trate test,[5] indicating the presence of ionic chloride. It appears, therefore, that the reaction occurs by hydrogenolysis of the chloroform to produce very small quantities of hydrogen chloride, which combines immediately with the amine as it is formed by reduction.

Experimental Section[6]

General Procedure.—The hydrogenations were carried out on a Parr apparatus as indicated in Table I followed by filtration through Hyflo-Supercel and evaporation of the solvent under reduced pressure. Unless otherwise indicated, the material left after evaporation to dryness was used for characterization.

Methyl 5-amino-5-deoxy-2,3,-*O*-isopropylidene-β-D-ribofuranoside hydrochloride (2) was obtained as a colorless solid, mp 189.5–190° dec. Recrystallization from absolute EtOH gave **2**, mp 200.5–201.5° dec (lit.[7] 201.5–202°).

***n*-Propylamine hydrochloride, *n*-butylamine hydrochloride, and benzylamine hydrochloride** were obtained as colorless solids, mp 153–154° (lit.[8] 155–158°), 201–203° (lit.[9,10] 195 and 215°), and 253–254° (lit.[11] 255–256°), respectively.

***p*-Toluidine hydrochloride** was obtained as a gray solid, mp 233.5–237.5°. Sublimation gave colorless material, mp 238.5–239.5° (lit.[12] 238–240°).

***n*-Heptylamine Hydrochloride.**—After filtration of the hydrogenation mixture through Hyflo-Supercel, the filtrate was evaporated to dryness. The residue was then washed with ether to give a colorless solid, which turned to a gel (200°) and became fluid at 256–259°. An authentic sample prepared by a Gabriel synthesis behaved identically.

Registry No.—2, 14131-79-2; chloroform, 67-66-3; *n*-propylamine HCl, 556-53-6; *n*-butylamine HCl, 3858-78-4; benzylamine HCl, 3287-99-8; *p*-toluidine HCl, 540-23-8; *n*-heptylamine HCl, 142-93-8.

(5) Pretested chloroform gave a negative silver nitrate test.

(6) All melting points were determined on a Thomas-Hoover capillary melting point apparatus in sealed capillaries and are corrected.

(7) N. J. Leonard and K. L. Carraway, *J. Heterocycl. Chem.*, **3**, 485 (1966).

(8) E. Linnemann and V. Zotta, *Justus Liebigs Ann. Chem.*, **161**, 45 (1872).

(9) E. Linnemann and V. Zotta, *ibid.*, **162**, 4 (1872).

(10) W. H. C. Rueggenberg and M. M. Falkof, *J. Amer. Chem. Soc.*, **67**, 2052 (1945).

(11) M. Konowalow, *Ber.*, **28**, 1861 (1895).

(12) C. A. Bischoff and P. Walden, *Justus Liebigs Ann. Chem.*, **279**, 130 (1894).

Metal-Amine Reactions.[1a,b] Selective 1,2′-Reductive Dimerization of Naphthalene

L. E. Harris[2] and E. J. Eisenbraun*

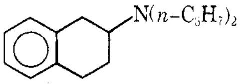
Department of Chemistry, Oklahoma State University,
Stillwater, Oklahoma 74074

P. W. Flanagan, M. C. Hamming, and G. W. Keen

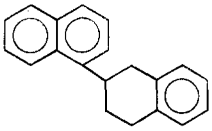
Research and Development Department,
Continental Oil Company, Ponca City, Oklahoma 74601

