zene solution of VII produced less than 0.1 mg. of residue. Intrinsic viscosities were then determined by running the viscosities of chlorobenzene or decalin solutions of various concentrations of VII at 100°. For comparison, the intrinsic viscosity of a polystyrene sample[12] of 110,000 molecular weight was determined under identical conditions.

Sample	Intrinsic viscosity
A, emulsion VII	0.38
B, emulsion VII	.49
C, emulsion VII	.59
Standard polystyrene[12]	.48

X-Ray Diffraction Study.[14]—Oriented fibers were prepared by drawing out a melted sample of the polymer VII on a glass rod and gently stretching the fibers over a hot-plate to 300 to 400% elongation. Examination of the X-ray diffraction pattern indicated that the poly-1,2-dimethylenecyclohexane (VII) was very highly crystalline. The unit cell was apparently monoclinic with the following constants: a = 11.75 Å.; b = 7.35 Å.; c = 10.38 Å.; β = 61°.

Infrared Absorption Spectrum.[15]—Attempts to prepare a transparent film of polydimethylenecyclohexane (VII) were not successful.[17] Since VII was not soluble in any common solvent at room temperature, infrared absorption spectrum was run on a mull of VII in mineral oil using a rock salt prism in a Perkin–Elmer model 12-C infrared spectrophotometer. No appreciable absorption was found in the 885–910 cm.$^{-1}$ region, which indicated little or no 1,2-addition.[18] Other interpretations of the absorption curve using model compounds will be reported later.

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[17] This failure to obtain a transparent film indicates that the second-order transition point of VII is below room temperature. An accurate determination of physical properties, including the second-order transition temperature for VII, is in progress and will be reported separately from another laboratory.

[18] W. S. Richardson and A. Sacher, *J. Polymer Sci.*, **10**, 353 (1953).

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Cyclic Dienes. VIII. 1,2-Dimethylenecyclopentane[1]

BY WILLIAM J. BAILEY[2] AND WAYNE R. SORENSON[3]

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By the use of a pyrolysis of a diacetate in the final step, 1,2-dimethylenecyclopentane (I) was synthesized in six steps, starting from malonic ester and trimethylene dibromide. The structure of this diene was proved by ultraviolet absorption and conversion through Diels–Alder reactions to solid derivatives.

Since the pyrolysis of esters gave excellent results in the synthesis of 1,2-dimethylenecyclohexane[4] and substituted 1,2-dimethylenecyclohexanes,[5] it was of interest to apply this method to the synthesis of other cyclic dienes. The synthesis of 1,2-dimethylenecyclopentane (I) was of special interest since the five-membered ring is fairly rigid and would produce an almost planar *cis*-diene. Poly-1,2-dimethylenecyclohexane,[6] even though it possessed an all-*cis* configuration very similar to natural rubber, was a high-melting crystalline solid. One possible reason for the difference in properties between these two all-*cis* polymers was the increase in steric hindrance to rotation due to the presence of the six-membered ring. Arnold and co-workers[7] showed that the steric requirement of a five-membered ring is considerably less than that of a six-membered ring. 1,2-Dimethylenecyclopentane (I), therefore, is of further interest because polymerization should produce an all-*cis* diene polymer with less steric hindrance than poly-1,2-dimethylenecyclohexane.

The cyclic diene I was synthesized in six steps from diethyl malonate and trimethylene dibromide (II). Perkin[8] prepared tetraethyl 1,1,5,5-pentanetetracarboxylate (IV) from diethyl malonate but did not report a yield. By following his directions, only a 25% yield of IV could be obtained under optimum conditions and decomposition of the unreacted halogen compounds during distillation was very troublesome. Cason and Allen[9] studied the reaction of diethyl malonate and II to form diethyl 1,1-cyclobutanedicarboxylate. Extrapolation of their results showed that if 12 moles of malonic ester reacted with 2 moles of sodium ethoxide and 1 mole of the dibromide II an 81% yield of the tetraester IV (based on II) could be obtained. Apparently the large excess of malonic ester suppressed the formation of the monoalkylated malonic ester anion III and therefore increased the concentration of enolate of malonic ester, giving a higher yield of the desired tetraester IV.

