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

Cyclic Dienes. XVI. 9,10-Dimethylene-1,7-dioxacyclohendecane-2,6-dione, A Cyclic Ester from 2,3-Di-(hydroxymethyl)-1,3-butadiene[1,2]

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

RECEIVED NOVEMBER 3, 1955

A cyclic diene, 9,10-dimethylene-1,7-dioxacyclohendecane-2,6-dione, that possesses two ester groups in an eleven-membered ring was prepared by ester interchange between 2,3-di-(hydroxymethyl)-1,3-butadiene and dimethyl glutarate. The dienediol was prepared in four steps from malonic ester in an over-all yield of 22%, based on unrecovered material. The bimalonic ester was, in effect, reductively acetylated with lithium aluminum hydride and acetic anhydride in a 34% yield. The resulting tetraacetate was pyrolyzed to produce an 84% yield of 2,3-di-(acetoxymethyl)-1,3-butadiene, which was subsequently hydrolyzed to the corresponding dienediol.

Although poly-1,2-dimethylenecyclohexane[4] is an all-*cis* polymer related in structure to natural rubber, this synthetic diene polymer does not possess any rubbery properties at room temperature but is a white crystalline solid melting at 165°. A research program was undertaken in order to determine the reason for the striking differences in properties of these all-*cis* polymers. One obvious structural difference in the two polymers was the presence of a cyclohexene ring in polydimethylenecyclohexane and the absence of a ring in natural rubber. For this reason a bicyclic diene, 2,3-dimethylenedecalin, that possessed a second cyclohexane ring per monomer unit was prepared.[5] However, it is possible that an additional ring located an appreciable distance from the polymer chain would have only a small effect on the properties of the polymer. It appeared desirable, therefore, to prepare a synthetic non-cyclic all-*cis* polymer. One promising approach was to prepare a cyclic diene similar to 1,2-dimethylenecyclohexane[6] but with some reactive group in the ring. If this reactive group was properly chosen, the cyclic diene could be polymerized to produce an all-*cis* polymer and then this reactive group could be treated with a reagent to open the ring to produce a non-cyclic all-*cis* diene polymer. In order to ensure that the final polymer is all *cis* this reactive group must be carefully chosen. In addition to being stable enough to allow ready synthesis, the active group must be stable to polymerization and must cleave in extremely high yield with a reagent that will not produce an ion or radical in the allylic position to the double bond or isomerize the double bond after cleavage. It appeared that an ester group derived from 2,3-di-(hydroxymethyl)-1,3-butadiene (I) would meet these requirements.

2,3-Di-(hydroxymethyl)-1,3-butadiene (I) was synthesized in a four-step procedure from diethyl malonate in an over-all yield of 22%. The method of Bischoff[7] for the coupling of sodiomalonic ester with iodine was improved by the use of bromine to produce an 80% yield of tetraethyl 1,1,2,2-ethanetetracarboxylate (II). The reduction of II to 2,3-di-(hydroxymethyl)-1,4-butanediol (III) with lithium aluminum hydride proved to be a difficult step. Although small runs gave a 65% yield of the tetraol III, reductions of larger quantities of II gave much poorer yields. Since II contains four reducible ester groups, the intermediate reduction products were only slightly soluble in ether; thus a large amount of ether had to be used and the reduction mixture had to be heated under reflux for 4 days. Since extraction of the aqueous solutions of the reaction mixture with various organic solvents was unsuccessful, the aluminum salts were removed as the insoluble hydroxide and the lithium salts were precipitated as the carbonate. The aqueous solution was then evaporated to obtain the tetraol. Acetylation of the tetraol III with acetic anhydride produced a 92% yield of 2,3-di-(acetoxymethyl)-1,4-diacetoxybutane (IV).

