[CONTRIBUTION FROM MONSANTO RESEARCH CORP.]

Synthesis of Polycyclic Hydrocarbons Containing Cyclopropyl Groups[1]

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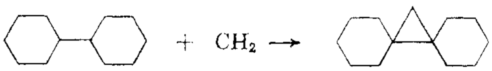
The elements of methylene, generated from diiodomethane and zinc-copper couple, were added to bicyclohexylidene, β-pinene, 1,5-cyclooctadiene, 2,5-norbornadiene and 4-vinylcyclohexene to produce, respectively, dispiro[5.1.5.0]tridecane, 6′,6′-dimethylspiro[cyclopropane-1,2′-norpinane], tricyclo[7.1.0.0^{4,6}]decane, tricyclo[3.2.1.0^{2,4}]oct-6-ene, tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane, 3-vinylnorcarane, 4-cyclopropylcyclohexene, and 3-cyclopropylnorcarane. The method has not previously been used to synthesize spiro links.

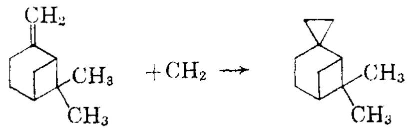
Seven new polycyclic hydrocarbons containing cyclopropyl groups have been prepared as a part of an Air Force program to develop new hydrocarbon jet fuels of high heat of combustion and high thermal stability.

Cyclopropane derivatives were formed from two monoolefins and three dienes by the method of Simmons and Smith,[2] using diiodomethane and zinc-copper couple. Although the exact nature of the reactive intermediate has not been determined, it is useful to consider that cyclopropane formation occurs via a carbene mechanism.[3]

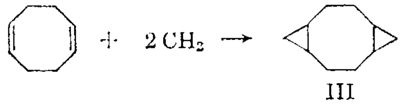
The products obtained from bicyclohexylidene, β-pinene, and 1,5-cyclooctadiene were dispiro[5.1.5.0]tridecane (I), 6′,6′-dimethylspiro[cyclopropane-1,2′-norpinane] (II), and tricyclo[7.1.0.0^{4,6}]decane (III), respectively.



I



II

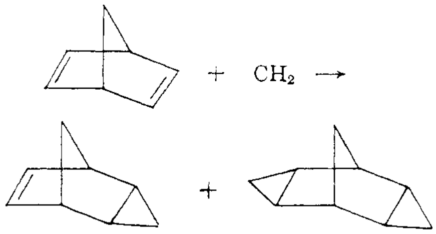


III

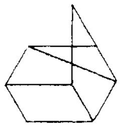
An excess of the carbene reagent was used in the reaction with 1,5-cyclooctadiene and no monoadduct, bicyclo[6.1.0]non-4-ene, was observed.

Preparation of I and II illustrates the use of this reaction for the synthesis of the spiro link.

Addition of carbene to 2,5-norbornadiene resulted in the formation of both the mono- and diadducts, tricyclo[3.2.1.0^{2,4}]oct-6-ene (IV) and tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane (V). The monoadduct was shown to have the structure IV, as claimed by Simmons and Smith,[2] rather than the tetracyclo[2.2.1.1^{2,6}.0^{3,5}]octane structure, VI, which would have resulted from transannular addition. This was demonstrated by infrared absorption at 1629, 1587, and 1558 cm.$^{-1}$, attributed to disubstituted ethylenic unsaturation in strained ring systems,[5] and at 1.66μ in the near infrared, attributed to a *cis* double bond.[6]

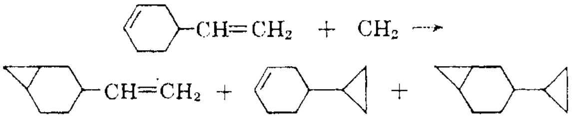


IV V



VI

The addition of carbene to 4-vinylcyclohexene resulted in the formation of two monoadducts, 3-vinylnorcarane (VII), and 4-cyclopropylcyclohexene (VIII), as well as the diadduct 3-cyclopropyl-



VII VIII IX

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(1) This work was presented in part before the Division of Organic Chemistry at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

(2) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958); H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(3) For convenience, the word *carbene* and the symbol CH_2 will be used to designate the reactive intermediate, regardless of whether its actual structure is iodomethylzinc iodide[2] or carbene.[4]

(4) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(5) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York (1958), p. 37.

(6) R. G. J. Miller and H. A. Willis, *J. Applied Chem.*, **6**, 386 (1956); R. T. Holman and P. R. Edmondson, *Anal. Chem.*, **28**, 1533 (1956); R. F. Goddu, *Anal. Chem.*, **29**, 1790 (1957).