Perkin[10] converted the tetraester IV to the tetraethyl 1,1,2,2-cyclopentanetetracarboxylate (V) and subsequently[11] converted this tetraester to 1,2-cyclopentanedicarboxylic acid (VII). He did not report the yield of either reaction. When the Perkin method, which used iodine instead of bromine, was modified by not isolating the intermediate tetraester V, and distilling off the ethyl acetate formed by ester interchange through a distillation column, the *trans*-1,2-cyclopentanedicarboxylic acid (VII) was produced in an over-all yield of 70% in a very clean-cut reaction.

VII, which was only slightly soluble in ether, was reduced with lithium aluminum hydride by adding VII to the reaction flask by means of an exhaustive ether extractor. If care was taken to heat the reaction mixture for 14 hours after the addition was complete and to avoid strong acids in the hy-

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[1] Previous paper in this series, THIS JOURNAL, **76**, 3009 (1954).

[2] Department of Chemistry, University of Maryland, College Park, Md.

[3] Office of Naval Research Fellow, Wayne University, 1949–1951; University of Maryland, 1952–1953; Union Carbide Fellow, University of Maryland, 1951–1952.

[4] W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953).

[5] W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **76**, 2251 (1954).

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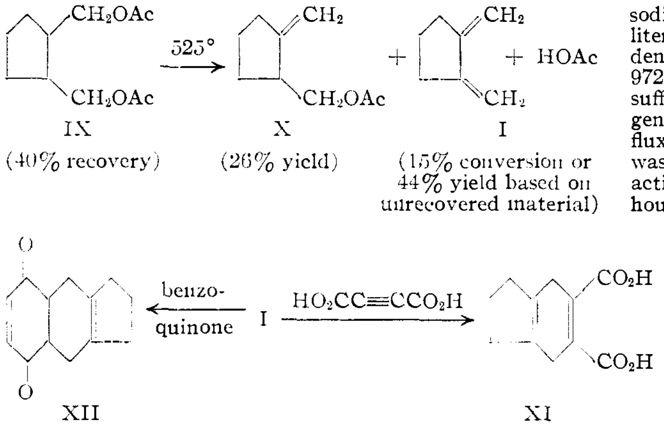
[11] W. H. Perkin, Jr., *J. Chem. Soc.*, **65**, 587 (1894).



drolysis, a 93% yield of the *trans*-1,2-di-(hydroxymethyl)-cyclopentane (VIII) was obtained. Acetylation with acetic anhydride and acetic acid produced the *trans*-1,2-di-(acetoxymethyl)-cyclopentane (IX) in 94% yield.

Pyrolysis of the diacetate IX was carried out by dropping the liquid ester through a helix-packed Vycor tube externally heated at 525°, according to a procedure similar to that described for the synthesis of 1,2-dimethylenecyclohexane.[4] When moderate quantities of the diester IX were used and conditions were adjusted so that 50% of the theoretical acetic acid was cracked out, a 15% conversion to pure 1,2-dimethylenecyclopentane (I), a 26% yield of 1-methylene-2-acetoxymethylcyclopentane (X), and a 40% recovery of the starting diester were obtained. The yield of the diene I, based on unrecovered material, was only 44%, in contrast to the high yield reported for pyrolysis of other diacetates.[4,5] With larger quantities of the diester, better yields undoubtedly could be obtained. However, it was not possible to crack out more acetic acid without encountering charring in the pyrolysis tube. Apparently the formation of a double bond exocyclic to a five-membered ring by pyrolysis requires a slightly higher temperature than the formation of one exocyclic to a six-membered ring.

The structure of 1,2-dimethylenecyclopentane (I) was proved by analysis, ultraviolet absorption, and conversion to two solid derivatives by Diels–Alder reactions. The diene I did not show a maximum above 220 mμ, but the ϵ was rising rapidly as the wave length was lowered and appeared to reach a maximum just below 220 mμ, indicating the presence of conjugated double bonds exocyclic to a ring. (1,2-Dimethylenecyclohexane possessed an ϵ maximum at 220 mμ.)