It appeared that a satisfactory synthesis could be developed only if the tetraacetate IV could be produced directly from the bimalonic ester II without the isolation of the water-soluble tetraol III. It was found that if the reduction of II was carried out for 4 days with lithium aluminum hydride in dibutyl ether and the salts were acetylated directly with a mixture of acetic acid and acetic anhydride, without the usual aqueous hydrolysis, the tetraacetate IV could be obtained in a 34% yield. This procedure for the reduction and acetylation of polyfunctional compounds with lithium aluminum hydride and acetic anhydride also has been successfully applied to the conversion of triethyl tricarballylate to 3-acetoxymethyl-1,5-diacetoxypentane in a 94% yield.[8]

The solid tetraacetate IV was pyrolyzed by the dropwise addition of a benzene solution of IV through a vertical Vycor pyrolysis tube packed with glass helices and externally heated at 480°. The conditions were adjusted to prevent charring, and the tube was swept out continuously with a stream of oxygen-free nitrogen. Under optimum conditions, 44% of two molar equivalents of acetic acid was liberated; if more vigorous conditions were used, charring occurred and the yield of products was lower. From this pyrolysis were obtained a 16% conversion to 2,3-di-(acetoxymethyl)-1,3-butadiene (VI), a 36% yield of the olefin triacetate V, and a 45% recovery of the starting tetraacetate IV. The yield of VI, based on unrecovered

---

[1] Previous paper in this series, THIS JOURNAL, **78**, 670 (1956).

[2] Presented in part before the Division of Polymer Chemistry at the 122nd Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

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

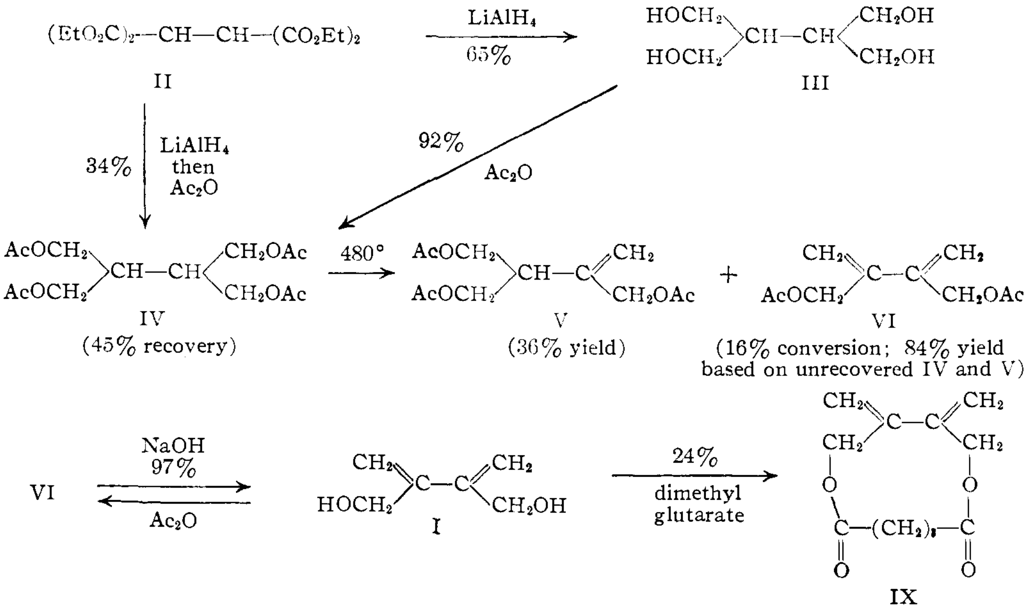
[4] W. J. Bailey and H. R. Golden, THIS JOURNAL, **76**, 5418 (1954).

[5] W. J. Bailey, C. W. Liao and G. H. Coleman, *ibid.*, **77**, 990 (1955).

[6] W. J. Bailey and H. R. Golden, *ibid.*, **75**, 4780 (1953).

[7] C. A. Bischoff, *Ber.*, **16**, 1046 (1883).

[8] W. J. Bailey and J. Economy, THIS JOURNAL, **77**, 1133 (1955).



IV and V, was 84%. Although IV possesses four acetoxy groups, only 2 moles of acetic acid can be eliminated readily since there are only two β-hydrogen atoms.

