recorded in the literature (bisacetamide, dihydrochloride, and dipicrate), with the correct melting points being observed.

Diindano[3,2-*b*;2′,3′-*f*]-13,16-diaza-5,7-diboraoxepane (VII).—Sublimation of the crude reaction mixture at 200° (0.015 mm) yielded crude pentacycle VII (35% by weight of crude, 17% yield based upon I). Several more sublimations provided an analytical sample which melted in a sealed capillary under nitrogen at 198–211° dec.

Anal. Calcd for $C_{16}H_{16}B_2N_2O$: C, 70.15; H, 5.89; N, 10.23; mol wt, 280. Found: C, 69.85; H, 6.10; N, 10.27; mol wt, 246 (Rast), 313 (osmometer).

In the infrared the substance showed no OH or NH absorption, but it did show a strong band attributable to BO at 1350 with two bands in the 757–729-cm^{-1} region, either of which, or both, could be assigned to *ortho* substitution. Acid-catalyzed deboronation of II yielded 37% N,N′-dibenzylethylenediamine, identified by its infrared spectrum.[22]

N-(*o*-Boronobenzyl)ethylenediamine-N′ Hydrobromide.—The analytically pure hydrobromide was obtained from those preparations of crude reaction mixtures wherein high purity I was used. Sometimes the yield was nil; it was never greater than 2% based upon I. This procedure was followed with the salt appearing as a white precipitate during the extraction with chloroform. The crystals were collected on a sintered-glass funnel, rinsed, and dried under vacuum: mp 305–306° dec, when introduced in an open capillary at 299°.

Anal. Calcd for $C_9H_{16}BBrN_2O_2$: C, 39.31; H, 5.87; Br, 29.06; N, 10.19. Found: C, 39.38; H, 5.54; Br, 29.57; N, 10.47.

The infrared spectrum was consistent for a boronic acid containing a primary amine hydrobromide moiety (primary ammonium band overlapping CH stretch).[20a] As evidenced by infrared spectra, a sample of this salt slowly sublimed unchanged at 306° (0.012 mm). No dehydration was noted, and the recovery was at least 89%.

A solution of 38 mg of N-(*o*-boronobenzyl)ethylenediamine-N′ hydrobromide (0.138 mmole) in 1.0 ml of water was agitated with 18 mg of silver oxide (0.155 mequiv, or 112% of theory)[23] for 15 min at 25°. Then the water was removed under vacuum from the resulting gray solids and the residue was extracted thrice with 1.0-ml portions of hot methanol. The methanol was filtered and concentrated to a yellow oil weighing 12 mg. This proved to be a free amine with an infrared spectrum very like that of materials from which the hemisulfate was obtained, and probably was unencumbered VIII. Unfortunately, it was not successfully purified, although it could be converted to the hemisulfate. The infrared spectrum of the oil was not that of N-benzylethylenediamine and the oil contained boron; hence no heavy metal-catalyzed deboronation was noted under these conditions.

Registry No.—I, 7481-16-5; *o*-(*t*-butylaminomethyl)-benzeneboronic acid hydrochloride, 7491-62-5; *o*-(*t*-butylaminomethyl)benzeneboronic acid, 7481-22-3; bis(2-*t*-butyl-1,2-boraazaindanyl-1) oxide, 7481-21-2; IV, 7492-95-7; VI, 7481-20-1; VIII hemisulfate, 7481-17-6; VII, 7481-18-7; N-(*o*-boronobenzyl)ethylenediamine-N′ hydrobromide, 7481-19-8.

Acknowledgment.—The authors express thanks for the technical assistance of Danny L. Elder, Doyle B. Stroup, Walter B. Sudweeks, Mrs. Clair H. Nelson, and Professor J. H. Wing, and gratitude is expressed to the National Institutes of Health for support and to Brigham Young University for a Faculty Research Fellowship granted to one of us (R. T. H.).

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[22] "Sadtler Standard Spectra," Midget ed., Sadtler Research Laboratories, Philadelphia, Pa., 1956, No. 6271.

