Effect of Ring Size on the Thermal Rearrangements of Bicyclo[*n*.1.0]alka-1,*n*-dienes[1]

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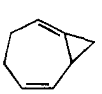
The bicyclo[*n*.1.0]alka-1,*n*-dienes (n = 5–10) have been synthesized and their thermal chemistry investigated. Products resulting from concerted sigmatropic processes or their structural equivalent in the form of biradicals where both carbon and hydrogen serve as the migrating group were observed, but the proportions of each were markedly controlled by ring size. When n = 5 spontaneous rearrangement (<25°) to 7-methylenebicyclo[4.1.0]hept-2-ene (**3**) occurs. At higher temperatures this compound undergoes rearrangement to give two new hydrocarbons identified as 4-methylenebicyclo[3.2.0]hept-2-ene (**4**) and 1-vinyl-1,3-cyclohexadiene (**5**). When n = 6 and 7 the products are 3-methylene-1,4-cyclooctadiene (**9**) and 3-methylene-1,4-cyclononadiene (**12**), respectively. When n = 8 the starting diene is much more thermally stable and gives a 2:1 mixture of 4-methylenebicyclo[5.3.0]dodec-2-ene (**16**) and 3-methylene-1,4-cyclodecadiene (**17**). The slower reaction rate is interpreted in terms of transannular nonbonded interactions within the ten-membered ring. Larger rings (n = 9 and 10) give 4-methylenebicyclo[6.1.0]undec-2-ene (**19**) and 4-methylenebicyclo[7.1.0]dodec-2-ene (**21**), respectively.

We have previously reported[3,4] the synthesis and thermolysis of the bicyclo[*n*.1.0]alka-1,*n*-dienes 1 and 2 (n = 5, 6). Since these two compounds exhibited very different thermal chemistry, it was of interest to investigate the effect of ring size on other accessible members of this family. In this paper we report more fully on compounds 1 and 2 and on four new bicyclo[*n*.1.0]alka-1,*n*-dienes where n = 7–10.



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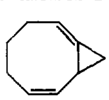

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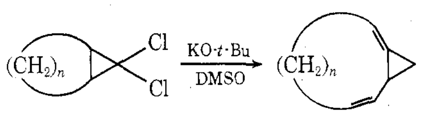
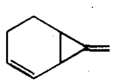
The bicyclo[*n*.1.0]alka-1,*n*-dienes were synthesized by treating the appropriate ω,ω-dichlorobicyclo[*n*.1.0]alkane with KO-*t*-Bu in DMSO[5] as shown by the general form of eq 1. For some of the larger rings the starting dichloride was a mixture of cis and trans isomers, but the stereochemistry is lost during the base-induced elimination–isomerization sequence.



n = 5–10

Bicyclo[5.1.0]octa-1,5-diene (**1**) was not isolated from the synthetic scheme, but suffered a methylenecyclopropane rearrangement under the reaction conditions (15–25°) to give 7-methylenebicyclo[4.1.0]hept-2-ene (**3**), which was isolated in 50% yield. Thermolysis of **3** was carried out in the gas phase between 126.1 and 186.2°, using a diffusively stirred flow system with nitrogen as the carrier gas.[6] Two major thermolysis products were isolated and identified as 4-methylenebicyclo[3.2.0]hept-2-ene (**4**) and 1-vinyl-1,3-cyclohexadiene (**5**). They were produced in a 1.15 ± 0.05 ratio at all temperatures. The study of the thermolysis is outlined in eq 2. Both reactions followed a first-order course with the indicated rate constants. Scheme I conveniently accounts for both **4** and **5** from **3**. The formation of **4** suggests this diradical path, since a one-step thermally allowed 1,3-sigmatropic shift requires an inversion at the migrating carbon, leading to an unknown trans-fused ring system, and the 3,3-sigmatropic shift is impossible because of severe geometrical restraints. The formation of **5** from **3** is accounted for through the fission[7] of the "1,4" diradical **6** to the tetraene **7** followed by a facile cyclization to **5**.[8]



