

identified. This mixture was separated by preparative GC. Identification of the isomers was unambiguous by comparison of their  $^{13}\text{C}$  NMR spectra with the known spectra<sup>7,11</sup> of the C-2 and C-6 monomethylated compounds.

**2 $\beta$ ,6 $\alpha$ -Dimethyl-*trans*-decahydroquinoline:** mp 38–39 °C; mp (for the picrate) 151–153 °C;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  61.77 (C-8a), 52.54 (C-2), 41.94 (C-4a), 41.06 (C-5), 34.90 (C-3), 34.09 (C-7), 33.66 (C-8), 32.57 (C-6), 32.41 (C-4), 22.97 (2- $\text{CH}_3$ ), 22.42 (6- $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{11}\text{H}_{21}\text{N}$ : C, 78.97; H, 12.65. Found: C, 79.05; H, 12.57.

**2 $\alpha$ ,6 $\alpha$ -Dimethyl-*cis*-decahydroquinoline:** mp (for the picrate) 174–175 °C;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  54.50 (C-8a), 53.32 (C-2), 35.03 (C-4a), 34.25 (C-5), 33.23 (C-6), 33.07 (C-8), 30.90 (C-4), 29.76 (C-3), 29.36 (C-7), 23.20 (2- $\text{CH}_3$ ), 22.77 (6- $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{24}\text{N}_4\text{O}_7$ : C, 51.51; H, 6.10. Found: C, 51.45; H, 6.23.

**2 $\beta$ ,6 $\beta$ -Dimethyl-*trans*-decahydroquinoline:** mp (for the picrate) 171–173 °C;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  62.69 (C-8a), 52.58 (C-2), 38.00 (C-5), 36.05 (C-4a), 35.01 (C-3), 32.63 (C-4), 30.79 (C-7), 28.11 (C-8), 27.72 (C-6), 22.99 (2- $\text{CH}_3$ ), 18.32 (6- $\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{24}\text{N}_4\text{O}_7$ : C, 51.51; H, 6.10. Found: C, 51.50; H, 5.93.

**2 $\beta$ ,8 $\alpha$ -Dimethyl-*trans*-decahydroquinoline.** 2,8-Dimethylquinoline<sup>14</sup> (15.7 g) was hydrogenated as reported above for 2,6-dimethylquinoline. The mixture of products was found by GC to consist of 50% 2 $\beta$ ,8 $\alpha$ -dimethyl-*trans*-decahydroquinoline besides five other isomers in smaller amounts. The compound was isolated by preparative GC and identified by comparison with authentic material.<sup>6</sup>

**2,3,3,4,4a,8a-Hexadeuteriodecahydroquinolines.** The deuterated analogues of 2 $\alpha$ - and 2 $\beta$ -methyl-*trans*-decahydroquinoline and 2 $\alpha$ -methyl-*cis*-decahydroquinoline (with the methyl protons also largely exchanged against deuterium) were obtained by reduction of 2-methyl-5,6,7,8-tetrahydroquinoline with sodium and ethan-*d*-ol followed by preparative GC as previously described.<sup>7</sup> In an analogous manner 2,3,3,4,4a,8a-hexadeuterio-8 $\beta$ -*tert*-butyl-*trans*-decahydroquinoline was prepared from 8-*tert*-butyl-5,6,7,8-tetrahydroquinoline.<sup>15</sup>

(15) M. Hönel and F. W. Vierhapper, *J. Chem. Soc., Perkin Trans. 1*, in press.

