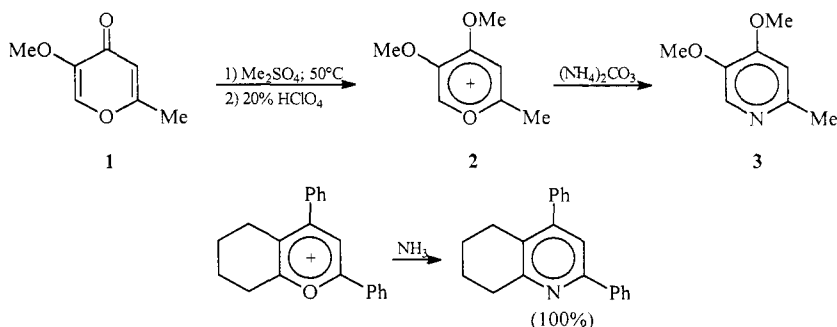


BAEYER Pyridine Synthesis

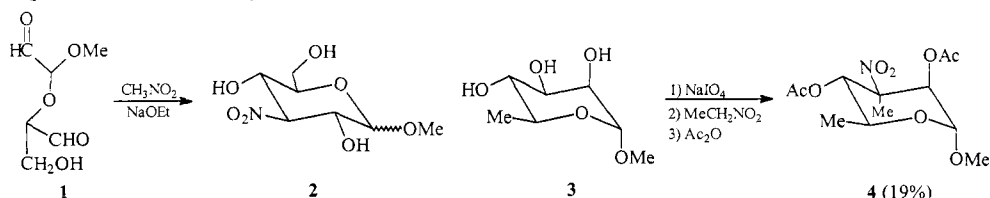
Synthesis of pyridines from pyrones (see 1st edition).



1	Baeyer, A.	<i>Chem. Ber.</i>	1910	43	2337
2	Nenitzescu, C.D.	<i>Liebigs Ann.</i>	1959	625	74
3	Cavallieri, L.F.	<i>Chem. Rev.</i>	1947	41	525
4	Dimroth, K.	<i>Angew. Chem.</i>	1960	72	331
5	Balaban, A.T.	<i>Liebigs Ann.</i>	1992		173

BAER-FISCHER Amino Sugar Synthesis

Synthesis of 3-nitro and derived 3-amino sugars by aldol condensation of sugar-derived dialdehydes with nitroalkanes (see 1st edition).

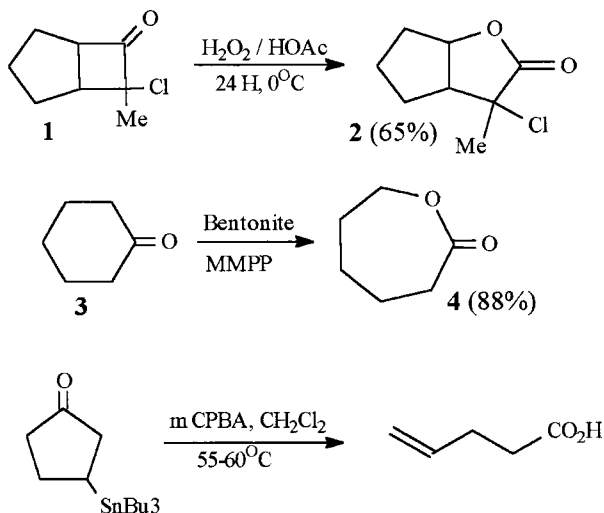


1	Baer, H.H.; Fischer, H.O.L.	<i>Proc. Nat. Acad. Sci. USA</i>	1958	44	991
2	Baer, H.H.	<i>Adv. Carbohydr. Chem.</i>	1969	24	67
3	Brimacombe, J.S.	<i>J. Chem. Soc. Perkin I</i>	1974		62
4	Santoyo-Gonzales, F.	<i>Synlett</i>	1990		715

Nitrosugar 4.³ Methyl-*L*-rhamnoside **3** (100 g; 0.55 mol) in 1000 mL water was treated with NaIO_4 (200 g; 0.83 mol) at 20°C . After 3 h NaHCO_3 was added, the mixture poured into EtOH (4000 mL) and filtered. The filtrate was concentrated and extracted with hot EtOH. The extract was cooled, filtered and treated with nitroethane (104.5 g; 1.4 mol) followed by a solution of Na (12 g; 0.52 at.g.) in EtOH (750 mL). After 4 h at 20°C the solution was treated with CO_2 , filtered and concentrated. The mixture was treated with pyridine (400 mL) and Ac_2O (300 mL) at 20°C for 12 h. Work up left a residue which dissolved in Et_2O :petroleum ether (1:1) (500 mL) and cooled afforded 36 g of **4** (19%), mp $137\text{--}138^\circ\text{C}$, $[\alpha]_D = -130^\circ$ (c 1).

BAEYER - VILLIGER Ketone Oxidation

Regioselective peroxide oxidation of ketones to esters or lactones with retention of configuration (see 1st edition).



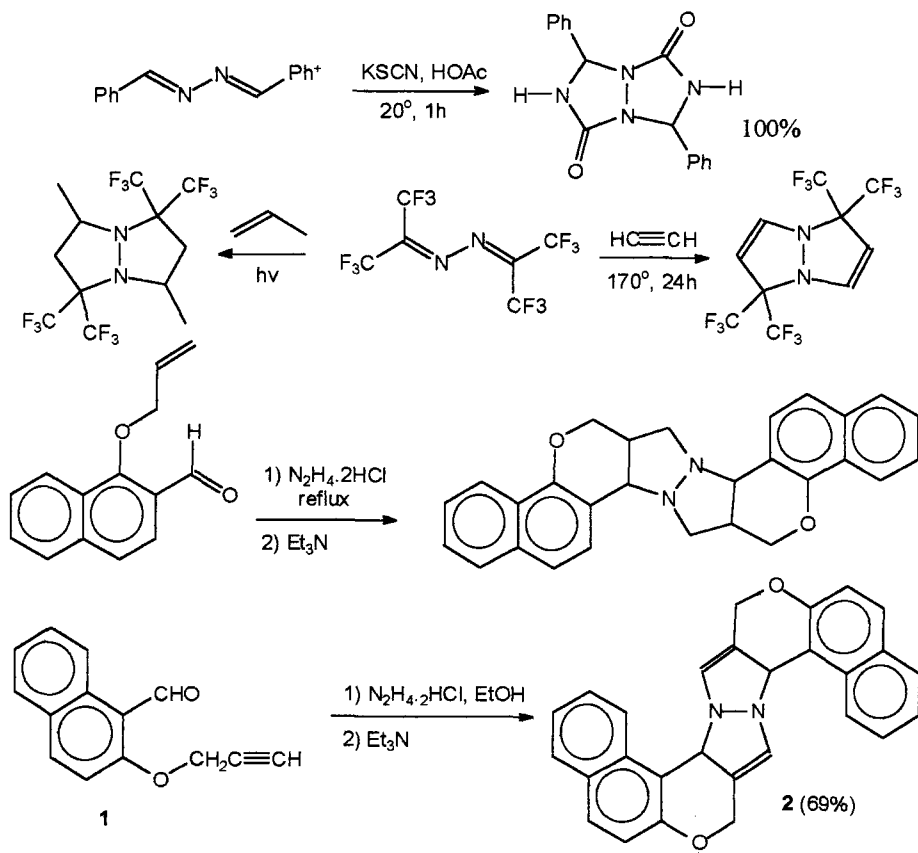
1	Bayer, A.; Villiger, V.	<i>Chem. Ber.</i>	1899	32	3625
2	Hassner, A.	<i>J. Org. Chem.</i>	1978	43	1774
3	Sarapanami, C.R.	<i>J. Org. Chem.</i>	1986	51	2322
4	Johnson, C.R.	<i>J. Am. Chem. Soc.</i>	1990	112	6729
5	Morimoto, T.	<i>Synth. Commun.</i>	1995	25	3765
6	Yamashita, M.	<i>J. Org. Chem.</i>	1997	62	2633
7	Hassal, C.H.	<i>Org. React.</i>	1957	9	73
8	Krow, G.R.	<i>Org. React.</i>	1993	43	251

Bicyclic lactone (2).² To a solution of **1** (790 mg, 5 mmol) in 90% HOAc (5 mL) at 0°C, was added 30% H₂O₂ (2.5 mL) in 90% HOAc (3 mL). The mixture was kept at 0°C for 24 h, poured into water and extracted with hexane. The organic layer after washing (NaHSO₃ and H₂O) was evaporated to give 570 mg of **2** (65%).

ε-Caprolactone (4). Cyclohexanone **1** (196 mg, 2 mmol) and moist bentonite clay (2 g) in MeCN (10 mL) was heated to 80°C with stirring and magnesium monoperoxyphthalate (MMPP) (3 mmol) was added in six portions at ten minute intervals. After additional 1 h stirring, followed by cooling, filtering and washing the precipitate with CHCl₃ (100 mL), evaporation of the solvent afforded 200 mg of **4** (88%).

BAILEY Crisscross Cycloaddition

A bis 3+2 cycloaddition between aromatic aldazines and olefins or acetylenes, called "crisscross" cycloaddition.

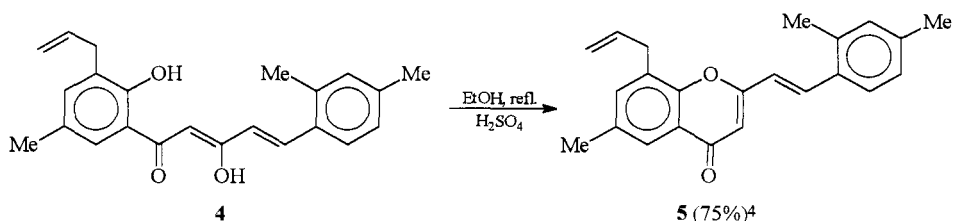
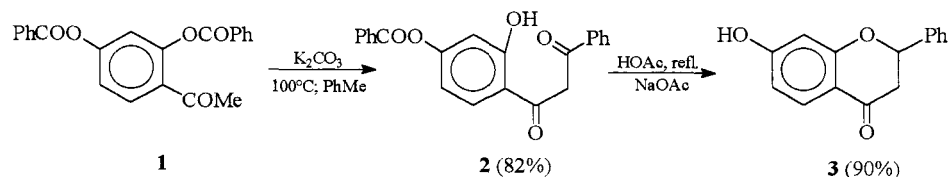


1	Bailey, J.R.	<i>J. Am. Chem. Soc.</i>	1917	39	279; 1322
2	Forshaw, T.P.	<i>J. Chem. Soc. (C)</i>	1971		2404
3	Forshaw, T.P.	<i>J. Chem. Soc. Perkin 1</i>	1972		1059
4	Shimizu, T.	<i>J. Org. Chem.</i>	1987	52	2277
5	Burger, K.	<i>Liebigs Ann.</i>	1982		853
6	Matur, S.S.	<i>J. Chem. Soc. Pekin 1</i>	1975		2479
7	Radl, S.	<i>Aldrichimica Acta</i>	1997	30	97

Diazabicyclooctadiene 2.⁴ A mixture of acetylenic aldehyde **1** (1.56 g, 5 mmol) and hydrazine.2HCl (260 mg, 2.5 mmol) in EtOH (80 mL) was refluxed for 4 h under stirring. To the cooled mixture (20°C) was added triethylamine (0.5 g, 5 mmol) and the mixture was stirred for 1 h at the same temperature. The crystals were filtered. Recrystallization afforded 1.042 g of **2** (69%), mp 276-278°C.

BAKER - VENKATARAMAN Flavone Synthesis

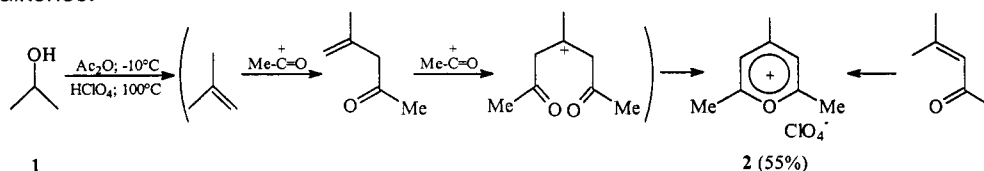
Rearrangement of aromatic *o*-keto esters of phenols to *o*-hydroxy-1,3-diketones followed by cyclization to flavones (see 1st edition).



1	Baker, W.	<i>J. Chem. Soc.</i>	1938		1381
2	Venkataraman, K.	<i>J. Chem. Soc.</i>	1939		1767
3	Kramm, E.	<i>J. Org. Chem.</i>	1984	49	3212
4	Krupadavam, G.L.D.	<i>J. Heterocycl. Chem.</i>	1996	33	1561
5	Levine, E.	<i>Chem. Rev.</i>	1954	54	493

BALABAN-NENITZESCU-PRAILL Pyrylium Salt Synthesis

Synthesis of pyrylium salts by acylation of unsaturated ketones or by diacylation of alkenes.

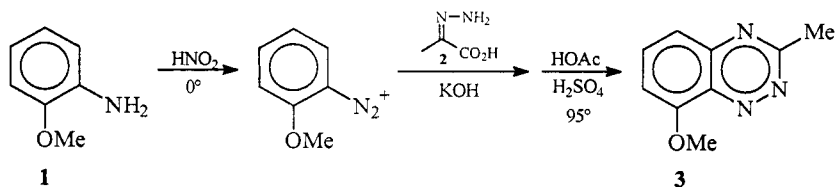


1	Balaban, A.T.; Nenitzescu, C.D.	<i>Liebigs Ann.</i>	1959	625	66; 74
2	Balaban, A.T.; Nenitzescu, C.D.	<i>J. Chem. Soc.</i>	1961		3553; 3561
3	Balaban, A.T.; Nenitzescu, C.D.	<i>J. Chem. Soc.</i>	1961		3564; 3566
4	Praill, P.F.G.; Whitear, A.L.	<i>J. Chem. Soc.</i>	1961		3573
5	Balaban, A.T.; Nenitzescu, C.D.	<i>Org.Synth.Coll.</i>		5	1106
6	Balaban, A.T.; Boulton, A.J.	<i>Org.Synth.Coll.</i>		5	1112; 1114

2,4,6-Trimethylpyrylium perchlorate 2.^{2,5} Anhydrous *t*-BuOH **1** (148 g; 2 mol) and Ac₂O (10 mL) at -10°C were cautiously treated with 70% HClO₄ (1.75 mol) and the temperature was controlled at 90-100°C. The mixture was heated at 100°C for 2 h. After cooling **2** was filtered and washed (AcOH, Et₂O) to give 205-215 g of **2** (53-57%), explosive when dry. The tetrafluoroborate or triflate⁵ are not explosive.

BAMBERGER Benzotriazine Synthesis

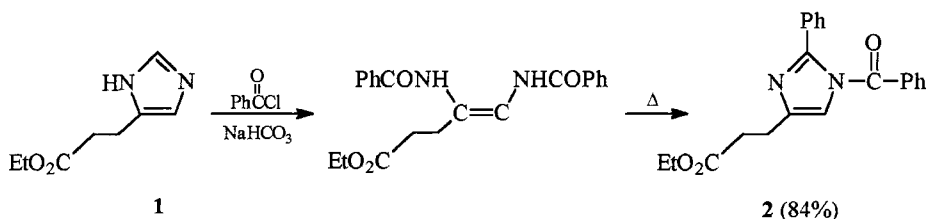
Synthesis of benzotriazines from pyruvic acid hydrazone **2** and aryldiazonium salts **1** (see 1st edition).



