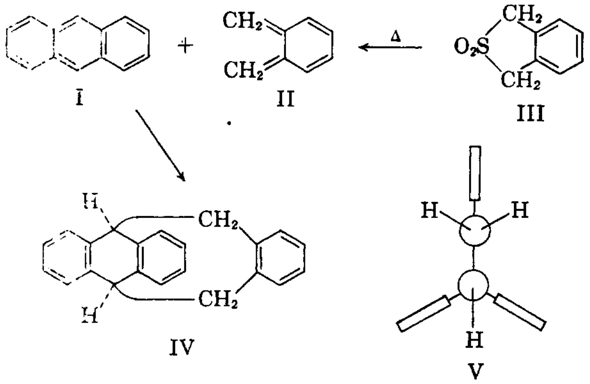
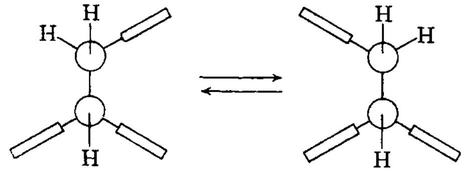
the reaction of I with *o*-xylylene or *o*-quinodimethane (II). II was obtained easily upon thermal decomposition of 1,3-dihydroisothianaphthene 2,2-dioxide (III) according to the method of Cava and Deana,[2] and was allowed to react *in situ* with I. Thus, heating of an almost equimolar mixture of I and III at 250–300° for thirty minutes, followed by chromatographic separation, furnished a 12% yield of 9,10-*endo*-*o*-xylylene-9,10-dihydroanthracene (IV), m.p. 179°. The constitution of IV was supported by its spectrographic properties.

Inspection of the molecular model of IV revealed that the symmetrical conformation (V)[3] can naturally be constructed only with substantial expansion of bond angles, but the fully eclipsed conformations (VIa and VIb) are devoid of such kind of strain. It is of interest to note signal of the bridgehead methine hydrogens has been observed as a triplet with integrated intensities in the approximate ratio of 1:2:1, while that of methylene hydrogens as a doublet of equal intensity. This fact indicates that each of the methine hydrogens is coupled with adjacent methylene hydrogens which are both completely equivalent. If the actual conformations are to be represented by VIa and VIb, these should be interchangeable with each other with low energy barrier separating them, or the *endo*-*o*-xylylene group must be almost free to flip over from one side to the other under conditions of NMR determination. The ultraviolet spectrum showed no anomaly which might have been expected from the interaction of two benzene rings closely situated in a rigid conformation (VIa or VIb).[4]





### EXPERIMENTAL[5]

*9,10-endo-o-Xylylene-9,10-dihydroanthracene* (IV). A mixture of 1.0 g. (0.0059 mole) of 1,3-dihydroisothianaphthene 2,2-dioxide (III)[2] and 1.1 g. (0.0062 mole) of anthracene in a small flask was heated at 250–260° for 15 min. in an oil bath. After an additional 15 min. at 300°, the reaction mixture was cooled and taken up in benzene. The benzene solution was chromatographed on a column of alumina. Elution with benzene afforded 0.2 g. (12% yield based on III) of colorless leaflets, m.p. 179° after two recrystallizations from ethanol. Considerable amounts of anthracene and polymeric materials were also isolated, besides a small quantity of anthraquinone (m.p. and mixed m.p. 274°).

*Anal.* Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.39; H, 6.48.

The NMR spectrum was obtained with a Varian spectrometer operating at 40 mc. on a *ca.* 0.1*M* solution of IV in carbon tetrachloride. Frequencies are given relative to water as an external standard. A doublet at −89 and −78 cps. (aromatic hydrogens), a triplet centering at 20.5 cps. with a separation of ±6.8 cps. (methine hydrogens), and a doublet centering at 62 cps. (methylene hydrogens) were observed, the integrated intensities being in the ratio of 6:1:2 in accordance with the formula given.

Ultraviolet absorption (in iso-octane): $\lambda_{max}$ 252 ($\epsilon$ 1000), 260 (610), 266 (1000), and 274 m$\mu$ (1350).

Infrared absorptions (potassium bromide): 3077, 3049, 2933, 2865, 1957 (w.), 1923 (w.), 1852 (w.), 1821 (w.), 1585, 1495 (s.), 1481 (s.), 1458 (s.), 1332, 1299, 1225, 1174, 1120, 1098, 1085, 1054, 1033, 963, 946, 915, 872, 825, 763 (v.s.), and 743 cm.$^{-1}$ (v.s.).

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[2] M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959).

[3] In formulas V, VIa, and VIb the top view of molecule IV has been shown. A thin square denotes an *o*-phenylene group.

[4] For an interesting example of "homoconjugation" interaction of benzene ring with an $\alpha,\beta$-unsaturated carbonyl group see J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **79**, 2569 (1957); **80**, 3667 (1958).