Received March 23, 1971

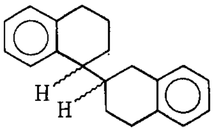
The reduction of naphthalene with sodium and amines yields numerous products, including 1,2-dihydronaphthalene (**1**), 1,4-dihydronaphthalene (**2**), 1,2,3,-4-tetrahydronaphthalene (**3**), reductive amination products, C_{20} dimers, and decreasing amounts of C_{30} and C_{40} products.[1a-c] The product distribution varies considerably depending on reaction conditions and the selection of the amine.[1a,b] If steric effects are present in the amine, reductive amination diminishes and reductive dimerization may increase; *e.g.*, piperidine gave 46% reductive amination of naphthalene and 11% of a mixture of C_{20} dimers, whereas dipropylamine caused formation of 6% of **4** and 55% of a mixture of reductive dimerization products[1a] now known to be **5**, **6**, and **7**. In our current work with sodium and dipropylamine using a specialized apparatus,[3a] the yield of **4** is 12% and the combined yield of **5**, **6**, and **7** is 62%. In the earlier work, two C_{20} dimers, 1,1′,2,2′,3,3′,4,4′-octahydro-2,2′-binaphthyl and 5,6,6a,6b,11,12,12a,-12b-octahydrodibenzo[*a,g*]biphenylene, were frequently observed, particularly with primary diamines.[1b] We now know there are, however, systems in which they are minor products or may not appear. One of these, sodium and dipropylamine, was chosen for detailed study because the resulting C_{20} dimer mixture was less complex. Indeed, we have learned that in this system a remarkably selective formation of 1,2′-coupled C_{20} dimers results. The major component of the dimer fraction,[3b] a colorless crystalline hydrocarbon, is shown to be 1′,2′,3′,4′-tetrahydro-1,2′-binaphthyl (**5**). It gives a molecular ion *m/e* 258.1408 and both analytical and spectral data are consistent with structure **5**. Hydrocarbon **5** shows uv absorption characteristic of an aliphatic-substituted naphthalene and forms a picrate that can be decomposed by stirring with petroleum ether and eluting through a column of basic alumina. The hydrocarbons **6** and **7** did not form picrates.



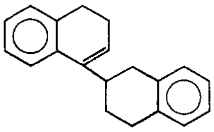
4



5



6



7

At room temperature, dimers **5**, **6**, and **7** were formed in the ratio 73:11:16, respectively. At higher temperatures (40–80°) dimer **5** was the C_{20} hydrocarbon formed almost exclusively.

To obtain pure **6**, a mixture of **5**, **6**, and **7** was treated with Pd/C in refluxing toluene[3c] and the resulting mixture of **5** and **6** was separated by column chromatography. The ir spectrum of **6** thus prepared from **7** is very similar[4a] to that of **6** obtained by hydrogenation

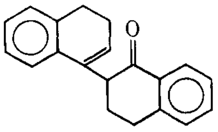
(1) (a) E. J. Eisenbraun, R. C. Bansal, D. V. Hertzler, W. P. Duncan, P. W. K. Flanagan, and M. C. Hamming, *J. Org. Chem.*, **35**, 1265 (1970); (b) R. C. Bansal, E. J. Eisenbraun, and P. W. K. Flanagan, *J. Amer. Chem. Soc.*, **88**, 1837 (1966); (c) L. Reggel, H. W. Sternberg, and I. Wender, *Nature (London)*, **190**, 81 (1961).

(2) Continental Oil Company Fellowship, 1970–1971, and National Aeronautical and Space Administration Trainee, 1969–1970.

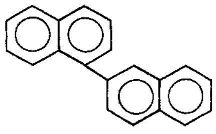
(3) (a) E. J. Eisenbraun and H. Hall, *Chem. Ind. (London)*, 1158 (1971). (b) Correspondence regarding this reference hydrocarbon and other samples should be addressed to Mr. A. J. Streiff, American Petroleum Institute, Carnegie-Mellon University, Pittsburgh, Pa. 15213. (c) L. E. Harris, W. P. Duncan, M. J. Hall, and E. J. Eisenbraun, *Chem. Ind. (London)*, 403 (1971).

(4) (a) Dimer **6** from both sources is a liquid. It should be recognized that **6** may possibly be a mixture of racemates and hence minor differences in the infrared spectra of samples from independent sources are to be expected. (b) J. M. Springer, C. W. Hinman, E. J. Eisenbraun, P. W. K. Flanagan, and M. C. Hamming, *J. Org. Chem.*, **35**, 1260 (1970). (c) H. L. Retcofsky, L. Reggel, and R. A. Friedel, *Chem. Ind. (London)*, 617 (1969). (d) We thank Mr. J. W. Burnham for a sample of **8** prepared by acid-catalyzed dimerization of 1-tetralone.