[23] This was at the suggestion of Professor H. R. Snyder, University of Illinois.

An Approach to the Synthesis of Tetrabenzo[*a*,*c*,*g*,*i*]heptalene

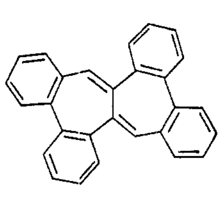
ERNST D. BERGMANN, ISRAEL AGRANAT, AND MENAHEM A. KRAUS

Department of Organic Chemistry, Hebrew University, Jerusalem, Israel

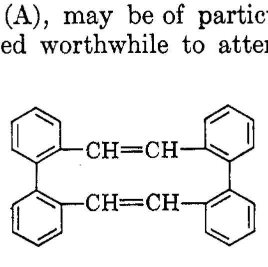
Received November 8, 1966

Diphendialdehyde and 2,2′-bis(cyanomethyl)biphenyl condense, in the presence of sodium ethoxide, to the tetrahydro derivative (IVa) of tetrabenzo[*a*,*c*,*g*,*i*]heptalene. 9,10-Dicyanophenanthrene was a by-product of this reaction. From diphendialdehyde and 2,2′-diaminobiphenyl, 9,20-diazatetrabenzo[*a*,*c*,*g*,*i*]cyclododecene (XIV) was obtained.

Calculations on the electronic structure and on the "pseudo-aromatic" character of heptalene have not yet led to unequivocal results.[1,2] As it has been predicted[1a] that higher benzologs of heptalene, such as tetrabenzo[*a*,*c*,*g*,*i*]heptalene (A), may be of particular theoretical interest, it seemed worthwhile to attempt to synthesize compound A, which is closely related to tetrabenzo[*a*,*c*,*g*,*i*]cyclododecene (B).



A



B

Diphendialdehyde (I) and 2,2′-bis(cyanomethyl)-biphenyl (II) condensed under the influence of sodium ethoxide to a product of the formula $C_{30}H_{20}N_2O$ which is composed of 1 mole each of I and II, minus 1 mole of water. Two formulas (IIIa and IVa) appeared possible *a priori*. The compound contained, indeed, two slightly different nitrile groups (doublet at 2240 and 2225 cm^{-1}) and a secondary hydroxyl; the acetyl derivative absorbed at 1745 cm^{-1} and was thus an ester, and not an amide, and the product could be oxidized to a ketone ($C_{30}H_{18}N_2O$) which absorbed at 1675 cm^{-1} and was thus of the arylalkyl ketone type. The nitrile doublet is explained by the fact that one of the nitrile groups is hydrogen bonded to the hydroxyl; thus, the acetyl derivative and the ketone show only *one* nitrile frequency.

A decision between IIIa and IVa and in favor of IVa was possible on the strength of the following observations: (a) the ultraviolet spectrum of the con-

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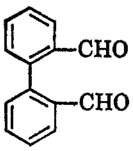
(1) (a) G. Berthier, B. Pullman, and J. Baudet, *J. Chim. Phys.*, **49**, 641 (1952); (b) E. D. Bergmann in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p 141.

(2) (a) T. Nakajima in "Molecular Orbitals in Chemistry, Physics and Biology," P. O. Loewdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p 451; (b) G. Wagnière and M. Gouterman, *Mol. Phys.*, **5**, 621 (1962); (c) H. J. Dauben and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4659 (1961).