[5] Temperatures are uncorrected. Microanalyses were performed by Miss Kenko Ogawa.

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# 1,1,5-Trichloro-1,3-pentadiene from the Pyrolysis of 5,5,5-Trichloro-4-acetoxy-1-pentene

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In an attempt to prepare 5,5,5-trichloro-1,3-pentadiene (I), 5,5,5-trichloro-4-acetoxy-1-pentene (II) was subjected to the usual pyrolytic conditions for elimination of acetic acid.[2] From the pyrolysis

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[1] National Science Foundation Fellow, 1956–1959.

[2] W. J. Bailey and R. Barclay, *J. Am. Chem. Soc.*, **81**, 5393 (1959).

there was isolated, although only in 3% yield, a liquid trichloropentadiene (III). However, the infrared, ultraviolet, and NMR spectra of III indicated the allylic isomer, 1,1,5-trichloro-1,3-pentadiene rather than the expected product, I. Confirmation of the pyrolysis product, III, as 1,1,5-trichloro-1,3-pentadiene was obtained by oxidative ozonization of III which yielded chloroacetic and $\beta,\beta$-dichloroacrylic acids, identified by comparisons of their *p*-bromophenacyl ester derivatives with authentic samples. As the infrared spectrum of II, the precursor of III, is in agreement with the assigned structure, the observed rearrangement must have occurred in the pyrolysis step.

Ester II and its precursor, 5,5,5-trichloro-1-pentene-4-ol (IV), have been mentioned in the literature,[3] but, because experimental details were not provided, our procedures are recorded in the Experimental section.

## EXPERIMENTAL[4]

*5,5,5-Trichloro-1-pentene-4-ol* (IV). In a 500-ml. three necked flask equipped with a mechanical stirrer, a pressure-equalized dropping funnel and a condenser protected by a drying tube, were placed anhydrous ether (200 ml.) and magnesium turnings (12 g., 0.5 mole). Stirring was started, a few drops of allyl chloride were added, and the mixture was warmed to initiate reaction. A mixture of allyl chloride (38.2 g., 0.5 mole, b.p. 44.0–44.7°) and chloral (74 g., 0.5 mole, b.p. 95.8–96.4° from phosphorus pentoxide) was then added from the dropping funnel over the course of 3 hr. and at a rate sufficient to maintain a gentle reflux. The reaction mixture was cooled and poured into 300 ml. of iced 2*N* hydrochloric acid, and the ether phase was separated, washed with two 250-ml. portions of water, and dried over magnesium sulfate. Solvent was removed by evaporation under reduced pressure and the residue was evaporatively distilled at 1 mm. and 80°. The distillate was than fractionated under reduced pressure in a tantalum spiral column to yield IV (42 g., 44%) as a colorless liquid, b.p. 77–80° (11.5 mm.), $n_D^{20}$ 1.4960 [lit.[3] b.p. 88° (17 mm.), $n_D$1.4960]. In the infrared (sodium chloride sandwich), this material exhibited absorption, among others, at 3400 (hydroxyl), 1640 (unsaturation), and 990 and 920 (terminal methylene) cm.$^{-1}$

A derivative, *5,5,5-trichloro-1-pentene-4-yl 3,5-dinitrobenzoate*, prepared by standard procedures,[5] melted at 83–84°.

*Anal.* Calcd. for $C_{12}H_9Cl_3N_2O_6$: Cl, 27.73. Found: Cl, 27.75.

*5,5,5-Trichloro-4-acetoxy-1-pentene* (II). Acetic anhydride (130 g., 1.27 moles), IV (65 g., 0.35 mole) and 1 drop of concd. sulfuric acid were heated under reflux for 4 hr. Excess acetic anhydride and acetic acid were removed by distillation through a tantalum spiral column at 47 mm. The pressure was then reduced and 5,5,5-trichloro-4-acetoxy-1-pentene (II) (73 g., 92%) was collected as a colorless liquid, b.p. 96–97° (16 mm.), $n_D^{20}$ 1.4694 [lit.[3] b.p. 97–98° (16 mm.), $n_D$ 1.4698]. In the infrared (sodium chloride sandwich), this material exhibited absorption, among others, at 1750 (ester carbonyl), 1637 (unsaturation), and 992 and 922 (terminal methylene) cm.$^{-1}$

*1,1,5-Trichloro-1,3-pentadiene* (III). *Pyrolysis of 5,5,5-Trichloro-4-acetoxy-1-pentene* (II). A total of 466 g. of II was pyrolyzed in batches of 25–160 g. at 475–510° and a flow rate of 0.6 g./min. by the usual flow technique.[2,6] The pyrolysates were diluted with carbon tetrachloride, washed with water until the washings were neutral to litmus, and dried over magnesium sulfate. Carbon tetrachloride was removed by distillation at atmospheric pressure through a tantalum spiral column; the pressure was then lowered and the distillation was resumed to give diene-rich material [b.p. <95° (17 mm.)] and recovered starting material [b.p. 95–100° (17 mm.)]. The recovered starting material was recycled.

