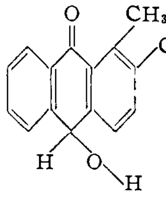
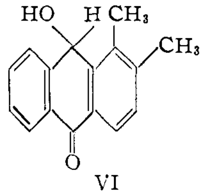
the oxanthrol from 1,2-dimethylanthraquinone, *viz.*, V and VI.

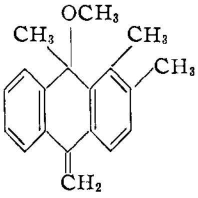


V

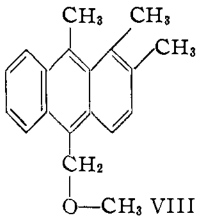


VI

The preferred structure is believed to be VI, *i.e.*, the carbon atom which is the more crowded is believed to be the one which becomes tetrahedral. Moreover there is a precedent for this type of structure in the 1,2-benzanthracene series.[17] It is also interesting that a mixture of the compounds VII and VIII has been isolated.[3] It is quite possible that the isomerization may be due to the resistance offered to the formation of a planar crowded molecule, which in this case is the hydroquinone.

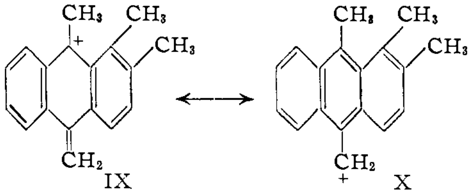


VII



VIII

From our study we conclude that compounds such as 1,2,9,10-tetramethylanthracene and the corresponding hydroquinones behave as crowded molecules. Superficially, from the standpoint of structure, I resembles the crowded molecule of octamethylnaphthalene.[18] The successful preparation of hydrocarbon I evidently requires, besides the driving force of aromatization, the added effect of a carbonium ion stabilized by the resonance forms IX and X.[3]



IX X

The unsuccessful demethoxylation[1] and dehydrogenation[2] attempts to prepare I, compared with the successful reactions where there is no 1,2-disubstitution, may involve an unfavorable reaction mechanism. Again it is possible that a hindered or unfavorable conformation of the starting material is involved, where a preferrred conformation for 9,10-elimination is necessary. Some recent interesting work has been carried out[19] which indicates that 9,10-dihydroanthracenes may be considered as cyclo-1,4-hexadienes and therefore may have bond orientations at the 9- and 10-positions which are not equivalent. For example, *cis*-9,10-dihydro-9,10-dimethylanthracene[19c] is stable to aluminum chloride in benzene, whereas the *trans* isomer[19c] is dehydrogenated under the same conditions.[20] Evidently in the former compound both hydrogen atoms are in equatorial positions, and in the latter compound one hydrogen is in an axial position. It should be mentioned, however, that the first compound, in spite of its stability to aluminum chloride in benzene, is dehydrogenated with sulfur without any difficulty.

Acknowledgment.—We take pleasure in expressing our appreciation to Dr. Richard T. Arnold of the Sloan Foundation for very stimulating discussions and suggestions, to Dr. Walter Harris for his help in connection with polarographic technique, and to Dr. Robert Christiansen for his help in the preparation and analysis of some of the compounds.

[17] R. B. Sandin and L. F. Fieser, THIS JOURNAL, **62**, 3098 (1940).

[18] (a) D. M. Donaldson and J. M. Robertson, *J. Chem. Soc.*, 17 (1953); (b) M. S. Newman and R. M. Wise, THIS JOURNAL, **78**, 450 (1956).

[19] (a) S. J. Cristol, W. Barasch and C. H. Tieman, *ibid.*, **77**, 583 (1955); (b) A. H. Beckett and B. A. Mulley, *Chemistry & Industry*, 146 (1955); (c) A. H. Beckett and B. A. Mulley, *J. Chem. Soc.*, 4159 (1955); (d) W. G. Ferrier and J. Iball, *Chemistry & Industry*, 1296 (1954).

