79.1°, in 40 ml. of 80% aqueous acetone was sealed in an ampule and placed in the 99.95° thermostat. After 5.8 hours the ampule was opened and the solvent evaporated under a stream of filtered air. The residue was extracted with chloroform and the insoluble phthalic acid was removed by filtration. The chloroform solution was extracted with three 10-ml. portions of ice-cold 5% sodium hydroxide which were combined and shaken with several portions of ether to remove the 5-methyl-2-cyclohexenol. The aqueous solution was acidified and the acid phthalate, which separated as an oil, was separated by extraction with chloroform. This solution was filtered and the solvent was removed by evaporation at room temperature. The infrared spectrum of the residue in chloroform was indistinguishable from that of pure Ia. Since as little as 1% of IIa in Ia can be detected by infrared analysis it is clear that the recovered acid phthalate contained less than 1% of the *trans* isomer, IIa.

When this experiment was repeated with *trans*-5-methyl-2-cyclohexenyl acid phthalate (IIa) the recovered acid phthalate was IIa containing less than 1% of the *cis* isomer Ia.

Isolation of Products from the Solvolysis of *cis*-(Ia) and *trans*-5-Methyl-2-cyclohexenyl Acid Phthalate (IIa) and from the Acid-catalyzed Isomerization of *cis*-5-Methyl-2-cyclohexenol (Ib).—The results of these experiments are given in Table IV. The indicated solutions (30 ml.) were sealed in ampules and thermostated at 99.95° for 5.5 hr. (4.4 half-lives for the solvolysis of the *cis*-acid phthalate Ia and 5.5 half-lives[22] for the solvolysis of the *trans*-acid phthalate IIa). The solutions were made alkaline and concentrated at room temperature to remove the acetone, and the resulting solutions were extracted with carbon disulfide. The carbon disulfide solution was filtered and concentrated to about 1 ml. The infrared spectra showed that these solutions contained only the isomeric 5-methyl-2-cyclohexenols and the compositions of the binary mixtures were determined from the infrared spectrum by the previously described method.[20]

In order to determine if the method of isolation results in fractionation, a synthetic mixture of the isomeric 5-methyl-2-cyclohexenols consisting of 48% of the *cis* isomer was dissolved in 60% aqueous acetone and isolated by the above procedure. The mixture of *cis*- and *trans*-5-methyl-2-cyclohexenol isolated was found to consist of 47% of the *cis* isomer by infrared analysis. It is thus clear that fractionation does not occur during the isolation.

TABLE IV

COMPOSITIONS OF THE MIXTURES OF *cis*-(Ib) AND *trans*-5-METHYL-2-CYCLOHEXENOL (IIb) FORMED IN THE ISOMERIZATION OF Ib AND IN THE SOLVOLYSIS OF THE ISOMERIC 5-METHYL-2-CYCLOHEXENYL ACID PHTHALATES IN 60% ACETONE AT 100°

Reactant (*M*)	Reagent (*M*)	Compn. of 5-methyl-2-cyclohexenols (% *cis* isomer)
Ia (0.05)	None	56
IIa (.05)	None	55
Ib (.07)	None	98
Ib (.07)	Phthalic acid (0 05)	53
Ib (.07)	Chloroacetic acid (0.05)	55

The Ethanolysis of *cis*-5-Methyl-2-cyclohexenyl Acid Phthalate (Ia).—A solution of 2.0 g. (0.77 mmole) of Ia in 80 ml. of absolute ethanol[23] was sealed in an ampule and heated at 100° for 68.5 hours.[24] The solution was diluted with an equal volume of water and extracted with two 70-ml. portions of hexane. After shaking with two 100-ml. portions of 5% sodium hydroxide to remove acidic components, the organic layer was fractionated. The only material obtained after removal of the hexane was a mixture of *cis*- and *trans*-ethyl 5-methyl-2-cyclohexenyl ether and a high boiling residue, presumably diethyl phthalate. The infrared spectrum of the mixture of isomeric ethers was a composite of the spectra of the pure isomers and from the absence of a band at 3.08 μ it is clear that 5-methyl-2-cyclohexenol was not present. The composition of the mixture, 74% of the *trans* isomer and 26% of the *cis* isomer, was determined from the percentage transmission at 9.05 and 9.85 μ, bands present in the spectrum of the *cis* isomer, but not of the *trans* isomer.