1	Bamberger, E.	<i>Chem. Ber.</i>	1892	25	3201
2	Abramovitch, R.A.	<i>J. Chem. Soc.</i>	1955		2326

BAMBERGER Imidazole cleavage

Synthesis of 2-substituted imidazoles from imidazoles via cleavage with acid chlorides to enediamides (see 1st edition).

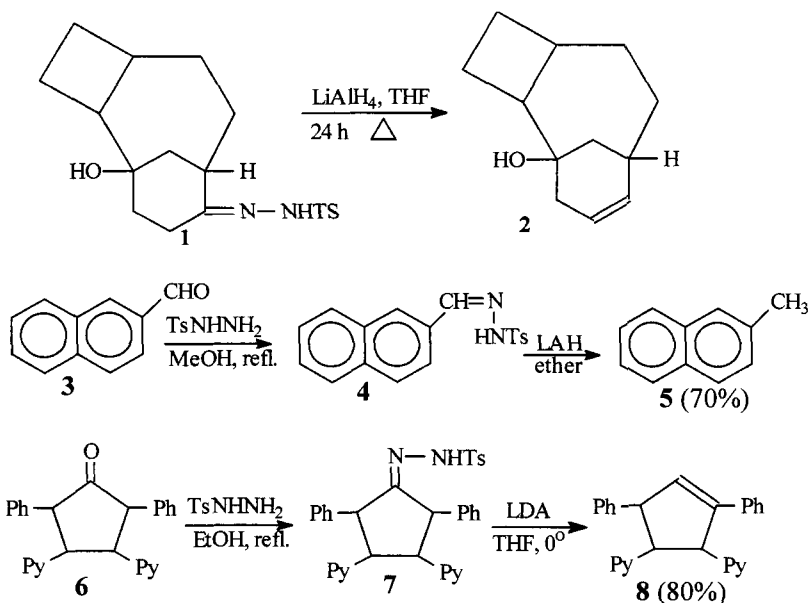


1	Bamberger, E.	<i>Liebigs Ann.</i>	1893	273	342
2	Babad, E.	<i>J. Heterocycl. Chem.</i>	1969	6	235
3	Grace, M.E.	<i>J. Am. Chem. Soc.</i>	1980	102	6784
4	Kimoto, H.	<i>J. Org. Chem.</i>	1978	43	3403
5	Altman, J.	<i>J. Chem. Soc. Perkin I</i>	1984		59

Imidazole 2.⁵ Imidazole **1** (9.2 g; 54 mmol) in EtOAc (140 mL) was treated with benzoyl chloride (15.7 g; 112 mmol) in EtOAc (40 mL) and 1M NaHCO₃ (380 mL) added simultaneously in 1 h under ice-cooling. The mixture was stirred for 1 h, then a further portion of benzoyl chloride (15.7 g; 112 mmol) in EtOAc and 1M NaHCO₃ (280 mL) was added followed by more 1M NaHCO₃ (200 mL). After 24 h the organic layer was concentrated and the residue dissolved in THF (300 mL). The THF solution was stirred with 10% NaHCO₃ (600 mL) for 24 h to decompose any N-formyl intermediate and to remove benzoic acid. Extraction with EtOAc, drying (Na₂SO₄), solvent evaporation and recrystallization from EtOAc:hexane afforded 16.24 g of **2** (84%), mp 128-129°C.

BAMFORD-STEVENS-CAGLIOTI-SHAPIRO Olefination

Conversion of ketones to olefins via tosylhydrazones with NaOR, LAH, LDA or BuLi. But 2-naphthaldehyde tosylhydrazone is reduced by LAH to 2-methylnaphthalene (see 1st edition).



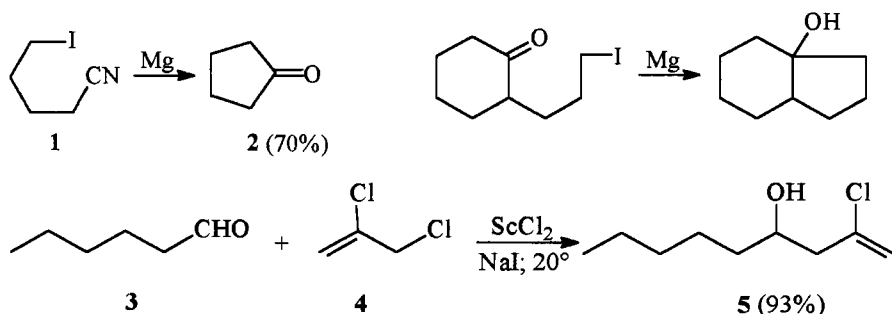
1	Bamford, W.; Stevens, T. <i>J. Chem. Soc.</i>	1952		4735
2	Farnum, D. G. <i>J. Org. Chem.</i>	1963	28	870
3	Nikon, A. <i>J. Org. Chem.</i>	1981	46	4692
4	Stadler, H. <i>Helv. Chim. Acta.</i>	1984	67	1379
5	Caglioti, R. <i>Tetrahedron Lett.</i>	1962		1261
6	Caglioti, R. <i>Tetrahedron</i>	1963	19	1127
7	Shapiro, R. H. <i>J. Am. Chem. Soc.</i>	1967	89	1442; 5734
8	Siemeling, E. <i>J. Org. Chem.</i>	1997	62	3407
9	Shapiro, R. H. <i>Org. React.</i>	1976	23	405

β -Methylnaphthalene 5.⁷ To a solution of **4** (2.0 g, 6.17 mmol) in THF (50 mL) was added LiAlH_4 (3.0 g, 78.9 mmol) and the mixture refluxed for 18 h. After careful decomposition of excess hydride with moist Et_2O and water, the organic phase was washed with dil. H_2SO_4 and water, dried and evaporated, to yield 620 mg of **5** (70.7 %).

1,3-Diphenyl-4,5-di(2-pyridyl)cyclopentene 8.⁸ A solution of **7** (30.2 g, 54 mmol) in THF (300 mL) was treated with LDA at 0°C . After 14 h stirring at 20°C , the mixture was quenched with brine at 0°C . Workup gave 16.2 g of **8** (80 %).

BARBIER Reaction

In situ Grignard generation in the presence of an electrophile (see 1st edition).

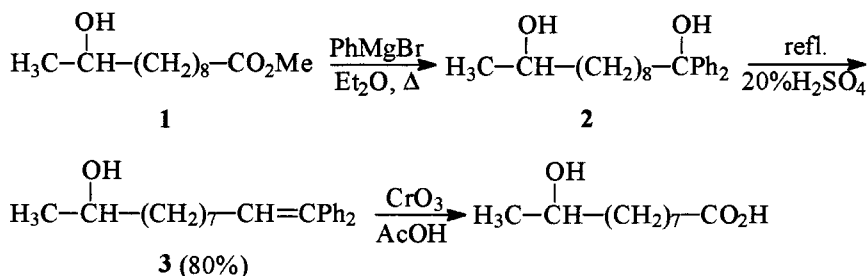


1	Barbier, P.	<i>C. R.</i>	1899	128	110
2	Grignard, V.	<i>C. R.</i>	1900	130	1322
3	Ashby, R.	<i>Pure & Appl. Chem.</i>	1980	52	545
4	Huang, X.Z.	<i>Tetrahedron Lett.</i>	1988	29	1395
5	Blomberg, C.	<i>Synthesis</i>	1977		18
6	Hassner, A.	<i>J. Organomet. Chem.</i>	1978	156	227
7	Imai, T.	<i>Synthesis</i>	1993		395
8	Banik, Bak.	<i>Tetrahedron Lett.</i>	2001	42	187

2-Chloro-1-nonen-4-ol 5.⁷ To **3** (500 mg; 5 mmol) and **4** (611 mg; 5.5 mmol) was added successively $\text{ScCl}_2 \cdot 2\text{H}_2\text{O}$ (1.7 g; 7.5 mmol) and NaI (1.1 g; 7.5 mmol). After 20 h stirring at 20°C, 30% NH_4F (10 mL) and Et_2O (20 mL) were added. Usual work up and chromatography followed by distillation gave 820 mg of **5** (93%).

BARBIER-WIELAND Degradation

A multi-step (Grignard reaction, elimination, oxidative cleavage) procedure for chain degradation of carboxylic acids (esters) (see 1st edition).

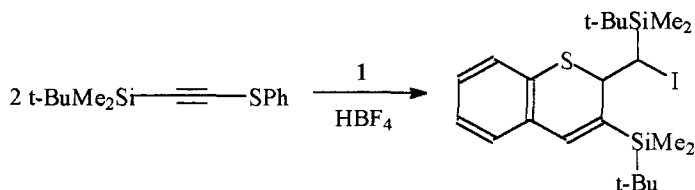
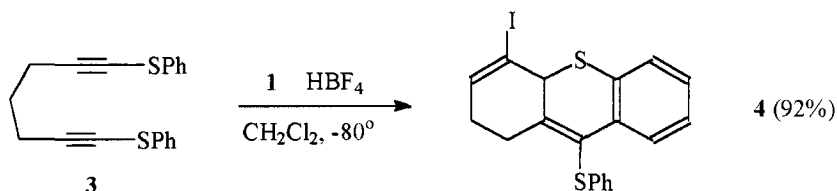
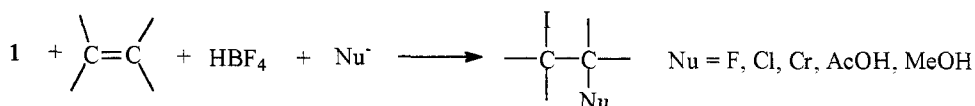
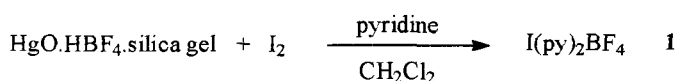


1	Barbier, P.	<i>C. R.</i>	1913	156	1443
2	Wieland, E.	<i>Chem. Ber.</i>	1912	45	484
3	Sarel, S.	<i>J. Org. Chem.</i>	1959	24	2081
4	Fetisson, M.	<i>C. R.</i>	1961	252	139
5	Djerassi, C.	<i>Chem. Rev.</i>	1946	38	526
6	Chadha, M.S.	<i>Synthesis</i>	1978		468

9-Oxodecanoic acid 4.⁶ To PhMgBr (from PhBr; 29.8 g, and Mg 4.6 g in Et₂O 100 mL) was added the hydroxy ester **1** (7 g; 32 mmol) in Et₂O (25 mL) over 1 h and refluxed for 2.5 h. Aq. NH₄Cl was added and the etheric extracts were concentrated to give diol **2** which was refluxed with 20% H₂SO₄ (100 mL) for 1 h. Extraction (Et₂O), washing and evaporation afforded 7.3 g of **3** (80%), distilled at 180°C (Bath) / 0.5 torr. CrO₃ (6 g; 60 mmol) in water (8 mL) was added to crude **3** (6.4 g) in AcOH (75 mL) over 1.5 h. After stirring at 35°C for 1 h, work up gave 2.2 g of **4** (60%), mp 48°C.

BARLUENGA Iodination Reagent

Bis(pyridine)iodonium(I) tetrafluoroborate reagent for 1,2-iodofunctionalization of isolated or conjugated olefins, or cyclization of alkynyl sulfides.

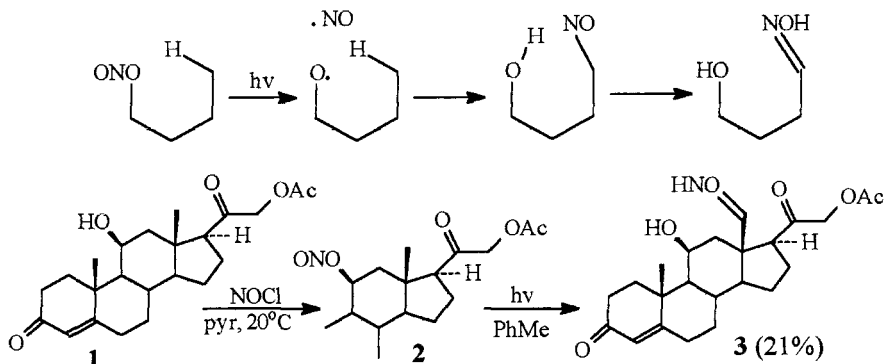


1	Barluenga, J.	<i>J.Chem.Soc.Perkin 1</i>	1984		2623
2	Barluenga, J.	<i>Angew.Chem.Int.Ed.</i>	1985	24	319
3	Barluenga, J.	<i>Tetrahedron Lett.</i>	1986	27	1715
4	Barluenga, J.	<i>J.Org.Chem.</i>	1990	55	3104
5	Barluenga, J.	<i>J.Org.Chem.</i>	1993	58	2058
6	Barluenga, J.	<i>Angew.Chem.Int.Ed.</i>	1993	32	893
7	Goldfinger, M.B.	<i>J.Am.Chem.Soc.</i>	1994	116	7895
8	Barluenga, J.	<i>J.Am.Chem.Soc.</i>	1997	119	6933
9	Barluenga, J.	<i>Tetrahedron Lett.</i>	1998	39	7393
10	Barluenga, J.	<i>Angew.Chem.Int.Ed.</i>	1998	37	3136
11	Barluenga, J.	<i>Pure Appl.Chem.</i>	1999	71	431
12	Barluenga, J.	<i>Angew.Chem.Int.Ed.</i>	2001	40	3389

Thiaanthracene 4.¹⁰ To a solution of IPy_2BF_4 **1** (3.72 g, 10 mmol) in CH_2Cl_2 (100 mL) cooled to -80°C was added HBF_4 (1.36 mL, 54% in Et_2O , 10 mmol). After 10 min a solution of diyne **3** (3.08 g, 10 mmol) in CH_2Cl_2 was added and the reaction mixture was stirred. Quenching with 10% $\text{Na}_2\text{S}_2\text{O}_3$, washing, drying and filtration through Al_2O_3 (elution with $\text{EtOAc} : \text{hexane}$) afforded 3.99 g of **4** (92%), mp $102\text{--}103^\circ\text{C}$.

BARTON Nitrite Photolysis

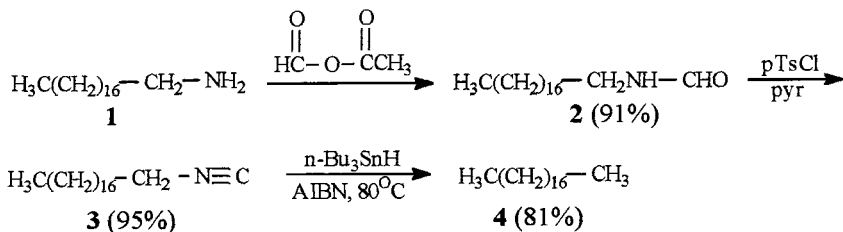
Long range functionalization of alcohols via nitrites leading to γ -hydroxy oximes (see 1st edition).



