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]

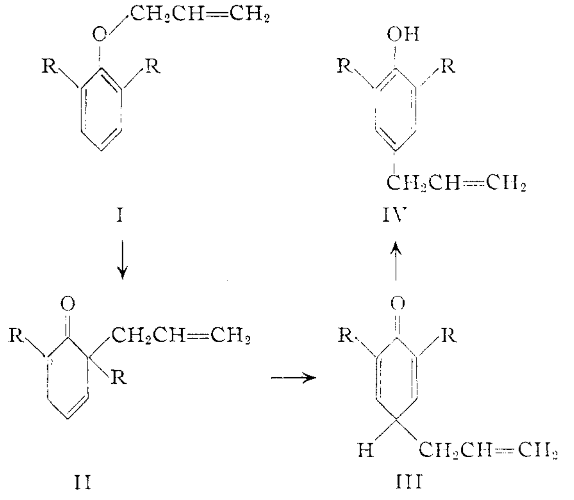
The Intermediate Dienone in the *para*-Claisen Rearrangement[1]

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).

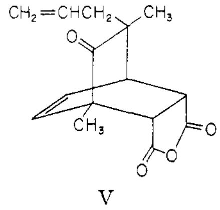
[13] C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939). Their mechanism did not explicitly include the dienone formulation. See also O. Mumm and J. Diederichsen, *Ber.*, **72**, 1523 (1939).

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

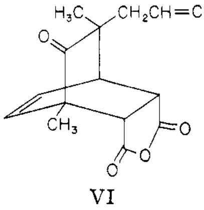
[15] H. Conroy and R. A. Firestone, *ibid.*, **75**, 2530 (1953).

adduct might not be so low as to prevent its isolation.[16]

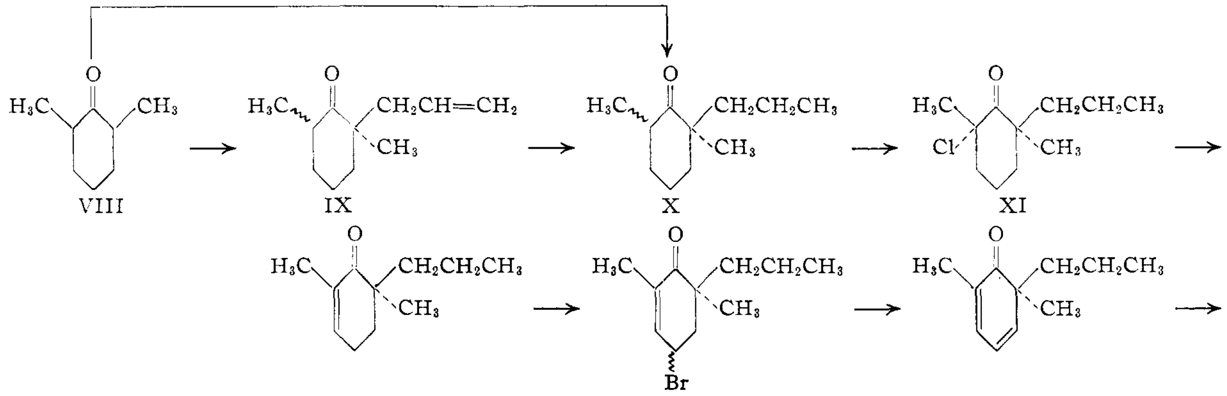
To ensure the best possible opportunity for interception of the dienone we chose a dienophile of high reactivity, present in high concentration; accordingly, the rearrangement of the ether (I, R = CH$_3$) was carried out in a solvent of molten maleic anhydride under conditions (200°, 2.5 hours) otherwise appropriate for conversion to IV. After removal of the excess maleic anhydride, and the neutral and weakly acidic (phenolic) products, two adducts,[17] m.p. 143° (in 6.3% yield) and m.p. 91° (in 0.65% yield) were isolated; these, in the sequel, have been assigned the formulas[18] V and VI, respectively. The functional groups expressed in V and VI are consistent with the spectral data: both adducts give absorption peaks at 1779 and 1845 cm.$^{-1}$, characteristic of a five-membered cyclic anhydride, and at 1718 cm.$^{-1}$, to be associated with the ketonic carbonyl. Both spectra contain weak bands at 1631 cm.$^{-1}$ due to the vinyl grouping. The 143° adduct shows no high intensity absorption in the near ultraviolet, but it does exhibit the characteristically weak ketone band at 303 mμ (ϵ 64). It was found to be insoluble in water, although slowly soluble in alkali, and it decolorized permanganate rapidly. It absorbed two equivalents of hydrogen to form a crystalline tetrahydro derivative VII, m.p. 115°, which was saturated to permanganate and which gave an infrared spectrum substantially identical with those of V and VI in the carbonyl region, but lacking the 1631 cm.$^{-1}$ band.

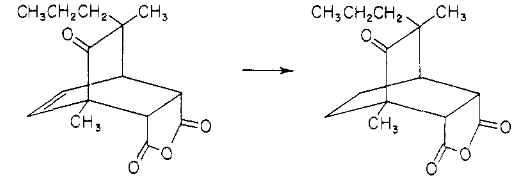


V



VI





An unequivocal proof of structure was most conveniently approached by synthetic means, as indicated in the diagram. As described,[19] 2,6-dimethylcyclohexanone (VIII) was prepared from 2,6-dimethylphenol: alkylation of the ketone with sodium hydride and allyl bromide followed by hydrogenation of the unsaturated ketone IX gave 2,6-dimethyl-2-propylcyclohexanone (X).[20] Direct propylation of VIII with propyl bromide also provided X, but this process was found to be inferior. The ketone X was readily chlorinated with sulfuryl chloride[21] to yield 6-chloro-2,6-dimethyl-2-propyl-

---

[16] Thus, using the values of Pauling ["The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, pp. 53, 131] for the bond energies, his value of 46 kcal./mole as typical of the phenolic or phenolic ether resonance energy and an estimate of 10 kcal./mole for the resonance energy of either dienone system, we compute the heats of formation as follows (R = CH$_3$): I, 2160; II and III, 2152; IV, 2171 kcal./mole. These results are in the expected order, that is, ignoring entropy, the presumed short-lived intermediates are less stable than the starting material, which in turn is considerably less stable than the product. If we assume a value of 5 kcal./mole for the resonance energy of conjugation in maleic anhydride, then the difference between the heats of formation of the adduct V and of maleic anhydride is 2172 kcal./mole which (again ignoring entropy) suggests that the adduct might well have considerable stability in this system. Considering the very rough nature of the computation this conclusion could not be taken seriously until it was borne out by the striking result obtained in the experiment with the trimethylated derivatives (*vide infra*).