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[22] This value was estimated by assuming that the rate constant (k_t) which is known for IIa in 90% acetone responds to a change in solvent composition in the same way that k_t for Ia does.

[23] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 359.

[24] The rate constant for the ethanolysis could not be determined because phthalic acid is esterified under the conditions of the reaction. A rate constant of 0.0181 hr.$^{-1}$ for the ethanolysis of Ia at 100° can be estimated from the rate constants in 80% and 90% acetone by the *mY* equation (E. Grunwald and S. Winstein, THIS JOURNAL, **70**, 846 (1948)). The half-period for the ethanolysis of Ia at 100° is thus estimated to be 38 hours.

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

Pyrolysis of Esters. III. Synthesis of 2-Vinylbutadiene[1,2]

BY WILLIAM J. BAILEY AND JAMES ECONOMY[3]

RECEIVED AUGUST 23, 1954

2-Vinyl-1,3-butadiene was synthesized in three steps from aconitic ester in an over-all yield of 40%. The crucial steps in the synthesis were the reductive acetylation with lithium aluminum hydride and acetic anhydride in a 94% yield and the pyrolysis of a triacetate in a 43% yield. The structure of the triene was proved by analysis, ultraviolet and infrared absorption and conversion to a known derivative through an intermediate Diels–Alder adduct.

The pyrolysis of esters has been shown to be an excellent method for the synthesis of strained dienes, such as 1,2-dimethylenecyclohexane[4] and 1,2-dimethylene-4-cyclohexene,[5] an isomer of *o*-xylene. It seemed likely that this excellent method could be applied to the synthesis of other highly unsaturated compounds that are difficult or impossible to prepare by other more conventional procedures. One such compound is 2-vinylbutadiene (I). This triene is of particular interest since it contains the simplest possible cross-conjugated system. Since it possesses two conjugated diene systems, it will form polymeric Diels–Alder adducts with bifunctional dienophiles. The triene I, for the same reason, should be of interest as a cross-linking agent for vinyl polymers. The Diels–Alder adducts of I with cyclic dienophiles appear to be excellent starting materials for the synthesis of condensed polynuclear aromatic

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[1] Previous paper in this series, THIS JOURNAL, **77**, 357 (1955).

[2] Presented at the 126th National Meeting of the American Chemical Society, New York, N. Y., September, 1954.

[3] Office of Naval Research Fellow, 1953–1954.

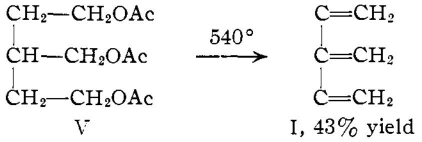
[4] W. J. Bailey and H. R. Golden, THIS JOURNAL, **75**, 4780 (1953).

[5] W. J. Bailey and J. Rosenberg, *ibid.*, **77**, 73 (1955).

hydrocarbons by employing the method by which 1,2-dimethylenecyclohexane was converted to pentacene,[6] hexacene and heptacene.[7]

Aconitic acid was esterified in a 96% yield to triethyl aconitate (II), which was reduced in a nearly quantitative yield to triethyl tricarballylate (III). Reduction of the ester III with lithium aluminum hydride was expected to produce the water-soluble glycol IV. However, the isolation of IV by decomposition of the complex by aqueous acid followed by extraction with ether did not appear feasible because of the low ether solubility of IV. By employing the method of reductive acetylation with lithium aluminum hydride that was successful for the synthesis of 1,4-diacetoxy-2,3-di-(acetoxymethyl)-butane from tetraethyl ethane-1,1,2,2-tetracarboxylate,[8] 1,5-diacetoxy-3-acetoxymethylpentane (V) was synthesized in a 94% yield directly from III. Thus III was reduced with lithium aluminum hydride and the complex decomposed with acetic anhydride and acetic acid to give the triacetate V in one step.

