Tetrahedron, 1964, Vol. 20, pp. 1843 to 1858. Pergamon Press Ltd. Printed in Northern Ireland

FREE-RADICAL TRANSANNULAR CYCLOADDITIONS TO *cis-cis*-1,5-CYCLOOCTADIENE[1]

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(*Received* 13 *February* 1964; *in revised form* 9 *April* 1964)

Abstract—Carbon tetrachloride, chloroform, N,N-dimethylformamide, N-t-butylformamide, acetaldehyde, butyraldehyde, butyrolactone, etc. react with *cis-cis*-1,5-cyclooctadiene in a free-radical transannular 1,5-cycloaddition to give derivatives of bicyclo[3.3.0]octane. Various transformations of the adducts as well as the proof of their structure are described.

IONIC reactions in the cyclooctane series, which have become well-known chiefly through the work of Cope *et al.*,[2] frequently lead to transannular rearrangements. Transannular reactions of cyclooctane derivatives involving carbene intermediates have also been described.[3] Free-radical reactions, however, have not been investigated.

Several years ago, after *cis-cis*-1,5-cyclooctadiene had become readily available, we were prompted by the absence of any information on the free-radical reactions in cyclooctane series to initiate the work which forms the subject of this paper.

Although close analogies to this system are lacking, *a priori cis-cis*-1,5-cyclooctadiene (hereafter referred to as 1,5-cyclooctadiene) could be predicted to form a mixture of 1:1 and 1:2 adducts with free-radical addends such as polyhalomethanes. Thus, with carbon tetrachloride the products would be (trichloromethyl)chlorocyclooctene and isomeric bis(trichloromethyl)dichlorocyclooctanes. Such a simple picture would be in line with the known addition of carbon tetrachloride to cyclohexene[4] as well as to other olefinic compounds.[5] On the other hand, the great propensity of the cyclooctane system to form bicyclic products, at least in the ionic[2] and carbene[3] reactions, would warrant a consideration of possible rearrangement through a transannular cycloaddition. Such a possibility seemed exciting even though free-radical rearrangements of this type occur so infrequently that Nesmeyanov *et al.*[6] were led to state that there is "little information about" such reactions.

Nevertheless, a few examples of free-radical rearrangements of interest in connection with the present work may be found in the literature. Thus, Berson *et al.*[7] have found that 2-azobornane gives on pyrolysis products some of which arise through a free-radical transannular reaction. Very recently, Huyser and Echegaray[8] have shown

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[1] A preliminary account of some of this work has been published: R. Dowbenko, *J. Amer. Chem. Soc.* **86**, 946 (1964).

[2] E.g., A. C. Cope, J. N. Grisar and P. E. Peterson, *J. Amer. Chem. Soc.* **82**, 4299 (1960).

[3] L. Friedman and H. Shechter, *J. Amer. Chem. Soc.* **83**, 3159 (1961).

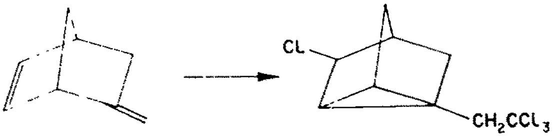
[4] E. C. Kooyman and E. Farenhorst, *Rec. Trav. Chim.* **70**, 867 (1951).

[5] For a critical review of free-radical polyhalomethane additions see C. Walling, *Free Radicals in Solution* J. Wiley, New York (1957).

[6] A. N. Nesmeyanov, R. Kh. Freidlina, V. N. Kost and M. Ya. Khorlina, *Tetrahedron* **16**, 94 (1961).

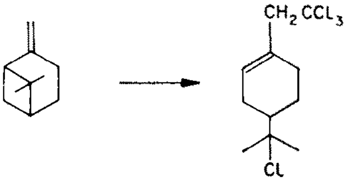
[7] J. A. Berson, C. J. Olson and J. S. Walia, *J. Amer. Chem. Soc.* **84**, 3337 (1962).

[8] F. S. Huyser and G. Echegaray, *J. Org. Chem.* **27**, 429 (1962).



I

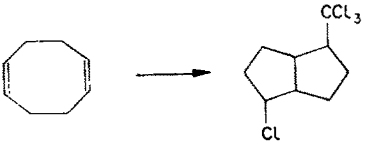
that 5-methylene-2-norbornene gives in a free-radical catalyzed reaction with carbon tetrachloride the nortricyclene derivative I. The corresponding reaction of β-pinene to give the adduct II is also well known.[9] In view of this, therefore, it appeared likely that 1,5-cyclooctadiene might also give rearranged products. That the free-radical additions to 1,5-cyclooctadiene are transannular and result in derivatives of bicyclo[3.3.0]-octane is shown below.



II

When 1,5-cyclooctadiene was refluxed with carbon tetrachloride and a small amount of benzoyl peroxide there was isolated, in addition to recovered starting material, a 63% yield of a 1:1 adduct which was accompanied by higher-boiling fractions showing strong benzoate absorption in the IR and by benzoic acid. Simple distillation afforded the pure compound which was homogeneous in gas chromatography. Irradiation of the mixture of the diene and carbon tetrachloride with a low intensity UV lamp or with a Sunlamp (General Electric Company) gave low yields of the 1:1 adduct. The same compound could be obtained in 73% yield when a mixture of 1,5-cyclooctadiene, carbon tetrachloride, isopropyl alcohol and a small amount of ferric chloride was refluxed for two days.[10]

All the evidence, both chemical and physical, indicated that the 1:1 adduct was 2-trichloromethyl-6-chlorobicyclo[3.3.0]octane (III). Thus, the compound did not



III

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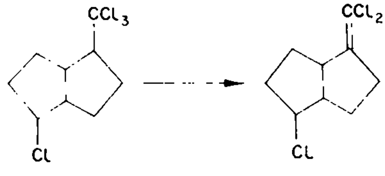
[9] D. M. Oldroyd, G. S. Fisher and L. A. Goldblatt, *J. Amer. Chem. Soc.* 72, 2407 (1950); G. DuPont, R. Dulou and G. Clement, *Bull. Soc. Chim. Fr.* 1056, 1115 (1950).

[10] For the iron and copper chloride catalyzed additions of carbon tetrachloride and chloroform to olefins, see M. Asscher and D. Vofsi, *Chem. & Ind.* 209 (1962); M. Asscher and D. Vofsi, *J. Chem. Soc.* 1887 (1963).

decolorize bromine in carbon tetrachloride, was unchanged on heating with aqueous potassium permanganate, and did not absorb any hydrogen in ethyl acetate solution (for further hydrogenation experiments, however, see below). The IR spectrum of the compound showed only two bands in the 3·4-μ region, and, unlike the spectra of cyclooctene and 1,5-cyclooctadiene, did not have any bands at wavelengths lower than 3·40 μ. Cyclooctene and 1,5-cyclooctadiene showed sharp bands at 3·30 and 3·34 μ, respectively, attributable[11] to the $=\overset{|}{\mathrm{C}}\text{—H}$ stretching vibrations. The absence of olefinic protons was also confirmed by PMR spectrum[12] which showed only traces of olefinic impurities at ca. 5·6 and 4·2 ppm, and consisted of two broad signals at 2·0 and 2·8 ppm and a weaker one at 4·05 ppm. If the resonance at 4·05 ppm is assigned to the hydrogen in the position 6, then the count of protons results in a total of 12. The broad resonance at 2·8 ppm appeared to represent 3 protons, probably those at positions 1, 2 and 5, while the resonance at 2·0 ppm was likely to be due to the remaining methylene protons.

In contrast to other similar products which give good yields of acids on hydrolysis of the trichloromethyl group[13] (also see below for hydrolysis of 2-(trichloromethyl)-bicyclo[3.3.0]octane), the compound III was either unreactive or gave uncharacterizable decomposition products. Thus, it was recovered unchanged on reflux with aqueous sodium hydroxide and on attempted hydrolysis with a small amount of water and ferric chloride in chloroform solution,[14] while hot phosphoric or sulfuric acid gave intractable tars. The last-mentioned reagents gave unchanged III under milder conditions. Concentrated nitric acid at 90° gave a small amount of an acidic material whose IR spectrum was similar to that of *endo-cis*-bicyclo[3.3.0]octane-2-carboxylic acid.

Dehydrochlorination of the bicyclooctane III with sodium methoxide in refluxing methanol gave a monodehydrochlorinated product, apparently IV. The reason for this preference over the alternative structure in which the chlorine in the ring is eliminated lies in the low reactivity of ring substituents in bicyclo[3.3.0]octane toward elimination[15] and also in the analogous behavior of 2-(trichloromethyl)-bicyclo[3.3.0]octane toward dehydrochlorination. In addition to this, the compound



IV

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[11] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* p. 38. Methuen Company, London (1954).