The structure of 2,3-di-(acetoxymethyl)-1,3-butadiene (VI) was proved by analysis and determination of neutral equivalent. The presence of conjugated double bonds in VI was indicated by the fact that the ultraviolet absorption spectrum possessed no maximum above 220 mμ but reached an ϵ of 19,500 at 220 mμ and appeared to reach a maximum just below 220 mμ. Treatment of the diene VI with maleic anhydride produced an 81% yield of the solid Diels–Alder adduct, 4,5-di-(acetoxymethyl)-Δ^4-tetrahydrophthalic anhydride (VII). Hydrolysis of VI with dilute sodium hydroxide produced a 97% yield of the solid 2,3-di-(hydroxymethyl)-1,3-butadiene (I).

The presence of conjugated double bonds in I was indicated by the fact that the ultraviolet absorption spectrum also did not possess a maximum or a minimum above 220 mμ but the ϵ increased to 26,000 at 220 mμ and appeared to reach a maximum just below 220 mμ. Treatment of the diol I with acetic anhydride regenerated the solid diacetate VI in an 84% yield, while reaction of I with benzoyl chloride and pyridine produced an 82% yield of the solid 2,3-di-(benzoxymethyl)-1,3-butadiene (VIII).

Before the synthesis of a cyclic ester from the diol I was attempted, several model reactions were studied. Carothers and Van Natta[9] had previously prepared the linear polymer, polytetramethylene carbonate, under non-dilute conditions and showed that, unlike polytrimethylene carbonate, the tetramethylene derivative was not reversibly converted to the monomeric cyclic ester. They showed that when the polymer was heated only a dimeric cyclic ester containing a fourteen-membered ring was produced. When an ester interchange between tetramethylene glycol and diethyl carbonate was carried out under dilute conditions, again no monomeric tetramethylene carbonate was isolated but only the fourteen-membered dimer was found. Since it did not seem likely that a seven-membered cyclic carbonate derivative of the dienediol I could be conveniently prepared, other cyclic esters were investigated. The study of Fisher–Hirschfelder models showed that, in contrast to carbocyclic rings, an eleven-membered glutarate ester ring had the best chance of being formed and yet that the polymer from this monomer would be an all-*cis* diene polymer. A model reaction involving the ester interchange between tetramethylene glycol and dimethyl glutarate under dilute conditions did yield the monomeric cyclic tetramethylene glutarate.[10] When an ester interchange was carried out between 2,3-di-(hydroxymethyl)-1,3-butadiene (I) and dimethyl glutarate under dilute conditions, a 24% yield of the eleven-membered cyclic diene, 9,-10-dimethylene-1,7-dioxacyclohendecane-2,6-dione (IX), was obtained.

The structure of IX was indicated by analysis and molecular weight determination. The presence of conjugated double bonds in IX was indicated by a maximum ϵ of 18,400 at 224 mμ. It is extremely interesting that, even though eleven-membered carbocyclic rings are difficult to prepare, the different bond angles of the oxygen atoms permit the synthesis of the eleven-membered cyclic esters IX and tetramethylene glutarate.

The polymerization and other reactions of I, VI, VIII and IX will be reported separately.

Experimental[11]

Tetraethyl 1,1,2,2-Ethanetetracarboxylate (II).—By a modification of the method of Bischoff,[7] 25 g. (1.0 mole) of sodium was dissolved in 500 ml. of absolute ethanol. To the cooled solution was added, with stirring, 160 g. (1.0 mole) of diethyl malonate at a rate sufficient to keep the enolate in solution. Then, with continued cooling, 80 g. (0.5 mole) of bromine was added at a very slow rate. When the addi-

---

[9] W. H. Carothers and F. J. Van Natta, This Journal, **52**, 314 (1930).

[10] C. N. Bird, Ph.D. Thesis, University of Maryland, 1956.

