The *p*-nitrobenzoate had mp 103–104° (hexane); nmr ($CDCl_3$), τ 1.90 (s, 4, ArH), 4.80 (m, 1, J = 6.8 cps, —CHOCO—), 5.12 (m, 2, $=CH_2$), 6.97 (m, 4, ring **H**).

Anal. Calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.78; H, 4.66; N, 6.10.

The tenth component had a retention time of 28.6 min and its relative abundance was 4.7%: ir (film), 3350, 2960, 2930, 2875, 1455, 1378, 1045, and 1018 cm^{-1} (no bands attributable to an olefinic group were present); nmr (CCl_4), τ 6.19 (m), 8.14 (m), 8.57 (m). From these data this component was assumed to be a polymeric alcohol.

Registry No.—2-Methylenecycloheptanol, 16240-38-3; *p*-nitrobenzoate of 2-methylenecycloheptanol, 17202-74-3; phenylurethan of 2-methylenecycloheptanol, 17202-75-4; 3,5-dinitrobenzoate of 1-cycloheptenylmethanol, 17202-84-5; XVIII, 3859-35-6; *p*-nitrobenzoate of XVIII, 17202-85-6; 3,5-dinitrobenzoate of XVIII, 17206-76-7; XIX, 931-43-1; 3,5-dinitrobenzoate of XIX, 7498-75-1; XXIII, 17202-79-8; *p*-nitrobenzoate of XXIII, 17202-80-1; XXIV, 4415-76-3; *p*-nitrobenzoate of XXIV, 17202-82-3; *p*-nitrobenzoate of 3-methylenecyclobutanol, 17202-83-4.

Acknowledgments.—The invaluable assistance of Dr. Jean-Marie Lehn of the Institute of Chemistry, University of Strasbourg, for the recording and interpretation of a portion of the nmr spectra is greatly appreciated. The generous financial assistance to L. M. K. from Schering Corporation, Bloomfield, N. J., is gratefully acknowledged.

Chemistry of Allene. III. Cyclooligomerization. Synthesis of 1,4,7-Trimethylenespiro[4.4]nonane and a New Pentamer

F. N. Jones and R. V. Lindsey, Jr.

Contribution No. 1406 from the Central Research Department, Experimental Station,
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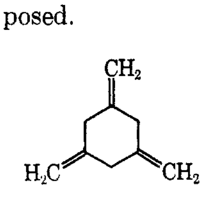
Received May 27, 1968

$[(C_6H_5)_3P]_3RhCl$ catalyzes the liquid phase cyclooligomerization of allene to a single tetramer, 1,4,7-trimethylenespiro[4.4]nonane (**5**), and a single pentamer of unknown structure.

Thermal oligomerization of liquid allene at 140° affords a mixture of cyclic products including two dimers, three trimers, two tetramers, and higher oligomers.[1] The structures of these oligomers have been the subject of recent papers.[2] The chemistry of allene is discussed more broadly in recent reviews.[3]

In earlier work[4] in these laboratories, it was found that allene cyclizes at 110° in solutions containing certain phosphorus-modified nickel catalysts, for example $[(C_6H_5)_3P]_2Ni[CO]_2$, to give products largely different from those obtained in the uncatalyzed reaction. The principal products were two trimers, **1** and **2**, and a tetramer, for which structure **3** was proposed.



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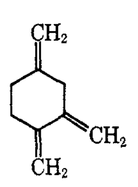

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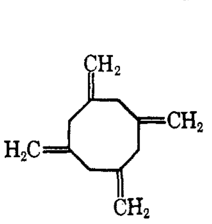

3

This paper describes the synthesis and characterization of some new cyclooligomers obtained with phosphine-modified rhodium catalysts.