[17] The work-up consisted in treatment of the total product with strong aqueous alkali, adjustment of the *p*H to 8-9 and extraction of the neutral and weakly acidic products; this left the adducts in the aqueous phase as the corresponding carboxylate anions, but the subsequent acidification evidently caused spontaneous cyclization back to the anhydride forms. Such behavior is not uncommon in cases of rigid or highly substituted succinic acids.

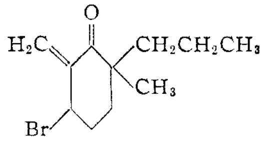
[18] The two adducts have been assigned the *endo* configuration solely on the basis of the rule of Alder [K. Alder and G. Stein, *Angew. Chem.*, **50**, 510 (1937); K. Alder, *Ann.*, **514**, 1 (1934); K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938)] which is somewhat ambiguous in this instance. Further, the adduct, m.p. 143°, obtained in larger amount is assigned the structure V because this is sterically more probable than the alternative VI. Finally, it will be conceded that although the constitution of the 143° adduct is regarded to be substantially proved in this study, the less abundant, 91° adduct is so written only on the basis of its elementary analysis, the close similarity of its infrared spectrum to that of the other, and because such an isomer might well be expected to be formed in addition to the main product.

[19] J. E. Nickels and W. Heintzelman, *J. Org. Chem.*, **15**, 1142 (1950).

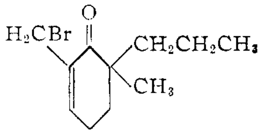
[20] The sample of X obtained was very probably a mixture of stereoisomers as suggested by the wide m.p. range of the 2,4-dinitrophenylhydrazone even though it was subjected to the usual purification procedures and gave satisfactory analytical figures.

[21] E. W. Warnhoff and W. S. Johnson, THIS JOURNAL, **75**, 494 (1953); B. Tchoubar and O. Sackur, *Compt. rend.*, **208**, 1020 (1939); P. Delbaere, *Bull. soc. chim. Belg.* **51**, 1 (1942).

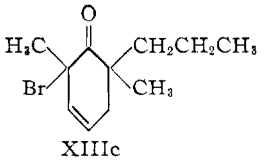
cyclohexanone (XI); a collidine dehydrochlorination furnished an unsaturated derivative, assigned the structure XII rather than the (unlikely) alternative of the exomethylene ketone on the evidence of the ultraviolet absorption: λ_{max} 237 mμ, log ϵ 3.88. The unsaturated 2,4-dinitrophenylhydrazone, which could also be prepared directly from the chloroketone XI, has λ_{max} 386 mμ.[22] N-Bromosuccinimide bromination of the cyclohexenone XII would be expected to provide XIII, and the results sustain the view that the latter predominated in the product obtained, although this may not have been entirely homogeneous. The bromoketone showed absorption characteristics (λ_{max} 237 mμ, log ϵ 3.99) similar to those of its progenitor, it was highly reactive toward alcoholic silver nitrate and it liberated iodine from sodium iodide in acetone on warming, properties which together appear to exclude any of the formal possibilities (XIIIa, etc.) as the major component. Further support for the structure XIII is found in the subsequent dehydrohalogenation to an homoannular diene. And as with the chloroketone, dehydrohalogenation occurred during the preparation of the 2,4-dinitrophenylhydrazone, since the derivative obtained from XIII was identical with that of 2,6-dimethyl-2-propyl-3,5-cyclohexadienone (XIV); this 2,4-dinitrophenylhydrazone has λ_{max} 407 mμ.[23] The dienone XIV itself was prepared from XIII with hot collidine. Its spectrum, containing two maxima at 242 mμ (log ϵ 3.65) and 312 mμ (log ϵ 3.48), is approximately that expected.[24a,b]



XIIIa

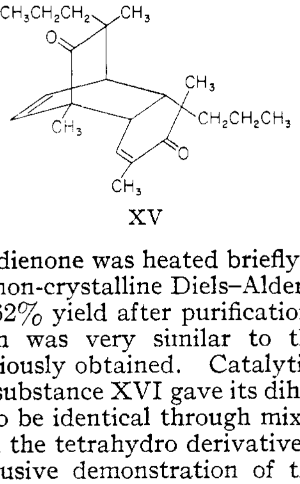


XIIIb



XIIIc

Any possibility of skeletal rearrangement in the over-all process leading to the dienone was ruled out, for catalytic hydrogenation of the preparation gave saturated ketonic material identical in its infrared spectrum with the 2,6-dimethyl-2-propylcyclohexanone (X) obtained earlier. The ready addition to maleic anhydride (*vide infra*) authenticates the formulation as an homoannular diene. The dienone sample initially was a mobile liquid, but upon storage (with a trace of hydroquinone) in the refrigerator it became more viscous, and in the course of several months turned nearly completely crystalline. The substance is considered to be the dimer XV, formed by self-condensation of the dienone in Diels–Alder fashion, and, except for the considerably reduced rate, in the manner so typical of the cyclopentadienone types. Partly dimerized material could be converted back to monomer upon distillation. The infrared spectrum of the purified crystalline dimer is quite different from that of the original dienone; the bands at 1672 and 1706 cm.$^{-1}$ indicate the presence of both conjugated and unconjugated ketonic groupings, and so exclude certain other formulations of the dimer. The conjugated system implied in XV is confirmed by the ultraviolet spectrum: λ_{max} 242 mμ, log ϵ 3.90.



XV

When the dienone was heated briefly with maleic anhydride a non-crystalline Diels–Alder adduct was obtained in 62% yield after purification; its infrared spectrum was very similar to those of the adducts previously obtained. Catalytic hydrogenation of this substance XVI gave its dihydro derivative, found to be identical through mixed m.p. and infrared with the tetrahydro derivative (VII) of V; thus a conclusive demonstration of the constitution of these latter compounds was provided.

Although the point is a formal one, since in this instance there is little reason to suppose that maleic anhydride could "cause" the formation of II from I, we may not conclude, merely from the isolation of the adduct V from the *para*-Claisen rearrangement, that the dienone II is actually present in the reaction mixture as normally run in the absence of maleic anhydride. It is a fortunate circumstance,

---

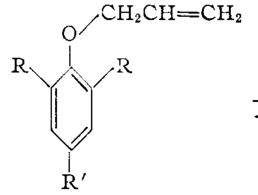
[22] *Cf.* E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945); J. D. Roberts and C. Green, THIS JOURNAL, **68**, 214 (1946); F. Ramirez and A. F. Kirby, *ibid.*, **74**, 4331 (1952).