[12] The author is grateful to Dr. D. P. Hollis of Varian Associates, Palo Alto, California, for obtaining this spectrum (Varian A-60 Spectrometer).

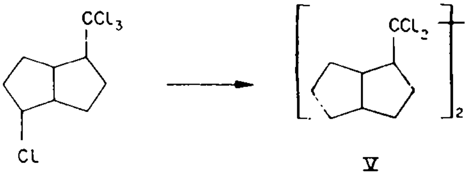
[13] E.g., M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.* **14**, 239 (1949).

[14] M. E. Hill, *J. Org. Chem.* **25**, 1115 (1960).

[15] A. C. Cope and T. Y. Shen, *J. Amer. Chem. Soc.* **78**, 3177 (1956).

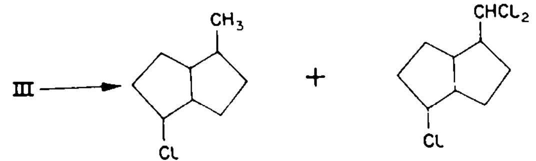
IV showed unsaturation at 6·11 μ in the IR, characteristic[16] of a chlorine-substituted double bond.

In the presence of Raney nickel and potassium hydroxide the compound absorbed 2·75 equivalents of hydrogen to give, in addition to a mixture of liquids which were not examined further, a low yield of a solid, m.p. 178·5–179·5°, whose IR spectrum was similar to that of the starting compound. According to the analysis, $C_{18}H_{24}Cl_4$ or $C_{18}H_{26}Cl_4$, the solid was probably V. This is in agreement with other cases of reductive coupling of trichloromethyl compounds.[17]



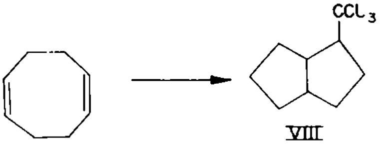
V

Hydrogenation of compound III in a mixture of methanol and triethylamine in the presence of Raney nickel led to absorption of about 2 equivalents of hydrogen and isolation of a mono- and a trichloro compounds which are formulated as VI and VII in analogy to a similar transformation of 2-(trichloromethyl)bicyclo-[3.3.0]octane (VIII) (see below).



VI VII

The reaction of chloroform with 1,5-cyclooctadiene was similar to the reaction of carbon tetrachloride in that it resulted, through a 1,5-cycloaddition, in a 37% yield of 2-(trichloromethyl)bicyclo[3.3.0]octane (VIII). After purification by distillation VIII was homogeneous in gas chromatography. Its IR spectrum, like that of III, showed only two bands in the 3·4-μ region, but no absorption at wavelengths lower than 3·4 μ which could be attributed to $=\overset{|}{C}-H$ stretching vibrations. Its NMR spectrum[18] showed two signals at 1·0–2·3 ppm and at 2·4–3·0 ppm in the ratio of 3:10, but no resonance due to olefinic protons.



VIII

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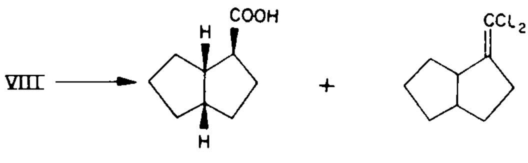
[16] Unpublished results; cf. also K. Pilgrim and F. Korte, *Tetrahedron Letters* 883 (1962).

[17] A. N. Nesmayanov, *Izv. Akad. Nauk SSSR* 211 (1960); cf. also *Chem. Abstr.* **46**, 1577 (1952).

[18] Obtained by Mr. F. E. Dickson of Mellon Institute, Pittsburgh, Pennsylvania on a Varian A-60 NMR Spectrometer.

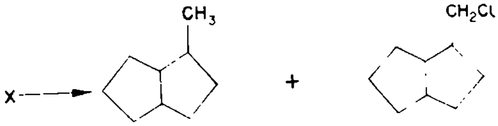
Hydrolysis of 2-(trichloromethyl)bicyclo[3.3.0]octane (VIII) by hot 85% phosphoric acid gave an acid and a neutral fraction. The acid fraction proved to be *exo-cis*-bicyclo[3.3.0]octane-2-carboxylic acid (IX) by analysis and by the m.p. of its amide which was not depressed by the admixture of the authentic amide.[19] The IR spectra of the two compounds were indistinguishable. This, together with the evidence given below, establishes the structure of the chloroform–cyclooctadiene adduct as *exo-cis*-2-(trichloromethyl)bicyclo[3.3.0]octane (IX).[20]



IX. X.

The neutral fraction from hydrolysis of VIII gave, after purification, a compound which analyzed correctly for 2-dichloromethylenebicyclo[3.3.0]octane (X). Its IR spectrum, like that of 2-dichloromethylene-6-chlorobicyclo[3.3.0]octane (IV), showed unsaturation (at 6·13 μ) which could be ascribed to the dichloromethylene group, but showed no $=\overset{|}{C}$—H stretching at about 3·4 μ.

Additional proof of this structure was sought in the oxidation of the double bond, but chromic acid in acetic acid at 50° or aqueous potassium permanganate at 60–70° proved to be ineffective. Although some carbonyl-containing impurities could be observed in the IR spectrum of the product, most of it was the starting material. Addition of bromine in carbon tetrachloride to X resulted in absorption of 1·8 equivalents of bromine with some evolution of hydrogen bromide, but the product, an orange viscous oil, decomposed on attempted distillation and gave an amorphous black solid. Hydrogenation of X in methanol–triethylamine in the presence of Raney nickel gave a mixture of two compounds which was composed of 14% of 2-methylbicyclo[3.3.0]octane (XI) (see below) and 86% of a compound which emerged between XI and 2-(dichloromethyl)bicyclo[3.3.0]octane, and which could thus be 2-(chloromethyl)bicyclo[3.3.0]octane (XII).



XI XII

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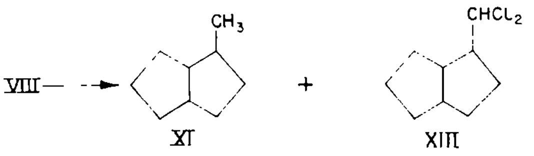
[19] A. C. Cope and M. Brown, *J. Amer. Chem. Soc.* **80**, 2859 (1958). I am thankful to Professor Cope for his kindness in furnishing a sample of *exo-cis*-bicyclo[3.3.0]octane-2-carboxamide.

[20] Although it is not unlikely that a rearrangement would take place under the rather drastic conditions of hydrolysis of the adduct of 1,5-cyclooctadiene and chloroform, and that, therefore, the acid IX would result from the rearrangement of the adduct and not from the simple hydrolysis of the trichloromethyl group, this possibility was not entertained after additional evidence on analogous reactions was obtained (see below).

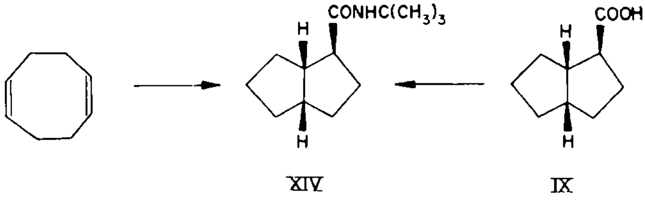
The synthesis of 2-(dichloromethylene)bicyclo[3.3.0]octane (X) was achieved through dehydrochlorination of VIII with potassium hydroxide in ethanol. The physical properties of this compound were the same as those of the neutral compound obtained in the hydrolysis of 2-(trichloromethyl)bicyclo[3.3.0]octane and their IR spectra were indistinguishable from each other.

Hydrogenation of VIII in methanol and triethylamine in the presence of Raney nickel gave two compounds. The first compound, a chlorine-free liquid, gave a correct analysis for 2-methylbicyclo[3.3.0]octane (XI). The higher-boiling compound gave a good analysis for 2-(dichloromethyl)bicyclo[3.3.0]octane (XIII), but showed weak absorption at 5·8 μ, apparently due to an aldehyde, probably arising from hydrolysis of the dichloromethyl group. The yield of compounds XI and XIII (by gas chromatography) was 53 and 22%, respectively, the rest of the material probably forming nonvolatile substances.