**Synthesis of *N*-Nitrosodecahydroquinolines and *N*-Nitrosoperhydroacridine (1–20).** In the same manner as in a literature procedure,<sup>1</sup> a solution of the parent amine in anhydrous THF was stirred in a stoppered flask at room temperature with a 5–10 molar excess of ethyl nitrite<sup>16</sup> until the starting amine had disappeared (TLC;  $\text{Al}_2\text{O}_3$  on  $\text{CHCl}_3$ ; detection by treatment with iodine vapor). The necessary reaction times varied, depending on the steric hindrance in the amine, between 1 (e.g., *trans*- or *cis*-decahydroquinoline) and 8 (for 8 $\alpha$ -*tert*-butyl-*trans*-decahydroquinoline) days. The recognition of the end of the reaction was facilitated by the disappearance of a precipitate originally formed in the reaction mixture. In the case of sterically less hindered amines the precipitate did not form. When the reaction was complete, solvent and excess ethyl nitrite were distilled off, and the residue was dissolved in petroleum ether and filtered. The petroleum ether was distilled off, and the residue was distilled in a Kugelrohr apparatus (bp 80–110 °C, air-bath temperature, 0.05 torr). If the compounds crystallized they were recrystallized from petroleum ether at low temperature; the melting points are included in Table II. All compounds gave satisfactory elemental (C, H) analysis. Care was taken in all handling of the compounds, bearing in mind their potential carcinogenic character.<sup>1</sup>

**Registry No.** 1, 15104-09-3; 2, 36041-75-5; 3, 73698-09-6; 4, 73698-10-9; 5, 73698-11-0; 6, 73698-12-1; 7, 73698-13-2; 8, 73698-14-3; 9, 73698-15-4; 10, 73698-16-5; 11, 73698-17-6; 12, 73698-18-7; 13, 7698-19-8; 14, 24506-23-8; 15, 73698-20-1; 16, 73698-21-2; 17, 73698-22-3; 18, 73698-23-4; 19, 73698-24-5; 20, 73698-25-6; 21, 73698-26-7; 22, 73698-27-8; 23, 73698-28-9; 2 $\alpha$ ,6 $\alpha$ -dimethyl-*cis*-decahydroquinoline, 73698-33-6; cyclohexen-1-ylpyrrolidine, 1125-99-1; methacrylonitrile, 126-98-7; 3 $\beta$ -methyl-*trans*-decahydroquinoline, 52679-13-7; 2-methylquinoline, 91-63-4; 2,6-dimethylquinoline, 877-43-0; 2 $\beta$ ,6 $\alpha$ -dimethyl-*trans*-decahydroquinoline picrate, 73698-34-7; 2 $\alpha$ ,6 $\alpha$ -dimethyl-*cis*-decahydroquinoline picrate, 73698-35-8; 2 $\beta$ ,6 $\beta$ -dimethyl-*trans*-decahydroquinoline picrate, 73698-36-9; 2,8-dimethylquinoline, 1463-17-8.

(16) W. L. Semon and V. R. Damerell, "Organic Syntheses", Collect. Vol. II, Wiley, New York, 1943, p 204.

## Notes

### New Synthesis of Perfluorocyclooctatetraene

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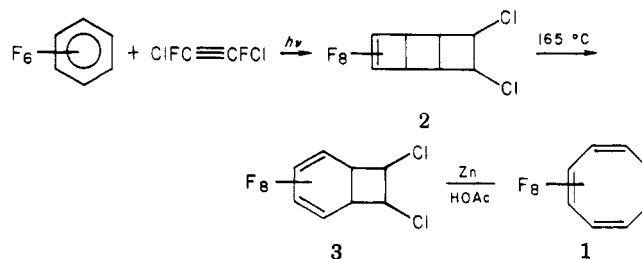
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Received June 12, 1979

Cyclooctatetraene serves as a precursor for a wide range of organic and organometallic compounds.<sup>3</sup> Eventually its perfluorinated counterpart (1) may assume a parallel role in the field of fluorocarbon chemistry.

Gerace, Lemal, and Ertl have reported a synthesis of this volatile white solid in four steps from perfluorobenzene (overall yield ~20%).<sup>4</sup> Photoisomerization of the benzene to its Dewar isomer<sup>5</sup> followed by ozonolysis yielded per-

Scheme I



fluorocyclobutene-3,4-dicarboxylic acid, which was converted to its anhydride and irradiated to give 1. Vapor-phase photolyses are not easy to scale up to the tens-of-grams level, and there are two such steps in this synthesis. Hence a new approach is needed if 1 is to become conveniently available in quantity.