[23] Although data on structurally analogous derivatives are apparently not available, the 2,4-dinitrophenylhydrazones of other dienones absorb in this region. *Cf.* C. Djerassi and E. Ryan, *ibid.*, **71**, 1000 (1949); A. Sandoval, L. Miramontes, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 990 (1951); J. Szmuszkovicz and H. Born, *ibid.*, **75**, 3350 (1953).

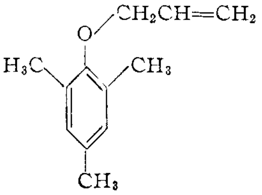
[24] (a) The literature does not provide many authentic examples of the 2,2,6-trialkylated 3,5-cyclohexadienone system, but as approximate models for ultraviolet absorption we may consider 2,2-diacetoxy-4-methyl-3,5-cyclohexadienone (λ_{max} 312 mμ, log ϵ 3.45) and 2-acetoxy-2,4-dimethyl-3,5-cyclohexadienone (λ_{max} 300 mμ, log ϵ 3.55) [F. Wessely and F. Sinwel, *Monatsh.*, **81**, 1055 (1950)]. The curves given by Wessely and Sinwel do not show a second, low wave length, maximum, although they fall to a minimum at *ca.* 270 mμ, and then rise to a value for log ϵ of 3.5 in the 230 mμ region, and so would indicate a maximum at perhaps 220–225 mμ. (b) Perhaps the infrared spectra of these **ketonic intermediates** deserve separate discussion. The carbonyl peaks of the unconjugated monocyclic ketones (VIII, IX, X, XI) all fall in the range 1689–1695 cm.$^{-1}$, values distinctly lower than those (1705–1725 cm.$^{-1}$) considered typical (L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 114). The effect may be general for compounds highly substituted in both of the positions adjacent to the carbonyl however, for such substitution would tend to widen the >C=O angle. The shift is in the direction expected on this basis, since it is well known, for example, that diminution of the carbonyl angle forced by inclusion in a small ring invariably results in a shift to higher wave numbers. The lack of exaltation in the case of the chloroketone XI as compared to X indicates an axial chlorine (R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2828 (1952); E. J. Corey, *ibid.*, **75**, 2301 (1953)) (propyl equatorial) which is to be anticipated in a non-epimerizable haloketone from the argument (E. J. Corey, *Experientia*, **9**, 329 (1953)) that the halogen will prefer to approach from the direction perpendicular to the plane of the stable enol. The cyclohexenones XII and XIII absorb at still lower wave numbers, *viz.*, 1656 and 1661 cm.$^{-1}$, while the dienone XIV exhibits a "carbonyl" peak at 1647 cm.$^{-1}$ and two others at 1631 and 1582 cm.$^{-1}$ associated with the unsaturated system.

again verified by experience in the conversion XIV → XVI, that the Diels–Alder reaction with these dienones will proceed under conditions far milder than those required for the formation of II from I. Thus, with a given sample of the pure ether (I, R = CH_3), and using the standard isolation technique, no trace of the adduct could be isolated from the reaction with maleic anhydride for three hours at 100°, but when a quantity of the same ether was first heated briefly at 200°, cooled and then treated with the dienophile for three hours at 100°, some adduct was obtained. The experiment shows (a) that the aromatic system I as such is unreactive in Diels–Alder addition, (b) that our sample of 2,6-dimethylphenyl allyl ether did not initially contain any significant amount of the dienone[25] and (c) *that the dienone is a normal component of the rearrangement reaction mixture.*

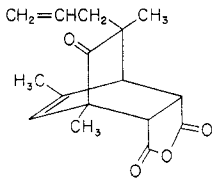
To eliminate the (nearly untenable) hypothesis that the product IV might be the precursor of II, rather than, for example, *vice versa*, the preparation of the adduct was attempted with a sample of 2,6-dimethyl-4-allylphenol under the same conditions, and again, with the standard isolation. No adduct(s) (V or VI) could be detected.



In order rigorously to prove that the dienone is a *bona fide* intermediate, it would be necessary to show not only that it is present, but that it is converted to the final product IV at a rate at least equal to that of the over-all transformation. Because of the difficulty in obtaining a pure sample of the allylated dienone, we have not yet been able to meet this requirement. But the Diels–Alder condensation is reversible, and it was found that pyrolysis of the adduct V under conditions similar to those of the rearrangement, yielded some of the phenol (IV), R = CH_3, isolated in 2.2% of theory as the phenylurethan. Evidently the dienone, when released from its adduct, can go on to form the phenol under the conditions, and it is therefore true that in the normal *para*-Claisen rearrangement, at least *some* of the *p*-allylphenol is formed *by way of* such a dienone.



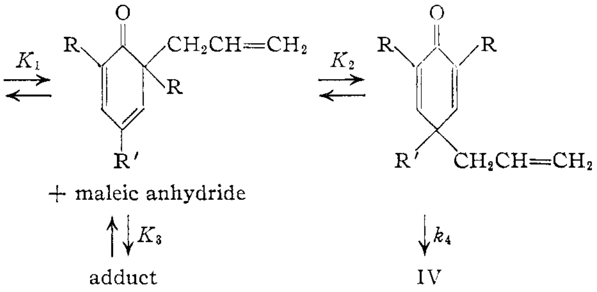
XVII



XVIII

We may profitably consider the behavior of a system, as implied in the case of the trimethylated derivative XVII, where the dienones should form normally, but where no rearranged phenolic product is possible. As anticipated, long heating of mesityl allyl ether alone at 200° left it practically unchanged. But treatment with a small excess of maleic anhydride at 200° for 45 min. gave a typical adduct XVIII in a yield (64%) sevenfold that which could be isolated in the analogous dimethylated series. The new adduct, as well as its dihydro derivative, shows the same carbonyl functions in the infrared as noted previously, and the reduced product is distinguished from its parent by the absence of the peak at 1631 cm.$^{-1}$, characteristic of the terminal methylene. The presence of the endocyclic, trisubstituted double bond can be deduced from the extinction[26] of 2600 at 220 mμ.

