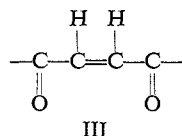


group ( $\tau$  6.62, 3 H) and absence of vinyl protons, in accord with system II; the dihydrodesoxy derivative of the methanol adduct, m.p. 243–244°,  $C_{29}H_{44}O_6$ ,  $[\alpha]^{27D} +6^\circ$ ,  $\lambda_{max}$  2.80, 5.78, and 5.83  $\mu$ ; the dehydro derivative (by oxidation with manganese dioxide),  $C_{28}H_{36}O_6$ , m.p. 276–277°,  $[\alpha]^{27D} +106^\circ$ ,  $\lambda_{alc}^{max}$  223 m $\mu$  ( $\epsilon$  14,700),<sup>8</sup>  $\lambda_{max}$  2.80 and 5.85–5.91  $\mu$ , n.m.r. spectrum showing the absence of ABX system of I and a new sharp signal at  $\tau$  3.20 (2 H), in accord with system III;

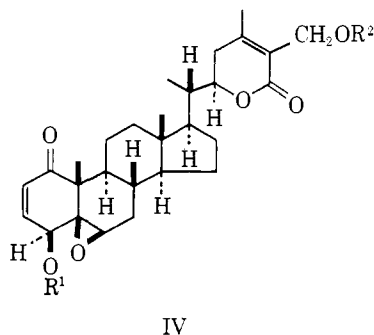


the *p*-bromobenzoate,  $C_{35}H_{41}BrO_7$ , m.p. 196–197°,  $[\alpha]^{28D} +63^\circ$ ;  $\lambda_{max}^{Nujol}$  2.85, 5.85, 5.92, and 13.20  $\mu$ ; and the *p*-bromobenzoate monoacetate,  $C_{37}H_{43}BrO_8$ , m.p. 179–180°,  $[\alpha]^{28D} +101^\circ$ ,  $\lambda_{max}^{Nujol}$  5.73, 5.84, 5.92, and 13.15  $\mu$ .

The *p*-bromobenzoate monoacetate crystallized from ethyl acetate in the orthorhombic system, space group  $P2_12_12_1$ , with cell dimensions  $a = 14.74$ ,  $b = 40.35$ ,  $c = 12.95$  Å. We found the crystal density to be 1.276 g. cm.<sup>-3</sup>, indicating that if the molecular formula of the *p*-bromobenzoate monoacetate is  $C_{37}H_{43}BrO_8$  then the asymmetric crystal unit consists of two molecules of  $C_{37}H_{43}BrO_8$  and one molecule of ethyl acetate ( $D_{calcd} = 1.276$  g. cm.<sup>-3</sup>); the crystallographic problem therefore involved the location of 96 independent carbon and oxygen atoms and 2 bromine atoms.

The initial positions of the two independent bromine atoms were derived from the three-dimensional Patterson synthesis and the carbon and oxygen atoms were then located by evaluating three-dimensional electron-density distributions with Fourier coefficients weighted according to the method proposed by Sim.<sup>9</sup> Three Fourier syntheses were used in the elucidation of the structure, and the approximate atomic coordinates are now being refined by the least-squares method. The present value of  $R$  for 3427 independent X-ray reflections is 18%. A most important verification of the structure lies in the fact that we find two crystallographically distinct but chemically identical molecules.

Our results establish that the *p*-bromobenzoate monoacetate has the structure and stereochemistry IV,  $R^1 = Ac$ ,  $R^2 = p\text{-}BrC_6H_4CO$ , from which it follows that compound A is represented by IV,  $R^1 = R^2 = H$ .



(8) Cf., e.g., the homocisoid enedione described by D. H. R. Barton, *et al.*, *J. Chem. Soc.*, 2988 (1951); 2210 (1952).

(9) G. A. Sim, *Acta Cryst.*, 12, 813 (1959); 13, 511 (1960); "Computing Methods and the Phase Problem in X-ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, Oxford, 1961, p. 227.

While this work was in progress, Lavie, *et al.*, reported the isolation<sup>10</sup> and partial elucidation of the structure of withaferin A<sup>11</sup> from *Withania somnifera* Dun. The similarity in physical properties of compound A to those reported for withaferin A led to direct comparison of the respective materials and to demonstration of their identity (by mixture melting point, mixed t.l.p.c., and infrared studies).<sup>12,13</sup> Consequently, we adopt the name withaferin A for IV,  $R^1 = R^2 = H$ .

(10) A. Yarden and D. Lavie, *J. Chem. Soc.*, 2925 (1962).

(11) D. Lavie, E. Glotter, and Y. Shvo, *Israel J. Chem.*, 2, 247 (1964); *J. Org. Chem.*, 30, 1774 (1965).

(12) We thank Professor David Lavie cordially for comparison samples of withaferin A and of withaferin.<sup>10</sup> Withaferin was found to be identical with the methanol adduct of withaferin A (see above).