Thus, from the result of hydrogenation of VIII in which a chlorine-free and a dichloro compound is obtained it appears certain that, by analogy, III should give two compounds: one with a methyl group and one with a dichloromethyl group, and that the structures of the hydrogenation products of III, therefore, are as shown in VI and VII.

In order to determine the generality of 1,5-cycloaddition to 1,5-cyclooctadiene other addends were used with this diene. t-Butylformamide which is known[21] to add to olefins to form 1:1 adducts gave 51% yield of an oil which after purification gave a highly crystalline solid, m.p. 134–135°. In accordance with the proposed structure XIV, the compound gave the expected analysis, showed strong bands at 3·08, 6·11 and 6·48 μ in the infrared and failed to absorb hydrogen in the presence of platinum oxide. The proof of structure of the amide was attempted by its saponification. All attempts, however, including heating it with base at 200° or fusing it with a mixture of potassium and sodium hydroxides at 200°, failed to saponify the amide XIV. In view of this, XIV appears to be one of the most difficultly saponifiable amides known. The structure of XIV was finally proved by preparing the compound



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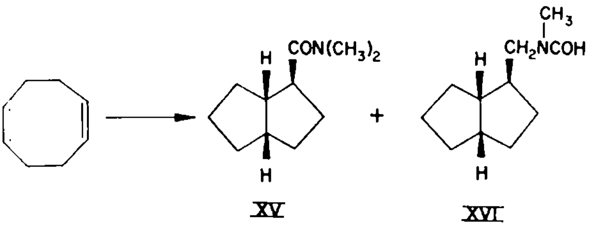
[21] L. Friedman and H. Shechter, *Tetrahedron Letters* 238 (1961).

from *exo-cis*-bicyclo[3.3.0]octane-2-carboxylic acid (IX) (via the acid chloride) and t-butylamine. Thus, the structure of XIV is as shown, namely, N-t-butyl-*exo-cis*-bicyclo[3.3.0]octane-2-carboxamide.

The reaction of 1,5-cyclooctadiene with dimethylformamide under the conditions similar to the reaction with t-butylformamide gave a mixture of two amides XV and XVI, in analogy to the usual mode of addition of this reagent.[21] Although the mixture could not be separated by fractional distillation, it could be saponified to give an acidic fraction which proved to be *exo-cis*-bicyclo[3.3.0]octane-2-carboxylic acid (IX). The basic fraction appeared to be the amine corresponding to the amide XVI, but the small amount of this material precluded its obtention in the pure state.



The reaction of 1,5-cyclooctadiene with aldehydes[22,23] gave the same general result as with other free-radical addends and resulted in a transannular 1,5-cycloaddition. Thus, acetaldehyde and 1,5-cyclooctadiene gave in the presence of benzoyl peroxide a ketone which proved to be methyl *exo-cis*-bicyclo[3.3.0]-2-octyl ketone (XVII). The m.p. of its semicarbazone, 180·8–181·8°, was in good agreement with the value reported[24] for this compound and the IR spectrum of the ketone and its retention time in gas chromatography were identical with that of a sample of the authentic compound prepared by a published procedure[24] from the acid IX through its chloride and reaction with methylcadmium. Butyraldehyde and 1,5-cyclooctadiene also gave a ketone, apparently the propyl homolog of XVII, which did not give a solid semicarbazone and which, despite many attempts at purification by fractional distillation, was not obtained pure.

Additional reactions of 1,5-cyclooctadiene with ethyl chloroacetate, ethyl trichloroacetate and butyrolactone[25] gave adducts whose structures, by analogy, are thought to be XVIII, XIX and XX, respectively. Although the structures of XIX and XX are fairly certain, XVIII may have the structure as shown or, alternatively, the compound may be derived from the addition of $\cdot CH_2COOEt$ and abstraction of chlorine from ethyl chloroacetate and thus have the analogous structure with chlorine in the position 6.

In view of the foregoing it is clear that the free-radical additions to 1,5-cyclooctadiene occur 1,5 in a transannular fashion and result in derivatives of bicyclo[3.3.0]octane. This mode of reaction was without precedent until recently when most

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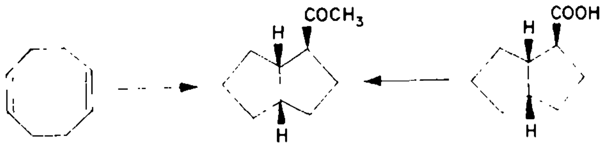
[22] M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.* **14**, 248 (1949).

[23] T. M. Patrick, Jr., *J. Org. Chem.* **17**, 1009 (1952).

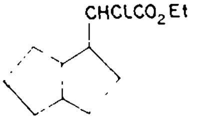
[24] A. C. Cope, M. Brown and H. E. Petree, *J. Amer. Chem. Soc.* **80**, 2853 (1958).

[25] G. I. Nikishin, G. U. Somov, Sh.-F. Wang and A. D. Petrov, *Izv. Akad. Nauk SSSR* 146 (1962); *Chem. Abstr.* **57**, 16390 (1962).

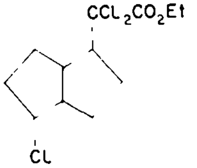


XVII

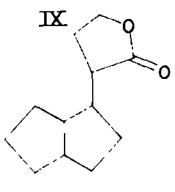
IX



XVIII

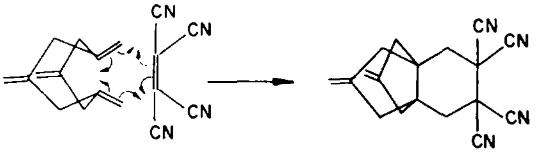


XIX

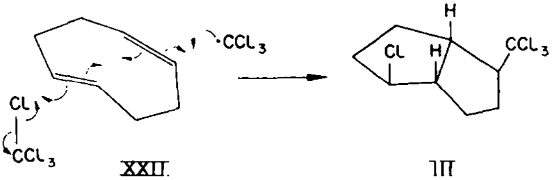


XX

of the present work was completed and a paper by Williams and Benson[26] appeared. These authors described the reaction of tetracyanoethylene with 1,3,5,7-tetramethylenecyclooctane in which the tricyclic compound XXI was formed. Although this type of reaction is usually classified as a cyclic or "no-mechanism" reaction,[27] the formation of XXI does furnish an interesting analogy to the free-radical cycloaddition in the 1,5-cyclooctadiene system, even though such an analogy may be purely formal.[28] The analogous over-all course of the two reactions may readily be seen by assuming free-radical mechanisms as shown.



XXI



XXII

III

The following may be said about the mechanism and stereochemistry of the free-radical cycloadditions to 1,5-cycloactadiene. Construction of molecular models shows that in the boat form (tub form)[29] of 1,5-cyclooctadiene the double bonds lie

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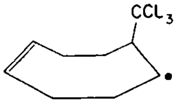
[26] J. K. Williams and R. E. Benson, *J. Amer. Chem. Soc.* **84**, 1257 (1962).

[27] W. v. E. Doering and W. R. Roth, *Tetrahedron* **18**, 67 (1962).

[28] For a recent formal analogy to the present case, see J. L. Kice and T. S. Cantrell, *J. Amer. Chem. Soc.* **85**, 2298 (1963) who describe a transannular 1,5-migration of hydrogen in 1,3,6-cyclooctatriene. Cf. also G. Büchi and E. M. Burgess, *Ibid.* **84**, 3104 (1962) and A. P. ter Borg, H. Kloosterziel and N. van Meurs, *Proc. Chem. Soc.* 359 (1962).

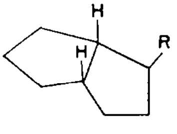
[29] K. Ziegler and H. Wilms, *Liebig's Ann.* **567**, 1 (1950).

parallel and in close proximity to each other, and that the transannular addition may take place in this conformation of the diene. On the other hand, in the stepwise reaction (as contrasted to a concerted one, XXII), the requirement of proximity may not be important, since the skeleton of a free radical such as XXIII can deform itself sufficiently so that the free radical site can approach the double bond and interact with it to form a new bond. However, no choice between the two mechanisms can be made on the evidence available at the present time.