The formation of XVIII in high yield in the presence of the dienophile, coupled with the evident lack of gross change when the ether XVII is heated alone, strongly indicates that the first two steps of the *para* Claisen rearrangement are both reversible. In the figure, $K_1 \ll 1$ and $K_1K_2 \ll 1$, from the fact that even when $k_4 = 0$ ($R' \neq H$) the dienones do not accumulate. But *a priori* $K_3 \gg 1$ and from the yield of adduct XVIII $K_1K_3 \geq 1$. The enolization rate k_4 is large (when $R' = H$) compared to the forward rate(s) of rearrangement, since it has been shown that the over-all rate is not appreciably affected by dimethylaniline.[5,12]



The mechanism supported by our evidence, is consistent with all other available data. When both *ortho* positions are open, no *para* migration occurs.[27] This is in accord with a route for the *para* rearrangement involving prior migration to the *ortho* position. *Meta* migration never occurs. The reaction is intramolecular[12,28] and of first order.[12] The fact that *para* migrations take place under the same conditions as *ortho*, and the close similarity exhibited by the *ortho* and *para* reactions with regard to their energies and entropies[5,12] of activation indicates that both rearrangements might well have a common (or similar) rate-determining step; the high negative entropy values suggest that this step involves a cyclic transition state. The single reported case[14,29] of α,γ-inversion in the *para* migration has been discredited[15]; others[4,30] proceed without inversion. An extension of the rule to the un-

---

(25) This point seemed important because it was quite conceivable that trace amounts of the same dienone might have been formed in the original preparation of the ether (I, R = CH_3) from 2,6-dimethylphenol and allyl bromide and then have eluded the purification process.

(26) P. Bladon, H. B. Henbest and G. W. Wood, *J. Chem. Soc.*, 2937 (1952).

(27) W. M. Lauer and R. M. Leekly, THIS JOURNAL, **61**, 3042 (1939).

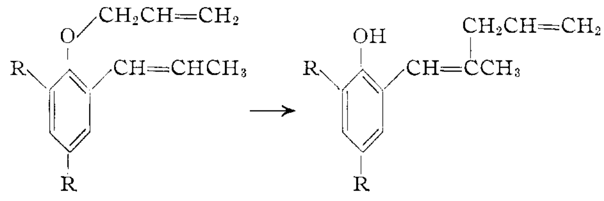
(28) H. Schmid and K. Schmid, *Helv. Chim. Acta*, **36**, 489 (1953).

(29) O. Mumm, H. Hornhard and J. Diederichsen, *Ber.*, **72**, 100 (1939).

(30) H. Staudinger, W. Kreis and W. Schilt, *Helv. Chim. Acta*, **5**, 743 (1922).

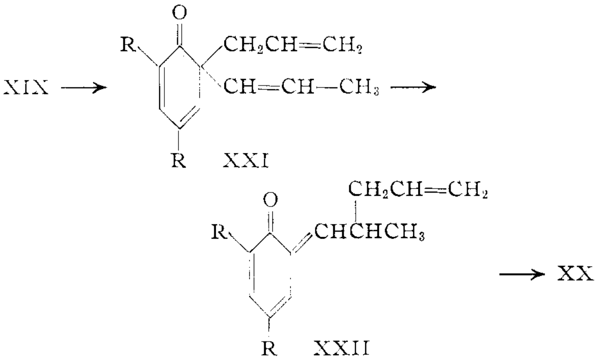
substituted allyl group was recently made possible with tracers.[11,28]

The second step (II → III) in the mechanism is analogous to the first in being a thermal rearrangement of a system in which both an allyl and a vinyl residue are attached to the same atom, although the central atom is carbon rather than oxygen. In 1926, Claisen made the remarkable observation[31] that phenyl allyl ethers rearrange on heating even when both *ortho* positions and the *para* position are blocked, provided that a propenyl group occupies one of the *ortho* positions; the allyl group then migrates to the β-carbon of the propenyl chain



XIX XX

Clearly the assumption of the dienone intermediate (XXI) and its further transformation to XXII allows a ready explanation, for migration of the allyl



XXI XXII

in this way is mechanistically closely similar to the *para* rearrangement itself, except that here the (reversible) *para* migration cannot ultimately allow return to the aromatic system. In a more recent and extensive study, Cope[32] has discovered a number of examples of rearrangement of substituted 1,5-hexadiene derivatives which show a strong resemblance to the changes (II → III) and (XXI → XXII).

Decarboxylation of *o*- and *p*-carboxyphenyl allyl ethers has been observed frequently during both *ortho*[33-35] and *para*[36,38] Claisen rearrangements, a result predictable from the mechanism, since dienones which are either β-keto acids or vinylogous β-keto acids would be involved. Inversion of the allyl group accompanies *ortho* displacement of carboxyl,[34,35] and *para* displacement occurs without inversion.[36]

Since the publication of our preliminary observations, there have appeared a number of elegant studies whose results tend to confirm an important corollary of the dienone mechanism:[37-39] that an allyl residue attached to the ether oxygen can gain equivalence with, exchange with, or displace one initially in the *ortho* position. In particular, Curtin and Johnson have obtained independent evidence for the *reversible* formation of the dienone II, as well as certain ancillary data tending to support the otherwise intuitive belief that this mechanism is in fact solely operative in the *para*-Claisen rearrangement.

Acknowledgment.—We would like to thank Professor Gilbert Stork for his guidance and generous assistance throughout this work.

Experimental

Reagents.—2,6-Dimethylphenol, m.p. 43.9–45.6°, b.p. 92° (20 mm.), was prepared by distillation of commercial material. 2,6-Dimethylphenyl allyl ether was prepared according to Tarbell and Kincaid[12]; reported: n^{25}D 1.5048, b.p. 67–68° (2 mm.); found: $n^{28.9}$D 1.5048, b.p. 73–76° (1.5 mm.). 2,6-Dimethyl-4-allylphenol (IV) was made by rearrangement of the ether for seven hours at 190–210° (bath temperature) and worked up as reported[12]; reported n^{25}D 1.5370, b.p. 90.5–91.4° (2 mm.), phenyl urethan m.p. 141–142.5°; found: $n^{30.5}$D 1.5352, b.p. 81–83° (0.3 mm.), phenylurethan m.p. 143.4–144.4°.

Diels–Alder Adducts (V and VI).—A mixture of 16.2 g. of 2,6-dimethylphenyl allyl ether (I) and 29.4 g. of maleic anhydride was heated under reflux in a carbon dioxide atmosphere for 2.5 hours at 200° (bath temperature). The reaction mixture was poured into concentrated aqueous sodium hydroxide, and after warming to dissolve any remaining acidic material, the suspension was cooled and extracted three times with petroleum ether. The aqueous portion was saturated with carbon dioxide and the extractions with fresh petroleum ether were repeated. The aqueous solution was then acidified with hydrochloric acid and extracted with diethyl ether in five portions. Upon evaporation of the solvent, a reddish gum was obtained; this was extracted with hot heptane which on cooling deposited a small amount of white crystalline material, used to seed the bulk of the product. The gum was allowed to stand for a few days to allow separation of the solid; two recrystallizations from 4:1 heptane–ethyl acetate afforded 1.63 g. (6.26%) of material with the m.p. 140–142°. Several further recrystallizations raised the m.p. to 143.3–143.6°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.3; H, 6.2.