(13) NOTE ADDED IN PROOF. Professor Lavie recently has informed us that his structural studies have led independently to proposal of the same structure for withaferin A: D. Lavie, E. Glotter, and Y. Shro, *J. Chem. Soc.*, in press.

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## Free Radical Additions of Carbon Tetrahalides to *cis*-Cyclooctene<sup>1,2</sup>

Sir:

The appearance of brief reports of evidence for a homolytic transannular reaction competing with normal 1,2 addition of bromotrichloromethane to methylenecycloalkanes<sup>3</sup> prompts us to make a preliminary communication about our study of additions of carbon tetrahalides to cyclooctene, a study which firmly establishes the occurrence of transannular hydrogen atom transfer during addition to an eight-membered ring and substantially delineates the energy requirements for the process.

Both photo- and thermally initiated<sup>4</sup> additions of carbon tetrachloride to *cis*-cyclooctene<sup>5</sup> give mainly isomeric  $C_9H_{14}Cl_4$  products.<sup>6</sup> In contrast to a patent claim that the thermal addition gives a 1,2-addition product,<sup>7</sup> we found that at least 97% of the  $C_9H_{14}Cl_4$

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant 1817-A4).

(2) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 13, 1965; Abstracts, p. 6S.

(3) (a) For addition to methylenecyclohexane, see M. Fisch and G. Ourisson, *Chem. Commun.* (London), 407 (1965). (b) For addition to the more rigid olefin, longifolene, see G. Ourisson, *Proc. Chem. Soc.* (London), 281 (1964).

(4) Photoinitiated additions were carried out in quartz flasks suspended in a Rayonet photochemical reactor and irradiated at 44° for 40 hr. with 2537 Å. light. Thermally initiated additions were accomplished without added initiator in a Parr medium pressure apparatus heated at 155° for 4.5 hr. Both reactions utilized about 4 moles of carbon tetrachloride per mole of cyclooctene.

(5) *cis*-Cyclooctene was generously given to us by Columbian Carbon Co., Lake Charles, La.

(6) Satisfactory analyses were obtained for all new compounds mentioned in this communication.

(7) F. Reicheneder and H. Suter, German Patent 1,036,847 (August 21, 1958); *Chem. Abstr.*, 54, 22416c (1960).

products from both additions is a mixture of *cis*- and *trans*-1-chloro-4-trichloromethylcyclooctane.<sup>8</sup>

The CCl<sub>4</sub>-cyclooctene product mixtures were fractionally distilled at reduced pressure. Several low boiling products containing 1-3 chlorines per 8-9 carbons were obtained in combined yield of about 17% (yields of individual compounds varied from traces to 5%), and substantial amounts of hexachloroethane, confirming the free radical nature of the reactions, were also isolated. The major fraction, C<sub>9</sub>H<sub>14</sub>Cl<sub>4</sub>, b.p. 97-116° (0.2 mm.), amounted to yields up to 73% and was separated into solid (33%,<sup>9</sup> m.p. 64.5-65.5°) and liquid (67%,<sup>9</sup> b.p. 127-130° (1.8 mm.)) isomers by low-temperature fractional crystallization from methanol. The geometrical isomerism was established by dehydrochlorination of either the solid or liquid isomer with 1.08 equiv. of potassium hydroxide in a mixed solvent of dimethyl sulfoxide, methanol, and water (10:4:1 by volume) to the same 1-chloro-4-dichloromethylenecyclooctane, b.p. 121-123° (3.5 mm.) (90% yield).

The dichloromethylenecyclooctane reacted sluggishly with ozone in CCl<sub>4</sub> solution at 0° to form an ozonide which was reduced with zinc dust and acetic acid to 4-chlorocyclooctanone (54% yield; infrared absorption at 1706 cm.<sup>-1</sup>; 2,4-dinitrophenylhydrazone m.p. 150-152°). This chloro ketone was identical with the one synthesized by conversion of 9-oxabicyclo[4.2.1]nonane<sup>10</sup> to 4-chlorocyclooctyl acetate (70% yield) by treatment with acetyl chloride and zinc chloride,<sup>11</sup> reduction of the ester to chloro alcohol with lithium aluminum hydride, and oxidation of the crude alcohol to 4-chlorocyclooctanone with chromic acid in aqueous acetone.

Photoinitiated (3500-Å. light) addition of bromotrichloromethane to *cis*-cyclooctene (4:1 molar equiv.) gives, along with small amounts of bromocyclooctenes and trichloromethylcyclooctane, addition product which is at least 97% 1-bromo-2-trichloromethylcyclooctane. The 1,2 isomer is readily distinguished from the 1,4 isomer by n.m.r. data.