[20] G. M. Badger, M. L. Jones and R. S. Pearce, *J. Chem. Soc.*, 1700 (1950).

EDMONTON, ALBERTA, CANADA

[CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The *para* Claisen Rearrangement: Rearrangement of 6-Allyl-2,6-dimethyl-2,4-cyclohexadienone[1]

BY DAVID Y. CURTIN AND ROBERT J. CRAWFORD

RECEIVED JANUARY 10, 1957

The synthesis of 6-allyl-2,6-dimethyl-2,4-cyclohexadienone from sodium 2,6-dimethylphenoxide and allyl bromide is here reported. The dienone rearranges to a mixture of 4-allyl-2,6-dimethylphenol and allyl 2,6-dimethylphenyl ether in a ratio of 2.7/1 when heated to 70°. On standing at room temperature it yields a dimer. The rates of the rearrangements have been measured at three temperatures. The results are compared with data of previous workers. The steady state concentration of dienone in the *para* Claisen rearrangement is shown by examination of the reaction mixture to be of the order of 0.1%.

Studies[2] of the mechanism of the *para* Claisen rearrangement have indicated that allyl-cyclohexadienones are intermediates in this reaction. It was the purpose of the present investigation to prepare such a compound and examine its behavior under the conditions of the Claisen rearrangement. The compound chosen for study was 6-allyl-2,6-di-

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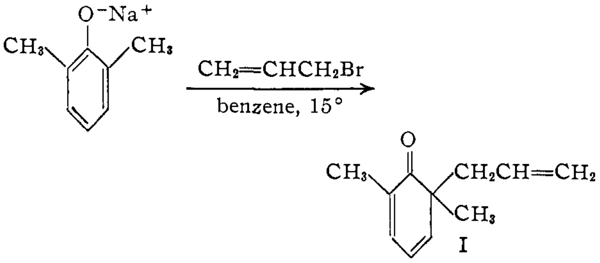
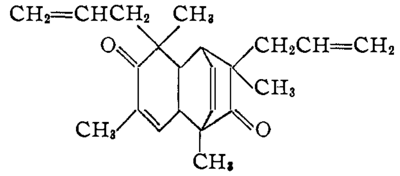
[1] Taken from a Ph.D. thesis submitted by Robert J. Crawford to the University of Illinois, August, 1956.

[2] See D. Y. Curtin and H. W. Johnson, Jr., THIS JOURNAL, **76**, 2611 (1956), for references.

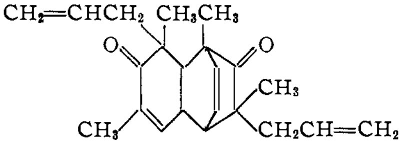
methyl-2,4-cyclohexadienone (I) which was prepared in 60% yield based on unreacted starting material by treatment of a suspension of the sodium salt of 2,6-dimethylphenol in benzene with allyl bromide.[3,4]