[11] The authors are indebted to Dr. Mary Aldridge and Kathryn Gerdeman for the analyses. The ultraviolet absorption spectra were determined with 95% ethanol solutions in a Beckman DU spectrophotometer. All melting points are corrected.

tion was completed, the reaction mixture was stirred slowly at room temperature for an additional hour. The reaction mixture was filtered to remove the sodium bromide and the clear reddish filtrate was cooled in a refrigerator for about 3 hours. The large mass of crystals was removed by filtration and washed with petroleum ether (60–80°). The ethanolic solution was concentrated and cooled again to produce a second crop of crystals. The combined solids were recrystallized from ether to yield 225 g. (80%) of tetraethyl 1,1,2,2-ethanetetracarboxylate (II), as silky white needles, m.p. 75–76° (reported[7] m.p. 75–76°, but no yield).

2,3-Di-(hydroxymethyl)-1,4-butanediol (III).—To a solution of 8 g. (0.21 mole) of lithium aluminum hydride in 300 ml. of absolute ether was added dropwise with stirring a solution of 10 g. (0.031 mole) of tetraethyl 1,1,2,2-ethanetetracarboxylate (II) in 50 ml. of absolute ether. After the addition had been completed, the reaction mixture was stirred and heated under reflux for an additional 80 hours. Water was then added dropwise to the reaction to decompose the excess hydride and to break up the reaction product complex. The ether was removed by distillation, and the insoluble lithium and aluminum salts were leached with five 600-ml. portions of hot water. After the combined aqueous washings were concentrated by evaporation to about half their original volume, a large excess of Dry Ice was added to the hot solution to precipitate the lithium salts as the carbonate. The lithium carbonate, which is less soluble in hot than in cold water, was removed by filtration. The resulting yellowish solution was evaporated to dryness, to produce a tan, gummy residue contaminated with a small amount of white inorganic matter. The organic matter was extracted with absolute ethanol. The ethanol was removed by evaporation to give 5.2 g. of crude tetraol. (This impure tetraol was usually acetylated without further purification.) Recrystallization of the crude product from dioxane yielded 3.0 g. (65%) of 2,3-di-(hydroxymethyl)-1,4-butanediol (III), m.p. 114°.

Anal. Calcd. for $C_6H_{14}O_4$: C, 48.04; H, 9.33. Found: C, 48.00; H, 9.30.

2,3-Di-(acetoxymethyl)-1,4-diacetoxybutane (IV). A. From **2,3-Di-(hydroxymethyl)-1,4-butanediol (III).**—To 50 g. (0.49 mole) of acetic anhydride, heated under reflux, was added dropwise with stirring the impure 2,3-di-(hydroxymethyl)-1,4-butanediol (III) [from 10 g. of tetraethyl 1,1,-2,2-ethanetetracarboxylate (II)] dissolved in 15 ml. of acetic anhydride and 5 ml. of acetic acid. After the mixture was heated under reflux for 15 hours, the solvents were removed at reduced pressure. The solid residue was recrystallized several times from ether to give 6.0 g. (60% overall yield for the two steps) of 2,3-di-(acetoxymethyl)-1,4-diacetoxybutane (IV), m.p. 67–68°.

Anal. Calcd. for $C_{14}H_{22}O_8$: C, 52.82; H, 6.91; sapon. equiv., 79. Found: C, 52.80; H, 7.21; sapon. equiv., 78.

B. From **Tetraethyl 1,1,2,2-Ethanetetracarboxylate (II).**—To a solution of 80 g. (2.1 moles) of lithium aluminum hydride in 5 liters of dibutyl ether was added dropwise 250 g. (0.79 mole) of tetraethyl 1,1,2,2-ethanetetracarboxylate (II) in 500 ml. of dibutyl ether. After the reaction mixture had been stirred and heated under reflux for 96 hours, about 250 ml. of acetic anhydride was added to react with the excess lithium aluminum hydride. Then 500 g. of acetic acid was added to decompose the complex, followed by 600 ml. of acetic anhydride to acetylate the tetraol II. It was usually necessary to add another 700 ml. of dibutyl ether to alleviate the thickening of the reaction. (In several runs the stirring could not be continued until the slurry was thinned by heating.) After the mixture was stirred and heated under reflux for 15 hours, it was filtered and the filtrate was concentrated by distillation under reduced pressure. The solid residue was recrystallized from ether to yield 85 g. (34%) of 2,3-di-(acetoxymethyl)-1,4-diacetoxybutane (IV), m.p. 67–68°.