TABLE I

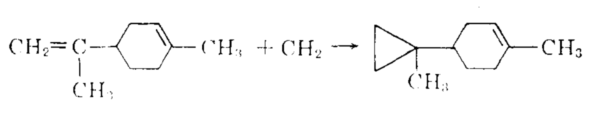
PROPERTIES OF POLYCYCLIC HYDROCARBONS CONTAINING CYCLOPROPYL GROUPS

Property	Compound				
	I[a]	II	III	V	IX
B.p./mm.	60/0.8	36.5/7 to 38.5/6	42–43/3.5	45–46/9	40/10
M.p.			38–39	−51	
Density					
d_4^{20}	0.918			0.991	0.8967
d_0^0				1.10	
$d_{37.4}^{37.4}$		0.8731	0.9076	0.9748	
$d_{98.9}^{98.9}$		0.8269	0.8599	0.9235	
$d_{146.1}^{145.1}$		0.7544			
$d_{177.8}^{177.8}$			0.7975		
n_D^{20}	1.4920	1.4762		1.5048	1.4756
Viscosity, centistokes					
−34.4°				10.87	
0°		5.29		4.607	
37.4°		2.29	2.76		
98.9°		1.03	1.09	0.90	
145°		0.78			
180°			0.541		
Net heat of combustion, Kcal./mole	1809	1550	1308	1222	
Thermal conductivity, cal./(sec.)(cm.)^2(°C./cm.)					
63°			0.00950	0.01036	
104°			0.00912	0.01028	
Specific heat, cal./(g.)(°C.) at 100°			0.485		

[a] 87% pure.

norcarane (IX). About twice as much IX was formed as the combined weight of the two monoadducts. The monoadducts were resolved by vapor phase chromatography to two peaks of 81 and 19%. The infrared spectrum of the two-component mixture of monoadducts showed strong vinyl unsaturation at 1639, 990 and 910 cm^{-1}. Absorption attributed to the cyclopropyl ring was noted at 3058, 2985, and 1015 cm^{-1}. The apparent molar extinction coefficient for the 1639 cm.$^{-1}$ absorption was calculated to be 23 after determination that the 1656 cm.$^{-1}$ cyclohexenyl unsaturation peak did not interfere appreciably with the intensity measurement. The extinction coefficient for a terminal double bond R—CH═CH$_2$ is reported[7] to be $\epsilon \simeq 24$–46 while that for an internal *cis* double bond is about $\epsilon = 5$–10. On this basis the 81% component of the monoadduct mixture was assigned the structure VII and the 19% component structure VIII.

In the case of D-limonene, Simmons and Smith[2] reported reaction exclusively on the isopropenyl group. The reaction has gone predominately the other way in the present case.



A run of the carbenation of 4-vinylcyclohexene made under the same conditions using the "simplified zinc-copper couple" of Shank and Shechter[8] resulted in about 70% recovery of unreacted diene and 30% yield of mixed monoadducts only. The simplified couple was not used with the other olefins.

The physical properties of previously unreported compounds prepared in this work are listed in Table I.

The reaction procedure has been modified to remove excess methylene iodide from the reaction mixture before the work-up. Distillation in the presence of methylene iodide causes further reaction and discoloration, even where strenuous efforts are made to exclude incident light. The modification consisted of the addition of 2-methylbutene-2 and an additional amount of zinc-copper couple to the reaction mixture at the completion of the normal reaction and additional reflux for another twenty-four hours. After this period vapor phase chromatograms showed that all of the excess methylene iodide had reacted with 2-methylbutene-2 to form 1,1,2-trimethylcyclopropane. Those two hydrocarbons, boiling at 38.6 and 52.5°, respectively, were readily removed by distillation.

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(7) R. N. Jones and C. Sandorfy, *Technique of Organic Chemistry, Vol. IX: Chemical Applications of Spectroscopy*, W. West, ed., Interscience, New York, 1956, pp. 287, 370.

(8) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

EXPERIMENTAL

Vapor phase chromatograms (v.p.c.) were run on a Perkin-Elmer Model 154C vapor fractometer. Conditions used were 95°, flow 130 cc. helium/min. on a 6′ column of 16% *m*-bis (*m*-phenoxyphenoxy)benzene on 35–80 mesh Chromosorb W, except where otherwise described.

All percentage compositions determined by v.p.c. are expressed in uncorrected area per cent.