An alternative route from II to V was investigated but was found to be inferior to the preceding



$$\begin{array}{l} CH_2{-}CH_2OAc \\ | \\ CH{-}CH_2OAc \\ | \\ CH_2{-}CH_2OAc \end{array} \xrightarrow{540^\circ} \begin{array}{l} C{=}CH_2 \\ | \\ C{=}CH_2 \\ | \\ C{=}CH_2 \end{array}$$

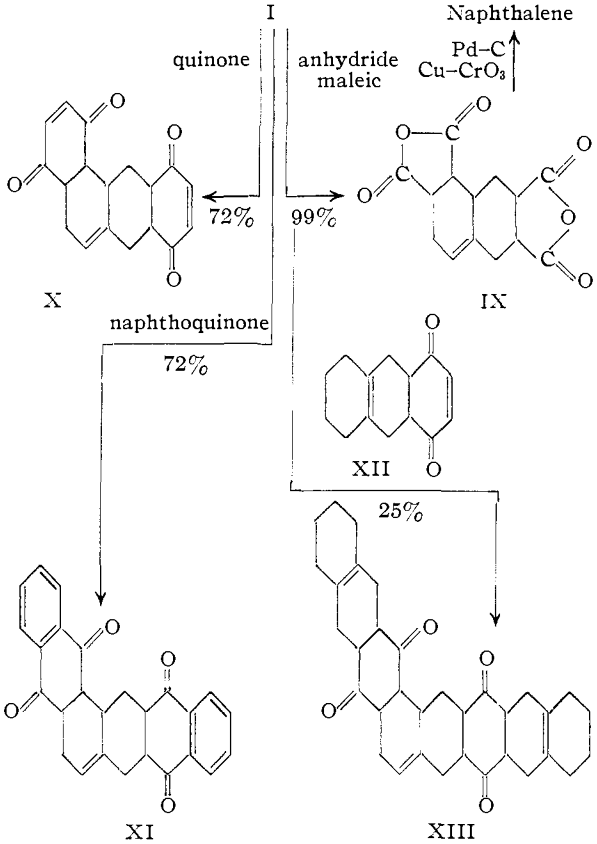
V I, 43% yield

method. Triethyl aconitate was reductively acetylated with lithium aluminum hydride and acetic anhydride to produce 1,5-diacetoxy-3-acetoxymethyl-2-pentene (VII) in only 40% yield. Apparently the reduction to the unsaturated glycol VI occurred in high yield but the triacetate VII lost a molecule of acetic acid when heated under the acidic conditions during acetylation and subsequent distillation. Both low boiling material and polymeric substances also were obtained. Catalytic reduction of pure VII gave only a 61% yield of the saturated triacetate V. Low boiling material obtained upon distillation indicated that partial hydrogenolysis of an acetoxy group had occurred.

Pyrolysis of the triacetate V by dropping the liquid ester through a Vycor tube packed with glass helices[4] at 540° produced a 43% yield of 2-vinylbutadiene (I). Even though 95% of three molar equivalents of acetic acid was liberated, the yield of I was reduced by the formation of a dimer during the pyrolysis and the distillation.

The structure of the 2-vinylbutadiene (I) was proved by analysis, ultraviolet and infrared absorption and conversion to a known derivative through an intermediate Diels–Alder adduct. The triene I possessed a broad absorption ϵ_{max} of 205,000 at 231 mμ, indicating a system of conjugated double bonds. The infrared absorption with strong peaks at 11.23, 10.02 and 10.16 cm.$^{-1}$ and moderate peaks at 13.25, 9.58, 9.39, 8.17, 7.60, 5.45 and 3.80 cm.$^{-1}$ is consistent with the structure assigned to the triene.

The 2-vinylbutadiene reacted readily with 2 moles of maleic anhydride to form the $\Delta^{1(9)}$-octalin-3,4,6,7-tetracarboxylic anhydride (IX). The maleic anhydride adds first to one of the conjugated diene systems to form the intermediate monoadduct VIII. The two remaining double bonds are still in conjugation and add the second mole of dienophile. The structure of the anhydride IX was indicated by its neutralization equivalent and by simultaneous dehydrogenation and decarboxylation to naphthalene. Mixed melting point determination with an authentic sample of naphthalene showed no depression.