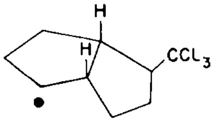


XXIII

It was shown that 2-(trichloromethyl)bicyclo[3.3.0]octane (VIII) yields on hydrolysis *exo-cis*-bicyclo[3.3.0]octane-2-carboxylic acid (IX). That this result is not merely that of isomerization of a primary product under the acid conditions of hydrolysis was further shown by the fact that the analogous product N-t-butylbicyclo[3.3.0]octane-2-carboxamide (XIV) and also methyl bicyclo[3.3.0]-2-octyl ketone (XVII) have the same stereochemistry, namely *exo-cis*, by preparation of those compounds from the authentic *exo-cis*-bicyclo[3.3.0]octane-2-carboxylic acid (IX). It is then certain that the stereochemistry of all the products which were obtained from addition of RH to 1,5-cyclooctadiene is as shown in XXIV ($R = CCl_3$, t-BuNCHO, $(CH_3)_2NCO$, CH_3CO, etc.), that is with a *cis* fusion in the bicyclooctane and R substituent being *exo*. The structure of the carbon tetrachloride adduct III remains to be considered. By analogy, it is assumed that the portion of the molecule of III which is common with other adducts XXIV is stereochemically identical with the latter. On mechanistic grounds, the only reasonable position for the chloro substituent is position 6. For the same reason, an intermediate such as XXV can form a bond with chlorine only from the *exo* side because of the prohibitive steric hindrance on the *endo* side of the bicyclooctane. It thus appears that the carbon tetrachloride adduct of 1,5-cyclooctadiene has the structure of *exo*-2-(trichloromethyl)-*exo*-6-chloro-*cis*-bicyclo[3.3.0]octane (III).



XXIV



XXV

EXPERIMENTAL

All m.ps and b.ps are uncorrected, except where stated to the contrary. The IR spectra of liquids were measured on pure liquids, of solids as mulls in Nujol. Analytical gas chromatography was carried out on a 2-ft, ¼ in column of 20% diethylene glycol succinate on Chromosorb W (Johns–Manville). Its resolving power was such that, for example, a mixture of dibutyl maleate and furmarate could be separated with a difference of about 2 min in their retention times. Longer columns resulted in decomposition of most of the compounds described here. Preparative gas chromatography was carried out on a gas chromatograph Autoprep Model A-700 (Wilkens Instrument and Research, Inc.) equipped with $\frac{3}{8}$ in columns.

Starting materials. In the initial runs, 1,5-cyclooctadiene was redistilled before use. The bulk of it distilled at 150–152°, n_D^{24} 1·4888–1·4912. The IR spectra of the fractions having different b.p. and refractive index were indistinguishable. The material was transparent in the UV and showed only one component in gas chromatography. Subsequently, 1,5-cyclooctadiene was not redistilled and used as received from the supplier (Cities Service Research and Development Company, Inc.). N-t-Butylformamide was prepared[21] and was obtained as a colourless liquid, b.p. 96–100° (22 mm), n_D^{25} 1·4319.

Reaction of 1,5-*cyclooctadiene and carbon tetrachloride.* A mixture of 325 g (3·00 mole) 1,5-cyclooctadiene, 14·55 g (0·06 mole) benzoyl peroxide and 3 l. CCl_4 was stirred and refluxed for 5 days. Four additional 7·26-g portions of benzoyl peroxide were added each day beginning with the second day of the reaction, thus making the amount of benzoyl peroxide used 43·6 g (0·18 mole). Most of the CCl_4 was removed by distillation and the residue dissolved in ether. The ether solution was washed thoroughly with $NaHCO_3$ aq and evaporated. The residue was distilled at ca. 15 mm to collect unreacted 1,5-cyclooctadiene which was redistilled to obtain 78 g (0·72 mole), b.p. 143–150°, n_D^{25} 1·4905. The rest of the material was distilled to obtain 457 g nearly colorless liquid, b.p. 54° (0·08 mm) to 178° (0·30 mm), and 41 g black residue (a band at 5·80 μ; Cl, 30·6, calc. for 3:1 adduct: Cl, 29·5%). The distillate was redistilled to obtain, in addition to 15·5 g of a forefraction, b.p. 53–82° (0·06 mm), $n_D^{25\cdot5}$ 1·5238, 374 g (63% based on unrecovered cyclooctadiene) of III, b.p. 84–87° (0·10 mm), $n_D^{25\cdot5}$ 1·5291, and two higher-boiling fractions: (1) b.p. 94–100° (0·1 mm) $n_D^{25\cdot5}$ 1·5334, 28·4 g, (2) b.p. 122–148° (0·1 mm), $n_D^{25\cdot5}$ 1·5468, 34·3 g. Redistillation of the main fraction gave the analytical sample, b.p. 83° (0·1 mm), n_D^{24} 1·5292. (Found: C, 41·21; H, 4·91; Cl, 53·90. Calc. for $C_9H_{12}Cl_4$: C, 41·25; H, 4·62; Cl, 54·13%).

When azobis(isobutyronitrile) was used as an initiator only a small amount of a higher boiling material was obtained. The reaction of 108·2 g (1·00 mole) cyclooctadiene and 500 ml CCl_4 which was run for 5 days at 60° and irradiated in a Pyrex flask with a GE Sunlamp gave 14·2 g (5·4%) substituted bicyclooctane III, b.p. 162–164° (20 mm), n_D^{25} 1·5278. A similar run in which an UV lamp was used gave 20 g substituted bicyclooctane.

When the reaction was carried out in a Vycor flask and irradiated with the same lamp, there was obtained from 27·1 g (0·25 mole) diene and 250 ml CCl_4, 22·0 g (33·5%) substituted bicyclooctane III, b.p. 83–84° (0·09 mm), $n_D^{25\cdot5}$ 1·5279.

In the $FeCl_3$-catalyzed reaction, a mixture of 27·0 g (0·25 mole) 1,5-cyclooctadiene, 125 ml CCl_4, 75 ml isopropyl alcohol and 1 g $FeCl_3{\cdot}6H_2O$ was refluxed (69·5°) 36 hr. The mixture was then washed with water and the organic layer evaporated to obtain 54 g liquid. This was distilled to obtain 48·4 g (73%) bicyclooctane III, b.p. 57–103° (0·6 mm) (mostly at 92–94°), n_D^{25} 1·5274, about 95% pure by gas chromatography. It showed the same retention time as authentic III.

The compound (III) obtained in the above reactions showed only one peak in the gas chromatogram. Its IR spectrum showed two bands in the 3·4-μ region, and unlike the spectra of cyclooctene and 1,5-cyclooctadiene, did not have any bands at wavelengths lower than 3·40 μ. The NMR spectrum of III (determined as a neat liquid with tetramethylsilane as internal standard) showed very weak signals due to traces of olefinic impurities at ca. 5·6 and 4·2 ppm and two broad signals at 2·0 and 2·8 ppm and a weaker one at 4·05 ppm.

Attempted oxidation of III was done by adding solid $KMnO_4$ to a stirred mixture of 13·1 g (0·050 mole) of the compound and 100 ml water at 70°. A total of 4·30 g permanganate was added and the mixture heated overnight. The excess $KMnO_4$ was removed by addition of methanol, the mixture filtered and extracted with ether. There were no acidic materials in the aqueous layer. The extract was evaporated and the residue distilled to obtain 9·0 g starting compound as a colorless liquid, b.p. 166–170° (21 mm) n_D^{25} 1·5289, homogeneous in gas chromatography.

On hydrogenation of 26·2 g (0·10 mole) of III in 100 ml ethyl acetate in the presence of 0·1 g PtO_2, the compound did not absorb any H_2 in 0·5 hr.

Attempted hydrolysis of 2-*trichloromethyl*-6-*chlorobicyclo*[3.3.0]*octane* (III). A mixture of 10·0 g (0·038 mole) III, 10 g (0·25 mole) NaOH and 50 ml water was refluxed 3 days. Extraction of the product and distillation of the residue gave 7·8 g nearly colorless liquid, b.p. 88–89° (0·06 mm), n_D^{26} 1·5282, essentially unchanged starting material.

Hydrolysis with H_3PO_4 was carried out by heating a mixture of 26·2 g (0·10 mole) of III with extracted with ether and the resulting ether extract separated into neutral and acidic fractions. While the acidic fraction contained only traces of material, the neutral fraction contained 5 g black tar which could not be distilled. In another attempt, hydrolysis was carried out as above, except that the temp was kept at about 160°. Extraction of the reaction mixture with a mixture of ether and benzene and separation into neutral and acidic fractions gave 10·8 g black neutral tar showing only a trace of chlorine but no carboxyl or lactone absorption in the IR; no acidic material. Prolonged heating of the neutral material with 10 g NaOH and 50 ml water at 100° gave back apparently unchanged starting material.