2,3-Di-(acetoxymethyl)-1,3-butadiene (VI) and 2,3,3-Tri-(acetoxymethyl)-1-propene (V).—Over a period of 100 minutes, 30 g. (0.095 mole) of 2,3-di-(acetoxymethyl)-1,4-diacetoxybutane (IV) in solution in 70 ml. of benzene was added dropwise to a Vycor pyrolysis tube externally heated at 480°. The system was flushed out with a slow stream of nitrogen and the pyrolysate was collected in a flask cooled in ice. The benzene solution was extracted with water and then dried over potassium carbonate. (Titration of aliquot portions of the aqueous extract of the pyrolysate indicated that 34% of two molar equivalents of acetic acid had been liberated.) After the benzene had been removed by distillation under reduced pressure, the residue was distilled through a 6-inch, Vigreux column to yield 3.1 g. (16%) of 2,3-di-(acetoxymethyl)-1,3-butadiene (VI), b.p. 103–107° (1.5 mm.), m.p. 43–44°; 9.0 g. (36%) of 2,3,3-tri-(acetoxymethyl)-1-propene (V), b.p. 138–139°, $n^{25}D$ 1.4518; and 13.4 g. (45% recovery) of the starting tetraacetate IV. The yield of the diene VI, based on unrecovered V and IV, was 84%. The diene VI could be conveniently recrystallized from ether.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.60; H, 7.07; sapon. equiv., 99. Found: C, 60.66; H, 7.21; sapon. equiv., 100. Calcd. for $C_{12}H_{18}O_6$: C, 55.82; H, 6.98. Found: C, 56.11; H, 7.00.

4,5-Di-(acetoxymethyl)-Δ^4-tetrahydrophthalic Anhydride (VII).—After a mixture of 0.7 g. (0.0035 mole) of 2,3-di-(acetoxymethyl)-1,3-butadiene (VI), 0.35 g. (0.0035 mole) of maleic anhydride, 45 ml. of benzene, plus a few milligrams of *m*-dinitrobenzene had been heated under reflux for 10 hours, the benzene was removed at reduced pressure and the solid residue was recrystallized several times from a chloroform–cyclohexane mixture to give 0.85 g. (81%) of 4,5-di-(acetoxymethyl)-Δ^4-tetrahydrophthalic anhydride (VII), m.p. 93–94°.

Anal. Calcd. for $C_{14}H_{16}O_7$: C, 56.75; H, 5.40. Found: C, 56.83; H, 5.51.

2,3-Di-(hydroxymethyl)-1,3-butadiene (I).—A solution of 6.0 g. (0.03 mole) of 2,3-di-(acetoxymethyl)-1,3-butadiene (VI) in 12 ml. of 95% ethanol was added to 4.0 g. (0.10 mole) of sodium hydroxide dissolved in 100 ml. of water plus a few milligrams of diphenylamine. After the mixture had been heated on the steam-bath for 2 hours, the cooled solution was extracted in a continuous ether extractor for 4 hours. Most of the ether was removed from the extract by distillation and the residue was dried under reflux with 300 ml. of toluene in a flask fitted with a Dean–Stark trap. After the toluene solution was concentrated to 75 ml., the solution was cooled to produce a white solid, which was recrystallized once more from toluene to give 3.3 g. (97%) of 2,3-di-(hydroxymethyl)-1,3-butadiene (I), m.p. 63–64°.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.15; H, 8.77. Found: C, 63.12; H, 8.78.

2,3-Di-(benzoxymethyl)-1,3-butadiene (VIII).—A mixture of 0.2 g. (0.0017 mole) of 2,3-di-(hydroxymethyl)-1,3-butadiene (I), 0.28 g. (0.0035 mole) of dry pyridine, 0.5 g. (0.0035 mole) of benzoyl chloride and 15 ml. of dry benzene was heated over a low flame for 8 minutes. The solvent was removed by evaporation and the residual solid was recrystallized from ether to give 0.45 g. (82%) of 2,3-di-(benzoxymethyl)-1,3-butadiene (VIII), m.p. 102–103°.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.33; H, 5.59. Found: C, 74.07; H, 5.56.