1	Barton, D.H.R.	<i>J.Am.Chem.Soc.</i>	1960	82	2640
2	Barton, D.H.R.	<i>J.Am.Chem.Soc.</i>	1961	83	4076
3	Barton, D.H.R.	<i>Pure Appl.Chem.</i>	1968	16	1
4	Baldwin, S.W.	<i>J.Am.Chem.Soc.</i>	1982	104	4990
5	Barton, D.H.R.	<i>Aldrichimica Acta</i>	1990	23	3

BARTON Deamination

Free radical deamination of primary amines via isocyanides (see 1st edition).

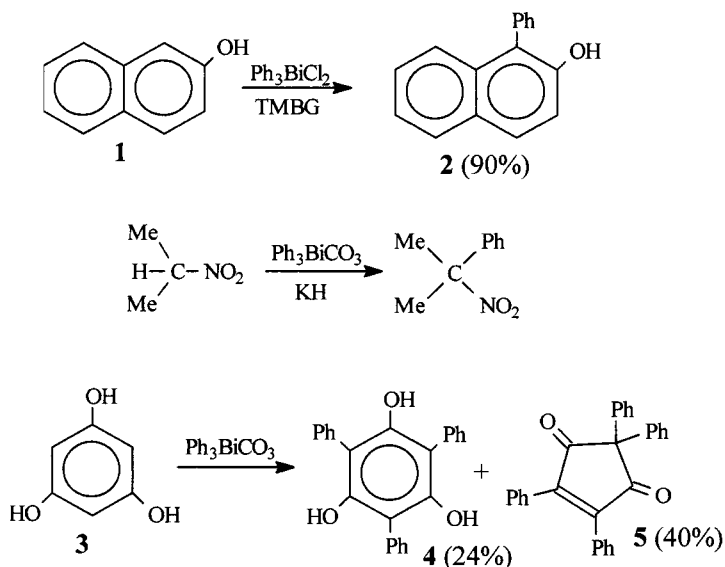


1	Barton, D.H.R.	<i>J.Chem.Soc.Perkin I</i>	1980		2657
2	Swindell, C.S.	<i>J.Org.Chem.</i>	1990	55	3
3	Barton, D.H.R.	<i>Aldrichimica Acta</i>	1990	23	3

Octadecane (4).¹ A solution of 3 (0.279 g, 1 mmol) and azoisobutyronitrile (AIBN) (0.1 g) in dry xylene (50 mL) was added dropwise to a solution of tri-*n*-butyl stannane (0.64 g, 2.2 mol equiv). A solution of AIBN (0.1 g) in xylene (50 mL) was slowly added at 80°C over 5 h. The solvent was removed in vacuum, the residue dissolved in pentane and iodine in pentane was added until the iodine color persisted. The solvent was evaporated and 4 was isolated by preparative TLC (silica gel, pentane). Sublimation in vacuum gave 0.205 g of 4 (81%), mp 29°C .

BARTON Phenylation of Phenols, Enols

Phenylation of phenols, enols and other anions by a pentavalent organo-bismuth reagent under neutral, acidic or basic conditions.



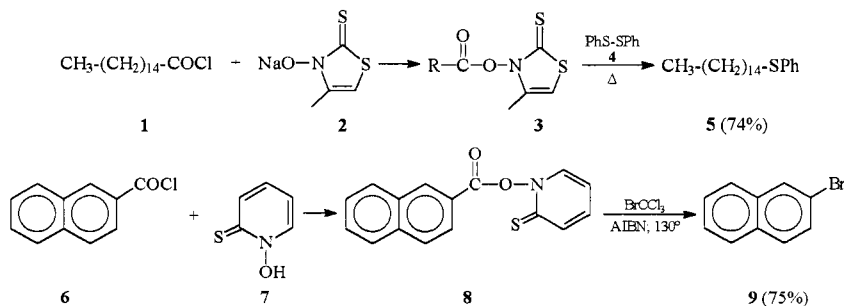
1	Barton, D.H.R.	<i>J.Chem.Soc.Chem.Comm.</i>	1980	246, 827
2	Barton, D.H.R.	<i>J.Chem.Soc.Chem.Comm.</i>	1981	503
3	Barton, D.H.R.	<i>Tetrahedron Lett.</i>	1982	23 3365
4	Barton, D.H.R.	<i>J.Chem.Soc.Perkin Trans</i>	1985	2657, 2667
5	Barton, D.H.R.	<i>Tetrahedron</i>	1988	44 3039
6	Barton, D.H.R.	<i>Aldrichim Acta</i>	1990	23 3

1-Phenyl-2-naphthol (2).⁴ To a stirred solution of Ph_3BiCl_2 (550 mg, 1.07 mmol) and 2-naphthol **1** (144 mg, 1 mmol) in THF (1mL) at 20°C under an Ar atmosphere was added tetramethyl-2-t-butylguanidine (TMBG) (500 mg, 0.11 mmol). After 5 h stirring, usual work up and chromatography (silica gel, Et_2O :hexane 1:4) afforded 198 mg of **2** (90%).

1,3,5-Trihydroxy-2,4,6-triphenylbenzene 4 and 2,2,4,5-tetraphenyl cyclopent-4-ene-1,3-dione (5).⁴ A mixture of phloroglucinol **3** (300 mg, 3.9 mmol) and Ph_3BiCO_2 (3.0 g, 6 mmol) in dioxane (10 mL) was heated to reflux under Ar for 11 h. After removing insoluble material by filtration, the solvent was evaporated and the residue chromatographed (hexane:EtOAc 7:3) to give 195 mg of **4** (24%) and 368 mg of **5** (40%). The same reaction but using a molar ratio of 3: Ph_3BiCO_3 =1:5.7 and heating for 24 h at 80°C afforded **4** in 60% yield.

BARTON Decarboxylation

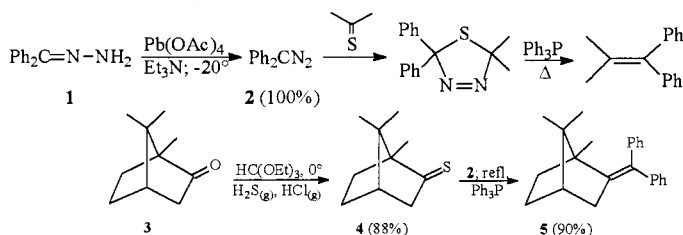
Decarboxylation of a mixed anhydride (thiohydroxamic-carboxylic) and interception of radicals as a sulfide, selenide or bromo derivative (see 1st edition).



1	Barton, D.H.R.	<i>J. Chem. Soc. Chem. Commun.</i>	1983		939
2	Barton, D.H.R.	<i>Tetrahedron Lett.</i>	1984	25	5777
3	Barton, D.H.R.	<i>Tetrahedron Lett.</i>	1985	26	5939
4	Tamm, Ch.	<i>Helv. Chim. Acta</i>	1995	78	403
5	Renault, P.	<i>Synlett</i>	1997		181
6	Barton, D.H.R.	<i>Aldrichimica Acta</i>	1990	23	3

BARTON-KELLOG Olefination

Olefin synthesis (especially tetrasubstituted) from hydrazones and thioketones via Δ^3 -1,3,4-thiazolidines (see 1st edition).

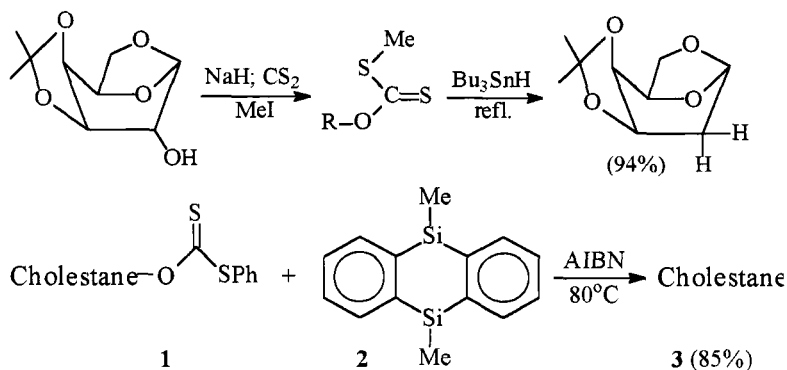


1	Barton, D.H.R.	<i>J. Chem. Soc. Perkin I</i>	1972		305
2	Barton, D.H.R.	<i>Chem. Soc.</i>	1970		1225
3	Kellog, R.M.	<i>Tetrahedron Lett.</i>	1970		1987
4	Kellog, R.M.	<i>J. Org. Chem.</i>	1972	37	4045
5	Barton, D.H.R.	<i>J. Chem. Soc. Perkin I</i>	1974		1794

(-)-2-Diphenylethylenecamphane **5. 2** (585 mg; 3 mmol) (from **1**, lead tetraacetate and TEA in CH_2Cl_2 at -20°C)⁵ and **4** (505 mg; 3 mmol) in THF (5 mL) were heated to reflux under N_2 for 3 h. After chromatography, the product was refluxed with Ph_3P (870 mg) in THF (5 mL) for 16 h and evaporated. The residue in petroleum ether was treated with 1 mL of MeI (exothermic) and stirred 2 h. Chromatography (silica) afforded 545 mg of **6** (90%), mp $69.5\text{--}72.5^\circ\text{C}$ (EtOH).

BARTON-MCCOMBIE Alcohol Deoxygenation

Deoxygenation of secondary alcohols to hydrocarbons via xantates (see 1st edition).

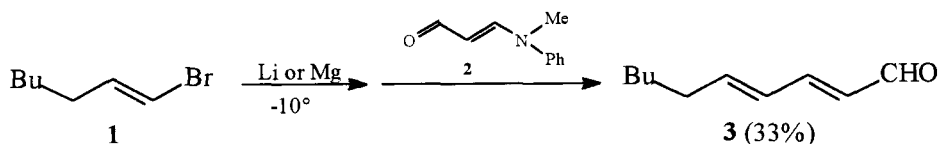


1	Barton, D.H.R.; McCombie, S.W.	<i>J. Chem. Soc. Perkin I</i>	1975		1574
2	Cristol, S.J.	<i>J. Org. Chem.</i>	1982	47	132
3	Barton, D.H.R.	<i>Tetrahedron</i>	1986	42	2329
4	McClure, C.K.	<i>J. Org. Chem.</i>	1991	56	2326
5	Chatgililoglu, C.	<i>Tetrahedron Lett.</i>	1995	36	3897
6	Crich, D.	<i>Aldrichimica Acta</i>	1987	20	36

Cholestane 3.⁵ To a stirred solution of **1** (100 mg; 0.19 mmol) and 5,10-dihydrosilanthrene **2** (67 mg; 0.32 mmol) in cyclohexane (20 mL) was added AIBN (5 mg) and the mixture was heated for 1 h at 80°C. Evaporation of the solvent and chromatography (hexane) gave 95 mg of **3** (85%).

BENARY Conjugated Aldehyde Synthesis

Formation of polyunsaturated aldehydes from vinyl halides and enaminonaldehydes (see 1st edition).

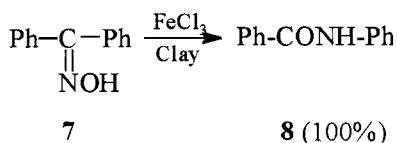
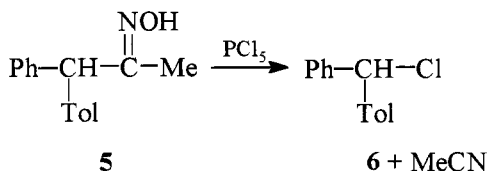
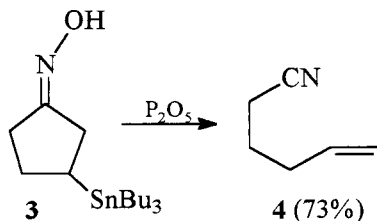
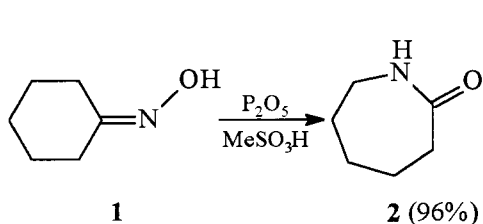


1	Benary, E.	<i>Chem. Ber.</i>	1930	63	1573
2	Normant, H.	<i>C. R.</i>	1958	247	1744
3	Schiess, P.	<i>Helv. Chim. Acta</i>	1972	55	2363
4	Näff, F.	<i>Helv. Chim. Acta</i>	1974	57	1317

3 (via Grignard reagent). **1** (4.42 g; 25 mmol) and Mg (0.6 g; 25 mmol) in THF followed by **2** (4.02 g; 25 mmol) and usual work up gave 1.32 g of **3** (33%), bp 95-103°C, as a mixture of 12% (*E,Z*) and 88% (*E,E*).

BECKMANN Rearrangement or Fragmentation

Acid catalyzed rearrangement of oximes to amides or cleavage of oximes to nitriles.



1	Beckmann, E.	<i>Chem. Ber.</i>	1886	19	988
2	Conley, R.T.	<i>J. Org. Chem.</i>	1963	28	210
3	Hassner, A.	<i>Tetrahedron Lett.</i>	1965		525
4	Eaton, P.E.	<i>J. Org. Chem.</i>	1973	38	4071
5	Nishiyama, H.	<i>Tetrahedron</i>	1988	44	2413
6	Johnson, C.R.	<i>J. Am. Chem. Soc.</i>	1990	112	6729
7	Samant, G.D.	<i>Synth. Commun.</i>	1997	27	379
8	Popp, I.	<i>Chem. Rev.</i>	1958	58	370
9	Heldt, W.Z.	<i>Org. React.</i>	1960	11	1
10.	Denz, y.	<i>Tetrahedron Lett.</i>	2001	42	403

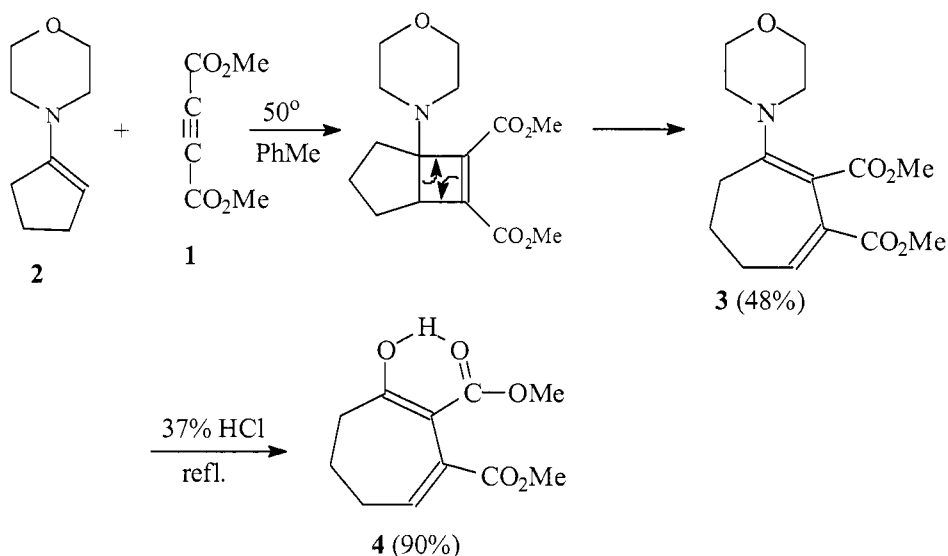
ε-Caprolactam 2.⁴ To a solution of P_2O_5 (36 g) in MeSO_3H (360 g) was added 1 (2 g; 20 mmol) under stirring. After 1 h at 100°C quenching with NaHCO_3 , extraction (CHCl_3), evaporation of the solvent and recrystallization from hexane gave 1.92 g of 2 (96%), mp $65\text{--}68^\circ\text{C}$.