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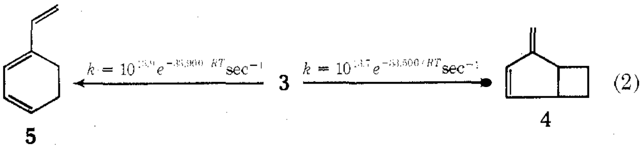
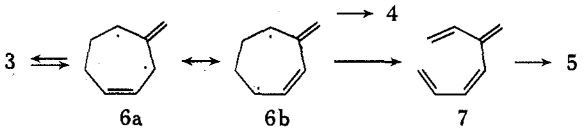
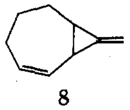


Scheme I

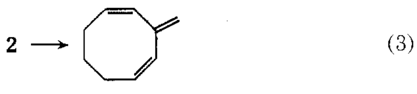


Bicyclo[6.1.0]nona-1,6-diene (**2**) was prepared from 9,9-dichlorobicyclo[6.1.0]nonane using the elimination–isomerization sequence illustrated in eq 1. The rearranged product analogous to **3**, compound **8**, was not detected, as shown by the reduction to *cis*-bicyclo[6.1.0]nonane and the absence of a prominent ir band at ~11.3 μ (methylenecyclopropane). Presumably **2** is, by virtue of the larger ring size, less strained than **3**, accounting for the preparation of **2** and not **8**.



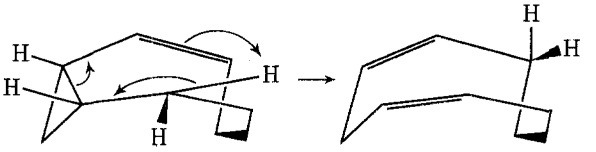
8

The thermolysis of **2** was studied in the liquid phase using DMF solvent and **2** was found to rearrange to 3-methylene-1,4-cyclooctadiene (**9**) by a first-order process, followed by NMR, giving $k = 10^{11}\ e^{-29{,}000/RT}$ sec^{-1} (eq 3).



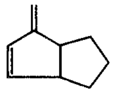
9

This rearrangement must involve a hydrogen migration. The marked contrast in the thermal chemistry of **1** and **2** is at first surprising. However, transannular interactions are well documented in C_8 rings[9] and similar, although less facile, rearrangements of related systems are well known[10] (eq 4). The strain energy associated with the methylenecyclopropane would be expected to accelerate **2** → **9**. In terms of conformation, compound **2** should be ideally disposed to form **9**, since labeling studies for the related systems[10] have



(4)

shown that the migrating hydrogen is trans to the cyclopropane ring. It may occur by the sequence **2** → **8** → **9**, or by a direct hydrogen shift in **8**. An argument against the intermediacy of **8** is that its expected rearrangement product,[4b] **10**, is undetected.



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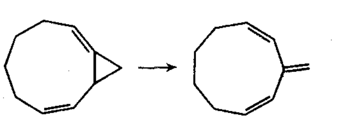
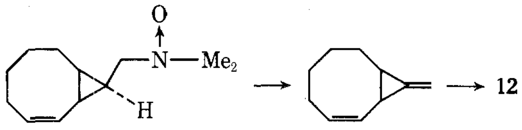
In strict analogy to eq 3 (**2** → **9**), bicyclo[7.1.0]deca-1,7-diene (**11**) rearranges exclusively to 3-methylene-1,4-cyclononadiene (**12**) (eq 5). This rearrangement is nearly complete in 30 min at 110° or 3 hr at 80°. The formation of **12** was also observed by Radlick, Fenical, and Alford[11] in a closely related reaction. When they attempted to prepare 9-methylenebicyclo[6.1.0]nona-2-ene (**13**) by thermolysis of the hydrated amine oxide **14**, **12** was obtained, presumably via **13** (eq 6). Compounds **11** and **13** are related by a methylenecyclopropane rearrangement. Molecular models reveal that **11** probably exists in the cis-syn stereochemical form. This assures favorable conformation for direct hydrogen migration, although the same mechanistic uncertainties exist as discussed earlier for the rearrangement of **2**.