Infrared spectra were determined on a Perkin-Elmer Model 21 double beam spectrophotometer with sodium chloride and lithium fluoride optics. Portions of the infrared spectra of compounds I, II, III, IV, V, VIII and IX have been published elsewhere.[11b]

Zinc-copper couple. The procedure is based on that of Simmons and Smith.[2,9] A mixture of 120 g. of zinc dust and 15 g. of cupric oxide was ground together in a mortar and pestle and placed in an 8 inch Vycor boat in a ceramic combustion tube. Three iron-constantan thermocouples were inserted into the mixture for accurate temperature information. The mixture was heated carefully in a stream of hydrogen to 450° over about 90–100 min. The reduction is highly exothermic and care should be taken to heat sufficiently slowly so that transient exothermic bursts do not carry the local temperature above 475°. The contents of the boat were held at 425–450° for an additional 4 hr. and allowed to cool in the hydrogen atmosphere. The product was a grayish powder, only occasionally containing solidified droplets of zinc.

General reaction procedure. The general procedure follows that of Simmons and Smith.[2] Diiodomethane from National Biochemical Co. was distilled before use and stored over mossy tin in a refrigerator. Anhydrous diethyl ether was stored over sodium. The quantity of ether was chosen so that the total volume of ether, diiodomethane and olefin, expressed in milliliters, equalled nine times the weight of the zinc-copper couple in grams. Per gram-atom of zinc, 6 mol.-% of iodine, 80–100 mol.-% of monoolefin and 100 mol.-% of diiodomethane were used. The reaction was refluxed for 48 hr. for the first stage.

In order to destroy the excess diiodomethane before distillation, the reaction mixture was treated with 2-methylbutene-2 and more zinc-copper couple in amount stoichiometrically equivalent to the original quantity of diiodomethane. This second phase of the reaction was carried out exactly as the first phase, including the use of 6 mol.-% of iodine to activate the couple.

The second stage of the reaction was allowed to reflux for 24 hr. After cooling, the mixture was centrifuged to remove the finely divided metals and the centrifugate extracted thrice with cold 5% hydrochloric acid, thrice with 5% sodium bicarbonate and twice with water. The organic phase was dried over a solid desiccant overnight. The solvent, 2-methylbutene-2 and trimethylcyclopropane were removed by a rotary evaporator by lowering the pressure to 27 mm. while the flask was immersed in ice water. The crude products were examined by v.p.c. to show the absence of diiodomethane and distilled.

Dispiro[5.1.5.0]tridecane. (I) Bicyclohexylidene of unambiguous structure was prepared from cyclohexanone pinacol by the method of Criegee, *et al.*[10] The sample melted at 54.5–55.5° uncorrected, lit.[10] m.p. 55°. Its purity by v.p.c. (165°, flow 150 cc. helium/min.) was over 99.8%.

Initial product of the carbene reaction on this olefin was a mixture whose v.p.c. showed 31.3% unchanged olefin, 60.0% desired dispiro[5.1.5.0]tridecane and 8.7% of an unknown hydrocarbon of higher retention time. Separation by distillation was not possible, since all three components boiled very close together. It was possible to remove a portion of the unreacted olefin by crystallization.

A second run of the carbene reaction on the mixture converted all of the remaining unreacted bicyclohexylidene, giving, after distillation, 13.3 g. of a mixture of 87% dispirotridecane and 13% of the unknown hydrocarbon (v.p.c. run at 200°, flow 100 cc. helium/min.). This mixture boils at 60°/0.8 mm., d_4^{20} 0.918, n_D^{20} 1.4920.

The unknown hydrocarbon is likely to be either a carbenation product from an isomeric olefin or a carbene insertion product. If the bicyclohexylidene were isomerized to cyclohexylcyclohexene in the presence of zinc iodide, the resulting product would be cyclohexylnorcarane. The latter is ruled out as being the principal product by the nuclear magnetic resonance spectrum cited below. The product of carbene insertion, if it should occur, would be methylbicyclohexyl or methylbicyclohexylidene.

Dispirotridecane was separated in pure form in small quantities from the above mixture by vapor phase chromatography.

An NMR spectrum was determined on the separated dispirane on a Varian spectrometer at an RF frequency of 40 mc., field 9400 gauss, using water as a reference. Two peaks were found, one at +3.38 ppm attributed to methylene protons from a six-membered carbocyclic ring, and one at +4.81 ppm attributed to methylene protons from a three-membered carbocyclic ring.