As hydrolysis with H_2SO_4 was equally unsuccessful, an attempt was made to hydrolyze III in the presence of $FeCl_3$. Thus, to a mixture of 16·2 g (0·10 mole) anhydrous $FeCl_3$ and 25 ml $CHCl_3$ there was added dropwise 26·2 g (0·10 mole) of the compound and 4·0 ml (0·22 mole) water. Hydrogen chloride evolution began almost immediately. After 0·5 hr, the mixture was heated to reflux for 1 hr, then cooled and extracted with ether. The ether extract did not have any acidic material but on distillation gave 12·1 g straw-coloured liquid, b.p. 158–168° (22 mm), n_D^{24} 1·5312, essentially starting material.

The compound (III) was also hydrolyzed with HNO_3. To 75 ml HNO_3 kept at 90° there was added dropwise with stirring over a period of 1 hr 10 g (0·038 mole) substituted bicyclooctane. After 2 days heating at 90°, the mixture was cooled and extracted with $CHCl_3$ and the extract washed well with water. Evaporation of the extract gave 1·5 g straw-coloured viscous oil, showing halogen by Beilstein test. Its IR spectrum had a band at ca. 5·9 μ and was similar to that of *endo-cis*-bicyclo[3.3.0]octane-2-carboxylic acid.

Dehydrochlorination of 2-*trichloromethyl*-6-*chlorobicyclo*[3.3.0]*octane* (III). A mixture of 78·5 g (0·30 mole) bicyclooctane, 32·4 g (0·60 mole) sodium methoxide and 1 l. methanol was refluxed 30 hr, then worked up as usual to obtain 70·2 g liquid, b.p. 122–163° (17 mm), n_D^{24} 1·5300, apparently containing some starting material. This was then refluxed with 135 g (2·5 mole) sodium methoxide and 1 l. methanol for 3 days, then worked up in the usual manner to obtain 50·0 g liquid, b.p. 118–152° (7 mm), showing predominantly one component in the gas chromatogram. There was no organic material in the aqueous phase. Several redistillations, in which lower-boiling components were removed, gave 26·0 g IV as a colorless liquid, b.p. 74–76° (0·15 mm), n_D^{24} 1·5373, showing one component in gas chromatography. It was transparent in the UV, but showed a double bond at 6·11 μ and no olefinic hydrogen around 3·4 μ. (Found: C, 48·15; H, 51·0; Cl, 46·80. Calc. for $C_9H_{11}Cl_3$: C, 47·92; H, 4·92; Cl, 47·16%).

In a dehydrochlorination with KOH, a mixture of 26·2 g (0·10 mole) III, 13·2 g (0·20 mole) 85% KOH and 75 ml t-butyl alcohol was refluxed (84°) 2 hr, then cooled and diluted with water. The resulting mixture was extracted with ether, the extract washed with water, dried and evaporated. The residue was distilled to obtain 16·9 g colorless liquid, b.p. 71–76° (0·15 mm), n_D^{25} 1·5358, showing a small amount of low-boiling impurities in the gas chromatogram. Preparative gas chromatography on neopentyl glycol succinate gave a liquid which was redistilled to obtain the analytical sample of IV, b.p. 75° (0·15 mm), n_D^{25} 1·5378, showing an IR spectrum identical with that of IV obtained from sodium methoxide and III. (Found: C, 47·84; H, 5·11; Cl, 47·12. Calc. for $C_9H_{11}Cl_3$: C, 47·92; H, 4·92; Cl, 47·16%).

Hydrogenation of 2-*trichloromethyl*-6-*chlorobicyclo*[3.3.0]*octane* (III). A mixture of 26·2 g (0·10 mole) III, 29·7 g (0·45 mole) 85% KOH, 10 ml Raney nickel and 150 ml 95% ethanol was shaken with H_2 and heated at 50° whereupon, in 4 hr, it absorbed 0·275 moles H_2 and then the absorption stopped. Most of the methanol was evaporated, the residue neutralized with acetic acid, taken up in ether and the ether solution washed with water. The ether solution was evaporated and filtered to obtain 0·75 g white solid, m.p. 175–178°. This was recrystallized from Skellysolve B to obtain 0·40 g V as a white solid, m.p. 178·5–179·5°. Its IR spectrum was similar to that of the starting compound. (Found: C, 56·41; H, 6·31; Cl, 37·33. Calc. for $C_{18}H_{24}Cl_4$: C, 56·7; H, 6·31; Cl, 37·1. Calc. for $C_{18}H_{26}Cl_4$: C, 55·7; H, 6·8; Cl, 36·9%).

Hydrogenation in the presence of Raney nickel, triethylamine and methanol, was carried out as follows. A mixture of 39·3 g (0·15 mole) III, 150 ml triethylamine, 40 ml methanol and 15 ml Raney nickel was shaken in a Parr hydrogenator at an initial press. of about 50 psi. Heat was evolved and the mixture absorbed most of the 0·30 mole H_2 during the first hr of shaking, whereupon absorption of H_2 nearly stopped. Addition of fresh catalyst did not cause more absorption. The mixture was combined with that from another run of the same size and worked up by filtering the catalyst, washing with methanol and dissolving the filtrate in ether. The ether solution was washed well with HCl aq, $NaHCO_3$ and water. Drying and evaporating the solution gave 56 g yellowish liquid which was distilled to obtain three fractions: (1) b.p. 72–78° (13 mm), 0·25 g; (2) b.p. 78–100° (13 mm), 12·1 g, and (3) b.p. 100° (13 mm) to 140° (6 mm), 26·3 g and 9·6 g of undistillable residue.

Fraction (2) was redistilled twice to obtain 9·3 g 2-methyl-6-chlorobicyclo[3.3.0]octane (VI) as a colorless liquid, b.p. 88–89° (19 mm), $n_D^{24.5}$ 1·4775. Its IR spectrum was transparent in the OH region and from 5 to 6·8 μ, but had a strong band at 6·9 μ and one at 8·1 μ. (Found: C, 68·03; H, 9·91; Cl, 21·75. Calc. for $C_9H_{15}Cl$: C, 68·12; H, 9·53; Cl, 22·35%).

Fraction (3) was fractionated several times to obtain, in addition to lower and higher-boiling fractions, 12·9 g 2-dichloromethyl-6-chlorobicyclo[3.3.0]octane (VII) as a colorless liquid, b.p. 66° (0·08 mm), n_D^{25} 1·5187. Preparative gas chromatography gave pure VII as a colorless liquid which was redistilled for analysis, b.p. 92° (0·2 mm), n_D^{24} 1·5208. Its IR spectrum did not show any absorption between 3 and 6 μ and was consistent with the assigned structure. (Found: C, 47·47; H, 5·59; Cl, 46·58. Calc. for $C_9H_{13}Cl_3$: C, 47·50; H, 5·76; Cl, 46·74%).

Reaction of 1,5-*cyclooctadiene and chloroform.* A mixture of 108·2 g (1·00 mole) 1,5-cyclooctadiene, 4·85 g (0·020 mole) benzoyl peroxide and 1 l. $CHCl_3$ was refluxed for 5 days with additions on consecutive days of four 2·42-g portions of benzoyl peroxide, thus making the total amount of peroxide used 14·53 g (0·060 mole). Most of the $CHCl_3$ and unreacted diene were removed at ca. 30 mm and the residue distilled to obtain 74 g liquid, b.p. 74–138° (0·12 mm), and 11 g residue. The liquid was redistilled to obtain 54 g of a fraction b.p. 53–56° (0·04 mm), and 17·2 g of a higher boiling liquid, b.p. 57–112° (0·1 mm), n_D^{25} 1·5313. The main fraction was refractionated to obtain 51 g (22%) colorless liquid, b.p. 129–135° (19 mm), n_D^{25} 1·5109. Refractionation of this gave forefractions containing crystals (benzoic acid by mixed m.p.) and 30·0 g of the analytically pure 2-(trichloromethyl)bicyclo[3.3.0]octane (VIII), b.p. 110–111° (9 mm), n_D^{25} 1·5110, showing one component in gas chromatography. Its IR spectrum, like that of III, showed no absorption at wavelength lower than 3·4 μ, attributable to $=$CH stretching vibrations. Its NMR spectrum (neat liquid, tetramethylsilane standard) showed two bands at 1–2·3 ppm and at 2·4–3·0 ppm in the ratio of 3:10, respectively, but no resonance due to olefinic protons down field from tetramethylsilane. (Found: C, 47·21; H, 5·37; Cl, 46·33. Calc. for $C_9H_{13}Cl_3$: C, 47·49; H, 5·75; Cl, 46·74%).