Treatment of the 2-vinylbutadiene (I) with cyclic dienophiles produced a series of polycyclic Diels–Alder adducts that should serve as starting materials for the synthesis of condensed polynuclear aromatic hydrocarbons. Thus, the triene plus quinone produced the benzanthracene derivative X, I plus naphthoquinone produced the hexaphene derivative XI, and I plus $\Delta^{2,8a(10a)}$-decahydroanthracene-1,4-dione (XII) produced the octaphene derivative XIII.

Diels–Alder polymers from 2-vinylbutadiene will be reported separately.

Experimental[8a]

Triethyl Tricarballylate (III).—Triethyl aconitate, b.p. 124–126° (0.7 mm.), $n^{20}D$ 1.4558 [reported[9] b.p. 250–253° (250 mm.), $n^{20}D$ 1.4556] was prepared from aconitic acid in a 96% yield by the azeotropic method using benzene and ethyl alcohol.

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(6) W. J. Bailey and M. Madoff, THIS JOURNAL, **75**, 5603 (1953).

(7) W. J. Bailey and C. Liao, *ibid.*, **77**, 992 (1955).

(8) W. J. Bailey and W. R. Sorenson, Abstracts of the 125th National Meeting of the American Chemical Society, Kansas City, Mo., March 1954.

(8a) All melting points are uncorrected. The authors are grateful to Mary Aldrich and Kathryn Gerdeman for the microanalyses.

(9) J. W. Bruhl, *Ann.*, **235**, 20 (1886).

At 50° and 3000 lb./sq. inch pressure 709 g. (2.75 moles) of triethyl aconitate (II) was hydrogenated in the presence of 70 g. of W-2 Raney nickel catalyst.[10] After the catalyst was removed by filtration, the filtrate was distilled through a 6-inch, helix-packed column to yield 706 g. (99%) of triethyl tricarballylate (III), b.p. 115° (1.0 mm.), $n^{25}\mathrm{D}$ 1.4329 [reported[11] b.p. 200–205° (12 mm.)] (Ingold prepared III by the condensation of diethyl malate and ethyl cyanoacetate followed by hydrolysis, decarboxylation and re-esterification).

Anal. Calcd. for $C_{12}H_{20}O_6$: C, 55.36; H, 7.74. Found: C, 55.52; H, 7.63.

1,5-Diacetoxy-3-acetoxymethylpentane (V). A. From Triethyl Tricarballylate (III).—To a solution of 113 g. (3.5 moles) of lithium aluminum hydride in 5000 ml. of dry ether was added dropwise 426 g. (1.60 moles) of triethyl tricarballylate (III) dissolved in 1000 ml. of dry ether. After the reaction mixture was stirred and heated under reflux for 1 week, 4000 ml. of dry butyl ether was added and the ethyl ether was removed by distillation until the temperature of the reaction mixture reached 120°. In order to decompose the excess lithium aluminum hydride, 300 ml. of acetic acid was added. To the reaction mixture heated under reflux was slowly added 4000 ml. of acetic anhydride. The precipitate became so thick that the stirring had to be discontinued. However, when the reaction mixture was heated for 24 hours, it became thin enough to permit stirring. After the mixture was heated for an additional 10 days, the salts were removed by filtration and the butyl ether, acetic acid and excess acetic anhydride were removed by distillation under reduced pressure. The residue, which still contained some unacetylated hydroxyl groups, was heated under reflux with 1,500 ml. of acetic anhydride for 72 hours. The acetic acid and acetic anhydride were removed by distillation under partial vacuum and an ether solution of the residue was washed consecutively with water, a saturated sodium bicarbonate solution and a saturated sodium chloride solution. The ether solution was dried over magnesium sulfate and the ether was removed by distillation. The dark brown residue was distilled through a 10-inch, Vigreux column to yield 400 g. (94%) of 1,5-diacetoxy-3-acetoxymethylpentane (V), b.p. 120° (0.5 mm.), $n^{25}\mathrm{D}$ 1.4410.

Anal. Calcd. for $C_{12}H_{20}O_6$: C, 55.36; H, 7.74. Found: C, 55.35; H, 7.44.