The separated dispirane was also examined by a high-resolution infrared spectrometer with a lithium fluoride prism over the range of 2700–3200 cm.$^{-1}$ Bands at 2855 and 2926 cm.$^{-1}$ exactly duplicated those in a reference determination on cyclohexane and were attributed to the C–H bond in the methylene protons of a cyclohexane ring. One additional band was found at 3035 cm.$^{-1}$ which agrees with the literature[11] assignment for the methylene group in cyclopropane.

The conventional infrared spectrum also showed a major absorption at 1020–30 cm.$^{-1}$, attributed to the cyclopropyl ring.

Analysis of the separated dispirane. Calcd. for $C_{13}H_{22}$: C, 87.6, H, 12.4. Found: C, 88.0, H, 12.3.

6′,6′-Dimethylspiro[cyclopropane-1,2′-norpinane]. (II) β-Pinene obtained from the Arizona Chemical Co. was redistilled. Vapor phase chromatographic analysis at 181°, flow 75 cc. helium/min., showed a composition of 74.3% β-pinene, 16.5% α-pinene and 3.4% of the next most concentrated component.

Carbenation of 151 g. of this redistilled material produced 153 g. of crude product which contained 84.3% of 6′,6′-dimethylspiro[cyclopropane-1,2′-norpinane] by v.p.c. at 181°, flow 75 cc. helium/min. The determination showed a complete absence of diiodomethane, α- and β-pinene.

Two vacuum distillations through a 30-cm. glass-helix packed column gave a 42 g. fraction boiling 36.5°/7 mm. to 38.5°/6 mm. After passage through a 10-cm. column packed with silica gel, 35.4 g. of purified material was obtained which showed a v.p.c. purity of 96.4% (at 146°, flow 75 cc. helium/min.), n_D^{20} 1.4762.

Absence of unsaturation in the infrared spectrum and absorptions at 3067 and 2985 cm.$^{-1}$ for cyclopropyl methylenes support the above structure.

Although the infrared spectrum also showed absorption in the 1010–1048 cm.$^{-1}$ region at 1010 cm.$^{-1}$, this cannot be cited as proof of the presence of a cyclopropyl ring in this case, since both α- and β-pinene, as well as many other terpenes, show strong absorptions in this region.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.9, H, 12.1. Found: C, 88.1, H, 12.0.

Tricyclo[7.1.0.0^{4,6}]decane. (III) Cyclooctadiene-1,5 was obtained from the Phillips Petroleum Co.

Carbenation of 108 g. of cyclooctadiene produced 102 g. of crude product.

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(9) We wish to thank Dr. H. E. Simmons for communicating some additional details on the preparation of the active couple.

(10) R. Criegee, E. Vogel, and H. Höger, *Chem. Ber.*, **85**, 144 (1952).

(11)(a) S. E. Wiberley, S. C. Bunce, and W. H. Bauer, *Anal. Chem.*, **32**, 217 (1960); (b) S. A. Liebman and B. J. Gudzinowicz, *Anal. Chem.*, **33**, 931 (1961).

After distillation a 65 g. fraction was obtained boiling 42–43°/3.5 mm. Vapor phase chromatography of the distilled product (150°, flow 80 cc. helium/min.) showed two major components of 52.7 and 42.4%, and two minor components of 4.4 and 0.4%. The two major components were separated on the chromatograph and their infrared spectra run separately and compared with the spectrum of the entire fraction. The major component of lower retention time, obtained in this separation, is a solid, m.p. 38–39°. The three spectra were very similar. Each showed the usual strong, sharp peaks at 3067 and 2994 cm.$^{-1}$ in the C–H region and a strong absorption at 1020 cm.$^{-1}$, all attributed to the cyclopropyl ring, and no absorption at 1661 cm.$^{-1}$ where the double bonds in the starting diene absorb strongly.

On this basis, the two major components are assigned the expected *cis* and *trans* structures of tricyclo[7.1.0.0^{4,6}]decane.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.2, H, 11.8. Found: C, 87.6, H, 12.0.

Tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane. (V) 2,5-Norbornadiene from Matheson, Coleman, and Bell was redistilled and 2 moles of the fraction boiling at 81–84° was used for the carbenation.

Approximately 200 g. of crude material was obtained which contained 40% monoadduct IV, 40% of the desired diadduct V, and no diiodomethane. Vacuum distillation produced a mixture of 86.5% diadduct and 4.7% of an unknown compound of higher retention time.