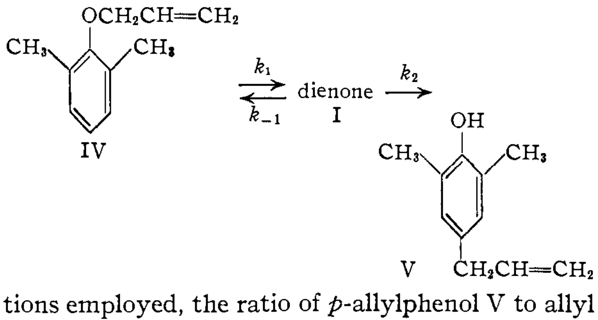
The allyldienone I rearranges readily when heated, but could be purified by distillation at reduced pressure. It was characterized by comparison of its infrared and ultraviolet spectra with those of other 2,4-cyclohexadienones. It reacted with maleic anhydride in benzene at 100° to form an adduct which is apparently identical with that which had been obtained by Conroy and Firestone[5] when they carried out the Claisen rearrangement of allyl 2,6-dimethylphenyl ether (IV) in the presence of maleic anhydride. When the dienone I was allowed to stand for several weeks, it was found to have undergone extensive reaction and eventually a crystalline compound, m.p. 92°, having twice the molecular weight of the dienone was formed. This substance is undoubtedly one of the diastereoisomers of the two Diels–Alder products II or III formed by condensation of the dienone I with itself. Evidence on which this conclusion is based includes the infrared and ultraviolet spectra, a molecular weight determination in camphor and the observation that hydrogenation over platinum resulted in the rapid uptake of three moles of hydrogen followed by a slower uptake of a fourth. The three unconjugated carbon–carbon double bonds in the structures II or III account for the rapid hydrogenation. The dimer when heated at 120° underwent what is apparently the reversal of its formation followed by a Claisen rearrangement of the dienone I to yield 4-allyl-2,6-dimethylphenol in 64% yield. A similar dimerization reaction was observed by Conroy and Firestone when they prepared 2,6-dimethyl-6-*n*-propyl-2,4-cyclohexadienone.[5b] The allyldienone I rearranges at temperatures above 70° to give a mixture of allyl 2,6-dimethylphenyl ether (IV) and 4-allyl-2,6-dimethylphenol (V). The reaction was conveniently carried out in cyclohexane solution. Under the conditions employed, the ratio of *p*-allylphenol V to allyl ether IV was 2.7.



II



III



Kinetics.—The rearrangement of the dienone I in cyclohexane at temperatures of 75–100° was conveniently followed with an ultraviolet spectrophotometer. At these temperatures the rearrangement of the allyl ether IV is negligible. Concentrations employed were low enough so that the Diels–Alder dimerization of I (which is presumably second order) was negligible. The disappearance of the dienone I followed a first-order rate law. If the reasonable assumption is made that dienone I is disappearing by two simultaneous first-order paths with constants k_{-1} and k_2 (each irreversible under the reaction conditions), then the measured rate constant is $k_{-1} + k_2$. Values of the experimental constants calculated from the data by the method of least squares are shown in Table I. The ratios k_2/k_{-1} in the table were obtained by an analysis of the products of the completed rearrangement with the ultraviolet spectrophotometer. It will be seen that this ratio is independent of temperature over the range studied.

TABLE I

RATE CONSTANTS FOR THE REARRANGEMENT OF THE DIENONE I

Run	Temp., °C.	Init. concn., M	10^5 $(k_{-1} + k_2)$, sec.$^{-1}$	k_2/k_{-1}	10^6k_{-1}	10^5k_2
1	75.00 ± 0.01	0.617	2.20			
2	75.00 ± .01	0.0305	1.44 ± 0.01	2.8	3.89	1.05
3	83.96 ± .01	.0249	3.56 ± .17	2.7	9.62	2.60
4	101.68 ± .01	.0305	20.7 ± .2	2.7	56.0	15.1

This conclusion was confirmed by the fact that infrared spectra of the products of rearrangement of 10% solutions at each of the temperatures studied were identical. The separate rate constants, calculated by partitioning the total rate constant, are shown in Table I. Quantities of activation calculated from these data are given in Table II.

The rate of rearrangement of the allyl ether IV to the 4-allylphenol V in diphenyl ether solution at 171.6° was measured by Tarbell and Kincaid.[6]

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[3] D. Y. Curtin and R. J. Crawford, *Chemistry and Industry*, 313 (1956). This reaction was suggested by the report of L. Claisen, F. Kremers, F. Roth and E. Tietze [*Ann.*, **442**, 210 (1925)] that the sodium salt of phenol underwent alkylation in an *o*-position when suspended in benzene and treated with allyl halides.

[4] The factors which determine whether the phenoxide ion undergoes alkylation on carbon to give dienone or on oxygen to give ether have been made the object of a more extended investigation and will be reported in a separate communication.