Cyclooligomerization Reactions.—A variety of Rh(I) compound such as $(CO)_4Rh_2Cl_2$ and $(AcAc)Rh(C_2H_4)_2$ catalyzed oligomerization of allene in solution at 50–100° to oily or semisolid mixtures. These mixtures contained small amounts of unidentified trimers and tetramers. When triphenylphosphine was added to these catalysts or, better, when a preformed phosphine complex was employed, the principal products were a single tetramer and a single pentamer produced in 42–60% and 5–16% yields, respectively. The reaction was conveniently effected using 0.5 to 2% $[(C_6H_5)_3P]_3RhCl$[5] or $[(C_6H_5)_3P]_2Rh[CO]Cl$[6] in chloroform. These two catalysts gave similar product compositions; however, because a large run using $[(C_6H_5)_3P]_2Rh[CO]Cl$ as catalyst detonated with great violence, the less active $[(C_6H_5)_3P]_3RhCl$ was used in most experiments.[7]

In a typical run, a solution of 150 g of allene, 1 g of $[(C_6H_5)_3P]_3RhCl$, and 0.1 g of hydroquinone in 75 g of chloroform was agitated in a 400-ml, silver-lined pressure tube at 80° for 16 hr; the pressure fell steadily to less than 1 atm. Gas chromatographic analysis of the resulting oil showed that the product contained traces of presumed dimers and trimers, a single tetramer (59% of the total product by weight), and a single pentamer (6%). The remainder was less volatile material probably containing at least two hexamers. Fractionation of the mixture gave tetramer, bp 80° (10 mm), and pentamer, bp 81–81.5° (1.2 mm). These fractions were established by gas chromatography (glpc) to be single compounds of >99.5% purity.

A reaction temperature of 80° appeared to be optimum for tetramer formation. At lower temperatures, the tetramer/pentamer ratio decreased and the re-

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[1] S. V. Lebedev and B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, **45**, 1249 (1913); *Chem. Zentr.*, **85**, 1410 (1914).

[2] (a) B. Weinstein and A. H. Fenselau, *Tetrahedron Lett.*, 1463 (1963); (b) B. Weinstein and A. H. Fenselau, *J. Chem. Soc., C*, 368 (1967); (c) B. Weinstein and A. H. Fenselau, *J. Org. Chem.*, **32**, 2278 (1967); (d) B. Weinstein and A. H. Fenselau, *ibid.*, **32**, 2988 (1967); (e) Y. M. Slobodin and A. P. Khitrov, *Zh. Organ. Khim.*, **1**, 1531 (1965); *J. Org. Chem. USSR*, **1**, 1553 (1965).

[3] K. Griesbaum, *Angew. Chem. Intern. Ed. Engl.*, **5**, 933 (1966). A. A. Petrov and A. V. Fedorova, *Russ. Chem. Rev.*, **33**, 1 (1964).

[4] R. E. Benson and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **81**, 4247 (1959).

[5] J. A. Osborne and G. Wilkinson, *Inorg. Syn.*, **10**, 67 (1967).

[6] L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

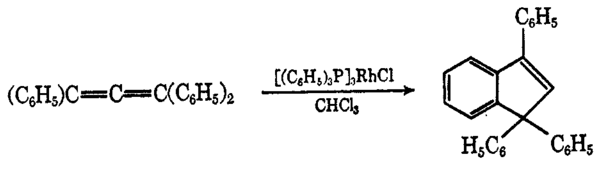
[7] While our manuscript was in preparation, S. Otsuka and A. Nakamura [*Polymer Lett.*, **5**, 973 (1967)] reported that they had observed the formation of allene tetramers with some of the same rhodium catalysts which we have employed.

action was much slower. At 100°, neither the rate nor product distribution was substantially altered.

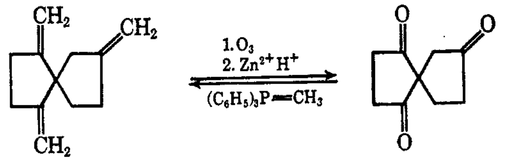
A small-scale experiment using $[(C_6H_5)_3P]_2Rh[CO]Cl$ as catalyst was complete within 6 hr at 70°. The product contained 56% tetramer and 13% pentamer. A larger scale experiment with this catalyst detonated violently.

Solid polymer was sometimes produced in small amounts. Polymer formation was repressed in most experiments by addition of hydroquinone. Addition of 1 drop of acetic acid seemed to accelerate the reaction slightly, but this was not established with certainty.