The combined diene-rich fractions were distilled through a 500 × 15 mm. Heli-Pak column to yield material, b.p. 88–89° (16 mm.), which was predominantly diene but which was contaminated by some carbonyl impurities as judged by its infrared spectrum. To remove the carbonyl impurities, this material was chromatographed on Woelm (activity 1) neutral alumina with petroleum ether (b.p. 60–68°) as the eluting solvent and it yielded, after removal of solvent and distillation, pure 1,1,5-trichloro-1,3-pentadiene (III) (10 g., 3%) as a pale yellow liquid, b.p. 38–40° (0.8–1.0 mm.), $n_D^{20}$ 1.5567.

*Anal.* Calcd. for $C_5H_5Cl_3$: C, 35.02; H, 2.94; Cl, 62.04. Found: C, 35.28; H, 3.12; Cl, 61.71.

In the infrared (sodium chloride sandwich), III exhibited absorption, among other, at 2920 (aliphatic C—H) and 1635 and 1585 (conjugated diene) cm.$^{-1}$ In the ultraviolet (iso-octane), III had $\lambda_{max}$ 250 m$\mu$ ($\epsilon$, 46,000). The NMR spectrum of III (20% in carbon tetrachloride) possessed absorption, relative to benzene as an external standard, at +94 and +100 (five-hydrogens, doublet) and at +5 (2-, 3-, and 4-hydrogens, center of unresolved multiplet) c.p.s. The areas were in the proportion, doublet:multiplet, 2:3.

*Ozonolysis of 1,1,5-trichloro-1,3-pentadiene* (III). Ozone, at a flow rate of 0.38 mmoles/min., was bubbled through a solution of III (0.368 g., 2.16 mmoles) in methylene chloride (50 ml.) at −80°. The operation was stopped after 6 min when ozone appeared in the effluent gases (aqueous potassium iodide indicator), the consumption of ozone amounting to 105% of theory for ozonization of *one* double bond. The solution was then evaporated under reduced pressure and the residue was stirred for 20 hr. at 60–70° with water (40 ml.) and 30% hydrogen peroxide (0.250 g., 2.2 mmoles). Excess hydrogen peroxide was decomposed with palladium black and the resulting solution was titrated with 0.1000*N* sodium hydroxide to the phenolphthalein endpoint, 46.35 ml. (107% of theory for the formation of two carboxylic acid fragments) being required.

After filtration, one-half of the neutralized solution was mixed with ethanol (20 ml.) and *p*-bromophenacyl bromide (0.90 g., 3.2 mmoles), heated under reflux for 2.75 hr., and then allowed to remain overnight at room temperature. Solvent was removed under reduced pressure and the residue was taken up in ether, washed with three 50-ml. portions of water, and dried over magnesium sulfate. The residue remaining after removal of the ether was chromatographed on 30 g. of 1:1 silicic acid:Hyflo Super Cel. Fraction A, eluted with 50:50 petroleum ether (b.p. 60–68°):benzene, amounted to 0.451 g. of *p*-bromophenacyl bromide. Fractions B and C were eluted, in order, with benzene, and Fraction D, 0.186 g. of *p*-bromophenacyl alcohol, was eluted with 2% ether in benzene.

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(3) G. I. Iotsitch, *Zhur. Russ. Fiz.-Chim. Obshchestva*, 42, 1083 (1910); *Bull. soc. chim. France*, [4], 10, 1148 (1911).

(4) We are indebted to Mr. William Saschek for the elemental analyses and to Mr. Carlos Rivas and Miss Yuet-May Huang for the infrared spectra. Infrared spectra were recorded on a Perkin-Elmer Model 21 infrared spectrophotometer, ultraviolet spectra on a Warren Spectracord ultraviolet-visible spectrophotometer, and NMR spectra on a Varian Associates 40 megacycle dual purpose spectrophotometer. Melting points are corrected.

(5) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 212.

(6) Extensive charring occurred even at temperatures below 450° where no conversion to diene was observed.

Fraction C melted at 101.5–102.7° and was identical with authentic[7] *p-bromophenacyl chloroacetate* (m.p. 102.0–103.2°, lit.[7] m.p. 103.7°) by the criteria of mixture melting point and infrared spectral comparison. It amounted to 0.050 g. (16% on diene III).

Fraction B melted at 120.7–121.5° and was identical with an authentic sample of *p*-bromophenacyl β,β-dichloroacrylate by the criteria of mixture melting point and infrared spectral comparison. It amounted to 0.070 g. (19% on diene III).