[5] H. Conroy and R. A. Firestone, (a) THIS JOURNAL, **75**, 2530 (1953); (b) **78**, 2290 (1956).

[6] D. S. Tarbell and J. F. Kincaid, *ibid.*, **62**, 1728 (1940).

TABLE II

QUANTITIES OF ACTIVATION FOR THE REARRANGEMENT AT 83.96° OF THE DIENONE I

Rate constant	E_a, kcal./mole	$\Delta H\ddagger$, kcal./mole	$\Delta S\ddagger$, cal./mole deg.	$\Delta F\ddagger$, kcal./mole
k_{-1}	26.8	26.1	−8.8	29.3
k_2	26.8	26.1	−7.1	

They found the reaction to be first order and quite insensitive to such changes in the reaction medium as added acetic acid or dimethylaniline or even omission of all solvent. In view of the results reported herein, it is likely that their rate constant is approximately that for the rearrangement of ether IV to dienone I, k_1.[7] In order to obtain a comparison of their data with those in this paper, the rate constant, k_{-1}, at 171.6° has been calculated by extrapolation to be 2×10^{-2} sec.$^{-1}$. In view of the aforementioned insensitivity of the rate to medium changes the extrapolation from cyclohexane used as solvent in the present work to diphenyl ether probably leads to no serious error. The rate constants together with the quantities of activation obtained by extrapolation of the present data may be compared with those of Tarbell and Kincaid. Their value for the entropy of activation was −10.1 e.u. at 171.6°. It was calculated from the Eyring equation with the assumption that $\Delta H^{\ddagger} = E_a$. A recalculation using the relationship[8] $\Delta H^{\ddagger} = E_a - RT$ gives a value of −12.1 e.u. A further correction must be applied before their value may be compared with that reported here for the reverse reaction. Their rate was the rate of rearrangement to two *o*-positions and must be corrected with a statistical factor of 2. Such a correction gives $\Delta S^{\ddagger}$ for rearrangment of the allyl ether IV to one *o*-position equal to −13.5 e.u. This is to be compared with the value of −8.5 e.u. for the reverse reaction obtained from the extrapolated values of $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$ in the present work. If interpreted literally, this difference requires that the entropy of the dienone I be lower than that of the ether IV by some 4 e.u.[9] However, in view of the possible errors in these values, it is not clear how valid such a comparison may be. It is of interest that ΔH for the process IV $\rightleftarrows$ I when calculated as $\Delta H_1^{\ddagger} - \Delta H_{-1}^{\ddagger}$ amounts to +3.5 kcal./mole as compared with the value of +7 calculated by Conroy and Firestone[5] from bond energies.

A further point of interest is the steady-state concentration of the dienone I in the rearrangement of the ether IV. From the integrated rate expression of Lowry and John[10] for two successive reversible reactions and the data discussed above, it has been calculated that the dienone concentration rises after about 100 seconds at 171° (when the reaction is 0.70% completed) to its steady state value of $10^{-3} \times$ the initial concentration of ether IV. A sample of the ether heated without solvent for 100 seconds at 172° and examined with the ultraviolet spectrophotometer contained some 0.1% dienone. Analysis of the ether used as starting material had shown 0.2% of dienone present, but a calculation of its rate of disappearance shows that the concentration of dienone remaining from that present initially would be less than 10^{-5}% at that time. It was reported by Conroy and Firestone[5a] that when the allyl ether IV was heated to 200° and treated with maleic anhydride at 100° (at which temperature it no longer rearranged), that the maleic anhydride adduct of the dienone I was obtained in small yield. Calculation of the yield from data given in the Experimental section of their paper[5b] indicates that it was 0.6% of incompletely purified product. This is in fair agreement with our value of 0.1% estimated from ultraviolet spectral data.