A Diels–Alder reaction with 1,2-dimethylenecyclopentane (I) and acetylenedicarboxylic acid produced 4,7-dihydroindan-5,6-dicarboxylic acid (XI). Treatment of the diene I with an equimolar quantity of benzoquinone produced the monoadduct, tetrahydrocyclopentanonaphthoquinone XII. The polymer from this diene will be reported later.

Experimental[12]

Tetraethyl 1,1,5,5-Pentanetetracarboxylate (IV).—In a modification of the method of Perkin,[8] 23 g. (1 mole) of sodium was dissolved in 500 ml. of absolute ethanol in a 3-liter, three-necked flask, fitted with a stirrer, a reflux condenser and a dropping funnel. The solution was cooled and 972 g. (6 moles) of diethyl malonate was added at a rate sufficient to keep the sodium enolate in solution by the heat generated. This solution was stirred and heated under reflux while 101 g. (0.5 mole) of trimethylene bromide (II) was added dropwise over a 3-hour period. After the reaction mixture was heated under reflux for an additional 12 hours, the ethanol was distilled off under reduced pressure.

To the concentrated residue was added 400 ml. of water containing a few drops of sulfuric acid to remove the sodium bromide plus any unreacted base. The aqueous layer was re-extracted two or three times with ether, and these ether extracts were combined with the original organic layer. The resulting ether solution was dried over magnesium sulfate, and the ether was removed under reduced pressure. The residue was fractionated through a 6-inch, Vigreux column to yield, after recovering the excess diethyl malonate, 146 g. (81%) of tetraethyl 1,1,5,5-pentanetetracarboxylate (IV), b.p. 198–202° (2.5 mm.) [Perkin[8] reported no yield and b.p. 259–262° (100 mm.)].

***trans*-1,2-Cyclopentanedicarboxylic Acid (VII).**—A modification of two procedures by Perkin[10,11] was used in this synthesis. To 400 ml. of absolute ethanol in a 2-liter, three-necked flask, equipped with a stirrer, a condenser protected by a drying tube and a dropping funnel, was added 31.3 g. (1.36 moles) of sodium. When the sodium had all reacted, 245 g. (0.68 mole) of tetraethyl 1,1,5,5-pentanetetracarboxylate (IV) was added dropwise to the solution. To the cooled reaction mixture was added, dropwise and very slowly with stirring, 109 g. (0.68 mole) of bromine. After the reaction mixture had been stirred at room temperature for an hour, the ethanol was removed by distillation under reduced pressure. The residue was washed several times with water to remove the sodium bromide plus any unreacted base, and the combined aqueous extracts were re-extracted with ether. The solvent was removed from these ether extracts, and the residue was combined with the original organic layer containing the crude tetraethyl 1,1,2,2-cyclopentanetetracarboxylate (V). The crude V was used without further purification for the subsequent hydrolysis and decarboxylation.

In a 2-liter, round-bottom flask, fitted with a 6-inch, helix-packed fractionating column, were placed the above crude ester, 250 ml. of concentrated sulfuric acid, 250 ml. of glacial acetic acid and 750 ml. of water. The mixture was heated under reflux for 3 hours until no more ethyl acetate was collected. The reaction mixture was cooled and a large quantity of tan crystals was filtered off. Concentration of the filtrate yielded an additional quantity of the tan crystals. The combined crude material was decolorized with charcoal and recrystallized from water to give 75 g. (70%) of white crystals of *trans*-1,2-cyclopentanedicarboxylic acid (VII), m.p. 161–162° (Perkin[11] reported m.p. 160° and no yield).