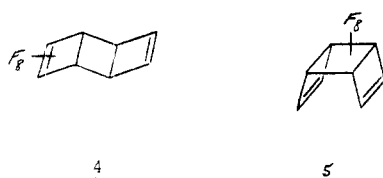
We now wish to describe a rather different three-step synthesis of 1 from the same progenitor, perfluorobenzene

(1) Goodyear Fellow, 1976–1977.  
 (2) Goodyear Fellow, 1978–1979.  
 (3) G. I. Fray and R. G. Saxton, "The Chemistry of Cyclooctatetraene and its Derivatives", Cambridge University Press, New York, 1978.  
 (4) M. J. Gerace, D. M. Lemal, and H. Ertl, *J. Am. Chem. Soc.*, **97**, 5584 (1975).

(5) G. Camaggi and F. Gozzo, *J. Chem. Soc.*, 489 (1969); G. Camaggi, F. Gozzo, and L. Cevidalli, *Chem. Commun.*, 313 (1966); I. Haller, *J. Am. Chem. Soc.*, **88**, 2070 (1966).

(Scheme I). Photochemistry again plays the key role, but here the single photochemical step can easily be carried out with hundreds of grams of a neat liquid mixture. Photocycloaddition of a *cis-trans* mixture of 1,2-dichloro-1,2-difluoroethylenes to perfluorobenzene<sup>6</sup> yields a stereoisomeric mixture of tricyclo[4.2.0.0<sup>2,5</sup>]octenes 2 containing little more than a trace of bicyclo[4.2.0]octadienes 3. The initially formed bicyclic adducts 3 photocyclize under the reaction conditions to give 2, but boiling under reflux reopens 2 to 3 essentially quantitatively. Reductive dechlorination of 3 with zinc in acetic acid yields 1, presumably via its less stable valence isomer perfluorobicyclo[4.2.0]octatriene.<sup>7,9</sup> The overall yield in this synthesis (25%) is only slightly improved relative to the original route,<sup>10</sup> but the convenience and flexibility of scale of Scheme I are great advantages.

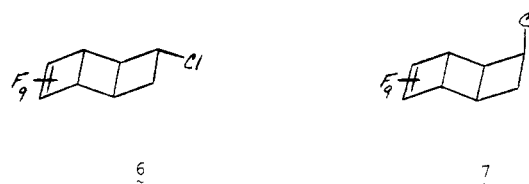
In principle, the order of the thermal ring-opening and reduction steps could be reversed, so that the *anti*- and *syn*-tricyclo[4.2.0.0<sup>2,5</sup>]octa-3,7-dienes 4 and 5 would be



formed as intermediates. Both 4<sup>4</sup> and 5<sup>11</sup> isomerize quantitatively to the cyclooctatetraene at 150 °C, but this sequence of reactions turns out to be a poor choice because the reduction of 2 proceeds in low yield.

In another variation on the theme presented in Scheme I, chlorotrifluoroethylene was substituted for the difluoro compound on the basis that the reductive elimination step should require a chlorine only at the site of attack by the metal.<sup>12</sup> This strategy was indeed successful, but it suffered by comparison with Scheme I with respect to both convenience and yield. In particular, the photocycloaddition step required weeks in sealed quartz tubes, and the zinc reductions gave poor yields. Again, the first step produced a stereoisomeric mixture of tricyclic adducts containing a lesser amount of bicyclic material. Analysis of the tricyclic fraction revealed that the two most abundant stereoisomers, by a wide margin, had the *exo* and *endo anti* configuration (6 and 7, respectively).<sup>11</sup>

A similar analysis of the mixture of tricyclic stereoisomers in Scheme I has not been performed, but it is a reasonable surmise that *anti* stereochemistry dominates



here as well. Only *anti* diene has been isolated from dehalogenation reactions run on this mixture.<sup>13</sup>

Aspects of both the organic and organometallic chemistry of perfluorocyclooctatetraene are currently under investigation in our laboratory.