Methylacetylene did not react under these conditions; the pressure remained constant. Only a trace of tetramer was obtained, and this is ascribable to the presence of allene in the methylacetylene. Indeed, treatment with a solution of $[(C_6H_5)_3P]_3RhCl$ may be an efficient way to remove allene from methylacetylene. 1,1-Dimethylallene gave an unstable yellow complex with $[(C_6H_5)_3P]_3RhCl$ in chloroform but no catalytic reaction. Tetraphenylallene cyclized in the presence of $[(C_6H_5)_3P]_3RhCl$ to indene **4**; HCl also catalyzes this cyclization.[8]



Structure of the Tetramer.—The tetramer was ozonized to give a crystalline, nine-carbon triketone in 65% yield. Absence of skeletal rearrangement was demonstrated by conversion of the triketone into the tetramer by Wittig's method. We have assigned structures **5** and **6**, respectively, to the tetramer and the triketone, primarily on the basis of their spectra.



5 **6**

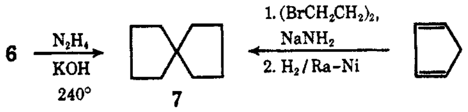
The ultraviolet spectrum of tetramer **5** in ethanol had no maximum; strong end absorption [227 mμ (ε 160), 200 (1600)] raised uncertainty about possible conjugation. The ultraviolet spectrum of triketone **6** showed maxima at 200 mμ (ε 1000), 287 (72), 295 (70), 306 (55), and 317 (38). In a mixture of 25% 0.5 *N* aqueous HCl and 75% ethanol λ_{max} was at 285 mμ (ε 76); the shoulders were not discernible. These low extinction coefficients show that **6** is neither a 1,2 nor an enolizable 1,3 triketone; cyclopentane-1,2-dione has $\lambda_{max}^{C_6H_{14}}$ 241 mμ (ε 10,000) and 300 (80),[9] and cyclopentane-1,3-dione has $\lambda_{max}^{0.1\,N\ HCl}$ 242 mμ (ε 20,000).[10]

The infrared spectrum of tetramer **5** has peaks associated with the unsaturated function at 3077 (m), 1758 (w), 1653 (s), 1648 (s), 1645 (s), and 875 (vs) cm^{-1}, all consistent with the presence of *exo*-methylene groups.[11] The frequencies are lower than expected for *exo*-methylene groups in three- or four-membered rings. The triketone had strong carbonyl peaks at 1721 and 1741 cm^{-1} with a shoulder at about 1766 cm^{-1}, consistent with the assigned structure but not consistent with structures having a single carbonyl group in a three-, four-, six-, or seven-membered ring.[11] The carbonyl peak of spiro[3.4]octan-5-one is at 1739 cm^{-1}.[12]

The mass spectrum of tetramer **5** had its most intense peak at *m/e* 160, the parent ion; this suggests a stable cyclic structure with no singly bonded side chains.

The nmr spectrum at 60 MHz of tetramer **5** in CCl_4 showed areas of resonance centered at δ 4.81 (6 H), 2.42 (8 H), and 1.73 (2 H). The δ 4.81 area, attributed to vinylic hydrogens, consisted of a strong, sharp peak overlapping some weaker resonances with fine splitting. The δ 2.42 area had a number of closely grouped peaks attributed to allylic protons.[2b,c] The δ 1.73 resonance was a triplet (J = 7.5 Hz) attributed to nonallylic protons and interpreted as being half of an A_2B_2 pattern whose other half is only partly visible in the δ 2.42 region. The nmr spectrum of triketone **6** in $CDCl_3$–TMS at 60 MHz consisted of a singlet (2 H) at −147 Hz, and two eight-line A_2B_2 patterns centered at −142 and −179 Hz. The spectrum at 100 MHz confirmed this interpretation. In structure **6**, one of the A_2B_2 patterns can be associated with the $-CA_2-CB_2-$ unit in the ring with one carbonyl, and the other can be associated with the –CAB–CAB– unit in the other ring. Only structures **5** and **6** seem consistent with the above spectral data.

To confirm the presence of the spiro[4.4]nonane skeleton in these compounds, degradation to spiro[4.4]-nonane (**7**) was attempted by various methods. For comparison, **7** was synthesized by a known route.[13]



7

Wolf–Kishner reduction of the triketone gave a gross mixture of substances including a trace of a substance whose glpc retention time was the same as that of **7**. The time-of-flight mass spectrum of the trapped glpc peak was substantially identical with that of **7**, but the yield of **7** in the degradation product was so small that the result was not regarded as conclusive.