Concentration of the mother liquors yielded 0.757 g. (2.91%) of a colorless, crystalline material, m.p. 82–135° (mostly at 82–84°) whose infrared spectrum was very similar to that of the adduct V. Further very slow evaporation of the mother liquors yielded an oil, along with some large cubic crystals, m.p. 83–90°, which were picked out carefully, and the oil discarded. After recrystallization from heptane the weight was 0.169 g. (0.65%) and the m.p. 88–90°; another recrystallization from heptane afforded pure material, m.p. 90.5–91.6°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.7; H, 6.3.

The infrared spectrum of the purified VI was substantially identical with that of the above crude, m.p. 82–135°. The total yield of the two isolated isomers amounted to 9.82%.

Attempted Reaction of Maleic Anhydride with the Phenol IV. (A).—A sample of the 2,6-dimethyl-4-allylphenol

---

(31) L. Claisen and E. Tietze, *Ann.*, **449**, 81 (1926).

(32) A. C. Cope and E. M. Hardy, THIS JOURNAL, **62**, 441 (1940); A. C. Cope, K. E. Hoyle and D. Heyl, *ibid.*, **63**, 1843 (1941); A. C. Cope, C. M. Hofmann and E. M. Hardy, *ibid.*, **63**, 1852 (1941); D. E. Whyte and A. C. Cope, *ibid.*, **65**, 1999 (1943); H. Levy and A. C. Cope, *ibid.*, **66**, 1684 (1944); E. G. Foster, A. C. Cope and F. Daniels, *ibid.*, **69**, 1893 (1947); G. R. Aldridge and G. W. Murphy, *ibid.*, **73**, 1158 (1951).

(33) L. Claisen and O. Eisleb, *Ann.*, **401**, 21 (1913).

(34) D. S. Tarbell and J. W. Wilson, THIS JOURNAL, **64**, 607 (1942).

(35) W. R. Nummy and D. S. Tarbell, *ibid.*, **73**, 1500 (1951).

(36) D. S. Tarbell and J. W. Wilson, *ibid.*, **64**, 1066 (1942).

(37) K. Schmid, W. Haegele and H. Schmid, *Helv. Chim. Acta*, **37**, 1080 (1954); *Experientia*, **9**, 414 (1953).

(38) D. Y. Curtin and H. W. Johnson, Jr., THIS JOURNAL, **76**, 2276 (1954).

(39) E. N. Marvel and R. Teranishi, *ibid.*, **76**, 6165 (1954).

(IV) (16.2 g.) was heated with 29.4 g. of maleic anhydride at 200° under carbon dioxide for 30 minutes. The mixture was treated with aqueous sodium hydroxide on the steam-bath for 20 minutes, until the gum was in solution. The aqueous solution was extracted once with petroleum ether, and it was then saturated with carbon dioxide. After another two extractions with petroleum ether, the aqueous portion was acidified with hydrochloric acid. The gummy precipitate was taken up in diethyl ether, in two portions. The gum remaining upon evaporation of the ether was extracted with hot heptane, as had been done previously, but the heptane extract deposited nothing on cooling. The infrared spectrum of the gum showed that it contained none of the familiar adduct V.

(B).—The phenol IV (16.2 g.) and maleic anhydride (29.4 g.) was heated at 200° under carbon dioxide for 2.5 hours, the mixture was treated with aqueous sodium hydroxide and the suspension was warmed on the steam-bath for two hours in order to dissolve the gummy material. The solution was washed with petroleum ether, the *p*H was adjusted to 8–9 with hydrochloric acid, and the solution was washed three times with ether, until non-volatile material was no longer extracted. The aqueous portion was then acidified strongly with hydrochloric acid and extracted five times with ether. A very hard red gum was left upon evaporation. An infrared spectrum of a Nujol mull of this gum showed no indication of adduct. Extraction of the gum with hot heptane yielded, upon evaporation, a trace of white material whose infrared spectrum showed no adduct. Extraction of the gum with heptane–ethyl acetate 4:1 for one hour on the steam-bath yielded upon evaporation only water-soluble crystalline material (the adducts are all insoluble in water). Repeated extraction of the gum with chloroform, in which all the adducts are very soluble, showed no sign of adduct in the infrared.

Attempted Low Temperature Additions to Pure and to Preheated Ether (I).—A sample (5 g.) of 2,6-dimethylphenyl allyl ether (I) from the same batch as used above for the preparation of V and VI, was heated with an equal weight of maleic anhydride for three hours on the steam-bath. The workup was the same as that described, except that no water-insoluble material appeared upon acidification, and no adduct could be obtained. However when 40.5 g. of the ether I was heated alone at 195–200° for ten minutes, cooled to room temperature, and then treated with 10 g. of maleic anhydride on the steam-bath for three hours adduct was obtained. The reaction mixture was extracted four times with aqueous sodium hydroxide and twice with water. The *p*H of the combined aqueous extract was adjusted to 8–9 with hydrochloric acid, and the solution was extracted three times with ether. The aqueous portion was then strongly acidified with hydrochloric acid, and extracted three times with ether. The red gum remaining upon evaporation was heated with heptane on the steam-bath; the heptane was decanted and allowed to cool slowly. There was obtained about 30 mg. of adduct, m.p. 133–137°. The mixed m.p. with authentic adduct of m.p. 138–142° was 132.5–141.5°, and the infrared spectrum was identical with that of the pure adduct V. One recrystallization brought the m.p. to 141.5–142.5°.

Pyrolysis of the Adduct (V).—A sample (0.52 g.) of adduct, with 15 ml. of Nujol as a diluent, was placed in a glass tube which was then flushed with carbon dioxide, evacuated and sealed. The tube was immersed in oil at 200° for 3.25 hours. After cooling, the contents of the tube were heated with aqueous sodium hydroxide on the steam-bath for several hours. The Nujol layer was separated and discarded, and the *p*H adjusted to 8–9 with hydrochloric acid. The product was extracted with ether and the combined extracts dried with magnesium sulfate. The solution was concentrated to a volume of 4–5 ml., three small drops of phenyl isocyanate and two drops of pyridine were added. The solvent was completely evaporated and the residue heated on the steam-bath for 30 minutes. The crystals which appeared on cooling were recrystallized twice from heptane to give material with the m.p. 141.5–143°, mixed m.p. with authentic IV phenylurethan, 141.5–144°. The infrared spectrum of this material, augmented with some of m.p. 139–142° obtained by concentration of the mother liquors, was identical with that of authentic phenylurethan.