***trans*-1,2-Di-(hydroxymethyl)-cyclopentane (VIII).**—In a 3-liter, three-necked flask, fitted with an exhaustive ether extractor and a Hershberg stirrer, was placed 11.7 g. (0.31 mole) of lithium aluminum hydride in 600 ml. of dry ether. In the reservoir of the exhaustive extractor was placed 25 g. (0.16 mole) of *trans*-1,2-cyclopentanedicarboxylic acid (VII), and the lithium aluminum hydride solution was heated under reflux in order to extract VII slowly into the reaction flask. After the addition of VII was complete, the reaction mixture was stirred and heated under reflux for an additional 14 hours. The excess lithium aluminum hydride was decomposed with 100 ml. of water, and just enough 10% hydrochloric acid was added to dissolve the aluminum salts. The ether layer was separated, and the aqueous layer was extracted for 30 hours with ether in a liquid–liquid exhaustive extractor. The ether extract was combined with the original ether layer, and the resulting solution was dried over anhydrous magnesium sulfate. The ether was removed by distillation and the residue was fractionated through a 6-inch, helix-packed column to yield 19.1 g. (93%) of clear, viscous *trans*-1,2-di-(hydroxymethyl)-cyclopentane (VIII), b.p. 127–129° (2.4 mm.), n^{25}D 1.4771.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.44; H, 10.76.

***trans*-1,2-Di-(acetoxymethyl)-cyclopentane (IX).**—To 153 g. (1.5 moles) of refluxing acetic anhydride in a 500-ml.,

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(12) All melting points are corrected. Analyses were performed by Vivian Kapuscinski and Mary Aldridge.

three-necked flask was added, dropwise over 30 minutes, 43 g. (0.33 mole) of *trans*-1,2-di-(hydroxymethyl)-cyclopentane (VIII) dissolved in 35 ml. of glacial acetic acid. After the mixture was heated under reflux for 14 hours, it was fractionated through a 6-inch, helix-packed column to yield 63 g. (94%) of colorless *trans*-1,2-di-(acetoxymethyl)-cyclopentane (IX), b.p. 116° (2 mm.), $n^{25}D$ 1.4471.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.11; H, 8.42. Found: C, 61.43; H, 8.48.

1,2-Dimethylenecyclopentane (I) and 1-Methylene-2-acetoxymethylcyclopentane (X).—A 25-mm. Vycor pyrolysis tube packed with Pyrex helices was externally heated with a 12-inch Hoskins furnace, as previously described,[4] and flushed out with a slow stream of oxygen-free nitrogen. Through this tube, heated at 525°, was dropped 75 g. (0.35 mole) of *trans*-1,2-di-(acetoxymethyl)-cyclopentane (IX) over a period of 65 minutes, and the pyrolysate was collected in a flask immersed in a Dry Ice–chloroform–carbon tetrachloride mixture. The pyrolysate was taken up in ether and washed several times with water to remove acetic acid, and the organic layer was dried over potassium carbonate. Titration of aliquot portions of the aqueous extracts indicated that 21 g. (0.35 mole or 50%) of acetic acid was cracked out. The ether was distilled from the organic layer, and the residue was fractionated through a 6-inch, helix-packed column to yield 5.0 g. (15%) of 1,2-dimethylenecyclopentane (I), b.p. 80–82° (130 mm.), $n^{25}D$ 1.4694, d^4_{25} 0.8553; 10.0 g. (26%) of 1-methylene-2-acetoxymethylcyclopentane (X), b.p. 90–91° (2.5 mm.), $n^{25}D$ 1.4526; and 30 g. (40% recovery) of the diacetate IX. The yield of I, based on unrecovered IX and X, was 44%.

Anal. Calcd. for C_7H_{10}: C, 89.36; H, 10.64. Found: C, 89.35; H, 10.65. Calcd. for $C_9H_{14}O_2$: C, 70.25; H, 9.11. Found: C, 70.22; H, 9.14.

4,7-Dihydroindan-5,6-dicarboxylic Acid (XI).—In a 50-ml. flask were placed 0.5 g. (0.0053 mole) of 1,2-dimethylenecyclopentane (I), 0.6 g. (0.0052 mole) of acetylenedicarboxylic acid, and 30 ml. of dioxane, and the mixture was heated under reflux for 6 hours. The dioxane was removed under reduced pressure, and the residue was recrystallized from ether twice to yield 0.9 g. (83%) of 4,7-dihydroindan-5,6-dicarboxylic acid (XI), m.p. 146–147°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.50; H, 5.77. Found: C, 63.21; H, 6.02.