The chemistry of compounds **5** and **6** was consistent with the assigned structures. Tetramer **5** was thermally stable at temperatures below 200°. At 225° it was slowly converted into a mixture of polymeric and isomeric substances.

Tetramer **5** was quite resistant to hydrogenation. Using prereduced PtO_2 at 25° (1 atm) or PtO_2 in hexane at 80° (500 atm), hydrogenation was incomplete. With Raney nickel in ethanol at 75° (400–700 atm), hydrogenation was complete in 5 hr. The product consisted of a 95:5 mixture of isomers. The predom-

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[8] D. Vorlander and C. Siebert, *Chem. Ber.*, **39**, 1024 (1966).

[9] G. Hesse and G. Krehbiel, *Ann. Chem.*, **593**, 35 (1955).

[10] (a) J. R. Beckwith and L. P. Hager, *J. Org. Chem.*, **26**, 5206 (1961); (b) J. H. Boothe, R. G. Wilkinson, S. Kirshner, and J. H. Williams, *J. Amer. Chem. Soc.*, **75**, 1732 (1953).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958.

[12] R. Mayer, G. Wenschuh, and W. Topelmann, *Chem. Ber.*, **91**, 1616 (1958).

[13] R. Ya. Levina and T. I. Tantsyreva, *Dokl. Akad. Nauk SSSR*, **89**, 697 (1953); *Chem. Abstr.*, **48**, 6972 (1954).

inant isomer was characterized as $C_{12}H_{22}$ by mass spectroscopy. This mass spectrum was readily interpreted as that of a trimethylspiro[4.4]nonane by comparison with the mass spectrum of spiro[4.4]-nonane. All major peaks in the spectrum of $C_{12}H_{22}$ had counterparts in the spectrum of spiro[4.4]nonane differing by *m/e* 0, 14, 28, or 42. Other spectral data were uninformative.

Tetramer **5** did not undergo reaction with tetracyanoethylene or maleic anhydride.

Treatment of triketone **6** with excess ethanedithiol gave mainly a bisdithioketal, not the expected trisdithioketal. The reason for the failure of the third keto function to react is unknown. Structure **6** offers little steric hindrance to trisdithioketal formation. The C=O peak of the bisdithioketal was at 1745 cm^{-1}, which is normal for a cyclopentanone derivative.[11] Evidence that the three keto groups of **6** are free of gross steric hindrance was provided by the facile formation of a trisphenylhydrazone.

The structure of the pentamer obtained from the phosphine-modified Rh(I)-catalyzed reactions has not been established. The uv spectrum shows strong end absorption [210 mμ (ε 11,200), 233 (2000), 257 (200)]. The nmr spectrum shows complex patterns in the vinylic and allylic proton regions: the vinylic/allylic ratio is 6:10 or 5:11. Both the nmr and the infrared spectra suggest the presence of methylene and internal double bonds. The chemical shifts in the allylic region suggest that two of the protons are doubly allylic (δ 2.68) and eight or nine are singly allylic (δ 2.5–1.9).

Experimental Section[14]

1,4,7-Trimethylenespiro[4.4]nonane (5) and Unknown Pentamer.—In a typical experiment a mixture of 125 g of allene, 50 g of chloroform, 1 g of chlorotris(triphenylphosphine)rhodium(I)[5] and 0.1 g of hydroquinone was agitated at 70–80° in a 400-ml pressure tube with a stainless steel liner for 16 hr. The pressure fell to less than 1 atm after 11 hr. Analysis of the crude product by glpc showed that it contained, besides chloroform, traces of volatile substances assumed to be allene dimers and trimers, 55% by weight of tetramer **5**, 16% of a single pentamer, and substantial amounts of less volatile substances assumed to be hexamers and heptamers. The product was combined with the products of three similar runs (whose glpc analysis showed 42–55% of tetramer, 12–16% of pentamer) and the chloroform was removed using a rotary evaporator and an aspirator at 25°. Trap-to-trap distillation of the residues at 0.1 μ gave 280 g of colorless liquid. Fractionation on a spinning-band column gave 202 g (40%) of tetramer **5**, bp 34–35° (0.65 mm), and 60 g (12%) of the pentamer, bp 70° (0.60 mm). In a separate experiment the boiling points of the tetramer and the pentamer were 80° (10 mm) and 81–81.5° (1.2 mm).