ω-Hexenenitrile 4.⁶ To 3 (99 mg; 0.5 mmol) in CH_2Cl_2 (2 mL) was added P_2O_5 (70 mg; 0.5 mmol). After 24 h at 20°C Et_2O (2 mL) and Et_3N (0.12 mL) were added followed by chromatography to afford 43 g of 4 (73%).

N-Phenylbenzamide 8.⁷ FeCl_3 (15 g) was dissolved in MeCN (60 mL) and Montmorillonit K-10 (10 g) was added. After 5 h stirring the clay was filtered, washed and dried (5 h at 280°C). Ketoxime 7 (400 mg; 2 mmol), clay catalyst (1 g) in PhMe was refluxed (TLC monitoring). Filtration and concentration in vacuum followed by chromatography (EtOAc :hexane) gave 400 mg of 8 (100%).

BERCHTOLD Enamine Homologation

Addition of acetylenic esters to cyclic enamines leading by rearrangement ring expansion to cyclic ketones with two more carbon atoms.



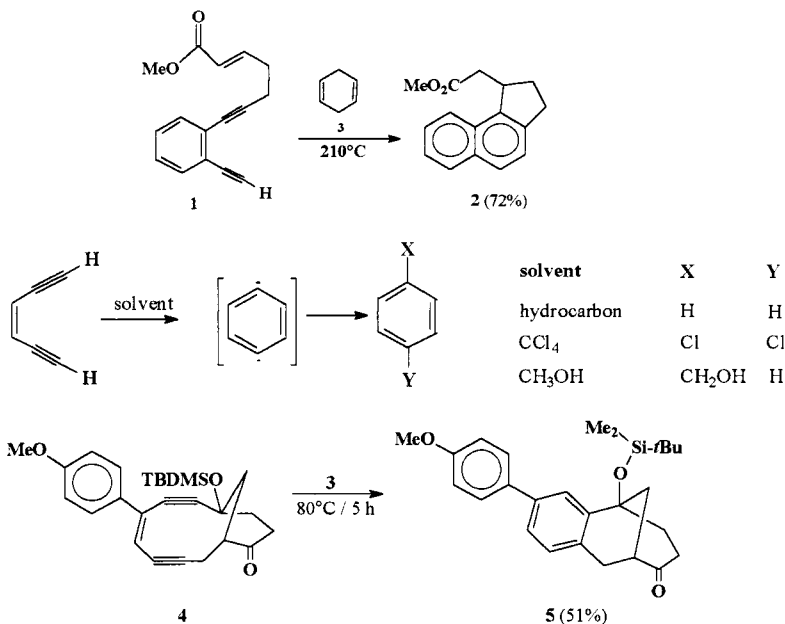
1	Brannock, K.C.	<i>J.Org.Chem.</i>	1961	26	625
2	Berchtold, G.A.	<i>J.Org.Chem.</i>	1961	26	3043
3	Berchtold, G.A.	<i>J.Org.Chem.</i>	1963	28	1459

1-(N-Morpholino)-2,3-dicarboxymethoxy-1,3-cycloheptadiene (3).³ Dimethyl acetylene dicarboxylate **1** (16.2 g, 77.4 mmol) was added to morpholinocyclopentene **2** (11 g, 77.4 mmol) in PhMe (40 mL) under N₂ with ice cooling and stirring at such a rate that the temperature never rose above 50°C. After a short supplementary stirring, the mixture was heated to reflux for 12 h. The solution was treated with excess of Et₂O under cooling and the precipitate was filtered off. Recrystallization from Me₂CO afforded 11.4 g of **3** (48%), mp 167-168°C.

2,3-Dicarboxymethoxy-3-cycloheptenone (4). A solution of **3** (1 g, 3.25 mmol) in MeOH (5 mL) and 32% HCl (1 mL) was heated to reflux. Water (2 mL) was added and the mixture was heated for another 10 min to reflux. After cooling the precipitate was crystallized from MeOH:H₂O 2:1 to give 610.5 mg of **4** (90%), mp 63.5-64°C.

BERGMAN Cycloaromatization

Ring annulation by radical cyclization of ene-diynes and (Z)-allene-ene-yne in a thermal reaction to give aromatics (electrocyclization).



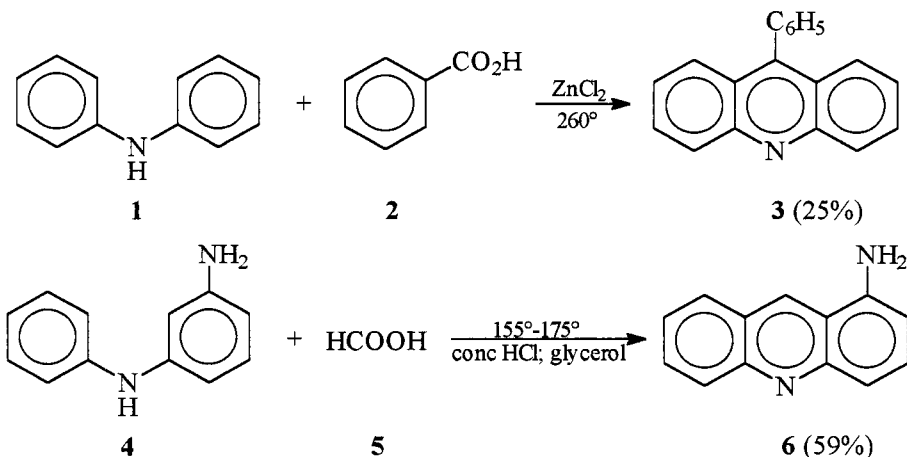
1	Bergman, R.G.	<i>J. Am. Chem. Soc.</i>	1972	94	660
2	Bergman, R.G.	<i>J. Am. Chem. Soc.</i>	1981	103	4082; 4091
3	Schreiber, S.L.	<i>J. Am. Chem. Soc.</i>	1988	110	631
4	Maier, M.E.	<i>Liebigs Ann.</i>	1992		855
5	Grissom, J.W.	<i>Tetrahedron Lett.</i>	1992	33	2315
6	Bergman, R.G.	<i>Acc. Chem. Res.</i>	1973	6	25
7	Myers, A.G.	<i>J. Am. Chem. Soc.</i>	1989	111	8057
8	Myers, A.G.	<i>J. Am. Chem. Soc.</i>	1992	114	9369
9	Ming-Jung Wu	<i>Tetrahedron Lett.</i>	1994	35	1879
10	Cramer, C.J.	<i>J. Am. Chem. Soc.</i>	1998	120	6269
11	Grissom, J.W.	<i>Tetrahedron</i>	1996	52	6453

3,4-Dihydrobenz-[e]-indene 2.⁵ A mixture of ene-diyne **1** (39.9 mg; 0.17 mmol), PhCl (1.8 mL) and 1,4-cyclohexadiene **3** (0.4 mL; 4.2 mmol) under N₂ was heated for 19 h at 210°C. Chromatography (silica gel, hexane:EtOAc 95:5) afforded 30.1 mg of **2** (72%). TLC (hexane:EtOAc 3:1), R_f = 0.48.

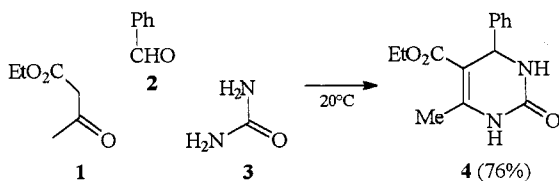
5-[tert-Butyldimethylsilyloxy]-3-(4-methoxyphenyl)-6,7,9,10-tetrahydro-5,9-methanobenzocycloocten-8(5H)-one 5.⁴ A solution of **4** (44 mg; 105 μmol) in **3** (2 mL) was heated under reflux for 5 h. The solvent was evaporated in vacuum and the residue purified by flash chromatography (petroleum ether:AcOMe 20:1) to afford 23.7 mg of **5** (51%) as a colorless oil. TLC (petroleum ether:AcOMe 4:1), R_f = 0.54.

BERNTHSEN Acridine Synthesis

Acridine synthesis from diphenylamine and carboxylic acids (see 1st edition).



1	Bernthsen, A	<i>Liebigs Ann.</i>	1878	192	1
2	Popp, F.D.	<i>J. Org. Chem.</i>	1962	27	2658
3	Albert, F.	<i>J. Org. Chem.</i>	1948		1225
4	Buu-Hoi, M.P.	<i>J. Chem. Soc.</i>	1955		1082

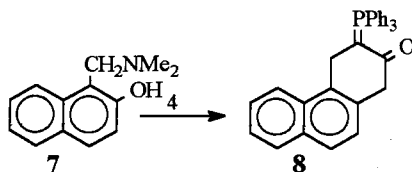
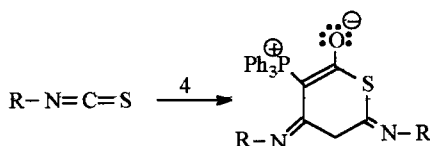
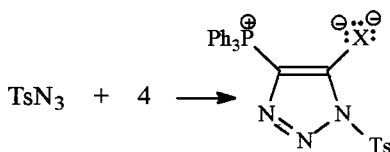
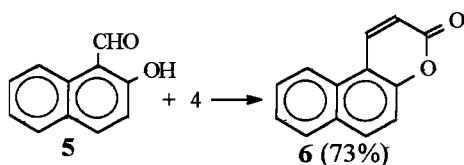
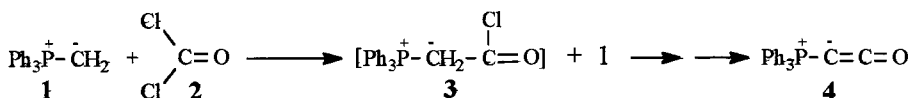
BIGINELLI Pyrimidone SynthesisPyrimidone synthesis from urea, an aldehyde and a β -keto ester.

1	Biginelli, P.	<i>Chem. Ber.</i>	1891	24	2962
2	Folkers, K.	<i>J. Am. Chem. Soc.</i>	1933	55	3361
3	Swett, I.	<i>J. Am. Chem. Soc.</i>	1973	95	8741
4	Zaugg, H.E.	<i>Org. React.</i>	1965	14	88
5	Kappe, C.O.	<i>J. Org. Chem.</i>	1997	62	7201
6	Wipf, P.	<i>Tetrahedron Lett.</i>	1995	36	7819

Pyrimidone 4.⁵ Ethyl acetoacetate **1** (1.3 g; 10 mmol), PhCHO **2** (1.06 g; 10 mmol) and urea **3** (0.6 g; 10 mmol) in MeOH (5 mL containing 1-2 drops of conc. HCl) was stirred 2 h at 20°C. A precipitate appeared and stirring was continued for 3 h to afford 1.98 g of **4** (76%), mp 106-107°C.

BESTMANN Cumulene Ylides

Phosphocumulenes ylides and phosphallene ylides in nucleophilic additions to $C=C$; $C\equiv N$ and $C\equiv C$ or cycloadditions (2+2; 4+2; 1,3-dipolar)



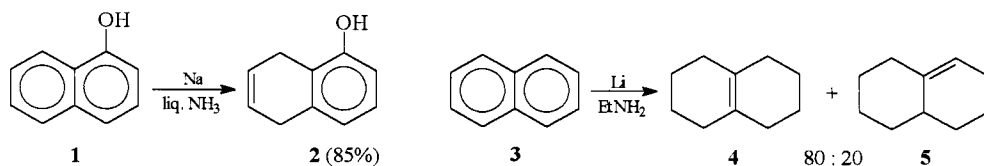
1	Bestmann, H.J.	<i>Angew.Chem.Int.Ed.</i>	1974	13	875
2	Bestmann, H.J.	<i>Liebigs Ann.</i>	1977	16	349
3	Bestmann, H.J.	<i>Angew.Chem.Int.Ed.</i>	1976	15	115
4	Bestmann, H.J.	<i>Angew.Chem.Int.Ed.</i>	1965	4	585, 645, 830
5	L'abbe, G.	<i>J.Org.Chem.</i>	1974	39	3770

Benzocoumarin (6).³ 1-Formyl-2-naphthol **5** (1.72 g, 10 mmol) is added slowly to a stirred solution of ylide **4** (3.02 g, 10 mmol) in PhH (30 mL). After 2-3 days stirring at 20°C or 24 h reflux, the solvent was removed in vacuum and the residue was crystallized from MeOH or i-PrOH. Recrystallization from i-PrOH or PhH/MeOH afforded 1.43 g of **6** (73%), mp 117°C.

Phosphorane (8).³ A solution of 1-(dimethylaminomethyl)-2-naphthol **7** (2.01 g, 10 mmol) and ylide **4** (3.02 g, 10 mmol) in anh. PhH (50 mL) was heated to reflux under stirring and N_2 . After complete evolution of Me_2NH , the mixture was refluxed for 5 hours, then the solvent was removed in vacuum and the residue, after recrystallization from EtOAc or PhH/EtOAc, afforded 3.15 g of **8** (69%), mp 217°C.

BIRCH-HÜCKEL-BENKESER Reduction

Reduction of aromatics, unsaturated ketones or conjugated dienes by alkali metals in liquid ammonia or amines.

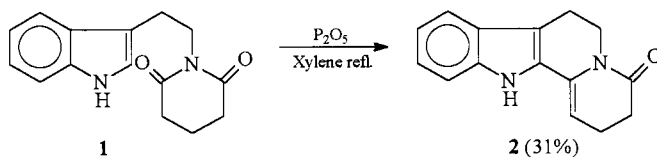


1	Hückel, W.	<i>Liebigs Ann.</i>	1939	540	156
2	Birch, A.I.	<i>J. Chem. Soc.</i>	1944		430
3	Benkeser, R.A.	<i>J. Am. Chem. Soc.</i>	1961	77	3230
4	Benkeser, R.A.	<i>J. Org. Chem.</i>	1964	29	955
5	Moody, C.J.	<i>Tetrahedron Lett.</i>	1986	27	5253
6	Silverstein, R.M.	<i>Synthesis</i>	1987		922
7	Robideau, P.W.	<i>Org. Reactions</i>	1992	42	1
8	Birch, A.I.	<i>Pure Appl. Chem.</i>	1996	68	553

5,8-Dihydro-1-naphthol 2.² To 1-naphthol 1 (10.0 g; 69 mmol) was added powdered NaNH₂ (2.7 g; 69 mmol), liquid NH₃ (100 mL), *t*-BuOH (12.5 g) and then Na (3.2 g; 0.139 at) in small pieces. After evaporation of the NH₃, the residue was extracted with Et₂O. Acidification gave an oil which solidified. Recrystallization gave 89.5 g of 2 (85%), mp 71-74°C.