4a,5,8,8a-Tetrahydro-6,7-cyclopentano-1,4-naphthoquinone (XII).—In a 50-ml. flask were placed 0.5 g. (0.0053 mole) of 1,2-dimethylenecyclopentane (I), 0.6 g. of benzoquinone (0.0055 mole), and 30 ml. of benzene, and the reaction mixture was heated under reflux for 8 hours. The benzene was evaporated and the crystalline residue was recrystallized three times from petroleum ether (30–60°) to yield 0.8 g. (75%) of 4a,5,8,8a-tetrahydro-6,7-cyclopentano-1,4-naphthoquinone (XII), m.p. 135–136°.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.22; H, 6.93. Found: C, 77.11; H, 7.17.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

Free Radical Additions Involving Fluorine Compounds. II. The Addition of 1-Chloro-1,2-dibromo-1,2,2-trifluorethane to Some Hydrocarbon Olefins[1,2]

BY PAUL TARRANT AND EARL G. GILLMAN

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Various hydrocarbon olefins have been found to react with 1-chloro-1,2-dibromo-1,2,2-trifluoroethane to give one-to-one addition products in the presence of peroxides. These adducts may be converted to olefins or to dienes containing the perfluorovinyl group.

Numerous reports have appeared in the literature on the peroxide-catalyzed addition of fluorohalomethanes to olefins[3–6] but very little information has been published on the addition to olefins of halogenated compounds containing more than one carbon atom. Feasley and Stover[7] carried out reactions of 1,1,2-trichloro-1,2,2-trifluoroethane with various straight-chain primary olefins; however, they apparently did not isolate any individual addition products.

It has been found that 1-chloro-1,2-dibromo-1,2,2-trifluoroethane, readily made by adding bromine to chlorotrifluoroethylene, reacts in the presence of benzoyl peroxide with ethylene, propylene, 2-butene, 2-methylpropene, 1-octene and 3-chloropropene to give good yields of the one-to-one addition products. The 1-chloro-1,2-dibromo-1,2,2-trifluoroethane is less reactive than bromotrichloromethane since the latter forms a one-to-one adduct with chlorotrifluoroethylene whereas the dibromide does not; however, it is more reactive than dibromodifluoromethane, which does not react to an appreciable extent with 3-chloropropene. The over-all reaction with ethylene is represented by the equation

$$CF_2BrCFClBr + CH_2{=}CH_2 \longrightarrow CF_2BrCFClCH_2CH_2Br$$

In reactions involving the homolytic scission of a carbon to bromine bond in $CF_2BrCFClBr$, it appears that either of the bromine atoms might be removed by the radical formed by the decomposition of the catalyst to give either $CF_2BrCFCl\cdot$ or $CFClBrCF_2\cdot$ and that with propylene, for example, the compound represented by either $CF_2BrCFClCH_2CHBrCH_3$ (I) or $CFClBrCF_2CH_2CHBrCH_3$ (II) might be formed. However, the carbon to bromine bond of the bromochlorofluoromethyl group is undoubtedly weaker than that of the bromodifluoromethyl group, and the compound represented by I was expected to be formed. Proof of this supposition was found in the transformation of the adduct to 1,1,2-trifluoro-1,3-pentadiene by the following reactions

$$CF_2BrCFClCH_2CHBrCH_3 \xrightarrow{\text{base}}$$

$$CF_2BrCFClCH{=}CHCH_3 \xrightarrow{\text{Zn}} CF_2{=}CFCH{=}CHCH_3$$

Had the other adduct II been obtained, the cor-

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[1] Previous paper in this series, THIS JOURNAL, **76**, 3466 (1954).

[2] The work was supported in part by the Office of Naval Research under Contract (Nonr 1017(00)).

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