This mixture was passed through a preparative-scale v.p.c. column (Gas Chromatography Ltd., London, England) 5 cm. in diameter and 180 cm. high. The packing was coated with dinonyl phthalate, temp. 140°, flow rate 2 l. nitrogen/min., and 1.5 ml. of hydrocarbon were injected per pass. Thirty grams of purified material were obtained in this way boiling at 45–46°/9.0 mm., d_4^{20} 0.991, n_D^{20} 1.5048. This product had a purity by v.p.c. of 96.5%, the balance being divided between three impurities.

Infrared spectra showed the usual, strong, sharp peaks at 3003 and 3058 cm.$^{-1}$ in the C-H region and a strong absorption at 1015 cm.$^{-1}$, all indicative of the cyclopropyl ring. Absorption at 1635 cm.$^{-1}$ attributed to the C=C and found in the spectrum of the starting diene was absent in the spectrum of the product. There was no evidence for methyl hydrogens in the infrared spectrum in the 1375 to 1380 cm.$^{-1}$ region or from 2800 to 3200 cm.$^{-1}$ determined through lithium fluoride optics.

Further proof of the absence of double bonds was obtained by the Raman spectrum on a Cary Model 81 Raman Spectrophotometer, which showed no frequency displacement, $\Delta \bar{\nu} \sim 1600$ to 1680 cm.$^{-1}$.

Anal. Calcd. for C_9H_{12}: C, 89.9, H, 10.1, M_D 36.4. Found: C, 90.1, H, 10.1, M_D 36.0.

Tricyclo[3.2.1.0^{2,4}]oct-6-ene (IV). The preparative v.p.c. run described above for V also yielded several grams of tricyclo[3.2.1.0^{2,4}]-oct-6-ene, boiling at 35–36°/8 mm., d_4^{20} 0.949, n_D^{20} 1.4867. Its purity was 91.5% by v.p.c. (flow rate 125 cc. helium/min.). Its infrared spectrum showed a strong band at 1030 cm.$^{-1}$ (cyclopropyl group) and peak at 1629, 1587, and 1558 cm.$^{-1}$ (unsaturation[5]). The near infrared spectrum (determined on a Cary Model 14 recording spectrophotometer) showed a band at 1.66μ, attributed[6] to a *cis* double bond. On this basis the structure IV rather than VI was assigned to this compound. The compound has been previously prepared by the same reaction,[2] b.p. 67–8°/100 mm., n_D^{25} 1.4874.

3-Cyclopropylnorcarane (IX). 4-Vinylcyclohexene was obtained from Matheson, Coleman, and Bell. Carbenation of 43.2 g. of 4-vinylcyclohexene produced 45.3 g. of crude product which had a composition by v.p.c. of 28.5% mixed monoadducts, 58.9% diadduct IX, and 3.4% of starting diene. On the column used, the retention times of IX and diiodomethane were the same.

The crude product was separated on the preparative scale v.p.c. described above. The diadduct IX was collected in 96% purity, b.p. 40°/10 mm., d_4^{20} 0.8967, n_D^{20} 1.4756. Infrared spectra showed the usual strong, sharp peaks at 2985 and 3058 cm.$^{-1}$ in the C-H region and a strong absorption at 1015 cm.$^{-1}$, all indicative of the cyclopropyl ring. There was no absorption assignable to vinyl or cyclohexenyl unsaturation which was strongly evident in the starting diene.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.2, H, 11.8, M_D 43.2. Found: C, 88.5, H, 11.7, M_D 42.8.

3-Vinylnorcarane and 4-cyclopropylcyclohexene (VII and VIII). Both monoadducts were collected from the preparative-scale v.p.c. as an unresolved single peak of 99% purity. This peak was separated on a 12′ v.p.c. column, 10% squalane on Chromosorb W, 128°, flow 125 cc. helium/min., to two well-resolved components of 81.2 and 18.8%. The interpretation of the infrared spectrum of this mixture has been given in the discussion above.

A mixture of 49.3% of this mixture of monoadducts and 49.2% diadduct IX boiled at 28–34°/10 mm. The v.p.c. separated mixture of monoadducts had n_D^{20} 1.4717.

Anal. Calcd. for C_9H_{14}: C, 88.5, H, 11.6. Found: C, 88.5, H, 11.6.

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We wish to thank Mr. J. V. Pustinger for the determination of nuclear magnetic resonance and near infrared spectra, Shirley A. Liebman for the determination and interpretation of infrared spectra and vapor phase chromatograms, Mr. B. J. Gudzinowicz and associates for the determination of some of the physical properties in Table I, and Dr. Carol K. Fitz for the microanalyses.

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