BISCHLER-NAPIERALSKI Isoquinoline Synthesis

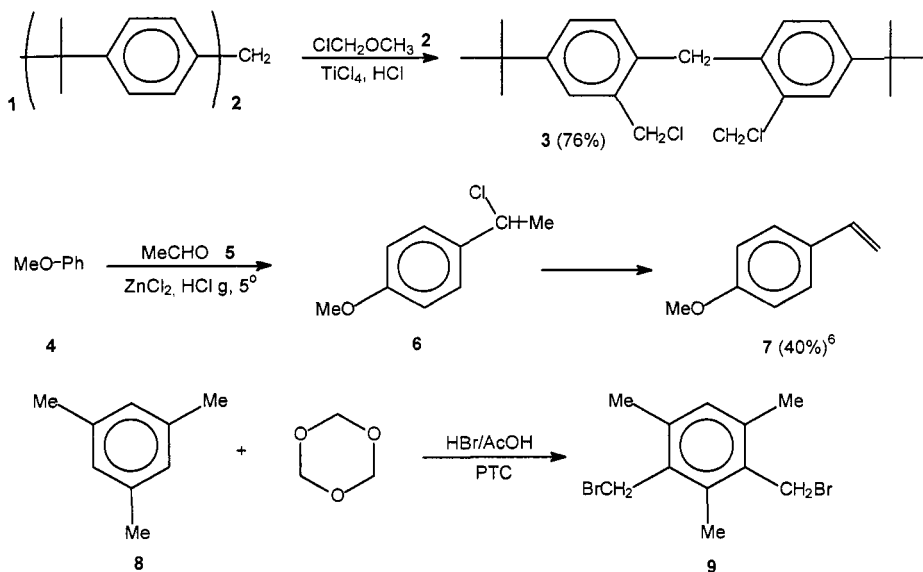
Isoquinoline synthesis from amides or phenethylamines (see 1st edition).



1	Bischler, A.; Napieralski, B.	<i>Chem. Ber.</i>	1893	26	1903
2	Morrison, C.G	<i>J. Org. Chem.</i>	1964	29	2771
3	Ramesh, D.	<i>Synth. Commun.</i>	1986	16	1523
4	Thygarayan, B.S.	<i>Chem. Rev.</i>	1954	54	1033
5	Fodor, G.	<i>Angew. Chem. Int. Ed.</i>	1972	11	919
6	Govindachari, T.R.	<i>Org. React.</i>	1951	6	74
7	Ishikawa, T.	<i>Tetrahedron Lett.</i>	1995	36	2795

BLANC-QUELLET Chloroalkylation

Lewis acid catalyzed aromatic chloromethylation (Blanc), chloroalkylation (Quellet).



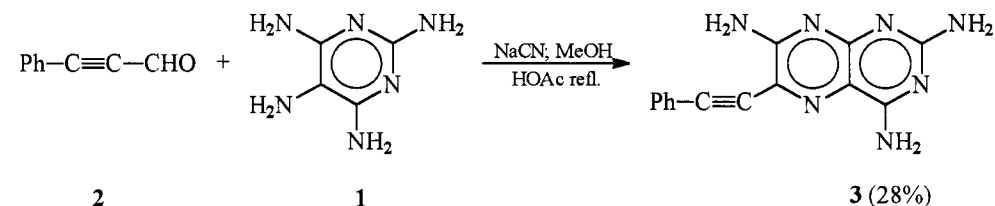
1	Grassi, G., Masselli, C.	<i>Gazz. Chim. Ital.</i>	1898	28	477
2	Blanc, G.	<i>Bull. Soc. Chim. Fr.</i>	1923	33	313
3	Tashiro Masashi	<i>J. Org. Chem.</i>	1978	43	1413
4	Fuson, R.	<i>Org. React.</i>	1942	1	63
5	Quellet, R.	<i>C. R.</i>	1932	195	155
6	Quellet, R.	<i>Bull. Soc. Chim. Fr.</i>	1940	7	196
7	Neda, V.	<i>J. Soc. Chem. Ind. Jpn.</i>	1944	47	565
8	Mitchel, R. H.	<i>Synlett.</i>	1989		55

2,2'-Di(chloromethyl) -4,4'-di(tert-butyl)diphenylmethane (3).³ To cooled (-5 °C) **1** (35 g, 125 mmol) and chloromethyl methyl ether **2** (80.5 g, 100 mmol) in CS₂ (150 mL) was added TiCl₄ (20 mL). The mixture was stirred for 1 h, poured into ice water (300 mL) and the organic layer extracted with PhH. Evaporation gave 36 g of **3** (76%), mp 90-91 °C(EtOH).

2,4-Bis (bromomethyl)-mesitylene (9).⁸ Mesitylene **8** (120 g, 1 mol) was added to a mixture of 48% HBr (475 mL) and glacial acetic acid (125 mL), followed by 1,3,5-trioxane (60 g, 2 mol) and tetradecyltrimethylammomium bromide (5 g). The mixture was then well stirred such that only a single layer could be seen and then heated to a gentle reflux for 24 h. After cooling to 20 °C the white solid was filtered, washed (water) and extracted with hot hexane-CH₂Cl₂. Finally there were obtained 290 g of **9** (94%), mp 133-4 °C

BLICKE - PACHTER Pteridines Synthesis

Condensation of aminopyrimidines with aldehydes and HCN followed by cyclization with NaOMe to pteridines.

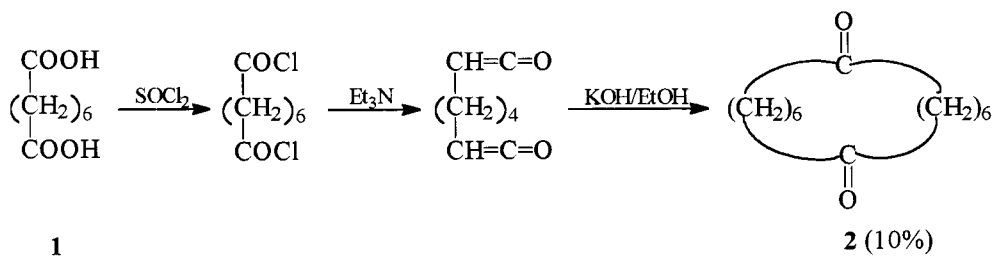


1	Blicke, F.F.	<i>J. Am. Chem. Soc.</i>	1954	76	2798
2	Pachter, I.J.	<i>J. Org. Chem.</i>	1963	28	1191
3	Pachter, I.J.	<i>J. Org. Chem.</i>	1963	28	1203

2,4,7-Triamino-6-phenylethynyl-pteridine 3.² 2,4,5,6-Tetraaminopyrimidine **1** (2.5 g; 14 mmol) in MeOH (12 mL) and HOAc (12 mL) was treated with NaCN (1.5 g; 30 mmol) in water (6 mL) and phenylpropargylaldehyde **2** (2.5 g; 19 mmol) in MeOH (3 mL). After 10 min stirring and boiling, cooling deposited yellow crystals, washed (MeOH, water and MeOH), 1.9 g (28%) of **3** (acetate).

BLOMQUIST Macrocycles Synthesis

Synthesis of large ring carbocycles by cyclization of bifunctional ketenes.

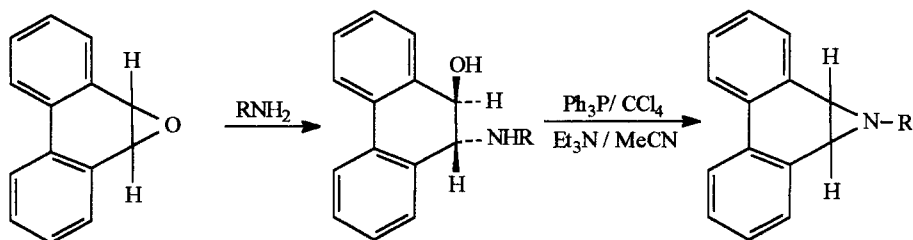
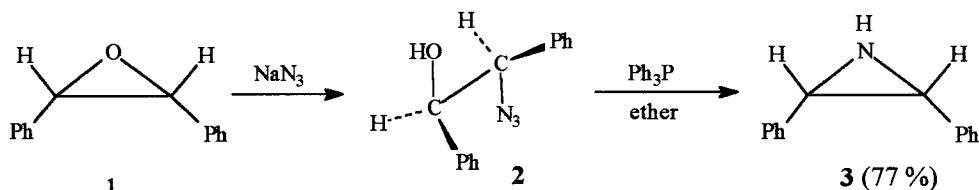


1	Blomquist, A.T.	<i>J. Am. Chem. Soc.</i>	1947	69	472
2	Blomquist, A.T.	<i>J. Am. Chem. Soc.</i>	1948	70	30

1,8-Cyclotetradecanedione 2.² Suberic acid **1** (3 g; 1.7 mmol) and SOCl_2 (0.4 g; 3.4 mmol) were heated at 55°C for 2 h and on a water bath until gas evolution ceased. Excess SOCl_2 was removed in vacuum and the acid chloride was diluted with Et_2O (200-300 mL). This was added to Et_3N (10-20 mL) in Et_2O (500-600 mL) over 26 h under gentle reflux. The decanted solution was washed with dil. HCl and water, dried (MgSO_4) and distilled. The yellow residue was treated with EtOH (5 mL) and KOH sol (1.8 g in 20 mL EtOH). After 10 h at 20°C and 2 h reflux, the mixture was diluted with water, extracted with Et_2O and the solvent evaporated to afford two crops of **2**, total yield 10%, mp 147.5-148°C.

B L U M Aziridine Synthesis

Synthesis of aziridines from epoxides via amino alcohols or azido alcohols and reaction with phosphines or phosphites (see 1st edition).



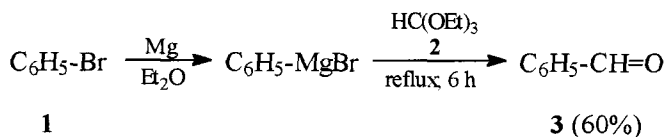
1	Blum, J.	<i>J.Org.Chem.</i>	1978	43	397, 4273
2	Shudo, K	<i>Chem.Pharm.Bull.</i>	1976	24	1013
3	Hassner, A	<i>J.Am.Chem.Soc.</i>	1970	92	3733
4	Hassner, A	<i>J.Am.Chem.Soc.</i>	1969	91	5046
5	Blum, J.	<i>J.Heterocycl.Chem.</i>	1994	31	837
6	Chiappe, C.	<i>Tetrahedron Asymm.</i>	1998	121	4079

Threo-2-Azido-1,2-diphenylethanol (2).¹ A mixture of cis-stilbene oxide 1 (3.92 g, 20 mmol) and NaN_3 (4.48 g, 70 mmol) in 50% aqueous acetone (60 mL) was refluxed for 3 h. The solvent was removed in vacuum and the residue extracted with CHCl_3 . The organic solution was washed with water, dried (MgSO_4) and concentrated. Distillation of the residue afforded 3.70 g of 2 (77%) as a pale yellow oil, bp 122 °C/0.15 mm.

Cis-2,3-Diphenylaziridine (3). A solution of 2 (0.84 g, 3.5 mmol) and triphenylphosphine (0.92 g, 3.5 mmol) in dry Et_2O (25 mL) was refluxed for 1 h. Et_2O (50 mL) was added and the mixture was allowed to stand overnight at 5°C to allow complete precipitation of triphenylphosphine oxide. Column chromatography on silica gel yielded 0.53 g of 3 (77%).

BODROUX-CHICHIBABIN Aldehyde Synthesis

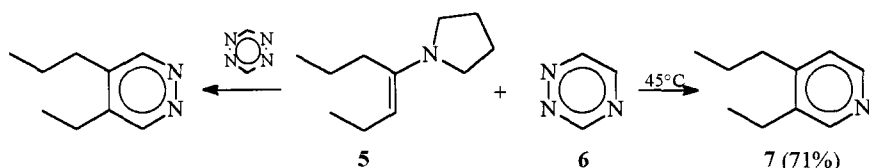
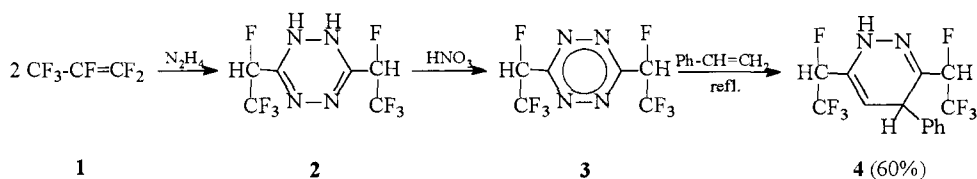
Aldehyde synthesis from Grignard reagents and trialkyl orthoformate; see also Bouveault (see 1st edition).



1	Chichibabin, A.E.	<i>J. Russ. Phys. Chem. Soc.</i>	1903	35	1284
2	Bodroux, F.	<i>C. R.</i>	1904	138	92
3	Smith, L.I.	<i>J. Org. Chem.</i>	1941	6	437

BOGER - CARBONI-LINDSEY Heterocycle Synthesis

Diels-Alder reactions of olefins, acetylenes, allenes with tetrazines or triazines to provide pyridazines or pyridines; reverse demand Diels-Alder reactions (see 1st edition).

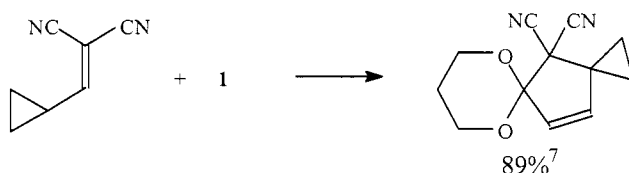
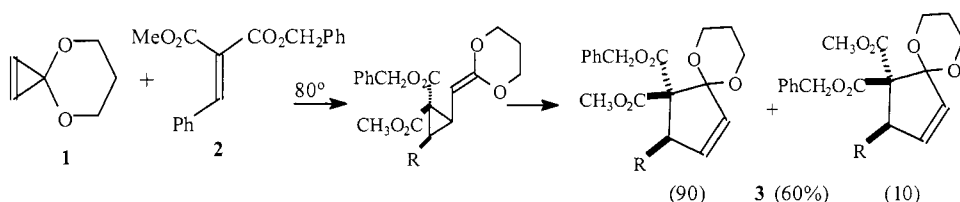


1	Carboni, R.A.; Lindsey, R.V.	<i>J. Am. Chem. Soc.</i>	1959	81	4342
2	Boger, D.L.	<i>J. Org. Chem.</i>	1981	48	2179
3	Boger, D.L.	<i>J. Org. Chem.</i>	1982	47	3736
4	Boger, D.L.	<i>J. Org. Chem.</i>	1983	48	621
5	Boger, D.L.	<i>J. Am. Chem. Soc.</i>	1985	107	5745
6	Boger, D.L.	<i>Chemtracts: Org. Chem.</i>	1996	9	149

3-Ethyl-4-n-propylpyridine 7. **2** (132 mg; 0.8 mmol) in CHCl_3 (0.5 mL) was added to a stirred solution of 1,2,4-triazine **6** (85 mg; 1.2 mmol) in CHCl_3 (0.5 mL) under N_2 at 25°C . The resulting dark orange solution was warmed at 45°C for 20 h. Chromatography (silica gel, 50% Et_2O in hexane) afforded 92 mg of pure **7** (71%).

BOGER Thermal Cycloadditions

Thermal cycloaddition of cyclopropenone ketal with olefinic acceptors to form cyclopentene derivatives.