N.m.r. signals for CH<sub>2</sub>CX (X = Cl, Br, or CCl<sub>3</sub>) and for HCCCl<sub>3</sub> appear at about -2.2 p.p.m. (A), while those for more remote methylenes appear at about -1.65 p.p.m. (B). For 1-chloro-4-trichloromethylcyclooctane, the ratio A:B (integrated areas) is 9:4, and the signal for HCCl is an unresolved multiplet at -4.2 p.p.m. For 1-halo-2-trichloromethylcyclooctane, the ratio A:B is 5:8 and the signal for HCCl or HCBBr is a doublet of triplets centered at -4.75 or -4.82 p.p.m., respectively.<sup>12</sup>

(8) Gas chromatographic analysis indicated that the C<sub>9</sub>H<sub>14</sub>Cl<sub>4</sub> fraction contained about 3% of material with retention time coincident with that of the 1,2 isomer.

(9) Analysis by comparison of infrared spectra of C<sub>9</sub>H<sub>14</sub>Cl<sub>4</sub> product mixture and standard mixtures prepared from separated isomers.

(10) (a) R. M. Moriarty and H. C. Walsh, *Tetrahedron Letters*, 465 (1965). (b) A. C. Cope, M. Gordon, S. Moon, and C. H. Park, *J. Am. Chem. Soc.*, **87**, 3119 (1965).

(11) A. C. Cope and A. Fournier, *ibid.*, **79**, 3896 (1957), describe the comparable reaction between 9-oxabicyclo[4.2.1]nonane and acetyl bromide. We found that the reaction of the less reactive acetyl chloride is facilitated by zinc chloride catalyst.

(12) (a) All chemical shifts are relative to internal tetramethylsilane. Data were obtained with a Varian HA-60 instrument. (b) The integrated n.m.r. spectrum of the 1-bromo-2-trichloromethylcyclooctane sample suggests about 3% contamination by the 1,4 isomer. (c) Analytical use of ratios similar to A/B has been described independently by C. L. McGehee and C. H. Sommers in "Developments in Applied Spectroscopy," Vol. 4, E. N. Davis, Ed., Plenum Press, New York, N. Y., 1965, p. 405.

Peroxide-initiated addition of trichloromethanesulfonyl chloride (0.45 mole) to *cis*-cyclooctene (0.35 mole) in refluxing benzene solution gave an 81% yield of C<sub>9</sub>H<sub>14</sub>Cl<sub>4</sub> addition product which was found by gas chromatographic and n.m.r. and infrared spectrophotometric analyses to be 30% 1-chloro-2-trichloromethylcyclooctane and 70% 1-chloro-4-trichloromethylcyclooctane (67% liquid isomer, 33% solid isomer).

Clearly the relative free energy requirements of the alternate reactions of intermediate 2-trichloromethylcyclooctyl radicals determine the course of the over-all reaction: Abstraction of chlorine from carbon tetrachloride requires more energy than transannular hydrogen migration, which requires more energy than abstraction of bromine from bromotrichloromethane; energy requirements for transannular hydrogen migration and for abstraction of chlorine from trichloromethanesulfonyl chloride are nearly the same.

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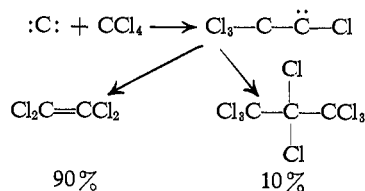
## The Reactions of Carbon Atoms with Chlorinated Hydrocarbons

Sir:

Previous communications from this laboratory have reported on reactions of carbon atoms with olefinic<sup>1-3</sup> and saturated<sup>4</sup> hydrocarbon substrates. We now report the extension of these studies to reactions with chlorinated hydrocarbons.

The reaction system used has been described.<sup>5</sup> Reactions occur in condensed phase at liquid nitrogen temperature. Products were isolated by vapor phase chromatography and their retention times and infrared and mass spectra compared with those of known compounds.

The reaction of carbon atoms with carbon tetrachloride yields two products, tetrachloroethylene and octachloropropane.



We postulate the initial reaction to be an insertion on a carbon-chlorine bond forming trichloromethylchlorocarbene as the intermediate. This intermediate can either stabilize by chlorine rearrangement, producing tetrachloroethylene, or can insert on the carbon-chlorine bond of a second carbon tetrachloride molecule, producing octachloropropane.

Carbon atoms react with chloroform in a similar manner, yielding trichloroethylene (84%) and 1,1,2,2,3,3-hexachloropropane (16%). The possibility that some of the trichloroethylene is produced from tri-

(1) P. S. Skell and R. R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).

(2) P. S. Skell and R. R. Engel, *ibid.*, **87**, 1135 (1965).

(3) P. S. Skell and R. R. Engel, *ibid.*, **87**, 2493 (1965).

(4) R. R. Engel and P. S. Skell, *ibid.*, **87**, 4663 (1965).

(5) P. S. Skell, L. D. Wescott, Jr., J.-P. Golstein, and R. R. Engel, *ibid.*, **87**, 2829 (1965).