In another similar run, a mixture of 325 g (3·00 mole) of 1,5-cyclooctadiene, 14·55 (0·060 mole) benzoyl peroxide and 3 l. $CHCl_3$ was refluxed 5 days with 4 additions of 7·26-g (0·020 mole) portions of benzoyl peroxide. After removing excess $CHCl_3$, the unchanged diene was distilled to obtain 176·6 g (1·63 moles) 1,5-cyclooctadiene, n_D^{24} 1·4920. The rest of the material was distilled to obtain 187 g liquid, b.p. 66–152° (0·1 mm), and 35·4 g of an undistillable residue. A solid (benzoic acid) which separated in the distillate was filtered off and discarded. Distillation of the liquid gave a fraction, b.p. 115° (13 mm) to 121° (8 mm), 129·9 g, and a fraction b.p. 82–102° (0·09 mm), 42 g. The former fraction was redistilled to obtain 117 g (37% based on unrecovered 1,5-cyclooctadiene) of VIII, b.p. 119–123° (7 mm), n_D^{24} 1·5110. The higher boiling fraction was redistilled to obtain 35·0 g liquid, b.p. 95–102° (0·10 mm), n_D^{24} 1·5330. This liquid showed a band at 5·84 μ and a weak doublet at 6·24–6·31 μ, but its gas chromatogram showed 4 peaks in a ratio of 13:74:3:10. Attempts at separation of individual components by distillation failed.

Hydrolysis of 2-(*trichloromethyl*)*bicyclo*[3.3.0]*octane* (VIII). A mixture of 11·5 g (0·050 mole) VIII and 50 ml 85% H_3PO_4 was refluxed (155°) 24 hr. Hydrogen chloride was evolved. The mixture was cooled, diluted with water, extracted with ether and the resulting extract separated into acidic and neutral fractions by means of $NaHCO_3$ aq. The acid fraction gave on distillation 2·8 g liquid, b.p. 93° (0·12 mm), which was redistilled to obtain 2·5 g *exo*-*cis*-bicyclo[3.3.0]octane-2-carboxylic acid (IX), b.p. 93° (0·12 mm), n_D^{26} 1·4847 showing a carbonyl band at 5·9 μ in the IR. Its gas chromatogram showed one component. (Found: C, 70·61; H, 9·00. Calc. for $C_9H_{14}O_2$: C, 70·10; H, 9·15%).

Its amide was prepared via the acid chloride and was obtained as white shiny platelets, m.p. 172–173°. Analytical sample was prepared by recrystallization from aqueous ethanol, m.p. 178–179° (corr). On admixture of authentic *exo*-*cis*-bicyclo[3.3.0]octane-2-carboxamide[19] the m.p. was 179° (corr). The IR spectra of the two compounds were indistinguishable. (Found: C, 70·65; H, 9·72, N, 9·22. Calc. for $C_9H_{15}NO$: C, 70·54; H, 9·87; N, 9·14%).

The neutral fraction was distilled to obtain 1·3 g impure X as a yellowish liquid, b.p. 54–70° (0·1 mm), n_D^{24} 1·5178.

In a larger scale run, a mixture of 111 g (0·484 mole) VIII and 500 ml 85% H_3PO_4 was refluxed

(154°) 24 hr. The usual work-up gave 29·4 g (39·5%) IX, b.p. 89° (0·1 mm), n_D^{25} 1·4839. The neutral fraction gave 32·2 g liquid, b.p. 55–90° (0·1 mm). It was redistilled to obtain, in addition to a small amount of a forefraction, 29·5 g of the main fraction, b.p. 107–119° (15 mm). The main fraction was redistilled again to obtain 3 fractions: (1) b.p. 103–111° (14 mm), n_D^{25} 1·5191, 2·5 g; (2) b.p. 111–113° (14 mm), n_D^{25} 1·5179, 22·3 g, and (3) b.p. 113–116° (14 mm), n_D^{25} 1·5169, 3·6 g. The fraction (2) was redistilled again to obtain a middle fraction of X for analysis, b.p. 68° (0·2 mm), n_D^{24} 1·5191. Its IR spectrum showed a band at 6·13 μ. It was homogeneous by gas chromatography. (Found: C, 56·80; H, 6·40; Cl, 35·37. Calc. for $C_9H_{12}Cl_2$: C, 56·56; H, 6·33; Cl, 37·11%).

Attempts to oxidize X by chromic acid in acetic acid at 50° or by $KMnO_4$ at 60–70° gave mostly starting material, but only traces of carbonyl-containing compounds.

Bromination of 2-(dichloromethylene)bicyclo[3.3.0]octane (XV) was carried out by adding a solution of Br_2 in CCl_4 to 11·26 g (0·050 mole) of a compound in 25 ml CCl_4. After only a small amount of Br_2 was added the mixture began to evolve HBr. A total of 14·4 g (1·8 equivs) Br_2 was added whereupon the solution did not decolorize bromine. Evaporation of the solution *in vacuo* gave 20·1 g orange viscous oil. On attempted distillation of this at 0·4 mm the oil charred forming a black brittle solid.

Hydrogenation of X was carried out by shaking with H_2 a mixture of 6·35 g (0·0332 mole) X, 100 ml methanol, 2 ml Raney nickel and 25 ml triethylamine. A total of 0·0243 mole H_2 was absorbed by the mixture. Filtration of the reaction mixture from the catalyst, washing with dil. HCl aq and water and evaporation gave 4·89 g yellowish oil. Gas chromatography showed two well-separated bands of 14% of XI (see below) and 86% of what was apparently XII. The retention time of the former was the same as that of the authentic XI but addition of 2-(dichloromethyl)bicyclo[3.3.0]-octane (XIII) to the hydrogenation product resulted in its separation as the highest boiling component in gas chromatography, thus showing the higher boiling component of the hydrogenation product to be different from, and lower boiling than, the component XIII.

Dehydrochlorination of 2-*(trichloromethyl)bicyclo*[3.3.0]*octane* (VIII). A mixture of 23·0 g (0·10 mole) VIII, 6·6 g (0·10 mole) 85% KOH and 50 ml absolute ethanol was refluxed overnight, then cooled and diluted with water. Extraction of the resulting mixture with ether, washing the extract with water, drying and distilling gave 14·6 g X as a liquid, b.p. 74–77° (1·2 mm), n_D^{25} 1·5160, which was 80% pure by gas chromatography. Preparative gas chromatography gave pure X, n_D^{24} 1·5197, showing a doublet at 3·43 μ and 3·52 μ and a medium band at 6·14 μ and being indistinguishable in its IR spectrum from that of the neutral compound obtained in the hydrolysis of VIII. (Found: C, 56·63; H, 6·38; Cl, 37·02. Calc. for $C_9H_{12}Cl_2$: C, 56·56; H, 6·33; Cl, 37·11%).

Hydrogenation of 2-*(trichloromethyl)bicyclo*[3.3.0]*octane* (VIII). A mixture of 22·9 g (0·10 mole) VIII, 50 ml methanol, 100 ml triethylamine and 10 ml Raney nickel was shaken with H_2. Heat was evolved and the mixture absorbed 0·212 mole H_2 in about 30 min. The mixture was combined with another run of the same size, the catalyst filtered off and the filtrate concentrated *in vacuo* to a small volume. The residue was dissolved in ether and the resulting solution washed with HCl aq, $NaHCO_3$ aq and water. Drying, removal of solvents and distillation of the residue gave two fractions: (1) b.p. 68° (47 mm) to 74° (50 mm), 7·5 g; (2) b.p. 64° (27 mm) to 155° (0·5 mm), 13·9 g, and some undistillable residue. Fraction (1) was refractionated to obtain 6·37 g colorless liquid, b.p 84–88° (106 mm), showing no chloroform by Beilstein test. The analytical sample was obtained by two more redistillations at atm press to obtain 5·48 g XI as a colorless liquid, b.p. 143–144°, n_D^{25} 1·4538. Its IR spectrum was transparent in the region of 3·6–6·8 μ, and showed C—H bands at 3·43 and 3·52 μ and a strong band at 6·9 μ. It was at least 98% pure by gas chromatography, the higher boiling material amounting to about 2%. (Found: C, 87·56; H, 12·50. Calc. for C_9H_{16}: C, 87·01, H, 12·99%).