From this reaction 71.8 mg. of adduct V was recovered. The weight of crude phenylurethan was 59.3 mg. The yield of fairly pure once-recrystallized material of m.p. 129–139° was 10.8 mg., and the 141.5–143° crystals amounted to 2.6 mg. Based on starting material not recovered, the three quantities represent 12.2, 2.2 and 0.54% of theory. The 2.2% is a conservative figure, because of not insignificant mechanical losses before this weighing was made.

Hydrogenation of the Adduct (V).—An acetic acid solution of 0.2889 g. of V containing platinum oxide was stirred under hydrogen at atmospheric pressure. A total of 56.3 ml. of hydrogen was absorbed (101% of two equivalents). After removal of catalyst and solvent the product was recrystallized from heptane–ethyl acetate; the m.p. was 115.1–115.4°. The substance VII did not decolorize permanganate.

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.2; H, 7.7.

2,6-Dimethylcyclohexanol.—A solution of 100 g. of 2,6-dimethylphenol, m.p. 43.9–45.6°, in 410 ml. of commercial absolute ethanol was hydrogenated at 150° with Raney nickel under a pressure of 900 lb./in.^{2} for about 20 hours. The catalyst and solvent were removed and the product distilled; reported[19]: b.p. 76–78° (20 mm.), n^{20}D 1.4600; found: 74° (*ca.* 15 mm.), $n^{26.6}$D 1.4586. The yield was 72.8 g. (68.7%), and some of the phenol was recovered as a higher cut.

2,6-Dimethylcyclohexanone (VIII).—This was prepared from the alcohol by oxidation with chromic acid, using the method of Nickels and Heintzelman,[19] in 82% yield; reported: b.p. 60° (20 mm.), n^{20}D 1.4470; found: b.p. 68° (*ca.* 17 mm.), n^{28}D 1.4441.

2,6-Dimethyl-2-allylcyclohexanone (IX).—A mixture of 750 ml. of benzene and 170 ml. of technical dimethylformamide was dried by partial distillation of the benzene. Sodium hydride (19.2 g.) and 100.8 g. of 2,6-dimethylcyclohexanone were added; the mixture was refluxed for three hours, when the hydrogen evolution had slackened, and then 96.8 g. of allyl bromide dissolved in a little dry benzene was added over a ten minute period, with stirring continued. The reaction was rapid and vigorous. The reaction mixture was refluxed for another 1.5 hours and then cooled; the addition of a little ethanol gave no reaction. The benzene solution was washed with water, 10% hydrochloric acid, and again twice more with water. The benzene was removed by distillation under reduced pressure, and the product distilled, b.p. 107–115° (25 mm.), n^{28}D 1.4648.

2,6-Dimethyl-2-propylcyclohexanone (X).—An ether solution of 4.76 g. of 2,6-dimethyl-2-allylcyclohexanone was hydrogenated in the presence of 0.1311 g. of platinum oxide at 26°; 711 ml. of hydrogen (97.4%) was taken up. After the catalyst had been filtered off the solvent was evaporated, and the product was distilled. The b.p. was 108–110° (25 mm.). A sample was redistilled for analysis and gave n^{25}D 1.4532.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.2; H, 12.0.

When the hydrogenation was repeated on a larger scale, 61.5 g. of the unsaturated ketone yielded 57.3 g. (92.6%) of distilled product. This material proved to be identical with that produced in the alkylation of 2,6-dimethylcyclohexanone with propyl bromide; the latter method proved to be vastly inferior both in yield and in time consumed.

The 2,4-dinitrophenylhydrazone of X was prepared with methanolic Brady reagent at room temperature, and purified by chromatography on alumina. After recrystallization from ethanol–water, the m.p. was 93–102°; λ_{max} 369 mμ, $\epsilon \cong 10^4$ ($CHCl_3$).

Anal. Calcd. for $C_{17}H_{24}N_4O_4$: C, 58.60; H, 6.94; N, 16.09. Found: C, 58.5; H, 6.9; N, 15.9.

2,6-Dimethyl-2-propyl-6-chlorocyclohexanone (XI).—Chlorination of X was effected by the method of Warnhoff and Johnson.[21] A 10% molar excess (9 ml.) of sulfuryl chloride was added to a solution of 16.8 g. of the ketone in 50 ml. of carbon tetrachloride. An immediate vigorous evolution of gas occurred and continued for about 15 minutes, the reaction mixture becoming slightly warm in this time. After another half-hour the reaction mixture was refluxed for several hours, cooled and washed twice with water, twice with saturated sodium bicarbonate solution and once more with water. The solution was dried over magnesium sulfate, the solvent evaporated and the product distilled, b.p. 122–126° (21 mm.). The yield was 16.3 g.

(80.5%). A sample was redistilled for analysis, giving n^{26}_D 1.4682.

Anal. Calcd. for $C_{11}H_{19}OCl$: C, 65.17; H, 9.45. Found: C, 64.8; H, 9.3.

The 2,4-dinitrophenylhydrazone was prepared with Brady reagent containing one equivalent of 2,4-dinitrophenylhydrazine. After five days, a small amount of dark red oil was deposited, which could not be crystallized. The supernatant liquid was refluxed for three hours, but nothing was precipitated upon cooling. The oil and solution were combined, diluted with water, and extracted four times with small amounts of chloroform. The residue upon evaporation of the chloroform was chromatographed on alumina, with hexane elution. The crystalline material obtained from the first fraction was recrystallized from methanol to give m.p. 125–126°. The derivative was identical by mixed m.p. and infrared with that of 2,6-dimethyl-6-propyl-2-cyclohexenone (XII) (*vide infra*).

2,6-Dimethyl-6-propyl-2-cyclohexenone (XII).—The chloro ketone XI (10.1 g.) was heated with 6.7 g. of dry 2,4,6-collidine under nitrogen. When the oil-bath temperature reached 187°, vigorous refluxing commenced, and this continued even though the oil-bath was removed. Upon cooling, the mixture was found to contain crystals, which were crushed with benzene, filtered and washed several times with fresh benzene. The dry weight of the solid was 7.5 g. or 96% of the theoretical amount of collidine hydrochloride. The benzene extract was washed twice with 10% hydrochloric acid saturated with sodium chloride, once with saturated sodium bicarbonate and once with water. The benzene was evaporated and the product distilled, b.p. 114.5–116° (25 mm.). The yield was 7.1 g. (86%). A small sample was redistilled for analysis, giving n^{31}_D 1.4733 and λ_{max} 237 mμ, log ϵ 3.88 (95% ethanol). *Anal.* Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.3; H, 10.9.