of **8**[4b-d] with Pd/C and its nmr spectrum is consistent with structure **6**. Dimer **7** was identified by its nmr and uv spectra and its facile disproportionation with Pd/C catalyst in boiling toluene to **5** and **6**.[3c]



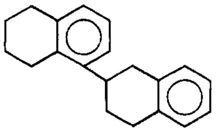
8



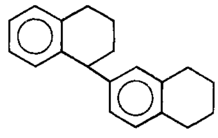
9

Evidence for the absence of any dimers with a 1,1′ or 2,2′ ring system among the reaction products was obtained by total aromatization. Treatment of the reaction mixture of **5**, **6**, and **7** with Pd/C at 350° gave a 92% yield of 1,2′-binaphthyl (**9**). Analysis of this dehydrogenation product by glc showed that 1,1- and 2,2′-binaphthyl were absent. A sample of the 1,2′-binaphthyl prepared by Pd/C dehydrogenation of **6** from **8** was compared with **9** from the dehydrogenation of **5**, **6**, and **7** and these were found through melting point of a mixture and spectral comparison to be identical.

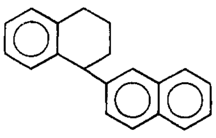
Additional evidence that **5** could not be represented by structure **12** was obtained by reducing **5** with Pd/C to **6**:**10** (62:38) and by reduction of **5** with sodium and diethylamine, and then treating with Pd/C in refluxing toluene[3c] to give **5**:**6**:**10** (62:1:37). Since glc studies of these mixtures showed that **11**[5] was not present, it is unlikely that **12** or **13** are formed. The presence of the latter would be revealed by its ready disproportionation to **6** and **12** in the presence of Pd/C in boiling toluene.[3c]



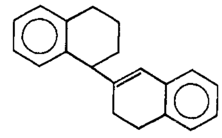
10



11



12



13

Experimental Section[6]

The amines, obtained from Union Carbide Co., were dried by stirring (24 hr) with KOH, decanting, and distilling from fresh KOH. The high-purity naphthalene was a gift from Sun Oil Co. The sodium (Matheson Coleman and Bell) was reagent grade, $^1/_{16}$ to $^1/_4$ in. spheres, and was washed with sulfuric acid treated petroleum ether[6a] before use. The 10% Pd/C catalyst was purchased as a stock item from Engelhard Industries, Newark, N. J.

Melting points were determined with a Hoover-Thomas capillary tube melting point apparatus and are corrected. The uv and ir spectra were obtained with a Cary Model 14 and a Beckman Model IR-5A spectrophotometer, respectively. The nmr spectra (CCl_4) were obtained with Varian HR-60 and HA-100 instruments (TMS standard) and mass spectra with a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer. The elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn.

Reduction of Naphthalene with Sodium and Dipropylamine.—To 12.8 g (0.1 mol) of naphthalene and 250 ml of di-*n*-propylamine (bp 109°) in the reaction flask[3a] was added 9.2 g (0.4 g-atom) of sodium over a period of several hours. A dark brown color developed within 20 min. The mixture was stirred at room temperature for 24 hr and then withdrawn from the unreacted sodium. The reaction mixture was poured cautiously over 400 ml of crushed ice and an orange emulsion resulted. This was extracted with 500 ml of ether (three portions) and the ether layer, which contained the hydrocarbons, was washed with water, twice with 10% aqueous HCl, and then with water until neutral. The acidic extracts and water washings were combined, made basic with NaOH, and extracted with ether. The ether layer was washed with water, dried (Na_2SO_4), and concentrated to yield 1.7 g of amine fraction.

The ether layer containing the amine-free hydrocarbons was dried (Na_2SO_4) and concentrated. The solution was steam distilled and both the pot residue and steam distillate were extracted with ether and dried (Na_2SO_4). Distillation of the extract of the steam distillate yielded 6.3 g of steam-volatile hydrocarbons. These were shown by glc analysis to be a mixture of unreacted naphthalene and **3** in a 93:7 ratio.

The ether extract of the steam-distillation pot residue was concentrated (rotary evaporator) to yield 6.4 g of a dark, viscous oil. This material was distilled [175–180° (0.2 mm)] to give 4.3 g (62%)[6c] of a light yellow oil which was shown by glc analysis to be a mixture of **5**:**6**:**7** (73:11:16).