Fraction (2) was redistilled several times to obtain 7·7 g colorless liquid, b.p. 108–112° (15 mm), showing one strong band and a small amount of 4 lower boiling components by gas chromatography. The analytical sample of XIII was obtained by preparative gas chromatography, colorless liquid, n_D^{25} 1·5005, showing a strong doublet at 3·43 and 3·53 μ and a weak absorption at ca. 5·8 μ. (Found: C, 56·1; H, 7·32; Cl, 36·77. Calc. for $C_9H_{14}Cl_2$: C, 55·97; H, 7·31; Cl, 36·72%).

In a different run, 11·5 g (0·050 mole) VIII, 50 ml triethylamine, 100 ml methanol and 10 ml Raney nickel was shaken with H_2. With the evolution of heat, the mixture absorbed 0·115 mole H_2 in about 1 hr whereupon the absorption stopped. The usual work-up gave 5·80 g crude reaction product which was analyzed by gas chromatography. It was found to contain 4 peaks: 57%, 1%, 6% and 36%. The first was 2-methylbicyclo[3.3.0]octane (XI), 0·0266 mole (53% yield), while the last was XII, 0·0108 mole (21·6% yield). The two middle peaks remain unidentified as well as the rest of the material.

Reaction of 1,5-*cyclooctadiene with* t-*butylformamide.* A mixture of 35·6 g (0·33 mole) 1,5-cyclooctadiene and 5·11 g (0·035 mole) di-t-butyl peroxide was added dropwise with stirring over a period of 12 hr to 1010 g (10·0 mole) t-butylformamide kept at 135–140° by external heating. Heating was continued for an additional 24 hr; then the mixture was distilled to obtain, in addition to a small forefraction, 959 g of t-butylformamide, b.p. 97° (21 mm) to 98° (18 mm), and a residue. On distillation the residue gave 35 g (51%) yellowish liquid, b.p. 115° (0·08 mm) to 165° (0·25 mm), which crystallized on standing. The undistillable residue amounted to 10·5 g. The solid was recrystallized from petroleum hexane, m.p. 125–128°. Two additional recrystallizations from aqueous ethanol, then from aqueous methanol gave 31 g nearly white amide (XIV), m.p. 125–130°. Several recrystallizations from a mixture of ether and Skellysolve F, and then from Skellysolve F alone gave the analytical sample of XIV as white, shiny leaflets, m.p. 134–135°. Its IR spectrum showed strong bands at 3·08, 6·11 and 6·48 μ and a weak sharp band at 3·30 μ. (Found: C, 75·09; H, 10·31; N, 6·76. Calc. for $C_{13}H_{23}NO$: C, 74·58; H, 11·07; N, 6·69%).

A solution of 10·45 g (0·050 mole) amide XIV in 75 ml ethyl acetate and 1·0 g 5% Pd-C was shaken with H_2 for 2·5 hr at an initial press. of ca. 50 psi. No absorption occurred. Working up the mixture gave a quantitative recovery of the starting amide, m.p. 130–132°.

Attempted saponification of exo-cis-N-*t-butylbicyclo*[3.3.0]*octane-2-carboxamide.* A mixture of 20·9 g (0·10 mole) XIV, 28 g KOH and 50 ml water was refluxed (112°) 4 hr. To dissolve XIV, 50 ml ethylene glycol was added and reflux (114°) continued. After 15 hr reflux, most of the amide sublimed on the sides of the flask. About 50 ml solvent was distilled, 75 ml butyl Cellosolve added and reflux (129°) continued for additional 19 hr during which time there was evolved a weak stream of a basic, volatile material through the condenser. Additional solvent was distilled off to raise the temp to 145°. After an additional 1·5 hr at this temp, volatile solvents were removed at 30 mm and ca. 50°, and the residue poured into water. The material which was initially oily crystallized on standing. Filtration, washing with water and drying gave 17·5 g unchanged amide, m.p. 131–132·5°. No acidic material could be isolated on acidification of the aqueous filtrate.

In another attempt, a mixture of 20·9 g (0·10 mole) XIV, 30·8 g KOH, 5 ml water, 15 ml diethylene glycol and 100 ml butyl Cellosolve was refluxed at 145° for 10 hr. Volatile solvents were evaporated at 50° (30 mm) and the residue was poured into water. Extraction with ether gave 16·8 g starting amide, m.p. 130–133°, but no acidic fraction on acidification of the aqueous phase.

In a run at a higher temp, a mixture of 20·9 g amide, 30·8 g KOH and 100 ml glycerin was heated at 175° for 23 hr. The usual isolation procedure gave impure amide, m.p. 120–124°, which was recrystallized from a mixture of petroleum pentanes and hexanes to give 18 g of the starting amide, m.p. 130–132°. The aqueous phase did not contain an acidic material.

Saponification in a bomb was carried out by heating at 200° a mixture of 10·45 g (0·050 mole) amide, 15·4 g KOH, 45 ml water and 5 ml butyl Cellosolve for 15 hr. Usual work-up gave 9·5 g starting amide, m.p. 126–130°, but no acidic material in the aqueous filtrate. A similar reaction run in a mixture of 25 ml water and 25 ml butyl Cellosolve also failed.

In another reaction, a mixture of 2·09 g (0·010 mole) amide, 2·80 g KOH and 2·00 g NaOH was heated without a solvent at 200° in a steel beaker. No acidic material could be obtained from this reaction.

Preparation of exo-cis-N-*t-butylbicyclo*[3.3.0]*octane-2-carboxamide* (XIV). A mixture of 3·0 g (0·019 mole) IX, b.p. 77–78° (0·07 mm), n_D^{25} 1·4820, and 15 ml thionyl chloride was refluxed gently for 1·5 hr. Excess thionyl chloride was removed *in vacuo* and the residue dissolved in 25 ml dry ether. The resulting solution was then added slowly to a solution of 20 ml t-butylamine in 30 ml dry ether and the resulting mixture allowed to stand at room temp for a few hr. The ether was evaporated and the residue filtered to obtain 3·7 g slightly yellowish solid, m.p. ca. 125°, which, on recrystallization from aqueous ethanol (charcoal) and then from a mixture of petroleum pentanes and hexanes, gave 2·6 g nearly white amide, m.p. 130–132°. Several recrystallizations from petroleum pentanes gave white solid, m.p. 133–134°. On admixture of the amide (m.p. 134–135°), obtained by addition of t-butylformamide to 1,5-cyclooctadiene, the m.p. was 133–135°. The two samples had identical IR spectra.

Reaction of 1,5-*cyclooctadiene and dimethylformamide.* A mixture of 108·2 g (1·00 mole) 1,5-cyclooctadiene and 14·6 g (0·10 mole) di-t-butyl peroxide was added dropwise during 12 hr to 2190 g (30·0 mole) dimethylformamide which was heated at 135–140°. After addition, the mixture was heated for additional 48 hr, then distilled to obtain 1848 g dimethylformamide. An additional 332·5 g formamide was obtained by distilling *in vacuo*, b.p. 54–56° (15 mm). Distillation of the remainder gave 28·8 g yellowish liquid, b.p. 93·5–175° (0·25 mm), and 11·0 g of an undistillable residue. Redistillation of the liquid gave 20·8 g (11·5%) slightly yellowish liquid, b.p. 83–85° (0·10 mm), n_D^{24} 1·5030, the mixture of XV and XVI. The liquid was composed, according to gas chromatography, of 2 major components containing a total of about 10% of two minor components. Its IR spectrum showed a weak hydroxyl band at 2·9 μ and a strong amide band (doublet) at 5·97 and 6·10 μ, but no absorption in the region of 6·1 to 6·7 μ. (Found: C, 74·31; N, 9·93; N, 6·64. Calc. for $C_{11}H_{19}NO$: C, 72·88; H, 10·56; N, 7·73%).

Preparative gas chromatography (20 in column of neopentyl glycol succinate) resulted only in a partial separation of the two main components.

Saponification of the mixture of N,N-*dimethylbicyclo*[3.3.0]*octane-2-carboxamide* (XV) *and* N-(*bicyclo*[3.3.0]*octane-2-methyl*)-N-*methylformamide* (XVI). A mixture of 20 g amides, 28 g KOH, 200 ml butyl Cellosolve and 10 ml water was refluxed (150°) 36 hr, then diluted with water and separated into a basic and an acidic fraction. The basic fraction gave after several redistillations 3·5 g colorless liquid, b.p. 90–91° (15 mm), n_D^{25} 1·4752, apparently impure amine corresponding to amide XVI. It was transparent from 3·7 to 6·7 μ and showed a band at 3·07 μ in the IR. (Found: C, 79·00; H, 12·41; N, 8·44. Calc. for $C_{10}H_{19}N$: C, 78·37; H, 12·50; N, 9·14%).