A similar run in which $[(C_6H_5)_3P]_2Rh[CO]Cl$[6] was used as catalyst detonated violently on heating to 80°.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.07; mol wt, 160. Found: C, 89.46; H, 1025; mol wt, 160 (mass spectroscopy).

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.07; mol wt, 200. Found: C, 89.65; H, 10.07; mol wt, 200 (mass spectroscopy), 202 (cryoscopic in benzene). The ir spectrum showed 1610 (s, sh), 1617 (s), 1650 (s), 1656 (s, sh), 1669 (m) cm^{-1}.

1,3,3-Triphenylindene (4).—A solution of 2.0 g (5.8 mmol) of tetraphenylallene and 0.15 g of chlorotris(triphenylphosphine)-rhodium(I)[5] in 10 ml of chloroform was heated at 110° for 15 hr in a sealed tube. The solvent was evaporated, and the semisolid residue was washed with hexane to give 1.15 g of solid, indicated by its ir spectrum to be a mixture of indene **4** and starting material. Three recrystallizations from ethanol gave 0.46 g (24%) of **4**, mp 128.5–130.5° (lit.[15] mp 135°).

Spiro[4.4]nonane-1,4,7-trione (6).—Ozone was bubbled through a stirred solution of 15 g of tetramer **5** in 300 ml of methylene chloride at −78° until the solution turned blue. The solution was flushed with nitrogen and allowed to warm to −20°; 300 ml of 50% aqueous acetic acid and 150 g of zinc dust were added. The mixture was stirred for 6 hr as the temperature rose to 25°. All methylene chloride was evaporated in a stream of nitrogen, and 500 ml of fresh methylene chloride was added. The mixture was stirred and filtered. The methylene chloride layer was separated and was washed in turn with water, saturated sodium bicarbonate, and water. It was dried with magnesium sulfate and concentrated to give 13 g of partly crystalline residue. Recrystallization from a mixture of toluene and hexane (*ca.* 9:1) gave 10.1 g (65%) of triketone **6** in three crops (8.0, 0.6, and 1.5 g) of mp 83–83.5, 81–82, and 77–78.5°.

Anal. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07. Found: C, 65.35; H, 6.06.

Conversion of Triketone 6 into Tetramer 5.—A Carius tube containing 3.6 g (10 mmol) of triphenylmethylphosphonium bromide and a magnetic stirrer was attached to a vacuum pump by an adapter having a serum bottle cap on a side arm. The tube was heated to 100° and then closed off and cooled. Tetrahydrofuran (10 ml) and 1.6 *M* *n*-butyllithium in hexane (8 mmol) were added by injection. After 15 min of stirring a solution of 0.20 g (1.2 mmol) of triketone **6** in tetrahydrofuran was injected. The tube was chilled with liquid nitrogen, evacuated, sealed, and stirred in an oil bath at 80–85° for 12 hr. Flash distillation at low pressure gave a solution which was shown by glpc analysis to contain 7 mg (3.6% yield) of $C_{12}H_{16}$. The time-of-flight mass spectrum was identical with that of a dilute THF solution of tetramer **5**.

Hydrogenation of Tetramer 5.—A mixture of 16 g (0.10 mol) of **5**, about 2 g of W-2 Raney nickel, and 80 g of ethanol was agitated in a stainless steel bomb at 75° under hyrogen at 400–700 atm. Uptake of hydrogen was complete after 5 hr. The product was isolated by glpc; two isomers in a 95:5 ratio were detected in the gas chromatogram. The product mixture was shown to be free of unsaturation by its ir and nmr spectra. The mass spectrum had its strongest peaks at *m/e* 166 (0.12), 123 (0.10), 110 (0.43), 109 (0.44), 95 (0.25), 82 (0.15), 81 (1.00), 80 (0.17), 69 (0.18), 67 (0.22), 55 (0.20), 41 (0.26), 39 (0.13), 29 (0.11) and 27 (0.12).