densation product showed only the biphenyl peak at 250 $m\mu$; therefore, no double bond is conjugated to the biphenyl system; (b) the infrared spectrum of the condensation product showed no absorption in the 1600–1800-cm^{-1} region where the ethylenic double bond should absorb; (c) the ketone showed an ultraviolet absorption [240, 325, 380 $m\mu$ (log ϵ 1.96)] which is more similar to the spectrum of acetophenone [242, 280, 320 $m\mu$ (log ϵ 1.90)] than to that of α-cyanodeoxybenzoin[3] [250, 288 $m\mu$ (log ϵ 4.04)]; such a cyano ketone would be largely enolized, and the longer absorption band at 288 $m\mu$ is very much stronger than in either our ketone or acetophenone; (d) also for mechanistic reasons, it would seem unlikely that the "symmetric" condensation to IIIa would be completed with elimination of only one molecule of water. The formation of IVa, on the other hand, can be rationalized as follows. The condensation of I and II leads to V, which is transformed into VI by an intramolecular Michael reaction; an aldol-like condensation leads from VI to IVa. The formula of 9a,18-dicyano-9,9a,18,18a-tetrahydro-9-hydroxyeterabenzo[*a,c,g,i*]heptalene (IVa) seems thus most plausible. Final proof was obtained by the nmr spectra of IVa[4] and its acetyl derivative (IVb). The spectrum of IVa contains a multiplet at $\delta = 7.10$–8.00 ppm (16 aromatic hydrogen atoms) and two quartets, both of the AB type. The first one is composed of a doublet at $\delta = 6.00$ ppm (one hydrogen atom), representing the hydroxyl hydrogen, coupled with a doublet at $\delta = 4.97$ ppm (one hydrogen, $J = 0.04$ ppm) related to H_A.[5] The second quartet, too, is composed of two doublets: $\delta = 4.65$ ppm (one hydrogen), corresponding to H_B, coupled with the doublet $\delta = 3.50$ ppm (one hydrogen of H_C, $J_{AB} = 0.13$ ppm). In the nmr spectrum of IIIa the vinylic hydrogen should have given a singlet, and the hydrogen α to the hydroxyl should have given rise to a higher splitting than a doublet (type ABC).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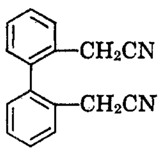
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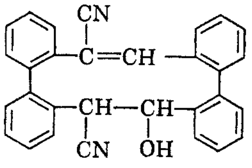
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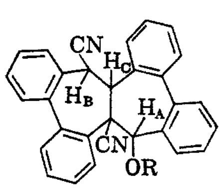
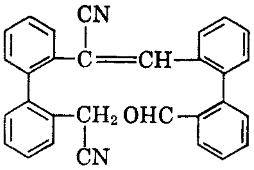

IVa, R = H
b, R = OAc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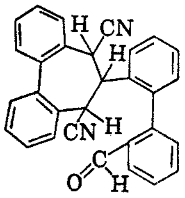
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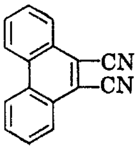
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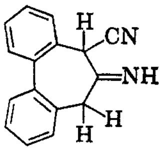
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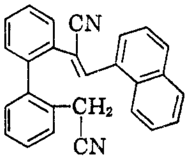
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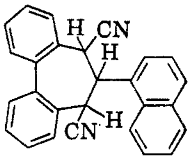
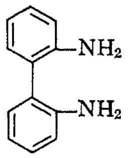

X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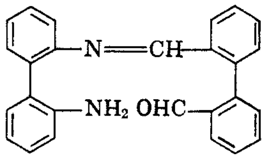
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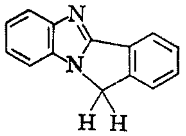
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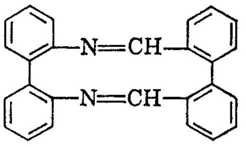
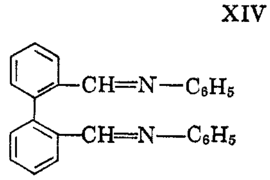

XIV


XV

In the nmr spectrum of the acetate IVb, which is similar to that of IVa, the deshielding effect of the acetoxy group is quite pronounced. Apart from the aromatic multiplet at $\delta = 6.65$–7.80 ppm (16 hydrogen atoms), the spectrum contains a singlet at $\delta = 6.19$ ppm (one hydrogen), a quartet composed of one doublet at $\delta = 4.29$ ppm (one hydrogen), and one at $\delta = 3.81$ ppm (one hydrogen, $J_{AB} = 0.22$ ppm), and a singlet at $\delta = 2.02$ ppm (3.5 hydrogen atoms, methyl group). The singlet at 6.19 represents H_A (which must give a singlet), the doublet at 4.29 H_B, coupled with H_C, which corresponds to the doublet at 3.81. The acetoxy group causes the shift of the H_A absorption to the lower field and the rise in the coupling constant of H_B and H_C as well as the decrease in the distance of the respective two doublets.[6]