Isolation and Identification of 1′,2′,3′,4′-Tetrahydro-1,2′-binaphthyl (5).—A portion (1 g) of the distilled dimer mixture was dissolved in absolute ethanol, and picric acid (1 g) was added. This mixture was heated until solution was complete, then allowed to cool slowly. The crystalline picrate was filtered out and washed with absolute ethanol. After recrystallization from the same solvent, the yellow needles melted at 101–104°. The hydrocarbon was regenerated by stirring the picrate with petroleum ether (bp 60–68°) and eluting through basic alumina. The clear oil obtained upon concentration of the solution was triturated with petroleum ether until crystals formed. Recrystallization from methanol gave **5** as white needles: mp 64–65°; ir (melt) 3030, 2820, 1600, 1580, 1515, 1498, 1458, 1439, 1402, 1255, 951, 799, 779, 760, and 743 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 258 (73), 154 (31), 153 (43), 130 (47), 128 (34), 104 (100); nmr (CCl_4) δ 8.08–6.72 (broad m, 11, Ar H, sharp s at 6.92), 3.91–2.44 (overlapping m, 5, Ar CH and Ar CH_2), and 2.28–1.61 (m, 2, CH_2); uv max (95% C_2H_5OH) 226 mμ (ϵ 83,600), 274 (7345), and 283 (8240).

Anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 93.15; H, 7.08.

Isolation and Identification of 1,1′,2,2′,3,3′,4,4′-Octahydro-1,2′-binaphthyl (6) and 1′,2′,3,3′,4,4′-Hexahydro-1,2′-binaphthyl (7).—The mother liquor recovered from the picrate preparation in the previous scheme was concentrated, petroleum ether was added, and the slurry was poured onto a column containing basic alumina. Elution with petroleum ether yielded a mixture of the three dimers **5**, **6**, and **7** in which the latter two were shown by glc studies to be the major constituents.

This dimer fraction (1.5 g) was mixed with 10% Pd/C (0.15 g) and 100 ml of toluene in a 200-ml, one-neck flask equipped with condenser and magnetic stirring bar. After being refluxed for 2 hr, the suspension was filtered to remove catalyst and concentrated to give 1.4 g of viscous oil containing **5** and **6** and none of **7**.

This oil was chromatographed (1.25 × 18 in. column) over silica gel (30–200 mesh) and basic and acidic alumina. Dimer **6** was eluted in the first fraction with petroleum ether.[6a] After distillation, **6** was obtained: bp 175–180° (0.2 mm); ir (film) 3010, 2925, 1700, 1670, 1490, 1450, 1435, 1040, 948, 762, 739 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 262 (8), 132 (21, 131 (100), 130 (30), 129 (17), 115 (15), and 91 (22); nmr δ 7.32–6.72 (m, 14, Ar H) and 3.08–1.12 (overlapping m, 14,

---

(5) An authentic sample of hydrocarbon **11** was kindly supplied by W. D. Vanderwerff, Sun Oil Co.

(6) (a) The petroleum ether, bp 60–68°, was distilled before use. (b) Glc analyses for the hydrocarbons were obtained on a Hewlett-Packard Model 5750 glc apparatus fitted with thermal conductivity and hydrogen flame detectors using helium as the carrier gas. For the dimer hydrocarbons, a 0.25 in. × 11 ft column of 5% UC W-98 methyl vinyl silicone rubber coated on acid-washed and DMCS-treated Chromosorb G (80–100 mesh) at 265° was used. For the steam-volatile hydrocarbons, a 0.25 in. × 10 ft column of 25% Carbowax 20M coated on Chromosorb W (30–60 mesh) at 190° was used. (c) This yield was calculated from the amount of unrecovered naphthalene and was based on the mixture of **5**, **6**, and **7**.

Ar CH, Ar CH_2 and CH_2); uv max (95% C_2H_5OH) 256 mμ (ε 2280), 267 (1935), and 274 (1950).

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.32; H, 8.67.