### Experimental Section

Perfluorocyclooctatetraene (1) was synthesized as follows. A mixture of 1,2-dichloro-1,2-difluoroethylene (Columbia Organic Chemicals, 36.3 g, 0.273 mol<sup>10</sup>) and perfluorobenzene (Columbia Organic Chemicals, 30.0 mL, 48.4 g, 0.260 mol) was introduced under nitrogen into a photochemical reactor containing a Hanovia 450-W type L medium-pressure mercury arc fitted with a Vycor filter (cutoff 215 nm). The reactor comprised a cylindrical three-necked Pyrex vessel containing in its central neck a water-cooled quartz well which surrounded the source. One of the small flanking necks was connected to a nitrogen bubbler, and the other was fitted with a serum cap. Efficient irradiation was achieved by filling the bottom part of the annular space for the reaction mixture with mercury (30 mL) up to ~2 cm below the lower edge of the lamp envelope. The assembly was cooled externally as well as internally with cold water (~15 °C).

The solution was irradiated for 76 h.<sup>14</sup> GLC analysis of the golden brown organic layer (46 mL, 78.8 g) indicated that the bicyclic fraction represented only 1–2% of the adduct mixture. Distillation through a small Vigreux column, first at atmospheric pressure and then under aspirator vacuum, gave about 3 g of starting olefin, 22.4 g of recovered perfluorobenzene (actually 23.8 g, 94% pure by GLC),<sup>15</sup> and 26.8 g of a colorless mixture of tricyclic and bicyclic photoadducts [~58 (31 mm)–80 °C (29 mm); 60% yield based on benzene consumed; IR(neat) 1760 cm<sup>-1</sup> (CF=CF)]. The mixture of photoadducts, already partially isomerized during distillation, was boiled under reflux for 11.5 h under a nitrogen atmosphere to complete ring opening of the tricyclic to bicyclic adducts.

The product was combined (portionwise addition is recommended) with acetic acid (130 mL) and zinc dust in large excess (27 g), and the mixture was heated with stirring at about 80 °C for 1.5 h. When cool, the reaction mixture was partitioned between ice-cold water (270 mL) and isopentane (210 mL, in two portions). After a washing with 60 mL of 10% aqueous sodium carbonate, the combined isopentane solution was dried over sodium sulfate. Roughly 90% of the isopentane was removed by distillation through a 9-in., silvered, vacuum-jacketed column packed with glass helices. The yellow residue was then distilled through a short Vigreux column to give 12.4-g (118–128 °C) and 1.9-g (128–135 °C) fractions of nearly colorless liquid. The first fraction largely crystallized, and the second partially crystallized. GLC analysis revealed that these fractions were approximately 83 and 64% pure perfluorocyclooctatetraene, respectively, corresponding to a 55% yield based on the photoadducts. Purification was accomplished by crystallization from isopentane at –20 °C, pressing of the somewhat oily crystals between filter papers, and sublimation at ~30 mm (bath up to 35 °C). Two crops of colorless crystals of

(6) For a review of photocycloadditions of perfluorobenzene, see M. Zupan, *Isr. J. Chem.*, 17, 92 (1978).

(7) As is the case with cyclooctatetraene itself (ref 3, p 10), the bicyclic isomer lies at least several kilocalories above the tetraene. Even passage of 1 through a tube at 500 °C followed by instantaneous quenching to –196 °C failed to reveal detectable amounts of the valence isomer. On the other hand, Diels–Alder reactions of 1, e.g., with 4-phenyl-1,2,4-triazoline-3,5-dione and maleic anhydride, give adducts which are formally (and presumably in reality) derived from the bicyclic form. B. B. Seiders and R. C. Petter, unpublished work in our laboratory.

(8) This experiment was similar in principle to that which permitted direct spectroscopic observation of the twist-boat form of cyclohexane. M. Squillacote, R. S. Sheridan, O. L. Chapman, and F. A. L. Anet, *J. Am. Chem. Soc.*, 97, 3244 (1975).

(9) Dehalogenation experiments employing aprotic media and activated zinc failed to improve the yield of 1.

(10) Commercial 1,2-dichlorodifluoroethylene, which was used in this synthesis, contains ~10% of the 1,1-dichloro isomer. This contaminant may cause a disproportionate lowering of the yield (1) because the 1,1-dichloro isomer is, in general, the more reactive one and (2) because some of the loss in purification of 1 should be attributable to the oily chloroheptafluorocyclooctatetraene, derived from the 1,1-dichloro olefin.