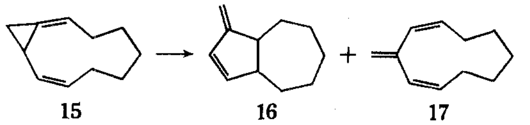


11 **12** (5)



14 **13** (6)

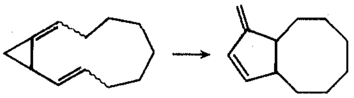
Unlike the other compounds in this series, bicyclo[8.1.0]undeca-1,8-diene (**15**) was found to undergo thermal reorganization by competing processes in which both carbon and hydrogen serve as the migrating atom. Thus, **15** rearranges slowly (16 hr at 140°) to give a 2:1 mixture (NMR) of 4-methylenebicyclo[5.3.0]deca-2-ene (**16**) and 3-methylenecyclodeca-1,4-diene (**17**) (eq 7).



15 **16** **17** (7)

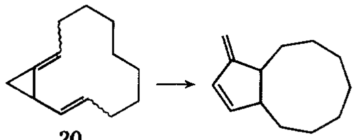
The marked thermal stability of **15** in comparison to **2** and **11** is at first surprising, but can be reconciled on the basis of geometrical restraints in the ten-membered ring. Models indicate that the cis-syn stereochemical form of **15** is the more favorable one and the observation of a major GC peak suggests one isomer. Nevertheless, this compound is highly encumbered sterically and this probably serves to retard the rate of rearrangement.

Larger rings give only rearrangement products resulting from sigmatropic processes involving carbon. Thus bicyclo[9.1.0]dodeca-1,9-diene (**18**) gives the cyclopentene **19** in nearly quantitative yield after refluxing in toluene at 105° for 4 hr (eq 8). A minor product, not identified, observed in the NMR spectrum of the crude product was shown to arise from thermal rearrangement of the product **19**.



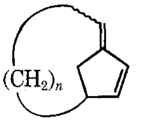
18 **19** (8)

Similarly, bicyclo[10.1.0]trideca-1,10-diene (**20**) yields only 4-methylenebicyclo[7.3.0]dodeca-2-ene (**21**) (eq 9).



20 **21** (9)

The question of concertedness vs. diradicals for the alicyclic counterpart of eq 7–9 has been discussed in several recent papers.[4] Geometrical restraints within the starting hydrocarbons probably rule out concerted [3,3]-sigmatropic processes for the systems under study here. All of the products can be accounted for through the regiospecific closure of diradicals (**22** is not observed) or vinylcyclopropane rearrangement of intermediate **23**.



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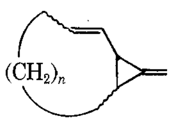

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Experimental Section

General. Infrared spectra were recorded as liquid films on a Beckman IR-8 spectrometer. NMR spectra were recorded on Varian A-56/60A and Perkin-Elmer R-12 spectrometers in CCl_4 solution and results are expressed in parts per million downfield from internal TMS (δ). GLC analyses were carried out on Hewlett-Packard Model 700 and Aerograph Autoprep A-700 instruments with thermal conductivity detectors using a 3 ft × 0.125 in. 15% column packed with β,β'-oxydipropionitrile on Chromosorb P. All boiling points are uncorrected and were run using a short-path distillation head.

Materials. Cycloheptene and cyclododecene were supplied by Chemical Samples Co. and used without further purification. Cyclooctene was used as received from Matheson Coleman and Bell. Potassium *tert*-butoxide was supplied by MSA Research Corp. Dimethyl sulfoxide (Aldrich) was distilled from CaH_2 and stored over 4A molecular sieves prior to use. All other solvents were reagent grade and used as received.

Cyclononene, cyclododecene, and cycloundecene were prepared by reduction of the corresponding allenes with sodium in ammonia.[12] Precursor allenes were prepared by the general ring-expansion methods of Moore and Skattebøl[13] using cyclooctene as a starting point. *gem*-Dichlorocyclopropanes were prepared after Skell and Garner.[14]