Treatment of Triketone 6 with Ethanedithiol.—A mixture of 5.2 g (0.031 mol) of triketone **6**, 30 ml (34 g, 0.36 mol) of ethanedithiol, 300 ml of benzene, and 40 g of $CaCl_2$ was saturated with HCl gas and stirred overnight. The solution was filtered and concentrated. The residue was recrystallized from ethanol to give 8.9 g (90%) of colorless bisdithioketal, mp 102–103°. The ir spectrum had one strong, sharp peak in the CO region at 1745 cm^{-1}. Retreatment with ethanedithiol gave no further reaction. Treatment with phenylhydrazine caused decomposition.

Anal. Calcd for $C_{13}H_{18}OS_4$: C, 49.02; H, 5.70; S, 40.26. Found: C, 48.99; H, 5.80; S, 40.27.

The triphenylhydrazone of **6** precipitated from an ethanol solution of triketone **6**, excess phenylhydrazine, and 1 drop of trifluoroacetic acid. Attempts to recrystallize the derivative failed. The crude substance melted with decomposition at 197–200°.

Anal. Calcd for $C_{27}H_{28}N_6$: C, 74.28; H, 6.47; N, 19.25. Found: C, 74.15; H, 6.40; N, 18.87.

Synthesis of Spiro[4.4]nonane (7).—Spiro[4.4]-1,3-nonadiene, bp 40–41.5° (7 mm), was prepared from cyclopentadiene and 1,4-dibromobutane as described.[13] The tetracyanoethylene adduct, mp 230–235° dec, was formed in acetonitrile and was recrystallized from a mixture of tetrahydrofuran and hexane.

Anal. Calcd for $C_{15}H_{12}N_4$: C, 72.56; H, 4.89; N, 22.57. Found: C, 72.56; H, 4.73; N, 22.61.

The diene was hydrogenated at 80°, 2000 psi, using W-2 Raney nickel. Spiro[4.4]nonene (**7**) was isolated by glpc. The nmr and ir spectra were consistent with the assigned structure. The mass spectrum had its strongest peaks at *m/e* 124 (0.17), 95 (0.48), 82 (0.84), 81 (0.23), 68 (0.19), 67 (1.00), 66 (0.11), 55 (0.16), 54 (0.13), 53 (0.12), 41 (0.33), 39 (0.26), and 27 (0.21).

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[14] Melting points and boiling points are uncorrected. Infrared spectra (linear in wavelength) were recorded using a Perkin-Elmer Model 21 spectrophotometer. Nmr spectra were determined with tetramethylsilane as internal standard using Varian A-60 and HR-100 devices.

[15] J. English and F. V. Brutcher, *J. Amer. Chem. Soc.*, **74**, 4279 (1952).

Wolf-Kishner Reduction of Triketone 6.—Triketone **6** (2.0 g) was reduced by a modification of the procedure of Durhan[16] using diethylene glycol as solvent. Distillation of the reaction mixture at 0.1 mm gave 14 g of a mixture of liquids more volatile than diethylene glycol; glpc indicated that a trace of spiro[4.4]-nonane was present. The time-of-flight mass spectrum of the peak was substantially identical with that of spiro[4.4]nonane.

Registry No.—**4,** 4614-01-1; **5,** 17396-77-9; **6,** 17396-18-8; triphenylhydrazone of **6,** 17414-33-4; **7,** 175-93-9.

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[16] L. J. Durham, D. J. McLeod, and J. Cason, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 510.

Nonplanar Cyclobutane. Evidence for a Conformationally Controlled, Classic Mechanism in the Deamination of *cis*- and *trans*-3-Isopropylcyclobutylamine[1]

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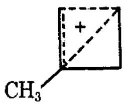
The synthesis and configurational assignments of *cis*- and *trans*-3-isopropylcyclobutylamine are described. Deamination yields the same five products for either isomer, but a major distinction in the ratios of two of these, cyclopropylisopropylcarbinol (68% from *cis* amine, 29% from *trans* amine) and *trans*-(2-isopropylcyclopropyl)-carbinol (0–2% from *cis* amine, 55% from *trans* amine) is observed; no *cis*-(2-isopropylcyclopropyl)carbinol is obtained from either reactant. These data are considered to be most compatible with concerted processes dependent on stereochemical differences; the cyclobutyldiazonium ion is implicated as the branching point in the formation of products, which arise through competing pathways. A mechanism is proposed in which the formation of major product *trans*-(2-isopropylcyclopropyl)carbinol is contingent on conformationally facilitated orbital overlap in the *trans* intermediate, whereas a similar process for the *cis* intermediate is opposed by unfavorable repulsive interactions. It is suggested that cyclobutylamine deaminations may follow a more classic course than has been hitherto generally accepted.