(11) A. C. Barefoot III, W. D. Saunders, J. M. Buzby, M. W. Grayston, and D. M. Lemal, submitted for publication in *J. Org. Chem.*

(12) M. Hudlicky, "Chemistry of Organic Fluorine Compounds: A Laboratory Manual", 2nd ed., Halsted Press, 1976, pp 481–5.

(13) In addition to 4, there was found a significant amount of *anti*-3-chloroheptafluorotricyclo[4.2.0.0<sup>2,5</sup>]octa-3,7-diene (probably derived from 1,1-dichlorodifluoroethylene<sup>10</sup>); mass spectrum *m/e* 266 and 264 (*M*<sup>+</sup>), 229 (–Cl), 179 (–CClF<sub>2</sub>); <sup>19</sup>F NMR (CDCl<sub>3</sub>, relative to internal CFCl<sub>3</sub>) multiplets at δ 101.37, 119.51 (2 F), 179.05, 184.26 (2 F), 186.25. The *anti* assignment is based on the close similarity of this spectrum to that of 4, as opposed to 5: <sup>19</sup>F NMR (CCl<sub>4</sub>, relative to external CFCl<sub>3</sub>) 4, δ 118.2, 182.1; 5, δ 113.2, 197.1. The chlorodiene is smoothly transformed at 160 °C into chloroheptafluorocyclooctatetraene, as expected.

(14) Similar results have been obtained with significantly shorter reaction times.

(15) All GLC analyses were carried out on a 10 ft × 1/4 in. SF-96 (20%) on Chromasorb W AW DMCS column with flow rates of ~80 mL/min and column temperatures in the range 100–150 °C.

the volatile perfluorocyclooctatetraene were obtained. The first weighed 8.15 g (mp 40–42.5 °C, ~97% pure by GLC) and the second weighed 0.60 g (mp 40–41.5 °C, ~94% pure by GLC). These crystals represent a 42% yield (uncorrected for impurities) based on photoadducts and thus a 25% overall yield from perfluorobenzene.

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**Registry No.** 1, 57070-35-6; 2, 72726-96-6; 3, 72726-97-7; 4, 72777-10-7; 1,2-dichloro-1,2-difluoroethylene, 598-88-9; perfluorobenzene, 392-56-3.

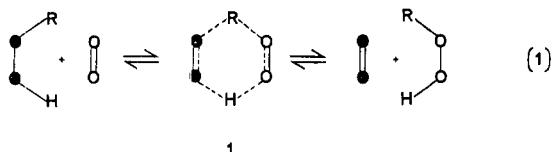
### Transfer of Hydrogen from (Trimethylsilyl)diazene

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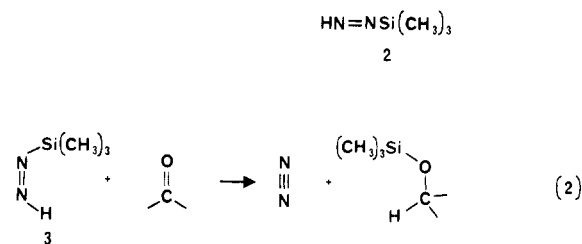
Received September 11, 1979

Structure 1 is a generalization of plausible transition states for the transfer of hydrogen during Meerwein-Ponndorf-Verley reductions,<sup>1</sup> Cannizzaro reactions,<sup>2</sup> reductions by Grignard reagents,<sup>3</sup> hydrogenations by *cis*-9,10-dihydronaphthalene<sup>4</sup> and diazene,<sup>5</sup> and other related reactions.<sup>6</sup> If ●=● is a volatile molecule with a low heat