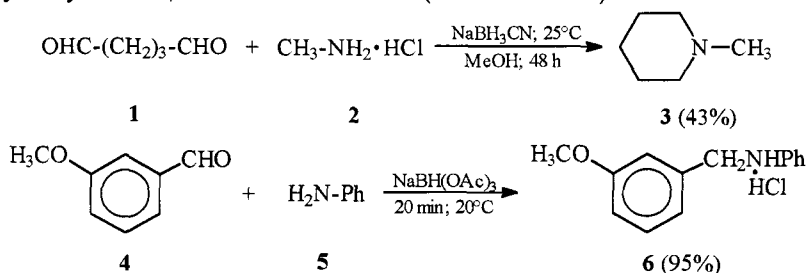


1	Boger, D.L.	<i>J.Am.Chem.Soc.</i>	1984	106	805
2	Boger, D.L.	<i>Tetrahedron Lett.</i>	1984	25	5611
3	Boger, D.L.	<i>J.Org.Chem.</i>	1985	50	3425
4	Boger, D.L.	<i>Tetrahedron</i>	1986	42	2777
5	Boger, D.L.	<i>Tetrahedron Lett.</i>	1984	25	5615
6	Boger, D.L.	<i>J.Am.Chem.Soc.</i>	1986	108	6695, 6713
7	Boger, D.L.	<i>J.Org.Chem.</i>	1988	53	3408

cis-Benzyl methyl 2-phenyl-6,10-dioxaspiro[4.5]dec-3-ene 1,1-dicarboxylate(cis).⁷

A solution of (Z)-benzyl methyl (phenyl methylene) malonate **2** (Z) (120 mg, 0.405 mmol) in MeCN-d₃ (0.4 mL) was treated with cyclopropenone 1,3-propanediyl ketal **1** (132 mg, 1.18 mmol, 2.9 equiv) under N₂. After 20 h heating at 80°C (shielded from light), the cooled mixture was concentrated in vacuum, and the residue filtered through a short column of SiO₂ (CH₂Cl₂). Evaporation of the solvent and chromatography (SiO₂ CH₂Cl₂) afforded: 8 mg of **2** (recovered), **1** (recovered) and a mixture of **3** (99 mg, 60%). Ratio cis:trans 90:10.

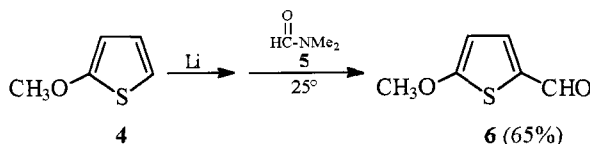
Reductive amination of aldehydes or ketones by cyanoborohydride (or triacetoxyborohydride)⁶ anion. Selective reduction of carbonyls to alcohols, oximes to N-alkylhydroxylamines, enamines to amines (see 1st edition).



1	Borch, R.F.	<i>J. Am. Chem. Soc.</i>	1969	91	3996
2	Borch, R.F.	<i>J. Am. Chem. Soc.</i>	1971	93	2897
3	Borch, R.F.	<i>J. Chem. Soc. Perkin I</i>	1984		717
4	Lane, C.F.	<i>Synthesis</i>	1975		135
5	Hutchins, R.O.	<i>Org. Prep. Proc. Int.</i>	1979	11	20
6	Abdel-Magid	<i>Tetrahedron Lett.</i>	1990	31	5595

Amine 6. Aldehyde **4** (1.36 g; 10 mmol) and aniline **5** (1.023 g; 11 mmol) in dichloroethane (40 mL) was treated with sodium triacetoxyborohydride (3.18 g; 15 mmol) under N₂ at 20°C to afford 2.37 g of **6** hydrochloride (95%).

Aldehyde synthesis from Grignard or Li derivatives with a formamide; see also Bodroux-Chichibabin (see 1st edition).

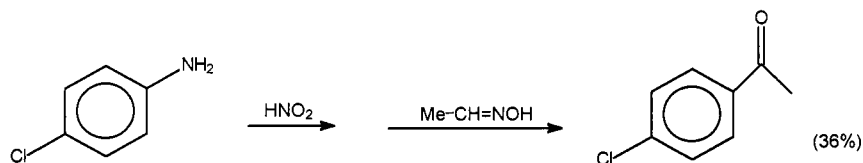
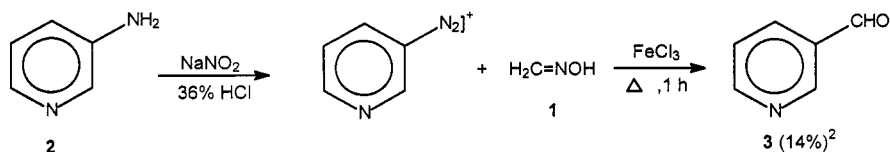


1	Bouveault, L.	<i>C. R.</i>	1903	137	987
2	Bouveault, L.	<i>Bull. Soc. Chim. Fr.</i>	1904	31	1306 (3)
3	Sice, J.	<i>J. Am. Chem. Soc.</i>	1953	75	3697
4	Einchorh, J.	<i>Tetrahderon Lett.</i>	1986	27	1791

5-Methoxy-2-thienaldehyde 6.³ 5-Methoxy-2-thienyllithium prepared from **4** (11.4 g; 0.1 mol) and Li in Et₂O (125 mL) was added slowly to ice cooled DMF **5** (8.0 mL; 0.11 mol) in Et₂O (75 mL) with efficient stirring and let stand at 20° overnight. The mixture was poured into ice, extracted with Et₂O and distillation gave 9.27 g of **6** (65%), bp 79-81°C/0.9 mm; mp 24-26°C (petroleum ether).

BORSCHÉ-BEECH Aromatic Aldehyde Synthesis

Synthesis of aromatic aldehydes and of alkyl aryl ketones from aldoximes or semicarbazones and aromatic diazonium salts (see 1st edition).

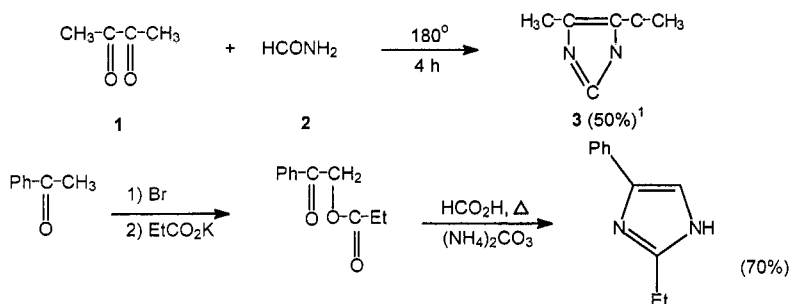


1	Borsche, C.	<i>Chem. Ber.</i>	1907	40	737
2	Beech, W. F.	<i>J. Chem. Soc.</i>	1954		1297
3	Woodward, R. B.	<i>Tetrahedron</i>	1958	2	1

Pyridine-3-aldehyde (3).² 3-Aminopyridine **2** (23.5 g, 0.24 mol), 36% HCl (68 mL), NaNO₂ (17.5 g, 0.25 mol) and water (75 mL) was made neutral (NaOAc) and treated with formaldoxime **1**. The mixture was acidified (pH-3) and after FeCl₃ (150 g) was added, it was boiled for 1 h. Usual work up gave 3.6 g of **3** (14%), bp 95-100 °C/16 mm.

BREDERECK Imidazole Synthesis

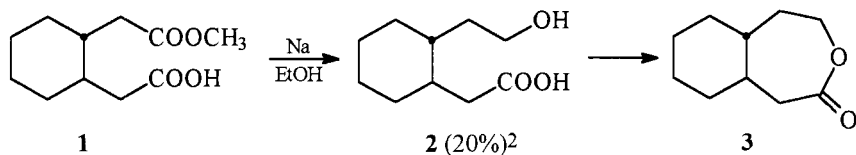
Synthesis of imidazoles from formamide (acetamide) and α-diketones, α-ketols, α-aminoketones, α-oximinoketones (see 1st edition).



1	Bredereck, H.	<i>Chem. Ber.</i>	1953	86	88
2	Grimmett, V.	<i>Adv. Heteroc. Chem.</i>	1970	12	113
3	Bredereck, H.	<i>Angew. Chem.</i>	1959	71	753
4	Schubert, H.	<i>Z. Chem.</i>	1967	7	461
5	Novelli, A.	<i>Tetrahedron Lett.</i>	1967		265

BOUVEAULT-BLANC Reduction

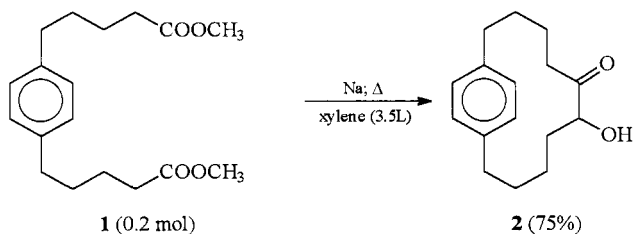
Reduction of esters to alcohols by means of sodium in alcohol (see 1st edition).



1	Bouveault, L.; Blanc, G.	<i>C.R.</i>	1903	136	1676
2	Paquette, L.A.	<i>J. Org. Chem.</i>	1962	27	2274
3	Ruhlmann, K.	<i>Synthesis</i>	1972		236
4	Chaussar, J.	<i>Tetrahedron Lett.</i>	1987	28	1173
5	Rabideau, P.W.	<i>Tetrahedron Lett.</i>	1980		1401

BOUVEAULT-HANSLEY-PRELOG-STOLL Acyloin Condensation

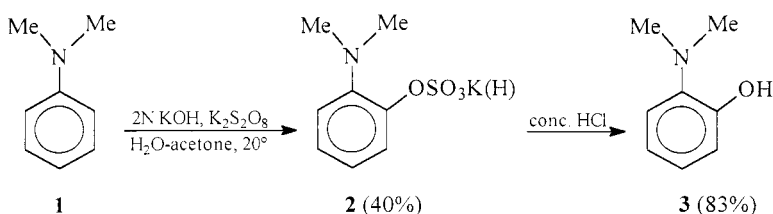
Condensation of two esters to an α -hydroxyketone by means of rapidly stirred (8000 rpm) Na suspension in boiling toluene or xylene (see 1st edition).



1	Bouveault, L.	<i>C. R.</i>	1905	140	1593
2	Hansley, V.L.	U.S. Pat. 2,228,268; cf. <i>Chem. Abstr.</i> , 1941 , 35, 2354			
3	Prelog, V.	<i>Helv. Chim. Acta</i>	1947	30	1741
4	Stoll, M.	<i>Helv. Chim. Acta</i>	1947	30	1815
5	Cramm, D.J.	<i>J. Am. Chem. Soc.</i>	1954	76	2743
6	Finley, K.T.	<i>Chem. Rev.</i>	1964	64	573
7	Ruhlmann, K.T.	<i>Synthesis</i>	1971		236

BOYLAND-SIMS *o*-Hydroxylaniline Synthesis

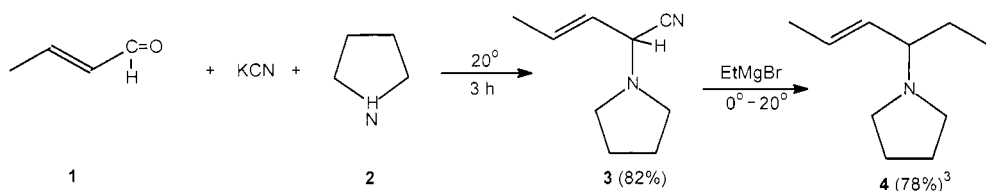
Oxidation of dialkylanilines or their N-oxides with persulfates to *o*-aminophenols (see 1st edition).



1	Boyland, E.; Sims, P.	<i>J. Chem. Soc.</i>	1953		3623
2	Boyland, E.; Sims, P.	<i>J. Chem. Soc.</i>	1958		4198
3	Behrman, E.J.	<i>J. Am. Chem. Soc.</i>	1967	89	2424
4	Behrman, E.J.	<i>J. Org. Chem.</i>	1992	57	2266
5	Behrman, E.J.	<i>Org. React.</i>	1988	35	432

BRUYLANTS Amination

Amination – alkylation of aldehydes via α -cyanoamines (see 1st edition).

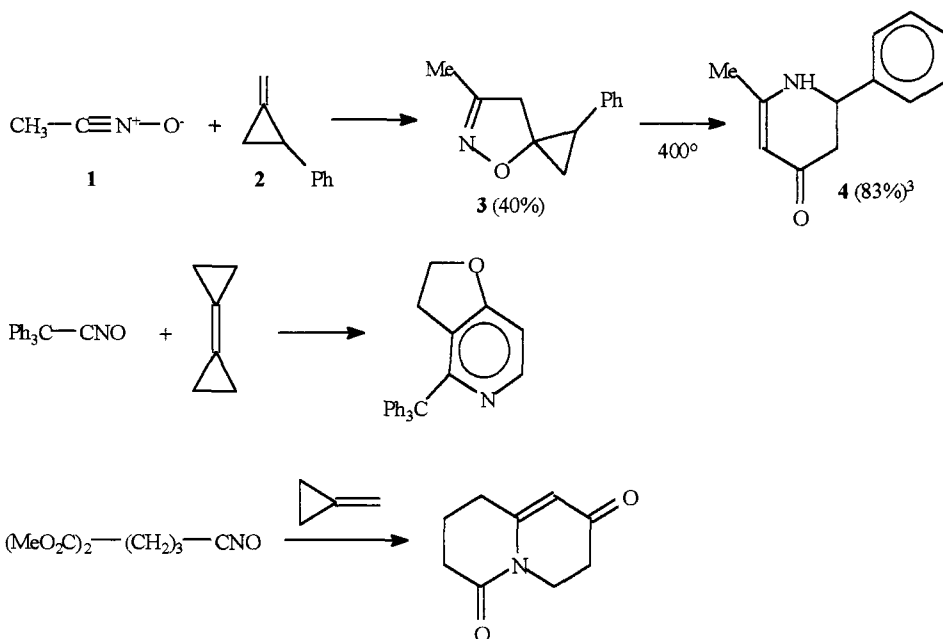


1	Bruylant, P.	<i>Bull. Soc. Chim. Belge</i>	1924	33	467
2	Bruylant, P.	<i>Bull. Soc. Chim. Belge</i>	1926	35	139
3	Bersch, H. W.	<i>Arch. Pharm.</i>	1978	311	1029
4	Ahlbrecht, H.	<i>Synthesis</i>	1985		743

N-(2-Hexene-4-yl)-pyrrolidine (4).³ To **3** (10.57 g, 70 mmol) in THF (20 mL) under Ar, EtMgBr (1 molar, 22 mmol) in THF is added slowly at 0 °C. The mixture was stirred for 3 h at 20 °C, diluted with Et₂O (50 mL) and worked up to give 8.35 g of **4** (78%), bp 83 °C (19 mm).

BRANDI-GUARNA Rearrangement

Synthesis of pyridine derivatives by rearrangement of isoxazolidone-5-spirocyclopropanes resulting from dipolar addition to methylenecyclopropanes.