Dimer **7**, isolated from the mixture by preparative gas chromatography (UC W-98 on acid-washed Gas-Pack W), was a viscous liquid: bp 180° (0.2 mm); ir (film) 3000, 2900, 2820, 1480, 1450, 1430, 1040, 1020, 806, 767, 737 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 260 (51), 131 (63), 130 (62), 129 (100), 128 (74), 115 (43), and 104 (69); nmr (CCl_4) δ 6.97 (m, 8, Ar H), 5.83 (t, 1, vinyl), 3.2–2.45 (m, 6, Ar CH_2), 2.4–1.4 (overlapping m, 5, Ar $CH_2\mathbf{CH_2}$ and >C=CHC**H**); uv max (95% C_2H_5OH) 202 mμ (ε 10,100) and 268 (5500).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.90.

Synthesis of 1,2′-Binaphthyl (9) by Dehydrogenation of C_{20} Dimers.—The dimer fraction (4.3 g of **5**, **6**, and **7**) was mixed with 10% Pd/C (0.5 g) in a 50-ml one-neck flask equipped with reflux condenser and gas outlet tube. As the flask was lowered into a preheated (350°) Woods metal bath, vigorous evolution of gas occurred. After 10 min, gas evolution had subsided, but heating was continued for 1 hr. After cooling, the residue was dissolved in petroleum ether,[6a] filtered, and concentrated to give 4.0 g of viscous yellow oil. The latter was distilled [153–158° (0.02 mm)] to give 3.9 g (92%) of light yellow solid. This constitutes a 57% yield of **9** based on the amount of reacted naphthalene. After elution through alumina and silica gel with petroleum ether,[6a] followed by concentration of the solution, a white solid was obtained: mp 76.5–77.5° (lit.[7] mp 76°); mmp with **9** prepared from **8**,[3c] 76–77°; mass spectrum (70 eV) *m/e* (rel intensity) 254 (100), 253 (72), 252 (53), 250 (13), 127 (10), 126 (27); nmr ($CDCl_3$) δ 7.18–8.05 (m).

Reduction of 5 with Sodium and Diethylamine.—To 6.5 g (0.025 mol) of **5** in 250 ml of diethylamine was added 2.3 g (0.1 g-atom) of Na over a period of several hours. A dark brown color developed in less than 1 min and persisted throughout the reaction time of 22 hr. The reaction mixture was quenched in ice and extracted with ether, and the ether solution was extracted with 10% HCl.

The ether remaining after washing with water was dried (Na_2SO_4) and concentrated to give 5.8 g of hydrocarbons. The acidic and aqueous extracts were combined, made basic with NaOH and extracted with ether, dried (Na_2SO_4), and concentrated to give 0.7 g of nonvolatile amines.

The hydrocarbon fraction showed a trace of **6** and **7**, 10% of **5**, and 89% of an undetermined mixture. When the latter (2.5 g) was treated as before with Pd/C (0.25 g) in 100 ml of refluxing toluene for 5 hr,[3c] a viscous oil (2.1 g) was obtained which showed the ratio **5**:**6**:**10** (62:1:37) by glc.[6b]

Isolation and Identification of 1′,2′,3′,4′,5,6,7,8-Octahydro-1,2′-binaphthyl (10).—The mixture from the preceding reduction was eluted with petroleum ether[6a] through a column of silica gel and basic, acidic, and neutral alumina. From the first fraction which eluted from the column, pure **10** was obtained: bp 175–180° (0.2 mm); ir (film) 2990, 2800, 2690, 1580, 1488, 1455, 1433, 772, 743, 716 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 262 (50), 131 (27), 130 (100), 129 (23), 115 (21), 104 (100); nmr (CCl_4) δ 6.96 (m, 7, Ar H), 3.30–2.45 (m, 9, Ar CH and Ar CH_2), 2.12–1.45 (m, 6, CH_2); uv max (95% C_2H_5OH) 258 mμ (ε 1208), 267 (1085), 274 (888).

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.83; H, 8.40.

Catalytic Reduction of 5, 6, and 7.—A mixture (3.6 g) of **5**:**6**:**7** (32:9:9) was stirred (Teflon-covered magnet) at 25° in a 500-ml fluted flask with 0.4 g of 10% Pd/C and 150 ml of 95% ethanol. Hydrogen (1 atm) was introduced and after 5 days, **5** and **7** had disappeared. After filtration (Dicalite Filter-aid) and concentration, a viscous oil remained (3.2 g) which proved to be a mixture of **6**:**10** (62:38) by glc analysis.