Experimental[11]

6-Allyl-2,6-dimethyl-2,4-cyclohexadienone (I).—A solution of 2,6-dimethylphenol (12.2 g., 0.10 mole) was treated with 5.6 g. (0.10 mole) of sodium methoxide in 300 ml. of dry benzene under a nitrogen atmosphere and the mixture distilled until the refractive index of the distillate corresponded to that of benzene (*ca.* 100 ml. of distillate). The mixture was then cooled to 15° and 30 ml. (0.38 mole) of freshly distilled allyl bromide added. After 44 hr. of stirring in a nitrogen atmosphere at 15°, the solid sodium bromide was removed by filtration and the filtrate extracted with Claisen alkali and then with water. The organic layer was dried over sodium sulfate and the benzene removed under reduced pressure to yield a yellow oil which, on distillation through a Holzmann column at 0.05 mm. pressure, gave 3.8 g. (60% based on unrecovered phenol) of dienone I, b.p. 36–37° (0.05 mm.), n^{25}_D 1.5050. The ultraviolet spectrum in cyclohexane showed λ_{max} *303 mμ, ε 4,400.* [Compare 2-acetoxy-2-methyl-3,5-cyclohexadienone[12] which has λ_{max} 292, log ε 3.6.] The infrared spectrum of a 10% solution in cyclohexane[13] showed maxima at 1663 and 1645 cm.$^{-1}$.

There was also a higher boiling neutral fraction (*ca.* 1 g., b.p. 72–73° (0.2 mm.)) which showed absorption at 1640 and 1670 cm.$^{-1}$ similar to that of the dienone I in the carbonyl region while the absorption maximum at 920 cm.$^{-1}$ was approximately double that of I. It seems likely that this material is a dienone–ether mixture formed from the reac-

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[7] ADDED IN PROOF.—It will be noted that application of the steady state approximation shows that the observed rate constant of Tarbell and Kincaid is equal to the constant $k_1 \times f$ where f is the fraction of dienone molecules which go on to 4-allylphenol rather than back to ether I. Their constant should therefore be multiplied by $1/f$ to give k_1 for their rearrangement. Unfortunately $1/f$ is unknown for their rearrangement conditions. In the present work it is 3.7/2.7 or 1.4 but previous results have suggested that it may be sensitive to changes in medium.[2] Since the correction is probably not large in any case no attempt has been made to apply one in the following comparisons of our data with those of Tarbell and Kincaid. While this paper was in press a report on the kinetics of the rearrangement of carbon-fourteen-labeled allyl 4-allyl-2,6-dimethylphenyl ether has appeared [F. Kalberer and H. Schmid, *Helv. Chim. Acta*, **40**, 13 (1957)].

[8] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., p. 97.

[9] For the calculation of the entropy change for the reaction IV $\rightleftarrows$ I the rate constant for the total rate of conversion of IV to I (*i.e.*, without the statistical correction for the two *o*-positions) has been used.

[10] T. M. Lowry and W. T. John, *J. Chem. Soc.*, **97**, 2673 (1910).

[11] Microanalyses were carried out by Mr. J. Nemeth, Mrs. K. Pih, Mrs. L. Chang, Mrs. E. Pett, Mr. R. N. Benassi and Miss C. Higham. Certain of the ultraviolet spectra were determined by Miss Gerardine Meerman. Infrared spectra were recorded by Mr. James Brader and Mrs. Louise Griffing. All melting points are corrected. The ultraviolet and infrared spectra and also detailed kinetic data are available in the Ph.D. Thesis, of Robert J. Crawford and reproduced by University Microfilms, Ann Arbor, Mich.

[12] F. Wessely and F. Sinwel, *Monatsh.*, **71**, 1055 (1950).