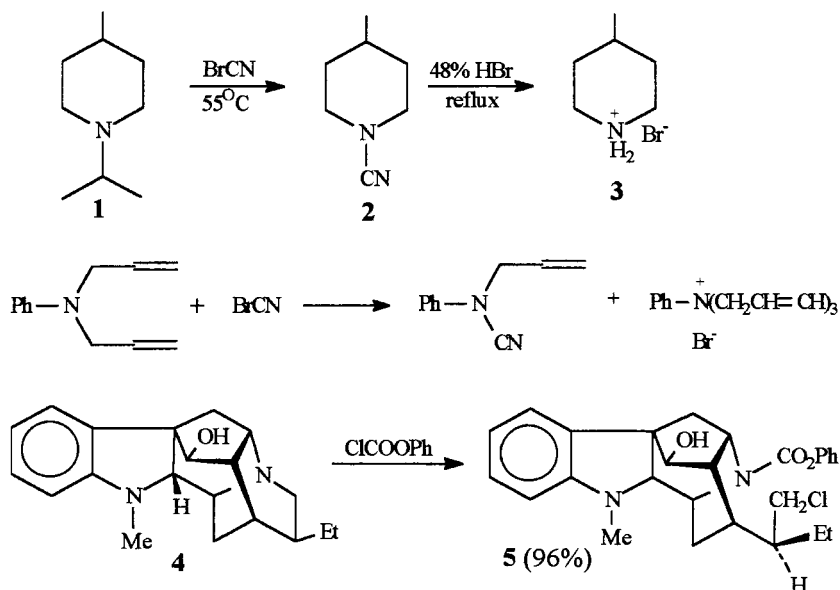
1	Brandi, A., Guarna, A.	<i>J.Chem.Soc.Chem.Comm.</i>	1985	1518
2	Brandi, A., Guarna, A.	<i>J.Org.Chem.</i>	1988	53 2426; 2430
3	Brandi, A.	<i>J.Org.Chem.</i>	1992	57 5666
4	Brandi, A.	<i>Tetrahedron Lett.</i>	1995	36 1343
5	Brandi, A. deMeijere, A.	<i>J.Org.Chem.</i>	1996	61 1665
6	Brandi, A., Guarna, A.	<i>Synlett</i>	1993	1

Spiro 4,5-dihydro-3-methylisoxazole-5,1'-2'-phenylcyclopropane (3).³ Nitroethane (1.3 g, 22 mmol) and Et_3N (262 mg, 2.6 mmol) in PhH (11 mL) was added over 1 h to a refluxing solution of 1-methylene 2-phenylcyclopropane 2 (1.88 g, 14.5 mmol) and methyl isocyanate 1 (1.24 g, 23 mmol) in PhH (10 mL) under stirring. After 18 h stirring at 20°C, the mixture was filtered and concentrated in vacuum. Unreacted 1 was recovered (45-65°C 0.5 torr) and the residue was chromatographed (CH_2Cl_2) to give 1 g of 3 (40%), mp 85°C.

2-Methyl-6-phenyl-dihydropyrid-4-one (4). Vapours of 3 (260 mg, 1.4 mmol) were passed at 0.04 Torr through a quartz tube heated at 400°C then led into a cold trap. Washing with petroleum ether afforded 216 mg of 4 (83%), mp 162°C (CHCl_3 - petroleum ether).

von BRAUN Amine Degradation

Degradation of tertiary amines with cyanogen bromide (BrCN), or ethyl, benzyl or phenyl chloroformate (see 1st edition).



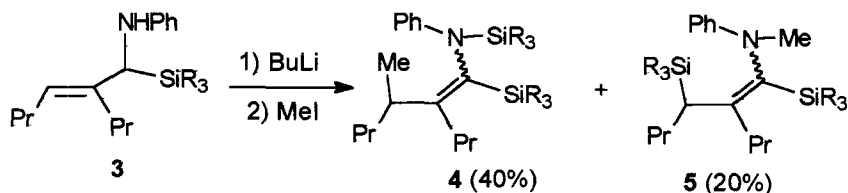
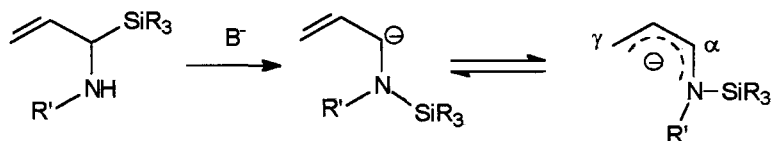
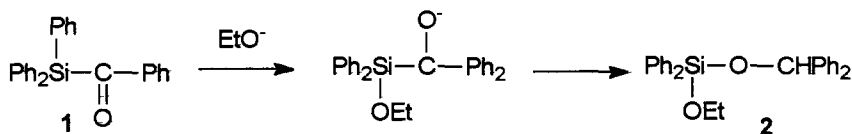
1	V. Braun, J.	<i>Chem. Ber</i>	1907	40	3914
2	Elderfield, R.C.	<i>J. Am. Chem. Soc.</i>	1950	72	1334
3	Boekelheide, V.	<i>J. Am. Chem. Soc.</i>	1955	77	4079
4	Wright, W.B.	<i>J. Org. Chem.</i>	1961	26	4057
5	Calvert, B.J.	<i>J. Chem. Soc.</i>	1965		2723
6	Rapoport, H.	<i>J. Am. Chem. Soc.</i>	1967	89	1942
7	Knabe, J.	<i>Arch. Pharm.</i>	1964	259	135
8	McCluskey, J.G.	<i>J. Chem. Soc. (C)</i>	1967		2015
9	Hageman, H.A.	<i>Org. React.</i>	1953	7	198

4-Pipecoline (3).² To a solution of BrCN (48 g, 0.46 mol) in PhH (100 mL) was added 1-isopropyl-4-pipecoline 1 (58 g, 0.41 mol) in PhH (275 mL) over 1 h at 40°C. The mixture was heated for 45 min at 55–60°C and was maintained at 20°C for 36 h. The basic material was extracted with HCl (100 mL) and the solvent was distilled to give 44 g of residue. The neutral product 2 was refluxed with 48% HBr (300 mL) for 10 h. After distillation of HBr, the residue was leached in a mixture of EtOAc:EtOH (80:20). Filtration of insoluble NH₄Br and concentration gave 3, mp 171–173°C.

Phenyl 21-chlorodeoxydihydrochanoajmaline-N-carboxylate (5).⁸ 21-Deoxy ajmaline 4 (1.55 g, 5.06 mmol) in CH₂Cl₂ (50 mL) was treated with phenyl chloroformate (0.86 g, 5.5 mmol) at 20°C for 18 h. Usual work-up, and chromatography afforded 2.24 g of 5 (96%).

BROOK Silaketone Rearrangement

Rearrangement of silaketone to silyl ethers (with chirality transfer) (see 1st edition).



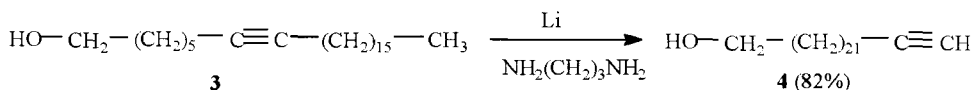
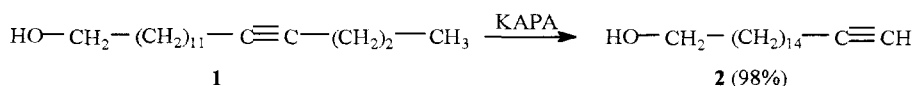
1	Brook, A.G.	<i>J.Org.Chem.</i>	1962	27	2311
2	Brook, A.G.	<i>Acc.Chem.Res.</i>	1974	7	77
3	Wilson, S.R..	<i>J.Org.Chem.</i>	1981	47	747
4	Kuwajima, J.	<i>Tetrahedron Lett.</i>	1980	21	623
5	Mori, M.	<i>J.Org.Chem.</i>	1996	61	1196
6	West, R.	<i>J.Am.Chem.Soc.</i>	1974	96	3214

Benzhydryloxy ethoxy diphenyl silane 2.² To a solution of benzoyltriphenylsilane 1 (2.5 g, 6.9 mmol) in PhH (25 mL) was added a solution of sodium ethoxide in EtOH (2 mL, 0.8 mmol). The solution was washed with water and the solvent removed in vacuum. The oily residue was dissolved in hot EtOH (15 mL) and cooled to give 2.1 g of 2 (74%), mp 67-75°C. Recrystallization from EtOH gave 1.8 g of 2 (64%), mp 77-78°C.

Silyl amines 4 and 5.⁵ To a solution of 3 in THF was added BuLi at -78°C and the solution was stirred for 30 min at the same temperature. MeI was added at -78°C and the mixture was stirred for another 30 min at the same temperature. After usual work-up are obtained 40% from 4 and 20% from 5.

BROWN Acetylene Zipper Reaction

Isomerization of internal acetylenes to the terminal position by means of potassium (or lithium) 3-aminopropylamide (KAPA).



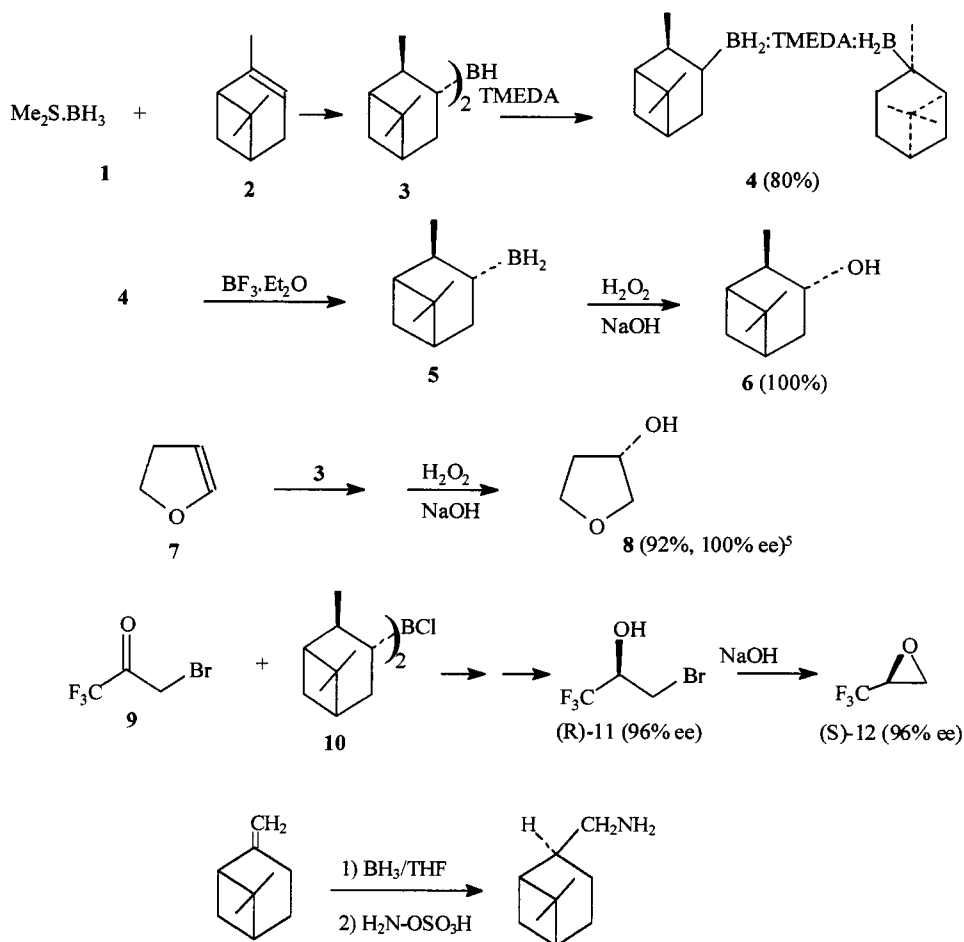
1	Brown, C.A.	<i>J. Am. Chem. Soc.</i>	1975	97	891
2	Brown, C.A.	<i>J. Chem. Soc. Chem. Commun.</i>	1976		959
3	Macaulay, S.R.	<i>J. Org. Chem.</i>	1980	45	734
4	Becker, D.	<i>J. Org. Chem.</i>	1984	49	2494
5	Abrams, S.R.	<i>Can. J. Chem.</i>	1984	62	1333

16-Heptadecyn-1-ol (2).⁴ A mixture of potassium (190 mg, 4.8 mmol) in 1,3-propanediamine **1** (5 mL) with ferric nitrate (1 mg) was heated to 90°C in an ultrasound cleaning bath. After 10-15 min potassium disappears and a green-brown solution of KAPA was formed. This mixture was cooled to 0°C and 12-heptadecyn-1-ol **1** (190 mg, 0.75 mmol) in THF (1 mL) was added. After 30 min stirring at 0°C, the mixture was poured into water (125 mL) and extracted with hexane (3 x 100 mL). The extract was dried with MgSO₄ and after evaporation of the solvent, there was obtained 185 mg of 16-heptadecyn-1-ol **2** (98%), mp 41°C.

23-Tetracosyn-1-ol (4).⁵ 1,3-Diaminopropane (10 mL) under N₂ was treated with Li (140 mg, 20 mmol) under heating (70°C) and stirring. After 2 h the mixture was cooled to 20°C, KO-t-Bu (1.3 g, 12 mmol) was added and stirring was continued for another 15 min when 7-tetracosyn-1-ol **3** (1.05 g, 3 mmol) was added. After 2 h stirring the mixture was quenched with water and normal work up gave after chromatography (silica gel, hexane : Et₂O 1:1) 860 mg of **4** (82%), mp 76-7°C.

BROWN Hydroboration

Hydroboration-regioselective and stereoselective (syn) addition of BH_3 (RBH_2 , R_2BH) to olefins. Synthesis of alcohols or amines including optically active ones from olefins. Also useful in synthesis of ketones by "stitching" of olefins with CO (see 1st edition).



1	Brown, H.C.	<i>J. Am. Chem. Soc.</i>	1956	78	2583
2	Brown, H.C.	<i>J. Org. Chem.</i>	1978	43	4395
3	Masamune, S.	<i>J. Am. Chem. Soc.</i>	1986	108	7401
4	Hoffmann, R.W.	<i>Angew. Chem. Int. Ed.</i>	1982	21	555
5	Brown, H.C.	<i>J. Am. Chem. Soc.</i>	1986	108	2049
6	Srebnik, M.	<i>Aldrichimica Acta</i>	1987	20	9
7	Brown, H.C.	<i>J. Org. Chem.</i>	1989	54	4504
8	Brown, H.C.	<i>J. Org. Chem.</i>	1995	60	41

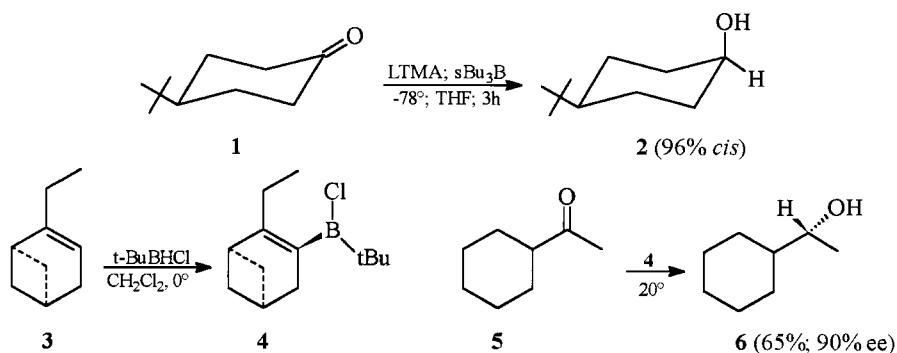
Isopinocampheol 6.² To a hot solution of borane-methyl sulfide **1** (2 mL, 20 mmol) in Et₂O (11.3 mL) was added (+)- α -pinene **2** (7.36 mL, 46 mmol), which led to quantitative formation of **3**. After addition of TMEDA (1.51 mL, 10 mmol), reflux was continued for 30 min. The adduct was filtered and washed with pentane to give 3.32 g of **4** (80%), mp 140-141°C (Et₂O). A solution of **4** (3.32 g, 8 mmol) in THF (16 mL) was treated with BF₃·Et₂O (1.97 mL, 16 mmol). After 1 h, the solid TMEDA·2BF₃ was removed and the solution of **5** was oxidized with alkaline H₂O₂ to give **6** (100%).