Reaction of 1,4-Butanediol and Diethyl Carbonate.—A flask was fitted with a device for effecting dilution of an added solution,[12] which in turn was connected to a 24-inch, helix-packed column with drying tubes protecting all openings. To 4000 ml. of dry toluene containing 10 ml. of absolute alcohol was added a small piece (*ca.* 0.1 g.) of sodium. When solution was accomplished, the excess ethanol was removed by distillation through the column. Through a dropping funnel attached to the dilution tube was added slowly a solution of 16.0 g. (0.175 mole) of 1,4-butanediol and 21 g. (0.175 mole) of diethyl carbonate in 500 ml. of toluene, to which had been added 12.0 ml. of absolute ethanol. Ethanol plus some solvent were removed by slow distillation. The amount of the ethanol was estimated from the refractive index of the distillate. When 66% of the theoretical amount of ethanol had collected, the reaction produced no more ethanol even with prolonged heating. The reaction mixture was cooled and filtered to remove a small amount of solid material, probably catalyst. Removal of the toluene by distillation yielded a white solid, which on recrystallization from chloroform gave 6.1 g. (29%) of dimeric tetramethylene carbonate, m.p., 175–176° (reported[9] m.p. 175–176°). When this reaction was carried out with moderate dilution, in 600 ml. of toluene, with the same conditions and amounts of materials, polytetramethylene carbonate was the main product.

---

(12) N. J. Leonard and R. C. Sentz, THIS JOURNAL, **74**, 1704 (1952).

9,10-Dimethylene-1,7-dioxacyclohendecane-2,6-dione (IX).—To a flask equipped with a 15-inch, helix-packed distilling column were added 1500 ml. of toluene and a small amount of sodium ethoxide prepared as described above. A solution of 3.0 g. (0.026 mole) of 2,3-di-(hydroxymethyl)-1,3-butadiene (I) and 4.2 g. (0.026 mole) of dimethyl glutarate in 300 ml. of toluene solution containing a trace of diphenylamine was added over a period of 4 hours. After the reaction mixture had been heated for an additional 6 hours, 71% of the theoretical amount of methanol (estimated by refractive index of the distillate) was removed. The solution was cooled and filtered, and the toluene was removed by distillation. The mushy residue was cooled to give a solid, which could be removed by filtration only with difficulty. Trituration of the solid with ether removed residual oily impurities, and further recrystallization from a benzene–ether–petroleum ether mixture gave 1.3 g. (24%) of the cyclic 9,10-dimethylene-1,7-dioxacyclohendecane-2,6-dione (IX), m.p. 95–96°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.66; mol. wt., 210. Found: C, 63.04; H, 6.72; mol. wt., (Rast) 220.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

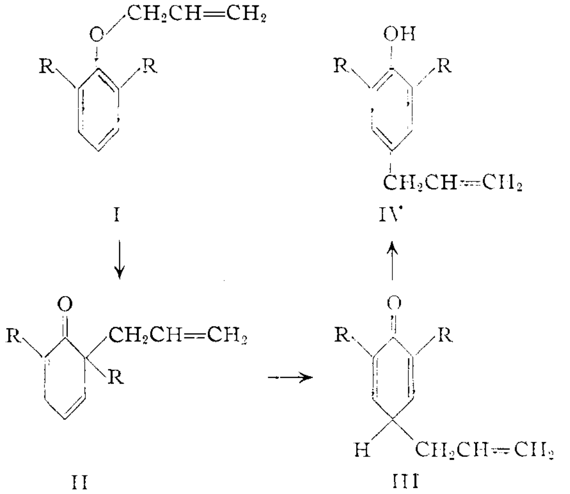
The Intermediate Dienone in the *para*-Claisen Rearrangement[1]

BY HAROLD CONROY[2] AND RAYMOND A. FIRESTONE

RECEIVED AUGUST 24, 1955

A 2,2,6-trisubstituted cyclohexadienone is a normal component of the reacting system undergoing the *para*-Claisen rearrangement, as shown by the isolation of a characteristic Diels–Alder adduct. The constitution of the adduct has been proved by an independent synthesis of its tetrahydro derivative. In the case of 2,4,6-trimethylphenyl allyl ether, where no rearranged *p*-allylphenol is possible, a remarkably high yield of the dienone–maleic anhydride adduct was obtained. Further evidence is presented to show that the mechanism of the rearrangement is most reasonably formulated in terms of intermediate cyclohexadienone derivatives, formed reversibly from the initial ether.