7-Methylenebicyclo[4.1.0]hept-2-ene (3). The preparation of this compound from 8,8-dichlorobicyclo[5.1.0]octane is representative of the preparations outlined for the other bicyclo[*n*.1.0]alka-1,*n*-dienes. In a 250-ml three-necked flask equipped with a stirrer and nitrogen purging system was prepared a solution of 28.1 g (0.25 mol) of KO-*t*-Bu in 100 ml of dry dimethyl sulfoxide. 8,8-Dichlorobicyclo[5.1.0]octane (21.5 g, 0.12 mol) was added dropwise with stirring over a 30-min period. The mixture was then stirred for 1 hr followed by addition of water. The aqueous layer was extracted with pentane and dried over sodium sulfate. The solvent was then removed, leaving 6.36 g (0.06 mol, 50%) of crude **3**. Further purification was accomplished by distillation to give 5.34 g (42%) of **3**, bp 23° (0.22 mm). The identification of **3** rested on its spectra: prominent ir band at 11.28 μ (methylenecyclopropane); NMR signals at δ 0.9–2.2 (6 H) and 5.20–6.25 (4 H). ^{13}C NMR shows eight distinct signals, one unattached to hydrogen. The mass spectrum showed a parent molecular ion at *m/e* 106.

Bicyclo[6.1.0]nona-1,6-diene (2). Addition of 9,9-dichlorobicyclo[6.1.0]nonane (19.3 g, 0.1 mol) to a solution of 23.6 g (0.21 mol) of KO-*t*-Bu in 100 ml of dry DMSO produced 4.8 g of **2** (40%

yield). Reduction of **2** to bicyclo[6.1.0]nonane was found identical with the sodium in ammonia reduction product of the starting *gem*-dichlorocyclopropane. The NMR is consistent with the structure: δ 0.5–0.85 (1 H), 1.05–2.83 (8 H), 5.6 (m, 2 H), 5.89 (m, 1 H). The ^{13}C NMR shows nine signals, one for carbon not attached to hydrogen.

Bicyclo[7.1.0]deca-1,7-diene (11). Addition of 10,10-dichlorobicyclo[7.1.0]decane (11.0 g, 0.053 mol) to a solution of KO-*t*-Bu (12.4 g, 0.11 mol) in 50 ml of DMSO at 125–125° gave **12** in 42% yield: bp 28° (0.2 mm); ir 3040 w, 3010 s, 2980 s, 2950 s, 2920 s, 2880 s, 2840 m, 2830 m (C–H), 1640 m (C=C), 1440 s, 1330 w, 1270 w, 1225 w, 1075 w, 980 m, 925 m, 730 s, 705 cm^{-1} w; NMR δ 0.6–1.0 (m, 2 H), 1.1–2.9 (m, 9 H), 5.15–6.1 (m, 3 H).

Bicyclo[8.1.0]undeca-1,8-diene (15). Treatment of 6 g of 11,11-dichlorobicyclo [8.1.0]undecane with KO-*t*-Bu (6.2 g, 0.56 mol) in 25 ml of DMSO gave 2.9 g (72% yield) of **15:** bp 55–57° (1.3 mm); ir 3040 w, 3020 m, 2970 s, 2940 s, 2930 s, 2870 s, 2830 m (C–H), 1640 w (C=C), 1450 s, 1430 m, 1420 m, 1340 w, 1310 w, 1260 w, 1245 w, 1200 w, 1140 w, 1100 w, 1020 m, 908 s, 940 m, 840 m, 820 m, 790 m, 740 m, 720 m, 695 cm^{-1} m; NMR δ 0.65–2.9 (m, 13 H), 5.0–5.95 (m, 3 H).

Bicyclo[9.1.0]dodeca-1,9-diene (18). 18, bp 68–70° (1.2 mm), was prepared in 69% yield by treating 12,12-dichlorobicyclo[9.1.0]dodecane with a solution of 11.7 g (0.104 mol) of KO-*t*-Bu in 50 ml of DMSO: ir 3040 w, 3010 m, 3070 s, 3030 s, 2850 s (C–H), 1630 w (C=C), 1450 s, 1430 s, 1390 w, 1330 w, 1260 w, 1010 w, 980 w, 970 w, 960 w, 920 w, 830 w, 740 cm^{-1} m; NMR δ 0.8–1.75 (m, 11 H), 1.75–2.6 (m, 4 H), 4.9–5.9 (m, 3 H).

Bicyclo[10.1.0]trideca-1,10-diene (20). This compound was prepared in 94% yield (crude) as described previously.[5a] Distillation of the crude material gives the product, bp 83–85° (1.3 mm), in 75% yield. The crude material is nearly as pure as the distilled product.