(-) 3-Hydroxytetrahydrofuran 8.⁵ To a suspension of (-) Ipc₂BH (diisopinocampheyl borane) **3** (7.1 g, 25 mmol) in THF, see above, at -25°C was added 2,3-dihydrofuran **7** (1.9 mL, 25 mmol). The reaction mixture was stirred at the same temperature for 6 h. The solid **3** disappeared, and formation of trialkyl borane was complete. The mixture was brought to 0°C, acetaldehyde (5.6 mL, 100 mmol) was added dropwise and stirring was continued for another 6 h at 25°C. Excess acetaldehyde was removed in vacuum (25°C, 12 mm Hg), and 20 mL of THF was added. The boronate thus obtained was oxidized with 25 mL of 3N NaOH and 3.75 mL of 30% H₂O₂, and maintained for 5 h at 25°C. The aqueous layer was saturated with K₂CO₃, extracted with 3.25 mL Et₂O and the organic layer dried (MgSO₄). The solvent was evaporated, the residue filtered through silica; pentane eluent removed - pinene, whereas the Et₂O eluent afforded the alcohol **8** which on distillation yielded 1.87 g, bp 80°C/15 mm (92%), GC purity 99%, $\alpha_D = -17.3^\circ\text{C}$ (c 2.4 MeOH, 100% ee).

(S)-(-)-(Trifluoromethyl)oxirane 12.⁸ B-chlorodiisopinocampheylborane **10** (8.8 g, 27.5 mmol) in Et₂O (25 mL) under N₂ was cooled to -25°C and **9** (4.7 g, 25 mmol) was added using a syringe. The reaction was followed by ¹¹B NMR (¹¹B: 32 ppm) for 96 h, when the reaction was complete. At 0°C was added diethanolamine (5.3 mL, 55 mmol), then the mixture was heated to 20°C and stirred for 2 h, whereupon the borane precipitated as a complex which was filtered and washed with pentane. The solvent was removed, the residue added to 15 N NaOH (10 equiv.) and heated at 95-100°C to distill the epoxide. This afforded 1.536 g of **12** (64%, 96% ee).

BROWN Stereoselective Reduction

Stereoselective reduction of ketones to alcohols by means of borohydride reagents (Li $s\text{-Bu}_3\text{BH}$) or $t\text{-BuClBR}^+$ for formation of chiral alcohols.



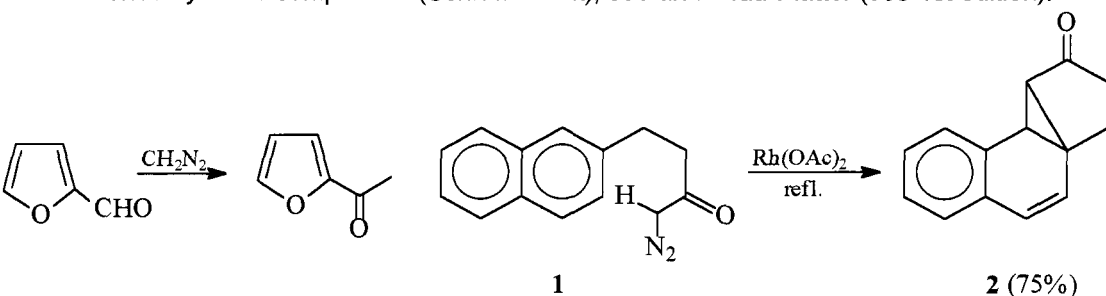
1	Brown, H.C.	<i>J. Am. Chem. Soc.</i>	1970	92	709
2	Brown, H.C.	<i>J. Am. Chem. Soc.</i>	1972	94	1750
3	Brown, H.C.	<i>Chem. Commun.</i>	1972		868
4	Brown, H.C.	<i>J. Am. Chem. Soc.</i>	1972	94	7159
5	Brown, H.C.	<i>J. Org. Chem.</i>	1989	54	4540
6	Brown, H.C.	<i>J. Org. Chem.</i>	1995	60	41

Cis-4-tert-butylcyclohexanol 2.⁴ To 1M lithium trimethoxyaluminium hydride (LTMA) (5.0 mL) in THF under N_2 , was added *sec*-butylborane (from 2-butene and diborane), 1.25 mL, 5 mmol. After 30 min the mixture was cooled to -78°C and **1** (390 mg; 2.5 mmol) was added. After 3 h, hydrolysis and oxidation (H_2O_2) gave **2** (96.5% *cis* and 3.5% *trans*).

(S)-Cyclohexylethanol 6.⁵ To 5.5 mmol of **4** in THF (from Li- $t\text{BuBH}_3$, HCl followed by (-)-2-ethylapopinene **3**, $\alpha_D = -42.78^\circ$) was added **5** (0.64 g; 5 mmol) under N_2 . After 2 days the solvent was removed, the residue dissolved in Et_2O (20 mL), diethanolamine (2.2 equiv.) was added and stirred for 2 h. After filtration and washing with pentane, the filtrates were concentrated and chromatography gave 0.42 g of **6** (65%), 90% ee.

BUCHNER-CURTIUS-SCHLOTTERBECK Homologation

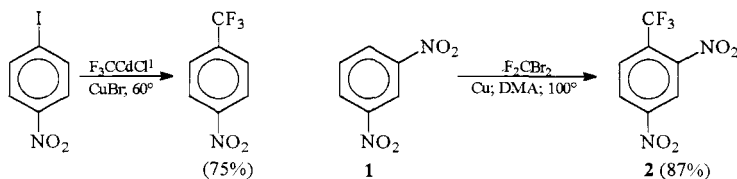
Ring enlargement of benzene derivatives by carbenes generated from diazo compounds (better in the presence of a Rh catalyst). Conversion of aldehydes to ketones by diazo compounds (Schlotterbeck); see also Pfau-Platter (see 1st edition).



1	Buchner, E.; Curtius, T.	<i>Chem. Ber.</i>	1885	18	2371
2	Buchner, E.	<i>Chem. Ber.</i>	1896	29	106
3	Schlotterbeck, F.	<i>Chem. Ber.</i>	1907	40	479
4	Ramonczay, J.	<i>J. Am. Chem. Soc.</i>	1950	72	2737
5	Doering, W.v.	<i>J. Am. Chem. Soc.</i>	1957	79	352
6	Anciaux, A.J.	<i>J. Org. Chem.</i>	1981	46	873
7	Manitto, P.	<i>J. Org. Chem.</i>	1995	60	484

BURTON Trifluoromethylation

Trifluoromethylation of aryl iodides or nitroarenes with Cd(Cu) reagents (see 1st edition).

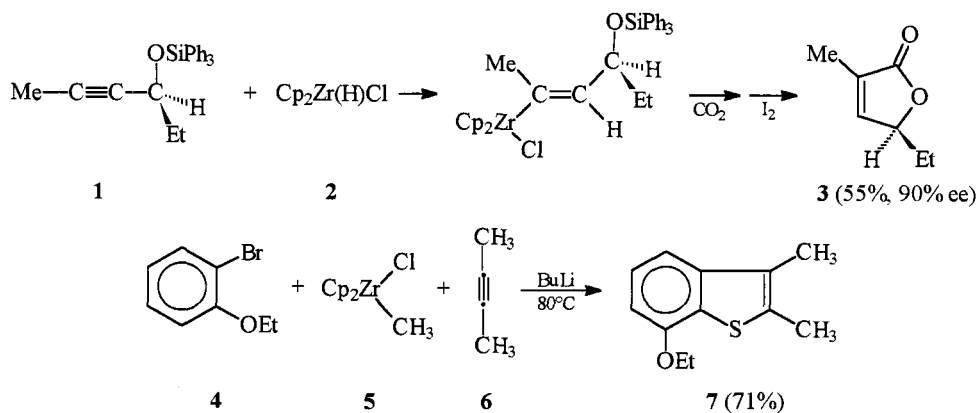


1	Burton, D.J.	<i>J. Am. Chem. Soc.</i>	1985	107	5014
2	Burton, D.J.	<i>J. Am. Chem. Soc.</i>	1986	108	832
3	Clark, J.H.	<i>J. Chem. Soc. Chem. Commun.</i>	1988		638
4	Clark, J.H.	<i>Tetrahedron Lett.</i>	1989	30	2133

1-Trifluoromethyl-2,4-dinitrobenzene 2.⁴ A mixture of *m*-dinitrobenzene **1** (840 mg; 5 mmol), metallic Cu (1.905 g; 30 mat), dibromodifluoromethane (2.43 g; 11 mmol), charcoal (1 g) (dried at 280°C) in dimethylacetamide (7.5 mL) was heated to 100°C under N₂, to afford 1.026 g of **2** (87%).

BUCHWALD Heterocyclization

Preparation of benzisothiazoles, butenolides or pyrroles using organo-zirconium reagents and acetylenes.



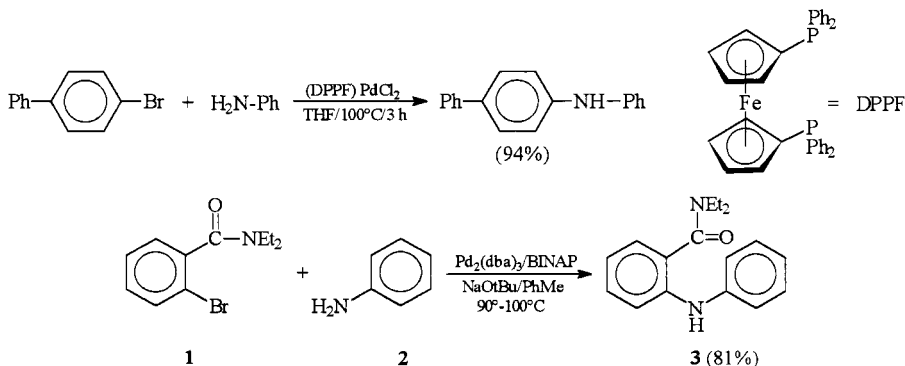
1	Buchwald, S.L.	<i>J. Am. Chem. Soc.</i>	1987	109	7137
2	Buchwald, S.L.	<i>Tetrahedron Lett.</i>	1988	29	3445
3	Buchwald, S.L.	<i>J. Am. Chem. Soc.</i>	1989	111	776
4	Buchwald, S.L.	<i>J. Org. Chem.</i>	1989	54	2793
5	Buchwald, S.L.	<i>J. Am. Chem. Soc.</i>	1991	113	4685
6	Buchwald, S.L.	<i>Chem. Rev.</i>	1988	88	1044
7	Gribble, G.W.	<i>Contemp. Org. Synth.</i>	1994	1	145

Chiral butenolide 3.² A mixture of **1** (995 mg; 2.79 mmol) and $\text{Cp}_2\text{Zr}(\text{H})\text{Cl} **2** (791 mg; 3.07 mmol) in PhH (30 mL) were stirred at 20°C under Ar for 16 h. After degassing, the mixture was stirred under a CO_2 atm for 6 h. A solution of I_2 (708 mg; 2.79 mmol) in PhH (20 mL) was added and stirring was continued for 1 h. Usual work up and chromatography (radial), pentane: Et_2O (9:1 to 7:3) gave 1.93 g of **3** (55%), 90% ee.$

7-Methoxy-2,3-dimethylbenzo[b]thiophene 7.⁴ To 2-bromoanisole **4** (385 mg; 2 mmol) in THF (10 mL) at -78°C was added BuLi (1.2 mL 1.68M; 2.2 mmol). After 15 min stirring, zirconocene(methyl)chloride **5** (570 mg; 2.1 mmol) in THF (10 mL) was added followed by 2-butyne **6** (130 mg; 2.4 mmol) and heated for 18 h at 80°C. Usual work up and recrystallization from pentane gave 274 mg of **7** (71%), mp 110-110.5°C.

BUCHWALD - HARTWIG Aryl Halide Amination

Amination of aryl halides in the presence of a base and $\text{Pd}_2(\text{dba})_3$ + BINAP (Buchwald) or $(\text{DPPF})\text{PdCl}_2$ (DPPF = 1,1'-bis(diphenylphosphino-ferrocene) (Hartwig).

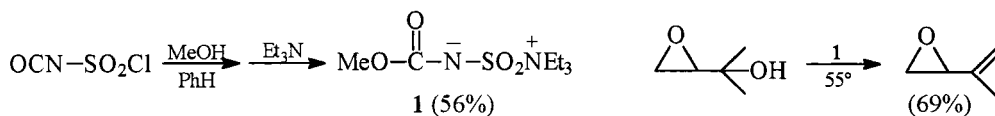


1	Buchwald, S.L.	<i>J. Am. Chem. Soc.</i>	1996	118	7215
2	Hartwig, J.F.	<i>J. Am. Chem. Soc.</i>	1996	118	7217
3	Snieckus, V.	<i>Synlett</i>	1998		419

Amide 3. **1** (505 mg; 1.97 mmol), **2** (0.21 mL; 2.30 mmol), NaOtBu (266 mg; 2.77 mmol), $\text{Pd}_2(\text{dba})_3$ (5 mg; 0.006 mmol), BINAP (11 mg; 0.017 mmol) and PhMe (5 mL) under N_2 were heated for 21 h at 90-100°C. Work up and chromatography afforded 426 mg of **3** (81%), mp 74-76°C.

BURGESS Alcohol Dehydration

Thermolysis of tertiary and secondary alcohols with (carbomethoxysulfamoyl) triethylammonium inner salt **1** or polymer linked reagent⁶ to give olefins; also conversion of amides to nitriles (see 1st edition).



1	Burgess, E.M.	<i>J. Org. Chem.</i>	1973	38	26
2	O'Grodnick, J.S.	<i>J. Org. Chem.</i>	1974	39	2124
3	Goldsmith, D.J.	<i>Tetrahedron Lett.</i>	1980	21	3543
4	Claremon, D.A.	<i>Tetrahedron Lett.</i>	1988	29	2155
5	Burgess, E.M.	<i>Org. Synth.</i>	1977	56	40
6	Wipf, P.	<i>Tetrahedron Lett.</i>	1996	37	4659
7	Wipf, P.	<i>Tetrahedron</i>	1998	54	6987
8.	Wipf, P.	<i>Chem. Rev.</i>	1995	95	2115