[13] Because of the small difference between the b.p. of the allyl ether IV, b.p. 50° (0.5 mm.), and the dienone I and because of the ease of rearrangement of I to IV, it was not possible to prepare dienone I demonstrably free from the ether IV. However, the ether IV has absorption at 837, 1097 and 1267 cm.$^{-1}$ in the infrared which is apparently absent in the dienone spectrum. Using these bands, it was possible to set an upper limit of approximately 5% on the amount of ether present in the best sample of dienone. This means that the ε (303 mμ) of 4400 could be low by that amount.

tion with allyl bromide with 4-allyl-2,6-dimethylphenol which was produced by a small amount of rearrangement of the dienone I under the reaction conditions.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.3; H, 9.0. Found: C, 83.1; H, 9.0.

Acidification of the alkaline extracts gave 7.0 g. of a phenol fraction which was estimated by infrared analysis to contain about 55% of 2,6-dimethylphenol and 44% of 4-allyl-2,6-dimethylphenol.

The maleic anhydride adduct (m.p. 139–140° uncor.) of dienone I was formed in 40% yield by heating 0.50 g. (0.0030 mole) of dienone with 0.35 g. (0.0035 mole) of maleic anhydride in a nitrogen atmosphere for 3 hr. at 100° and washing the product with ether after it solidified.

Dimerization of Dienone I.—A sample of the dienone I after 3 weeks at room temperature showed an entirely different ultraviolet and infrared spectrum and eventually crystallized. The product after recrystallization from petroleum ether melted at 92–93°. The infrared spectrum of a 10% solution in carbon tetrachloride shows weak absorption at 1638 cm.$^{-1}$ and strong bands at 1680 and 1715 cm.$^{-1}$. The ultraviolet spectrum (in cyclohexane) had a shoulder at 237 mμ, ε 5700.

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.5; H, 8.7; mol. wt., 324. Found: C, 81.9; H, 8.8; mol. wt., 320.

Hydrogenation of the dimer in ethyl acetate at room temperature with hydrogen at one atmosphere pressure and Adams platinum catalyst led to the rapid absorption of 2.95 moles of hydrogen and an additional mole over a period of 4 hr., after which no further hydrogen reacted. No attempt was made to isolate the reduced product.

When the dimer of I (0.5 g.) was heated at 150° for 3 hr. and the product distilled (only a portion was distillable), 4-allyl-2,6-dimethylphenol was formed as shown by its solubility in alkali and the identity of its infrared spectrum with that of a known sample. The dimer when heated at 120° for 8 hr. gave 64% of the phenol.

Rearrangement of Dienone I.—After 12 hr. at 135°, the product from 2 g. of dienone was added to 15 ml. of cyclohexane, extracted with Claisen alkali washed with water, dried over sodium sulfate and the solvent evaporated at room temperature. Distillation of the remaining oil gave 0.55 g. of the allyl ether IV, b.p. 63° (1.2 mm.), $n^{25}\text{D}$ 1.5045. The ultraviolet spectrum showed no absorption at 303 mμ (where the dienone has strong absorption) but instead λ_{max} 270, ε 500, in agreement with that characteristic of the allyl ether IV.

Acidification of the Claisen alkali-soluble fraction above followed by extraction with 15 ml. of cyclohexane, drying over magnesium sulfate, evaporation of the solvent and distillation of the residual oil under vacuum gave 1.0 g. of 4-allyl-2,6-dimethylphenol (V), b.p. 87° (1.8 mm.), $n^{25}\text{D}$ 1.5365 (lit.[6] b.p. 90.5° (2 mm.), $n^{25}\text{D}$ 1.5370).

Determination of the Rates of Rearrangement of the Dienone I.—Since the dienone rearranges slowly at room temperature, only freshly prepared samples could be employed. Its infrared spectrum was determined as a check on its purity. There was always a trace of the ether IV present which could be determined by its absorption at 1098 cm.$^{-1}$. The sample was diluted to the appropriate concentration and stored at −10° until used. The cyclohexane was purified by washing with cold concentrated sulfuric acid and fractionation from calcium oxide through a 30-cm. Widmer column. The first and last 10% fractions were discarded.