B. From 1,5-Diacetoxy-3-acetoxymethyl-2-pentene (VII).—At 80° and 2300 lb./sq. inch pressure, 104 g. (0.403 mole) of 1,5-diacetoxy-3-acetoxymethyl-2-pentene (VII) was hydrogenated in the presence of 10 g. of W-2 Raney nickel catalyst.[11] After the catalyst was removed by filtration, the filtrate was distilled through a 6-inch, helix-packed column to yield 64 g. (61%) of 1,5-diacetoxy-3-acetoxymethylpentane (V), b.p. 126–129° (0.8 mm.), $n^{25}\mathrm{D}$ 1.4410. A considerable amount of a lower boiling forerun was also obtained.

1,5-Diacetoxy-3-acetoxymethyl-2-pentene (VII).—To a solution of 144 g. (3.8 moles) of lithium aluminum hydride in 5000 ml. of dry ether was added dropwise 450 g. (1.745 moles) of triethyl aconitate (II) dissolved in 1000 ml. of dry ether. After the reaction mixture was stirred and heated for 9 days, the excess hydride was decomposed with 350 ml. of acetic acid. Three liters of butyl ether was added and the ethyl ether was removed by distillation until the temperature of the reaction mixture reached 120°. While the mixture was heated under reflux, 4000 ml. of acetic anhydride was added slowly. The mixture became so thick that stirring was discontinued, but after the mixture was heated for 24 hours it became thin enough to permit stirring. In order to ensure complete acetylation the mixture was heated under reflux for an additional 10 days. The salts were removed by filtration and butyl ether, acetic acid and excess acetic anhydride were removed by distillation under reduced pressure. An ether solution of the crude ester was washed consecutively with water, a saturated sodium bicarbonate solution and a saturated sodium chloride solution. (It was found that small traces of acid catalyzed the decomposition of the ester during the subsequent distillation.) After the ether solution was dried over potassium carbonate, the ether was removed by distillation. The dark brown residue was distilled through a 10-inch Vigreux column to yield 180 g. (40%) of 1,5-diacetoxy-3-acetoxymethyl-2-pentene (VII), b.p. 120–130° (0.3 mm.). (This material was not purified but was used directly for the catalytic reduction.)

2-Vinyl-1,3-butadiene (3-Methylene-1,4-pentadiene) (I).—The pyrolysis of the 1,5-diacetoxy-3-acetoxymethylpentane (V) was carried out in an apparatus previously described.[4] At a rate of 1.5 g. per minute, 102 g. (0.39 mole) of the triester V was dropped through a vertical Vycor tube packed with 1/8-inch glass helices. The tube was externally heated at 540° and continuously flushed out with a stream of oxygen-free nitrogen. (In order to avoid the accumulation of a carbon deposit that might cause polymerization or isomerization,[5] the original pyrolysate tube was replaced with a clean tube midway through the run). The pyrolysate, which was collected in a receiver immersed in a dry ice–acetone-bath, was washed with four 25-ml. portions of ice-water to remove the acetic acid. (Titration of the aqueous extracts indicated that 95% of three molar equivalents of acetic acid had been liberated.) The crude triene I was extracted with a saturated sodium bicarbonate solution and a saturated sodium chloride solution and dried over potassium carbonate. After removal of the drying agent, the triene was flash distilled from the high-boiling residue at reduced pressures and collected in a dry ice trap. Redistillation of this condensate through a 6-inch, helix-packed column produced 13.5 g. (43%) of 2-vinylbutadiene (I), b.p. 32° (200 mm.), $n^{20}\mathrm{D}$ 1.4559.

Anal. Calcd. for C_6H_8; C, 90.00; H, 10.00. Found: C, 90.02; H, 10.21.

Distillation of the residue produced 15.4 g. (49%) of a hydrocarbon, b.p. 40–60° (0.3 mm.), $n^{25}\mathrm{D}$ 1.5090. The high refractive index probably indicates that this material is a cyclic dimer of the triene I.

$\Delta^{1(9)}$-Octalin-3,4,6,7-tetracarboxylic Anhydride (IX).—A solution of 0.40 g. (0.005 mole) of 2-vinylbutadiene (I) in 5.75 ml. of toluene was added to a solution of 1 g. (0.010 mole) of maleic anhydride in 4 ml. of toluene and the mixture was heated for 30 min. on a steam-bath. After the mixture was cooled, the precipitate was removed by filtration and recrystallized from a mixture of toluene and dioxane to yield 1.37 g. (99%) of $\Delta^{1(9)}$-octalin-3,4,6,7-tetracarboxylic anhydride (IX), m.p. 248–250°.