Registry No.—**5,** 32675-22-2; **6,** 27426-98-8; **7,** 23439-78-3; **9,** 4325-74-0; **10,** 32675-26-6; naphthalene, 91-20-3.

Acknowledgments.—We are grateful to the American Petroleum Institute and the Research Foundation, Oklahoma State University, for their assistance. We thank Dr. O. C. Dermer for having read the manuscript.

---

[7] H. A. Weidlich, *Ber.*, **71B**, 1201 (1938).

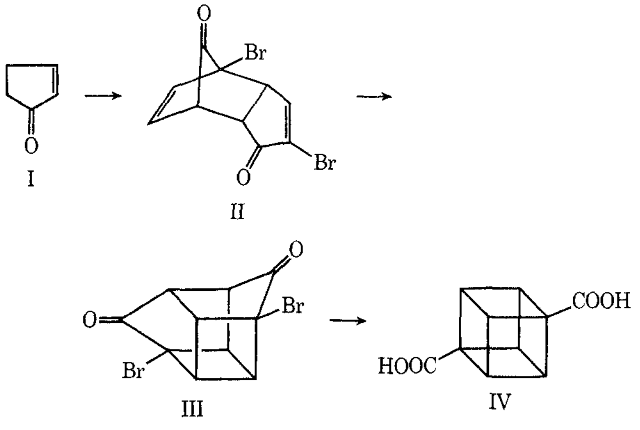
On the Preparation of 1,4-Dicarboxycubane[1]

TIEN-YAU LUH AND LEON M. STOCK*

Department of Chemistry,
University of Chicago, Chicago, Illinois 60637

Received June 30, 1971

The synthesis of cubane and several important derivatives including the 1,4-diacid was reported in a communication in 1964.[2] Recently, Chapman and his associates[3] have reported a closely related alternative route, chosen because of difficulties encountered in their attempts to follow the preparative method outlined by Eaton and Cole[2] for the synthesis of 1,4-disubstituted cubanes. We wish to report that we have employed the original approach without difficulty. The procedures derive from those employed by Cole[4] and are described fully in the Experimental Section. We note in particular that the conversion of the caged dimer III to 1,4-dicarboxycubane (IV) was accomplished with potassium hydroxide in 55% yield and with sodium hydroxide in 44 (first experiment), 70, 75, 78, and 72% yield, respectively.



Experimental Section

2-Cyclopentenone (I).—A mixture of cyclopentendiols (100 g, 1.0 mol) was converted to 2-cyclopentenone by the method of Depuy and Eilers.[5] A second fractionation of the initial product provided colorless 2-cyclopentenone (47 g, 57%, bp 151–154°).

2,4-Dibromo-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (II).—2-Cyclopentenone (50 g, 0.61 mol) was added to a slurry of *N*-bromosuccinimide (240 g, 1.45 mol) in carbon tetrachloride (700 ml). The reaction mixture was heated to reflux, stirred vigorously, and illuminated with a General Electric sun lamp to start the reaction. After the initial exothermic reaction had subsided, additional 2-cyclopentenone (50 g) was added. The solution was refluxed for 3 hr. The cooled reaction mixture was filtered and the filtrate was concentrated *in vacuo* at room temperature. The residue was dissolved in anhydrous ether (1 l.) previously saturated with lithium bromide (dried overnight at 100° *in vacuo*). The solution was cooled to −30°. Bromine (1.17 mol) was then added dropwise at a rate approximately equal to the reaction rate. The bath temperature was maintained at −30 to −35°. After the bromination reaction was complete,

---

[1] This research was supported by a grant from the National Science Foundation.

[2] P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 962, 3157 (1964).

[3] N. B. Chapman, J. M. Key, and K. J. Toyne, *J. Org. Chem.*, **35**, 3860 (1970).

[4] T. W. Cole, Jr., Dissertation, University of Chicago, 1966.

[5] C. H. Depuy and K. L. Eilers, *Org. Syn.*, **42**, 38 (1962).