Thermolysis of 7-Methylenebicyclo[4.1.0]hept-3-ene (3). Thermolysis of **3** was carried out in the gas phase using the flow system which has been described previously.[4b,6] Products **4** and **5** were obtained from the condensed effluent by preparative GLC using a 10 ft × 0.125 in. column packed with 15% FFAP on Chromosorb P. The uv of **4** shows the diene structure, λ_{max} 238 nm (ϵ 15,000); the proton NMR is well resolved, δ 1.5–2.7 (m, 4 H), 3.24 (m, 2 H), 4.62 (s, 1 H), 6.2 (s, 2 H). **5** is a known compound.[15] Its uv max absorption and NMR spectrum are indistinguishable from those kindly supplied by Dr. Ziegenbein. Kinetic measurements were carried out between 126.1 and 186.2° as described earlier for several related systems.[4b]

Thermolysis of Bicyclo[6.1.0]nona-1,6-diene (2). The thermolysis of **2** was carried out in DMF at 80–100°. The product **9** is shown by the λ_{max} 250 nm and the skeleton by reduction to methylcyclooctane with PtO$_2$ in ether. The NMR is too simple to allow a structure of lesser symmetry: δ 1.44 (m, 2 H), 2.55 (m, 4 H), 4.93 (s, 2 H), 5.33 (dt, 2 H, J = 11.5, 8.4 Hz), 6.24 (d, 2 H, J = 11.5 Hz).

Thermolysis of Bicyclo[7.1.0]deca-1,7-diene (11). A solution of **11** (0.5 g) was heated at 110° in 21 ml of toluene for 30 min, after which analysis by NMR showed nearly complete conversion to 3-methylene-1,4-cyclononadiene (**12**). In benzene (80°) it takes 3 hr. Identification of the very sensitive **13** rested on its NMR spectrum, which was identical with that reported.[11]

Thermolysis of Bicyclo[8.1.0]undeca-1,8-diene (15). A solution of **15** in xylene was heated at 140° for 16 hr. After this time ~90% of **15** was converted to a 2:1 mixture of 4-methylenebicyclo[5.3.0]dec-2-ene (**16**) and 3-methylene-1,4-cyclodecadiene (**17**). No suitable GLC column and conditions were found to adequately separate the high-boiling, easily polymerized compounds. Column chromatography through 25% AgNO$_3$ on silica gel resulted in purification of **16**, but **17**, which was first to emerge from the column, could only be enriched. Compound **17** was readily identified by the very close resemblance of its NMR spectrum to that of **13.** The olefinic portion shows a narrow multiplet at δ 4.87 (2 H, =CH$_2$), doublet triplet at 5.30 (2 H, J = 11, 8.5 Hz), and a doublet triplet at 6.05 (2 H, J = 11, 1 Hz). Compound **16** shows NMR signals at δ 1.5–2.0 (m, 10 H), 2.65–3.1 (m, 2 H) 4.57 (s, 1 H), 4.8 (s, 1 H), and 5.65–6.1 (m, 2 H).

Thermolysis of Bicyclo[9.1.0]dodeca-1,9-diene (18). 18 was completely converted to 4-methylenebicyclo[6.3.0]undec-2-ene (**19**) by refluxing in xylene at 140° for 30 min or toluene for 3 hr at 119°. Column chromatography (25% AgNO$_3$ on silica gel) gave pure **19:** ir 3080 w, 3060 w, 2920 s, 2860 m (C–H), 1720 w (C=C), 1625 s (C=CH$_2$), 1460 s, 1535 m, 850 s, 790 cm^{-1} m; NMR δ 5.7–6.1 (m, 2 H), 4.65 (d, 2 H, J = 13 Hz), 2.45–3.0 (m, 2 H), 1.15–1.9 (m, 12 H).