In addition to IVa, two other compounds were isolated from the condensation of I with II: (a) a compound of mp 290°, which has very many peaks in the ultraviolet spectrum and shows in the infrared mainly the nitrile absorption; it was identified as 9,10-dicyanophenanthrene (VII)[7] and is obviously obtained by a dehydrogenation of II; and (b) the known product[8] (VIII) of an intramolecular Thorpe reaction of II, 5-cyano-5,7-dihydro-6-imino-6H-dibenzo[*a,c*]cycloheptene.

The reaction between I and II is thus not analogous to the condensation between *o*-phthaldehyde and *o*-bis(cyanomethyl)benzene which leads to a derivative of dibenzocyclooctatetraene.[9]

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[3] P. B. Russell, *J. Am. Chem. Soc.*, **74**, 2654 (1952).

[4] The nmr spectrum of IVa was measured by Dr. U. Scheidegger, Varian A. G., Zurich, Switzerland. We are grateful to Dr. Scheidegger for his courtesy.

[5] The assignment has been proved correct by means of the exchange of the hydroxyl hydrogen by deuterium.

[6] It is recalled that also in benzyl alcohol the hydrogen α to the hydroxyl group absorbs at 4.58 ppm, while its absorption lies at 5.08 ppm in benzyl acetate: NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1963, Spectra No. 161 and 530.

[7] (a) D. G. Coe, E. W. Garnish, M. M. Gale, and C. J. Timmons, *Chem. Ind.* (London), 665 (1957); (b) W. L. Mosby, *J. Org. Chem.*, **24**, 421 (1959).

[8] J. Kenner and E. G. Turner, *J. Chem. Soc.*, 2101 (1911).

[9] L. E. Fieser and M. M. Pechet, *J. Am. Chem. Soc.*, **68**, 2577 (1946).

It seemed of interest to compare the course of the above-described reaction between I and II with the reaction of II and an aromatic monoaldehyde, *e.g.*, α-naphthaldehyde. In all stoichiometric ratios used, only an 1:1 product was isolated, which had neither a double bond nor a hydroxyl group, but showed the nitrile absorption at 2230 cm^{-1}. In view of the results reported here it is assumed that the reaction leads first to IX which undergoes internal Michael reaction to X; here the reaction ends, and no further (aldol) condensation with a second naphthaldehyde molecule occurs.

It was also deemed worthwile to compare the reaction of I and II with that of I and 2,2′-diaminobiphenyl (XI). Formally, the free amino group in the primary product XII could add to the azomethine double bond, but the likelihood of this reaction is much lower than that of an intramolecular Michael reaction. Such reactions do occur in the condensation of diphendialdehyde (II) and *o*-phenylenediamine[10] or phthalaldehyde and *o*-phenylenediamine (to XIII).[11] In fact the condensation product obtained has formula XIV of 9,20-diazatetrabenzo[*a*,*c*,*g*,*i*]cyclododecene. This has been shown by the nmr spectrum of the compound: singlet at $\delta = 8.05$ ppm (two vinylic hydrogen atoms), multiplet at $\delta = 7.75$–7.20 ppm (14 aromatic hydrogen atoms), multiplet at $\delta = 7.08$–6.60 (two hydrogen atoms, *ortho* to the methine groups). For comparison, we quote the vinyl absorption of benzylideneaniline at $\delta = 8.47$ ppm[11b] and—perhaps even more significant—the vinyl absorption of the dianil (XV) of diphendialdehyde at $\delta = 8.35$ ppm.