The facile interconversions which often occur among related cyclobutyl, cyclopropylcarbinyl, and homoallyl derivatives in carbonium ion reactions have long been intriguing mechanistically. The bicyclobutonium ion rationale attempts to explain these transformations in terms of a common system of nonclassical carbonium ion intermediates.[3] This concept, while effective in reconciling reactivity for the parent cyclobutyl and cyclopropylcarbinyl derivatives, is less persuasive in application to substituted systems. It was observed that deamination of 1-, 2-, and 3-methylcyclobutylamine[3b] gave no ring rearrangement in the first case, exclusive production of one cyclopropylcarbinol in the second, and a mixture of cyclopropylcarbinols in the third. Preferred stabilization of different bicyclobutonium ions (**1** and **2**) for, respectively, the 1- and 2-methylamines was invoked to explain the disparity, with a pair of interconverting bicyclobutonium ions (**3** and **4**) accounting for the 3-methyl case. However, it is difficult to understand why such interconversion would occur solely in the latter instance and not the former two. Entry into the same system of rapidly equilibrating intermediates is anticipated in theory, and were electrical stabilization a predominant factor, the same major product(s) might be reasonably expected. Further, although not reflecting a mandatory requirement, absence of homoallylic product implicit in the formulation of the several bicyclobutonium ions was encountered.



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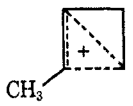

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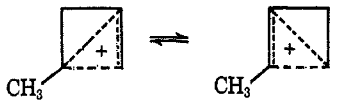

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Recently, convincing evidence[4–8] has accumulated that the ion derived from the cyclopropylcarbinyl system possesses an unrearranged structure rather than the bicyclobutonium ion structure previously proposed.[3] More recently, extended Hückel theory quantum mechanical calculations have supported a completely classical cyclobutyl cation derived from cyclobutane, with nonclassical structures involving 1,3 bridging in rings with varying dihedral angle all being of higher energy.[9] Further, calculations on the tricyclobutonium ion proposed as a possible initial or intermediary pathway in these reactions[3g] showed that it is of such high energy as to eliminate it clearly from consideration. The suggestion has been previously made that the cyclopropyl cation is in equilibrium with the classical cyclobutyl cation.[10]

It would thus appear that while factors of electrical stability are undoubtedly important in explaining deamination of cyclobutylamines, the specific concept of a system of common, interconverting bicyclobutonium ions must bear renewed examination, particularly

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[1] Preliminary reports of this work have been presented: 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstracts, p 167s; I. Lillien and R. A. Doughty, *Tetrahedron Lett.*, 3953 (1967).

[2] Taken in part from the thesis submitted by R. A. D. to the Graduate School of the University of Miami in partial fulfillment of the requirements for the Ph.D. degree in chemistry. Work done primarily at the University of Miami, Coral Gables, Fla.

[3] (a) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1331 (1965); (b) M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *ibid.*, **83**, 3671 (1961); (c) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961); (d) E. Renk and J. D. Roberts, *ibid.*, **83**, 878 (1961); (e) M. S. Silver, P. R. Schaeffer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960); (f) R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959); (g) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509, 3542 (1951).

[4] M. Vogel and J. D. Roberts, *ibid.*, **88**, 2262 (1966).

[5] H. L. Goering and K. E. Rubinstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, p 11K.

[6] H. G. Richey, Jr., and J. M. Richey, *J. Amer. Chem. Soc.*, **88**, 4971 (1966).

[7] C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998 (1965); N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, **87**, 3000 (1965).

[8] P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

[9] R. E. Davis and A. Ohno, *Tetrahedron*, **24**, 2063 (1968).

[10] H. C. Brown, "The Transition State," Spec. Publ. No. 16, The Chemical Society, London, 1962, p 140.