Authentic *p-bromophenacyl β,β-dichloroacrylate* (m.p. 121.5–122.0°) was prepared by standard procedures[8] from β,β-dichloroacrylic acid (m.p. 74–75°, lit.[9] m.p. 76–76.5°) which was obtained as described by Levas.[9]

*Anal.* Calcd. for $C_{11}H_7BrCl_2O_3$: C, 39.08; H, 2.09. Found: C, 38.71; H, 2.30.

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(7) H. Lund and T. Langvad, *J. Am. Chem. Soc.*, **54**, 4107 (1932).

(8) Ref. 5, p. 200.

(9) M. Levas, *Ann. Chim.* [12], **7**, 713 (1952).

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# The Chemistry of Trinitromethane. II. Reactions with Esters of Unsaturated *N*-Methylolamides[1]

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Benzoate esters of various saturated *N*-methylolamides have been prepared for purposes of identification[2], but the reactions of these esters have apparently not been investigated. This note reports the results of the investigation of the reactions of esters of unsaturated *N*-methylolamides with trinitromethane (I) in polar and nonpolar solvents.

In an attempt to add compound I to *N,N'*-bis(benzoxymethyl)fumaramide[3](II) the desired reaction did not occur. Instead, the ester was cleaved and the only products isolated were benzoic acid (III) and *N,N'*-bis(trinitroethyl)fumaramide[4] (IV). The same products were obtained when two or three equivalents of compound I were employed. The reaction was carried out in nitromethane because it was the only solvent in which compound II was found to be appreciably soluble. (When a mixture of benzene and carbon tetrachloride was employed, ester II was recovered quantitatively). The formation of compound IV from the interaction of compounds I and II must have involved alkyl-oxygen fission. If ester I had undergone the usual acyl-oxygen fission, characteristic of esters of primary alcohols, the products would have been trinitromethyl phenyl ketone and *N,N'*-bis(methylol)fumaramide.

*N,N'*-Bis(acetoxymethyl)fumaramide,[3] for which no suitable solvent could be found was recovered unchanged when treated with compound I in a variety of organic solvents. When water was used as a solvent at 100° vigorous decomposition was observed. A small amount (2%) of compound IV was isolated and 90% of the ester was recovered unchanged. The formation of compound IV from the acetate ester on prolonged heating in water may not involve the same mechanism as the cleavage of the benzoate ester (II) under anhydrous conditions. It was observed that some of the acetate ester was cleaved by boiling water alone to *N,N'*-bis(methylol)fumaramide, and it has been established[4] that this compound reacts with compound I in a Mannich type reaction to yield compound IV.

The reaction of *N*-benzoxymethylmethacrylamide (V) with compound I to yield *N*-trinitroethylmethacrylamide (VI) and compound III occurred at 25° in anhydrous ethylene chloride as well as in water. The highest yield (65%) of compound VI was obtained when ester V was treated with two equivalents of compound I for three hours at 25°. When the reaction time was increased to twelve hours, compound III was obtained in an almost quantitative yield but none of compound VI. The only other product was a noncrystallizable red oil which probably was formed from a secondary reaction of compound VI with compound I. For we had observed that samples of compound VI, contaminated with compound I, decompose on standing to a noncrystallizable red oil.

In aqueous solution at 25° compound V reacted with compound I in thirty minutes to give compounds III and VI in yields of 33% and 63% respectively.

$$\underset{\text{V}}{H_2C{=}C(CH_3)CONHCH_2OCOC_6H_5} + \underset{\text{I}}{HC(NO_2)_3} \xrightarrow[25^\circ]{(CH_2Cl)_2\text{ or }H_2O} \underset{\text{III}}{C_6H_5CO_2H} + \underset{\text{VI}}{H_2C{=}C(CH_3)CONHCH_2C(NO_2)_3}$$

In the case of *N*-benzoxymethylacrylamide (VII), no cleavage of this ester occurred at 40° in the absence of a solvent, instead compound I added across the double bond with the formation of *N*-benzoxymethyl-4,4,4-trinitrobutanamide (VIII).

$$\underset{\text{VII}}{H_2C{=}CHCONHCH_2OCOC_6H_5} \xrightarrow[40^\circ]{\text{I}} \underset{\text{VIII}}{(O_2N)_3C(CH_2)_2CONHCH_2OCOC_6H_5}$$

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(1) From the Ph.D. thesis of Una E. Lynch, Purdue University, 1952.

(2) A. Einhorn and R. Feibelmann, *Ann.*, **361**, 141 (1908).

(3) H. Feuer and Una E. Lynch, *J. Am. Chem. Soc.*, **75**, 5027 (1953).

(4) H. Feuer and Una E. Lynch-Hart, *J. Org. Chem.*, **26**, 391 (1961).