Experimental Section

2,2′-Bis(cyanomethyl)biphenyl (II), mp 76–78° (from ethanol), was prepared according to Cope and Smith;[12] diphendialdehyde, (I) was prepared by ozonolysis of phenanthrene.[13] The aldehyde is best purified by distillation [bp 180° (3 mm)] and not by recrystallization from aqueous alcohol.

Condensation of I and II.—A solution of (10%) sodium ethoxide in anhydrous alcohol was *slowly* added to a boiling solution (inert atmosphere) of 10.5 g of I and 11.5 g of II in 150 ml of absolute alcohol. After 5 min the heating was interrupted and the addition of the ethoxide solution continued until suddenly (after about another 3 min) a white precipitate appeared (only 40% of the theoretical amount of base was necessary). The mixture was stirred for 3 hr and the product (10 g, 47%) was filtered and recrystallized from butanol or nitromethane. Thus pure 9a,18-dicyano-9,9a,18,18a-tetrahydro-9-hydroxytetrabenzo[*a*,*c*,*g*,*i*]heptalene (IVa), mp 295–297°, was obtained: $\lambda_{max}^{CH_3CN}$ 250 mμ (log ε 4.27); $\tilde{\nu}_{max}^{Nujol}$ 3575, 2240, 2225, 1480 cm^{-1} (and many other bands).

Anal. Calcd for $C_{30}H_{20}N_2O$: C, 84.9; H, 4.7; N, 6.6; mol wt, 424. Found: C, 84.9; H, 4.4; N, 6.5; mol wt, 424 (mass spectrum).

The nmr was measured in deuteriodimethyl sulfoxide.

From the mother liquor, there separated after 24 hr another high-melting compound, from butanol, mp 290°, which was identified as 9,10-dicyanophenanthrene (VII): λ_{max}^{EtOH} 213 mμ (log ε 4.47), 236 (4.57), 249 (4.53), 260 (4.51), 320 (3.94), 334 (4.19), 361 (3.31), 380 (3.26); $\tilde{\nu}_{max}^{Nujol}$ 2220, 1600, 1560, 1520, 1480, 1450 cm^{-1}. For comparison, the literature data[15] are given: mp 286 and 290–292°; $\tilde{\nu}_{max}$ 2222 cm^{-1}; λ_{max}^{EtOH} 213 mμ (log ε 4.43), 236 (4.54), 259 (4.58), 320 (4.07), 333 (4.18), 360 (3.30), 380 (3.28).

Anal. Calcd for $C_{16}H_8N_2$: C, 84.2; H, 3.5; N, 12.3; mol wt, 228. Found: C, 83.7; H, 3.4; N, 12.5; mol wt, 228 (mass spectrum).

When the mother liquor of VII was evaporated, a colorless compound was obtained which did not depress the melting point (190°) of a sample of VIII, prepared according to Kenner and Turner,[8] and gave the correct analysis.

The ratio between the three products of the reaction is markedly dependent on the conditions of operation.

Acetate (IVb) of IVa.—When 1 g of IVa was refluxed for 15 hr with 50 ml of acetic anhydride, part of the acetate crystallized spontaneously. The solvent was evaporated and the product (IVb) triturated with methanol: yield 1 g (88%); mp 300°; $\lambda_{max}^{CH_3CN}$ 248 mμ (log ε 4.33); $\tilde{\nu}_{max}^{Nujol}$ 2230, 1745, 1450 cm^{-1}.

Anal. Calcd for $C_{32}H_{22}N_2O_2$: C, 82.4; H, 4.7; N, 6.0. Found: C, 82.6; H, 4.7; N, 5.8.

The nmr spectrum was determined in deuteriochloroform.

9a,18-Dicyano-9,9a,18,18a-tetrahydrotetrabenzo[*a*,*c*,*g*,*i*]heptalen-9-one.—From 11.5 g of chromic anhydride and 40 ml of dry pyridine the complex was prepared[14] and stirred for 12 hr with a solution of 5 g of IVa in 50 ml of pyridine. The mass was poured into ice-cold dilute hydrochloric acid and the brownish precipitate was filtered, refluxed with dilute hydrochloric acid for 25 min, and recrystallized from butanol: yield 5 g (quantitative); mp 271–273°; $\lambda_{max}^{CH_3CN}$ 240 mμ (s) (log ε 4.30), 325 (3.25), 380 (1.96); $\tilde{\nu}_{max}^{Nujol}$ 2225, 1675, 1580, 1475, 1450 cm^{-1}.