The 2,4-dinitrophenylhydrazone was formed when the ketone was treated with Brady reagent for two days at room temperature. The m.p. was 124–126°, λ_{max} 386 mμ, $\epsilon \cong 10.^4$

Anal. Calcd. for $C_{17}H_{22}O_4N_4$: C, 58.94; H, 6.40; N, 16.18. Found: C, 58.6; H, 6.1; N, 16.1.

2,6-Dimethyl-4-bromo-6-propyl-2-cyclohexenone (XIII).—To 5.7 g. of the unsaturated ketone XII dissolved in 75 ml. of carbon tetrachloride was added 6.9 g. (10% molar excess) of N-bromosuccinimide and 200 mg. of benzoyl peroxide. This mixture was refluxed for 18 hours with a 60-watt bulb and reflector against the side of the flask. The solid floating at the surface was removed and washed; it weighed 3.79 g. (98.2% of the theoretical amount of succinimide). The rather dark solution was washed with dilute potassium hydroxide, then dilute hydrochloric acid and water and dried over magnesium sulfate. After evaporation of the solvent the product was distilled, b.p. 123–134° (10 mm.), and 89–104° (2 mm.). The yield was 6.39 g. (74.3%). When a small amount was redistilled in a fractionating tube, there was evidence of slow decomposition. The refractive index (at 31–32°) ranged from 1.5057 for the most volatile of four fractions to 1.5125 for the least volatile. The latter gave λ_{max} 237 mμ, log ϵ 3.99, and the following analytical figures.

Anal. Calcd. for $C_{11}H_{17}OBr$: C, 53.89; H, 6.99. Found: C, 55.2; H, 7.1.

The 2,4-dinitrophenylhydrazone was prepared by refluxing 0.35 g. of the ketone with 0.31 g. of 2,4-dinitrophenylhydrazine in 35 ml. of methanol containing three drops of concentrated hydrochloric acid. After five hours the mixture was diluted with water, shaken with chloroform and filtered. The chloroform layer was evaporated and the unreacted ketone removed by distillation in a small sublimer for 3–4 hours on the steam-bath using the water-pump. The residue was chromatographed on alumina, with a benzene elution; the first band contained the derivative, which after recrystallization twice from methanol had the m.p. 135–136° and λ_{max} 407 mμ. The substance was found by infrared and mixed m.p. to be identical with the derivative prepared from 2,6-dimethyl-2-propyl-3,5-cyclohexadienone.

Anal. Calcd. for $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85. Found: C, 59.1; H, 5.8.

2,6-Dimethyl-2-propyl-3,5-cyclohexadienone (XIV).—A sample of 3.10 g. of the bromo ketone XIII was mixed with 1.69 g. of collidine (1.1 equivalents) and heated under nitrogen. Solid began to appear in the reaction flask when the oil-bath temperature reached about 120°. The bath was kept at 130–140° for 15 minutes, until further formation of solid appeared to have ceased. After cooling, the reaction mixture was crushed with benzene and the solid washed with benzene several times. The weight of collidine hydrobromide was 2.09 g. (81.7%). The combined benzene extracts were washed twice with cold dilute hydrochloric acid, once with saturated sodium bicarbonate and once with water. After evaporation of the benzene, the product was distilled, b.p. 88° (10 mm.). The yield was 0.87 g. (41.3%). The ultraviolet spectrum in 95% ethanol showed two bands, at 239 mμ (log ϵ 3.72) and 312 mμ (log ϵ 3.43). After chromatography on alumina (Woelm's "neutral," strength 2), eluting with 0.01% methanol in hexane, the first fraction of 250 ml. was evaporated and the product distilled at 6 mm. and 90° (bath temperature). The purified product absorbed in the ultraviolet at 242 mμ (log ϵ 3.65) and 312 mμ (log ϵ 3.48) and had n^{26}_D 1.4877; the infrared spectrum in chloroform indicated peaks at 1647 (S), 1631 (M) and 1582 (W) cm.$^{-1}$.

The 2,4-dinitrophenylhydrazone was prepared from 0.33 g. of the dienone, 0.40 g. of 2,4-dinitrophenylhydrazine, 25 ml. of methanol and three drops of concentrated hydrochloric acid, with a 4-hour reflux period. The derivative was obtained substantially as given above and had the m.p. 132–134°.

A few drops of the dienone in glacial acetic acid was hydrogenated at atmospheric pressure for two hours, using platinum oxide. The acetic acid and catalyst were removed, and the infrared spectrum of the residual material, except for three very small peaks carried over from the dienone, was identical with that of the saturated ketone X.

Dimer of 2,6-Dimethyl-2-propyl-3,5-cyclohexadienone (XV).—A sample of the dienone stored (with a trace of hydroquinone) in the refrigerator gradually became more viscous, and eventually turned nearly completely crystalline. The original monomeric dienone could be regenerated on distillation. Two recrystallizations of the solid dimer from petroleum ether furnished material with the m.p. 104–106°.

Anal. Calcd. for $C_{22}H_{32}O_2$: C, 80.44; H, 9.82. Found: C, 80.4; H, 9.9.

Diels–Alder Adduct XVI. 2,6-Dimethyl-2-propyl-3,5-cyclohexadienone–Maleic Anhydride.—The dienone XIV (0.0543 g.) was mixed with 0.0356 g. (1.1 equivalents) of maleic anhydride and a trace of hydroquinone inhibitor, and heated to just below boiling over a free flame for about 10–20 seconds. A very viscous oil was obtained upon cooling. This was dissolved in hot aqueous potassium hydroxide and kept hot on the steam-bath for 3–4 hours. After cooling, the alkaline solution was washed twice with ether, acidified with hydrochloric acid and extracted three times with chloroform. Upon evaporation of the chloroform to constant weight, the adduct weighed 0.0539 g. (62.2%) but could not be crystallized. Its infrared spectrum was very similar to that of the original adduct V. Chromatography on Florex XXX afforded colorless material whose infrared spectrum was unchanged, but which still did not crystallize.

Hydrogenation of Adduct XVI. Compound VII.—The non-crystalline XVI was dissolved in acetic acid, platinum oxide was added and the suspension was stirred in an atmosphere of hydrogen. After the catalyst and solvent were removed, the product was recrystallized twice from heptane–ethyl acetate 4:1. The m.p. was 113.3–114.2°; the mixed m.p. with VII (m.p. 115.1–115.4°) was 113–114.5°. The infrared spectra were identical.