Anal. Calcd. for $C_{14}H_{12}O_6$: C, 60.87; H, 4.35. Found: C, 61.17; H, 4.51.

Simultaneous dehydrogenation and decarboxylation of the anhydride IX were carried out by heating IX for 3 hours at 270° in the presence of 0.1 g. of 5% palladium-on-carbon and 0.1 g. of copper chromite catalyst. During the reaction 0.012 g. (26%) of naphthalene, m.p. 79°, sublimed to the cold finger. A mixed melting point determination with an authentic sample of naphthalene showed no depression.

The $\Delta^{2,6(6a),9(10)}$-Dodecahydrobenzanthracene-1,4,8,11-tetraone (X).—A solution of 0.30 g. (0.00376 mole) of 2-vinylbutadiene (I) in 6 ml. of toluene was added to a solution of 0.91 g. (0.0084 mole) of benzoquinone in 6 ml. of toluene. After the mixture had stood at room temperature for 24 hours, it was heated on a steam-bath for an additional 24 hours. A yellow solid was removed from the cooled mixture by filtration and recrystallized from toluene to produce 0.80 g. (72%) of $\Delta^{2,6(6a),9(10)}$-dodecahydrobenzanthracene-1,4,8,11-tetraone (X), m.p. 204–206°.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 72.97; H, 5.41. Found: C, 72.67; H, 5.55.

5,5a,6,8,8a,9,14,14a,15,15a,15b,16-Dodecahydrohexaphene-5,9,14,16-tetraone (XI).—A solution of 0.22 g. (0.00275 mole) of 2-vinylbutadiene (I) in 4 ml. of toluene was added to a solution of 1.0 g. (0.0063 mole) of 1,4-naphthoquinone in 7 ml. of toluene. After the mixture had stood for 24 hours at room temperature, it was heated on the steam-bath for an additional 48 hours. The white flocculent precipitate was removed by filtration of the hot solution and recrystallized from methyl ethyl ketone to yield 0.78 g. (72%) of 5,5a,6,8,8a,9,14,14a,15,15a,15b,16-dodecahydrohexaphene-5,9,14,16-tetraone (XI), m.p. 249–252°.

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.78; H, 5.05. Found: C, 78.55; H, 5.17.

$\Delta^{4a(20a),8(8a),11a(15a)}$-Octacosahydroöctaphene-6,10,17,19-tetraone (XIII).—A solution of 0.15 g. (0.0019 mole) of 2-vinylbutadiene (I) and 0.9 g. (0.0042 mole) $\Delta^{2,8a(10a)}$-deca-

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[10] A. A. Pavlic and H. Adkins, THIS JOURNAL, **68**, 1471 (1946).

[11] C. K. Ingold, *J. Chem. Soc.*, **119**, 340 (1921).

hydroanthracene-1,4-dione (XII)[6] in 10 ml. of toluene was allowed to stand at room temperature for 24 hours and was heated under reflux for an additional 48 hours. The hot toluene solution was filtered to yield 0.24 g. (25%) of white crystalline $\Delta^{4a(20a),8(8a),11a(15a)}$-octacosahydroöctaphene-6,10,17,19-tetraone (XIII), m.p. 291–293°.

Anal. Calcd. for $C_{34}H_{32}O_4$: C, 79.69; H, 7.81. Found: C, 79.77; H, 7.73.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XXII. The 1,3-Dichloro-2-butenes[1]

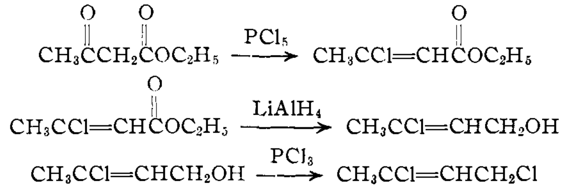
BY LEWIS F. HATCH AND ROBERT H. PERRY, JR.[2]

RECEIVED AUGUST 23, 1954

Pure α- and β-1,3-dichloro-2-butene have been prepared by unambiguous syntheses. The geometrical configurations of the various compounds involved in this synthesis were determined by the method of synthesis, the relative ease of dehydrochlorination and their infrared spectra. The configuration of α- and β-1,3-dichloro-2-butene was established by conversion to the corresponding *cis*- and *trans*-2-chloro-2-butene by means of lithium aluminum hydride and by their infrared spectra. The reactivity of α- and β-1,3-dichloro-2-butene was determined with potassium iodide in acetone and sodium ethoxide in ethanol.