Thermolysis of Bicyclo[10.1.0]trideca-1,10-diene (20). The rearrangement of **20** to **21** was complete after 4 hr in toluene reflux (110°): ir 3080 w, 3060 w, 2970 m, 2930 s, 2850 s (C–H), 1720 w (C=C), 1625 s (C=CH$_2$), 1460 s, 1435 s, 1340 w, 850 m, 780 cm^{-1} m; NMR δ 1.0–2.0 (m, 14 H), 2.45–3.0 (m, 2 H), 4.65–5.1 (m, 2 H), 4.7 (d, 2 H, J = 12 Hz, C=CH$_2$).

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Registry No.—2, 36398-97-7; **3,** 36398-96-6; **4,** 36399-02-7; **5,** 1192-86-5; **9,** 36399-01-6; **11,** 54643-82-2; **12,** 28569-70-2; **15,** 54643-83-3; **16,** 54643-84-4; **17,** 54643-85-5; **18,** 54643-86-6; **19,** 54643-87-7; **20,** 54643-88-8; **21,** 54643-89-9; 8,8-dichlorobicyclo[5.1.0]octane, 6498-42-6; 9,9-dichlorobicyclo[6.1.0]nonane, 6498-44-8; 10,10-dichlorobicyclo[7.1.0]decane, 52512-01-3; 11,11-dichlorobicyclo[8.1.0]undecane, 54643-90-2; 12,12-dichlorobicyclo[9.1.0]dodecane, 54643-91-3.

References and Notes

(1) Presented in part at the Southwest Regional Meeting of the American Chemical Society, San Antonio, Tex., 1971.

(2) (a) Alfred P. Sloan Foundation Fellow, 1973–1975. (b) Taken in part from the M.S. Thesis of B. A. Baker, Rice University, 1973. (c) National Science Foundation Predoctoral Fellow.

(3) For a preliminary account, see W. E. Billups, K. H. Leavell, W. Y. Chow, and E. S. Lewis, *J. Am. Chem. Soc.,* **94,** 1770 (1972).

(4) See also (a) W. E. Billups, W. Y. Chow, K. H. Leavell, and E. S. Lewis, *J. Org. Chem.,* **39,** 274 (1974); (b) W. E. Billups, K. H. Leavell, E. S. Lewis, and S. Vanderpool, *J. Am. Chem. Soc.,* **95,** 8096 (1973); (c) J. C. Gilbert and D. P. Higley, *Tetrahedron Lett.,* 2075 (1973); (d) A. S. Kende and E. E. Riecke, *J. Am. Chem. Soc.,* **94,** 1397 (1972); (f) W. R. Roth and Th. Schmidt, *Tetrahedron Lett.,* 3639 (1971).

(5) (a) W. E. Billups, T. C. Shields, W. Y. Chow, and N. C. Deno, *J. Org. Chem.,* **37,** 3676 (1972); (b) T. C. Shields and P. D. Gardner, *J. Am. Chem. Soc.,* **89,** 5425 (1967).

(6) The system is essentially the same as that described by E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Am. Chem. Soc.,* **90,** 662 (1968).

(7) For studies on 1,4 diradicals, see P. D. Bartlett and N. A. Porter, *J. Am. Chem. Soc.,* **90,** 5317 (1968).

(8) Tetraene **7** might also arise by a concerted process, but the similar activation parameters for the formation of **4** and **5** seem to suggest a common intermediate.

(9) For a review see A. C. Cope, M. M. Martin, and M. A. Mckervey, *Q. Rev., Chem. Soc.,* **20,** 119–152 (1966).

(10) D. S. Glass, R. S. Borkess, and S. Winstein, *Tetrahedron Lett.,* 999 (1966), and references cited therein.

(11) P. R. Radlick, W. Fenical, and G. Alfrod, *Tetrahedron Lett.,* 2707 (1970).

(12) P. D. Gardner and M. Narayana, *J. Org. Chem.,* **26,** 3518 (1961); R. Vaidyanathaswamy, G. C. Joshi, and D. Devaprabhakara, *Tetrahedron Lett.,* 2075 (1971).

(13) W. R. Moore and H. R. Ward, *J. Org. Chem.,* **27,** 4179 (1962); L. Skattebøl, *Acta Chem. Scand.,* **17,** 1683 (1963).

(14) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.,* **78,** 3409 (1956).

(15) W. Ziegenbein, *Angew. Chem., Int. Ed. Engl.,* **4,** 70 (1965).