Anal. Calcd for $C_{30}H_{18}N_2O$: C, 85.3; H, 4.3; N, 6.6; mol wt, 422. Found: C, 85.2; H, 4.2; N, 6.6; mol wt, 422 (mass spectrum).

5,7-Dicyano-5,7-dihydro-6-(α-naphthyl)-6H-dibenzo[*a*,*c*]cycloheptene (X).—A stirred solution of 5,3 g of α-naphthaldehyde (0.034 mole) and 4.0 g of II (0.017 mole) in 50 ml of methanol and of 0.23 g of sodium (0.01 mole) in 5 ml of methanol was refluxed for 1.5 hr in an atmosphere of nitrogen. The solid product (5 g, 78%) was recrystallized from acetonitrile and melted at 276°. The same product was obtained when the molar ratio of the reactants was 1:1: $\lambda_{max}^{CHCl_3}$ 252 mμ (log ε 4.24), 275 (4.04), 285 (4.04), 293 (3.82), 315 (2.76), 320 (2.58); $\tilde{\nu}_{max}^{Nujol}$ 2250, 1580, 1450 cm^{-1}.

Anal. Calcd for $C_{27}H_{18}N_2$: C, 87.6; H, 4.9; N, 7.6; mol wt, 370. Found: C, 87.7; H, 4.9; N, 7.4; mol wt, 370 (mass spectrum).

9,20-Diazatetrabenzo[*a*,*c*,*g*,*i*]cyclododecene (XIV).—When 1 g of diphendialdehyde (I) and 0.9 g of 2,2′-diaminobiphenyl (XI)[15] were stirred in 30 ml of methanol at room temperature for 30 min, the product separated within 2 hr. From butanol, colorless crystals were obtained: 1 g (59%), mp above 300°; $\lambda_{max}^{CHCl_3}$ 310 mμ (log ε 3.78); $\tilde{\nu}_{max}^{Nujol}$ 1625, 1600, 1560, 1475, 1450 cm^{-1}. The nmr spectrum was measured in deuteriochloroform.

Anal. Calcd for $C_{26}H_{18}N_2$: C, 87.2; H, 5.0; N, 7.8; mol wt, 358. Found: C, 86.9; H, 5.0; N, 7.9; mol wt, 358 (mass spectrum).

Registry No.—I, 1210-05-5; II, 3526-27-0; IVa, 7443-44-9; IVb, 7444-75-9; VII, 2510-54-5; VIII, 7443-47-2; X, 7431-10-9; XIV, 7428-21-9; 9a,18-dicyano-9,9a,18,18a-tetrahydrotetrabenzo[*a*,*c*,*g*,*i*]heptalen-9-one, 7443-51-8.

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(10) F. Sparatore, *Chem. Abstr.*, **54**, 16446 (1960); F. Sparatore and G. Bignardi, *ibid.*, **61**, 11985 (1964); J. O. Hawthorne, E. L. Mihelic, M. S. Morgan, and M. H. Wilt, *J. Org. Chem.*, **28**, 2831 (1963).

(11) (a) J. Thiele and K. G. Falk, *Ann.*, **347**, 112 (1906); (b) D. Amos and R. G. Gillis, *Australian J. Chem.*, **17**, 1440 (1964).

(12) A. C. Cope and R. D. Smith, *J. Am. Chem. Soc.*, **78**, 1012 (1956).

(13) *Org. Syn.*, **41**, 41 (1961). A gift of 25 g of the aldehyde was obtained from U. S. Steel International (New York), Inc., through the courtesy of Mr. E. H. Carlock.

(14) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

(15) St. von Niementowsky, *Ber.*, **34**, 3325 (1901).