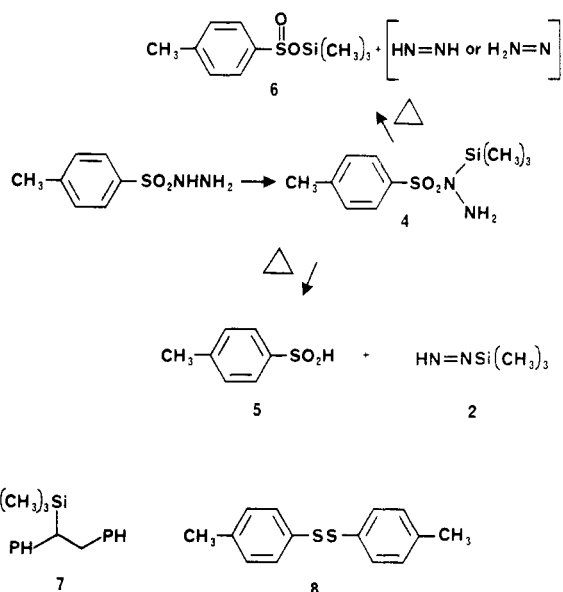
of formation which contributes to the stabilization of transition state 1, then reaction 1 should be rapid and virtually irreversible. In reductions of symmetrical multiple bonds by diazene, for example, transfer of hydrogen and formation of nitrogen are coupled effectively.<sup>5,7</sup> Reductions of the polar double bonds of aldehydes and ketones by diazene commonly are much less efficient, however,<sup>8</sup> but we hoped that the great strength of single bonds between silicon and oxygen<sup>9</sup> would make (trimethyl-

silyl)diazene (2) a more effective agent for the reduction of carbonyl compounds (eq 2). Note that synchronous



transfer of the elements of trimethylsilane requires (*Z*)- (trimethylsilyl)diazene (3). Evidence for the geometrical isomerization of diazene itself in the gas phase<sup>10</sup> suggested that both (*Z*)- and (*E*)- (trimethylsilyl)diazene might serve as agents for the transfer of hydrogen and encouraged us to try the experiments described below.

We hoped that pyrolysis of 4-methylbenzenesulfonic acid 1-(trimethylsilyl)hydrazide (4) would generate (trimethylsilyl)diazene and 4-methylbenzenesulfinic acid (5).



The reaction of 4-methylbenzenesulfonic acid hydrazide with equimolar amounts of triethylamine and chlorotrimethylsilane (THF, 25 °C) efficiently produced hydrazide 4,<sup>11</sup> but pyrolysis of this compound at 170 °C (0.10 torr) yielded primarily trimethylsilyl 4-methylbenzenesulfinate (6, 64%).<sup>12</sup> Its infrared spectrum included a strong band at 1140 cm<sup>-1</sup> characteristic of the esters of sulfinic acids,<sup>13</sup> and hydrolysis in aqueous THF at 25 °C quantitatively converted sulfinate 6 into sulfinic acid 5. Since pyrolysis of (trimethylsilyl)hydrazide 4 at 170 °C in diglyme in the presence of diphenylacetylene provided 1,2-diphenylethane (57%), diazene<sup>5</sup> or isodiazene<sup>14</sup> presumably are among the primary products of decomposition. Formation of (1,2-diphenylethyl)trimethylsilane (7, 21%)<sup>12</sup> under these conditions suggested that a competing mode of decom-

(1) A. L. Wilds, *Org. React.*, **2**, 178 (1944); W. von E. Doering and T. C. Aschner, *J. Am. Chem. Soc.*, **75**, 393 (1953); V. J. Shiner, Jr., and D. Whittaker, *ibid.*, **85**, 2337 (1963).

(2) T. A. Geissman, *Org. React.*, **2**, 94 (1944); E. Pfeil, *Chem. Ber.*, **84**, 229 (1951); D. Luther and H. Koch, *ibid.*, **99**, 2227 (1966).

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(7) E. J. Corey, D. J. Pasto, and W. L. Mock, *J. Am. Chem. Soc.*, **83**, 2957 (1961).

(8) E. E. van Tamelen, R. S. Dewey, M. F. Lease, and W. H. Pirkle, *J. Am. Chem. Soc.*, **83**, 4302 (1961); E. E. van Tamelen, M. Davis, and M. F. Deem, *Chem. Commun.*, **71** (1965); D. C. Curry, B. C. Uff, and N. D. Ward, *J. Chem. Soc. C*, 1120 (1967); J. J. Looker, *J. Org. Chem.*, **32**, 472 (1967).

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(11) N. Wiberg, S. K. Vasisht, G. Fischer, and E. Weinberg, *Chem. Ber.*, **109**, 710 (1976).

(12) The assigned structure was consistent with the elemental analysis and the IR, NMR, and mass spectra of this new substance.

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