The concerted, cyclic mechanism for the *ortho*-Claisen rearrangement was first put forward by Claisen[3] and more clearly restated by Mumm[4]; it has since gained continuous acceptance. The concept can be reconciled with data pertaining to reaction order,[5] intramolecularity,[6–8] inversion of the allyl group[3,6,8–11] activation energies and entropies,[5,12a] and the reported[12b] but quantitatively uncertain degree of retention of optical activity of the allyl group. It was a logical extension to consider[13] that the *para* rearrangement, occurring in analogously constituted, but *ortho* disubstituted allyl ethers, proceeds initially in the same way, although the first dienone (II) so produced cannot enolize, and must rearrange further to III before aromatization is possible. Mumm abandoned this thesis on spurious experimental grounds, which have only recently been corrected,[14] and the mechanism of the *para* migration seemed uncertain for a considerable period. The first *specific* experimental evidence in support of an intermediate cyclohexadienone in the *para*-Claisen rearrangement appeared in a preliminary communication[15]; we now wish to record our observations in detail.



Even before the results of Rhoads, *et al.*, became available to us, the bulk of the evidence seemed to justify serious consideration of the dienone mechanism. There was reason to hope that the dienone II might be trapped, and thereby deferred from further rearrangement to III and IV, by combination with a suitable dienophile to form a Diels–Alder adduct. Diels–Alder addition to an homoannular diene can be exceedingly rapid and calculation shows not only that the over-all formation of adduct from I should be exothermic but that even in the event that equilibria between all species involved were to be attained the concentration of

---

[1] Taken from the dissertation of Raymond A. Firestone submitted in May, 1954, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

[2] To whom inquiries should be directed at School of Science, Brandeis University, Waltham 54, Mass.

[3] L. Claisen and E. Tietze, *Ber.*, **58B**, 275 (1925).

[4] O. Mumm and F. Möller, *ibid.*, **70**, 2214 (1937).

[5] J. F. Kincaid and D. S. Tarbell, THIS JOURNAL, **61**, 3085 (1939).

[6] C. D. Hurd and L. Schmerling, *ibid.*, **59**, 107 (1937).

[7] A. S. Fomenko, G. P. Miklukhin and E. A. Sadovnikova, *Doklady Akad. Nauk (S.S.S.R.)*, **62**, 91 (1948) [*C.A.*, **43**, 602*i* (1949)]; A. S. Fomenko and E. A. Sadovnikova, *Zhur. Obshchei Khim.*, **20**, 1898 (1950) [*C.A.*, **45**, 2895*h* (1951)].

[8] H. Schmid and K. Schmid, *Helv. Chim. Acta*, **35**, 1879 (1952).

[9] W. M. Lauer and P. A. Sanders, THIS JOURNAL, **65**, 198 (1943).

[10] C. D. Hurd and F. L. Cohen, *ibid.*, **53**, 1917 (1931).

[11] J. P. Ryan and P. R. O'Connor, *ibid.*, **74**, 5866 (1952).

[12] (a) D. S. Tarbell and J. F. Kincaid, *ibid.*, **62**, 728 (1940); (b) E. R. Alexander and R. W. Kluiber, *ibid.*, **73**, 4304 (1951).

[13] C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939). Their mechanism did not explicitly include the dienone formulation. See also O. Mumm and J. Diederichsen, *Ber.*, **72**, 1523 (1939).

[14] S. J. Rhoads, R. Raulins and R. D. Reynolds, THIS JOURNAL, **75**, 2531 (1953); **76**, 3456 (1954).

[15] H. Conroy and R. A. Firestone, *ibid.*, **75**, 2530 (1953).