The two isomers of 1,3-dichloro-2-butene have been the subject of several investigations with the object of assigning configuration[3] and relating geometrical configuration to relative reactivity.[4] The two isomers were prepared by the addition of hydrogen chloride to chloroprene,[5] a process which produced essentially pure α-1,3-dichloro-2-butene and only relatively impure β-1,3-dichloro-2-butene.

The two isomers have now been prepared from ethyl acetoacetate as represented by the equations



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 \xrightarrow{PCl_5} CH_3CCl{=}CH\overset{\overset{O}{\|}}{C}OC_2H_5}$$

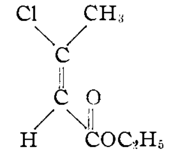
$$\mathrm{CH_3CCl{=}CH\overset{\overset{O}{\|}}{C}OC_2H_5 \xrightarrow{LiAlH_4} CH_3CCl{=}CHCH_2OH}$$

$$\mathrm{CH_3CCl{=}CHCH_2OH \xrightarrow{PCl_3} CH_3CCl{=}CHCH_2Cl}$$

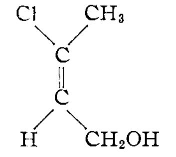
The treatment of ethyl acetoacetate with phosphorus pentachloride gave a mixture of ethyl β-chloroisocrotonate and ethyl β-chlorocrotonate.[6] This mixture was separated, by distillation, into ethyl β-chloroisocrotonate and a mixture of ethyl β-chlorocrotonate and ethyl acetoacetate.

The ethyl β-chlorocrotonate thus produced could not be separated from the ethyl acetoacetate. It was purified by conversion to β-chlorocrotonic acid, which was then esterified to obtain pure ethyl β-chlorocrotonate. In this respect it is of interest to note that Errera and Lepingle[7] determined the dielectric constant for a material they assumed to be pure ethyl β-chlorocrotonate but which, from the index of refraction they reported, must have contained a considerable amount of ethyl acetoacetate.

The configuration of ethyl β-chloroisocrotonate and ethyl β-chlorocrotonate have been established,[8] and reduction of these esters with lithium aluminum hydride produced β- and α-3-chloro-2-buten-1-ol, respectively.



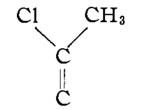
ethyl β-chloroisocrotonate



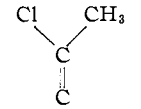
β-3-chloro-2-buten-1-ol

Geometrical configuration was retained in each case, since in neither reduction was a mixture of the two chloroalcohols produced. The configurations thus established were the same as those previously assigned from data obtained by the dehydrochlorination of the less pure chloroalcohols.[3] The physical data for the α-3-chloro-2-buten-1-ol were essentially the same as those previously reported[3,4] but the data for the β-3-chloro-2-buten-1-ol were somewhat different. The infrared spectra and the dehydrochlorination of these chloroalcohols (Table I) confirmed the assignment of configuration.

The chloroalcohols were converted to the corresponding dichlorides by phosphorus trichloride in pyridine. The α-1,3-dichloro-2-butene had essentially the same physical properties as those previously reported[5] but the physical properties of the β-isomer were appreciably different. The configuration of these dichlorides was confirmed by transforming the dichlorides to the corresponding 2-chloro-2-butene using lithium aluminum hydride.[9]



β-1,3-dichloro-2-butene



cis-2-chloro-2-butene

The infrared spectra also agree with the assigned configurations. Of particular interest is the presence of a band at 8.01 μ which is indicative of the $RR'C{=}CHCH_2Cl$ structure.[10] The configurations

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[1] Presented in part at the Northwest Regional Meeting of the American Chemical Society, Pullman, Washington and Moscow, Idaho, June 11 and 12, 1953.

[2] Eastman Kodak Company Fellow, 1951–1952.

[3] L. F. Hatch and P. S. Hudson, THIS JOURNAL, **72**, 2505 (1950).

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