The acid fraction gave 7·0 g liquid, b.p. 77–78° (0·07 mm), n_D^{25} 1·4820, whose IR spectrum was indistinguishable from that of IX. (Found: C, 70·25; H, 9·27. Calc. for $C_9H_{14}O_2$: C, 70·10; H, 9·15%).

Its amide was obtained as a nearly white solid, m.p. 165–167°. Several recrystallizations from aqueous ethanol gave the amide as shiny platelets, m.p. 176–178° (corr). The m.p. was not depressed on admixture of the authentic *exo-cis*-bicyclo[3.3.0]octane-2-carboxamide, m.p. 178–179° (corr). The IR spectra of the two compounds were identical.

Reaction of 1,5-*cyclooctadiene and acetaldehyde.* A mixture of 108·2 g (1·00 mole) 1,5-cyclooctadiene, 176·4 g (4·00 mole) acetaldehyde and 4·84 g (0·020 mole) benzoyl peroxide was placed in a bomb and heated at 80° for 48 hr. The bomb was then cooled and opened, and the liquid was poured into a beaker and allowed to evaporate at room temp. The residue was distilled to obtain, in addition to a small forefraction and residue, the following three fractions: (1) b.p. 77–95° (89 mm), 82 g; (2) b.p. 86–96° (10 mm), 10·5 g; (3) 104–145° (5 mm), 6·6 g. Fraction (3) contained about 10 components by gas chromatography and was not examined further. Fraction (1) was redistilled at atm press to obtain, in addition to 14·3 g forefraction, b.p. 78–148°, 65·3 g (0·602 mole) 1,5-cyclooctadiene, b.p. 149–152°, n_D^{24} 1·4912. Fraction (2) was redistilled to obtain 8·1 g impure methyl *exo-cis*-2-bicyclo[3.3.0]octyl ketone (XVII), b.p. 88·97° (10 mm), n_D^{24} 1·4772, showing a strong band at 5·87 μ, but no bands at 3·0 μ in the IR (literature[24] b.p. 94–95° (10 mm), n_D^{25} 1·4655). Gas chromatography showed essentially one component. It was further purified through its semicarbazone, m.p. 177–179°, from which the ketone was recovered through the action of $NaNO_2$ in acetic acid.[30] The analytical sample was obtained as a colorless liquid, b.p. 93° (5·0 mm), n_D^{25} 1·4732. (Found: C, 78·57; H, 10·59. Calc. for $C_{10}H_{16}O$: C, 78·89; H, 10·59%).

Methyl *exo-cis*-2-bicyclo[3.3.0]octyl ketone semicarbazone was prepared as described in the literature[24] and was obtained as a white solid, m.p. 180·8–181·8° (dec, corr) (reported[24] m.p. 181·0–182·4°, dec, corr). Its IR spectrum showed bands at 2·94, 3·03 and 3·17 μ and a strong doublet at 5·94 and 6·03 μ. (Found: 62·59; H, 9·11; N, 19·96. Calc. for $C_{11}H_{19}N_3O$: C, 63·12; H, 9·15; N, 20·07%).

Authentic methyl *exo-cis*-2-bicyclo[3.3.0]octyl ketone was prepared from IX by a published procedure[24] and was obtained as a colorless liquid, m.p. 84–86° (8 mm), n_D^{25} 1·4728. Its IR spectrum was indistinguishable from that of the ketone obtained from acetaldehyde and 1,5-cyclooctadiene.

Reaction of 1,5-*cyclooctadiene and butyraldehyde.* A mixture of 54 g (0·50 mole) 1,5-cyclooctadiene, 108 g (1·50 mole) butyraldehyde and 2·42 g (0·010 mole) benzoyl peroxide was refluxed (80°) 24 hr, an additional 2·42 g (0·010 mole) benzoyl peroxide was added and reflux continued for a total of 48 hr. The mixture was distilled to obtain 83·4 g (1·16 mole) butyraldehyde, b.p. 75–78°, and 3

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[30] S. Goldschmidt and W. L. C. Veer, *Rec. Trav. Chim.* **65**, 796 (1946).

fractions of higher boiling materials: (1) b.p. 32–42° (100 mm), 6·7 g; (2) b.p. 78° (100 mm) to 84° (85 mm), n_D^{25} 1·4883, 33·5 g, (3) b.p. 87° (83 mm) to 162° (0·3 mm), 35·9 g. Fraction (3) was refractionated to obtain, in addition to lower boiling forefraction and higher-boiling residues, 10·8 g propyl *exo-cis*-2-bicyclo[3.3.0]octyl ketone, b.p. 62–64° (0·09 mm), n_D^{22} 1·4720, showing a strong band at 5·88 μ and a weak band at 2·9 μ. Its gas chromatogram showed a small amount of a well-separated low-boiling component in addition to the main component. The former could not be removed by repeated redistillations. (Found: C, 78·37; H, 11·03. Calc. for $C_{12}H_{20}O$: C, 79·94; H, 11·18%).

Reaction of 1,5-*cyclooctadiene and ethyl chloroacetate.* A mixture of 10·8 g (0·10 mole) 1,5-cyclooctadiene and a portion (ca. 0·9) of 122·6 g (1·0 mole) ethyl chloroacetate was heated at 140° while a solution of 3·65 g (0·025 mole) di-t-butyl peroxide in the remainder of ethyl chloroacetate was added dropwise over a period of 6·5 hr. Heating at 140° was continued for an additional 7·5 hr, then the reaction mixture was distilled to obtain 118·7 g liquid, b.p. 34–46° (15 mm), mostly ethyl chloroacetate, and 6·42 g liquid, b.p. 78–108° (0·30 mm). The higher-boiling fraction was redistilled to obtain the analytical sample of XVIII as a colorless liquid, b.p. 70° (0·08 mm) to 77° (0·10 mm), n_D^{26} 1·4820, 5·43 g. It showed a strong band at 5·73 μ in the IR. (Found: C, 62·49; H, 8·17, 8·17, Cl, 15·33. Calc. for $C_{12}H_{19}ClO_2$: C, 62·47; H, 8·30; Cl, 15·36%).

Reaction of 1,5-*cyclooctadiene and ethyl trichloroacetate.* To a mixture of 21·6 g (0·20 mole) 1,5-cyclooctadiene and 170 g (0·888 mole) ethyl trichloroacetate there was added dropwise at 140° over a period of 9 hr a solution of 3·65 g (0·025 mole) di-t-butyl peroxide in 21·5 g (0·112 mole) ethyl trichloroacetate. After an additional 3 hr heating at 140° the mixture was distilled to obtain, in addition to 170 g recovered ethyl trichloroacetate, b.p. 61–67° (22 mm), 24·9 g liquid, b.p. 106–144° (0·1 mm), and 8·2 g of an undistillable residue. The liquid was redistilled to obtain 22·7 g bicyclooctane XIX, b.p. 99–102° (0·10 mm), n_D^{24} 1·5073. The compound showed a strong band at 5·72 μ in the IR. (Found: C, 48·60; H, 6·11; Cl, 35·95. Calc. for $C_{12}H_{17}Cl_3O_2$: C, 48·10; H, 5·72; Cl, 35·50%).

Reaction of 1,5-*cyclooctadiene and* γ-*butyrolactone.* A mixture of 21·6 g (0·20 mole) 1,5-cyclooctadiene and 7·30 g (0·050 mole) di-t-butyl peroxide was added dropwise over a period of 6 hr to 172·2 g (2·00 mole) γ-butyrolactone which was heated at 155–160°. Heating at the same temp was continued for an additional 2 hr, then the mixture was distilled to obtain, in addition to 168 g liquid, b.p. 77–78° (6·5 mm), n_D^{25} 1·4350 (mostly butyrolactone), 10·5 g lactone XX, b.p. 97° (0·10 mm) to 134° (0·40 mm). This was redistilled to obtain 8·2 g colorless liquid, b.p. 96–98° (0·10 mm) n_D^{26} 1·5011, showing a strong band at 5·76 μ in the IR. Its gas chromatogram showed a small amount of two low-boiling impurities. (Found: C, 75·15; H, 9·39. Calc. for $C_{12}H_{18}O_2$: C, 74·19; H, 9·34%).

Acknowledgements—The author wishes to thank Messrs. R. F. Cornuet and J. A. Muir for the able technical assistance, and Drs. H. L. Gerhart and S. W. Gloyer for permission to present this work for publication. Many helpful discussions with Professor C. D. Hurd and Dr. W.-H. Chang are acknowledged with pleasure.