Pyrex tubing (6 mm. o.d.) was cut into 10-cm. lengths and soaked in a solution of chromium trioxide in sulfuric acid. The tubes were thoroughly rinsed in deionized water and dried. They were then sealed at one end, constricted at a distance of 3 cm. from the unsealed end, flushed with dry nitrogen and filled with the dienone in cyclohexane (concentrations indicated in Table I). The contents were frozen in a brine–ice mixture and the tubes sealed. The tubes were then inserted into an oil-bath thermostatically regulated to within ±0.05°. The temperature of the bath was measured with a totally immersed thermometer graduated in tenths of a degree and calibrated by the Bureau of Standards.

At the proper time intervals the samples were removed from the bath and immersed in an isopropyl alcohol–Dry Ice mixture. After completion of the reaction the tubes were brought to 20°, opened and the solutions diluted to the appropriate concentrations (*ca.* 3×10^{-4} *M*) with cyclohexane. The absorbancies at 303 mμ were determined by the use of a Cary model 11 ultraviolet recording spectrophotometer using 1.00-cm. matched cells. At this wave length ε for the dienone I is 4,400 while the ether IV has $\epsilon <$ 5 and the *p*-allylphenol V has ε 30. The infinity absorbance is thus negligible compared to the measured absorbance over the range studied.

The complete spectrum was recorded for a control tube and for the infinity tube at each temperature. The infrared spectrum of the product (10% solution in cyclohexane) of a rearrangement for ten half-lives at each temperature confirmed the product analysis with the ultraviolet spectrophotometer. The rate constants ($k_{-1} + k_2$) were evaluated from the equation

$$\ln A_0 - \ln (A) = kt$$

where A_0 = initial absorbancy and A = absorbancy at time t, using the method of least squares.[14] At each temperature the reaction was followed to greater than 60% completion, and the least squares calculation is based on measurements of twelve points.[10]

Use of the ultraviolet spectrum to calculate the composition of the product mixture is illustrated by the data for the run at 75 ± 0.01°. The absorbancy at 303 mμ was used to calculate the concentration (1.0×10^{-5} *M*) of dienone I remaining in the sample assuming that the absorbancies of ether IV and *p*-allylphenol V are negligible. The concentration of total starting material was 3.57×10^{-4} *M*. These data together with the absorbancy at 280 mμ where the dienone has ε 2200, the phenol has ε 1630 and the ether has ε 38 were used to calculate the concentrations of *p*-allylphenol (2.31×10^{-4}) and ether (1.16×10^{-4}). However, the starting material was shown to contain 0.33×10^{-4} *M* ether (from comparison of its infrared spectrum with those of authentic samples) and the ether concentration of 1.16×10^{-4} was corrected by the subtraction of this amount to yield the amount of ether formed in the reaction (0.83×10^{-4}). The ratio ether/*p*-allyl ether formed in the reaction is therefore 2.78. Values of 2.7 were obtained for reactions at each of the other temperatures employed. The individual rate constants were calculated using the assumption that the measured $k = k_{-1} + k_2$ and that k_2/k_{-1} = 2.7.

Detection of Dienone I in the Rearrangement of the Ether IV.—A sample of allyl 2,6-dimethyl ether sealed in a Pyrex tube was heated in refluxing phenetole (b.p. 172°) for 100 seconds. Samples of the product and the unheated starting solution were diluted to concentrations of 1.00×10^{-2} *M* in cyclohexane and their ultraviolet spectra determined. The absorbancy at 303 mμ showed that the unheated sample contained 0.20% of dienone I, whereas the heated sample contained 0.13%. Calculation from the rate constants ($k_{-1} + k_2$) for the rearrangement of the dienone I shows that only 1×10^{-5} % of the dienone present in the heated sample can be left from the dienone originally present.

URBANA, ILLINOIS

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[14] L. P. Hammett, "Introduction on the Study of Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, pp. 410–411.