Mesidine.—A sample of 98.0 g. of nitromesitylene[40] was dissolved in 600 ml. of ethanol and hydrogenated in the Parr shaker at about 50 p.s.i., in portions, in the presence of Raney nickel. The expected amount of hydrogen was absorbed rapidly, and the mixture became warm. The catalyst was removed, the ethanol was evaporated and the mesidine taken up in dilute hydrochloric acid. The aqueous solution was washed three times with ether, made alkaline with sodium hydroxide, and extracted with several portions of ether. The extract was dried over sodium hydroxide pellets and the ether and then the product, were distilled. The yield of mesidine, b.p. 115° (*ca.* 15 mm.), was

---

[40] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 449.

73.5 g. (91.7%). The properties of samples of N-acetylmesidine[41] and N-benzoylmesidine[42] prepared as derivatives agreed closely with those reported.

Mesitol.—Mesidine (2.30 g.) was dissolved in a solution of 100 ml. of water and 2.30 g. of concentrated sulfuric acid. This was cooled in an ice–salt mixture, and a solution of 1.3 g. of sodium nitrite in water was added slowly, with stirring, until the solution gave a starch–iodide coloration. Aqueous urea was added until the solution was almost inert to starch–iodide, and then the diazonium salt was warmed on the steam-bath under reflux until the evolution of gas ceased. The solution was extracted with ether, the extract was washed with hydrochloric acid, the ether solution was dried over magnesium sulfate. The mesitol was sublimed on the steam-bath after removal of the ether. The yield was 2.09 g. (86.4%) of material with m.p. 72–72.5°. The m.p. reported[41] is 70–71°. The phenylurethan prepared in the usual way and recrystallized from heptane had m.p. 143.2–143.6°; Hey[41] reports 141–142°.

Mesityl Allyl Ether (XVII).—Since mesitol of good appearance was produced directly from the diazonium salt, the crude mesitol from a large run was used without further purification to make the allyl ether: A solution of 83.8 g. of mesidine in one liter of water containing 84 g. of sulfuric acid was diazotized, using 47.3 g. of sodium nitrite. The ethereal solution of crude mesitol was washed with dilute hydrochloric acid, dried with magnesium sulfate and most of the ether evaporated. The mesitol was then added to a solution of 13 g. of sodium dissolved in 230 ml. of commercial absolute ethanol. The solution was heated to reflux and 80 g. of allyl bromide was added, producing an immediate copious white precipitate. Refluxing was continued for two hours after the last of the allyl bromide had been added. The reaction mixture was poured into one liter of water, the organic layer was separated, and the aqueous layer was extracted twice with petroleum ether. The combined organic layers were washed twice with 20% aqueous sodium hydroxide, once with water, and dried over magnesium sulfate. After evaporation of the solvent, the mesityl allyl ether was distilled, b.p. 56° (0.20 mm.), yield 85.6 g. (78.2% based upon mesidine). Redistillation over a range 76.5–78.2° (2.3 mm.) provided four fractions whose infrared spectra and refractive indices, n^{28}D 1.5051, were all identical.

Anal. Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.08. Found: C, 81.8; H, 9.1.

The spectrum of this product contained two weak but disturbing bands in the conjugated carbonyl region, which might have been caused by dienones produced by C-alkylation during the preparation. In view of the intended purpose the presence of such impurities might invalidate the results and, accordingly, a procedure specific for the removal of ketonic material was employed, as follows: The mesityl allyl ether (10.54 g.) was stirred for seven hours with 1.0 g. of lithium aluminum hydride in 40 ml. of anhydrous ether. The excess of hydride was decomposed by the addition first of ethyl acetate, and then water. Dilute hydrochloric acid was added until the precipitate dissolved. The ether layer was washed once with water, some benzene was added and the solvent evaporated. The product was heated with 6 g. of phthalic anhydride and 6 ml. of dry pyridine for 50 minutes on the steam-bath. Benzene was added, and the solution was washed three times with 5% aqueous sodium hydroxide. After washing once with water, twice with 10% hydrochloric acid saturated with sodium chloride and once more with water, the solvent was removed and the purified mesityl allyl ether was distilled, b.p. 65–69° (2 mm.), n^{26}D 1.5068. The infrared spectrum was free from carbonyl bands, but was otherwise identical with that of the previously prepared material.

Attempted Thermal Rearrangement of Mesityl Allyl Ether.—A sample of mesityl allyl ether was heated at 200° under nitrogen, and portions were withdrawn at various times for spectroscopic examination. After 45 minutes, and after 1.5 and 4 hours the spectra were virtually identical with that of unheated material, and it is concluded that *within the limitations of the instrument* (perhaps 2 or 3%) this ether does not change on heating.

Diels–Alder Adduct (XVIII).—A sample of 3.52 g. of the purified mesityl allyl ether (XVII) was heated with 3.0 g. of maleic anhydride and 1 mg. of hydroquinone for 45 minutes at 200° (bath temperature) under nitrogen. Refluxing, which was quite vigorous at first, steadily declined throughout the reaction. The reaction mixture was allowed to cool to 80° slowly in the oil-bath; it was then warmed with 5% potassium hydroxide for 90 minutes on the steam-bath, cooled and extracted twice with hexane. Upon acidification with concentrated hydrochloric acid, a copious precipitate appeared, which became completely crystalline on standing. The solid was filtered and washed thoroughly with water to remove maleic acid. Its infrared spectrum indicated that it consisted partly of the anhydride and partly of the open diacid. Upon heating to the melting point, the liquid effervesced, and heating was stopped when this ceased. The resulting oil could not be crystallized, and so it was chromatographed on Florex XXX, with a benzene elution. There was obtained, upon evaporation of the solvent to constant weight, 3.49 g. (63.7%) of a colorless oil whose infrared spectrum corresponded so closely to that of the original Diels–Alder adduct (V) that there could be no doubt that it was the desired compound. This oil could not be crystallized, but it took up hydrogen readily in glacial acetic acid, using platinum oxide, to yield a crystalline dihydro adduct. In one run, 0.1794 g. of the chromatographed oil took up 16.3 ml. of hydrogen at 28° (1.00 molar equivalent). Three recrystallizations from heptane gave a product with m.p. 120.5–121.5°, λ_{max} 304 mμ (log ϵ 2.23), with log ϵ 3.42 at 220 mμ.

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.54; H, 7.30. Found: C, 69.5; H, 7.0.

WALTHAM, MASS.

---

(41) D. H. Hey, *J. Chem. Soc.*, 1590 (1931).

(42) H. Hubner, *Ber.*, **10**, 1711 (1877).