nitrate, has no effect on the activity coefficient of the olefin in the carbon tetrachloride solution. Moreover, K_E is complicated further by the necessity of assuming that the salting out effects of silver nitrate on the two olefins are those of potassium nitrate.

The composition of an unknown mixture of trimethylethylene and cyclohexene can be evaluated directly from K_W or from K_O of the mixture, or empirically from K_D or K_E of the mixture. It is probable that a mixture of any two olefins could be analyzed by distribution measurements.

Experimental

Materials.—Trimethylethylene was obtained by the careful fractionation through a seven-foot total reflux column of the amylene prepared by heating *t*-amyl alcohol with oxalic acid[3]; b. p. 38.2–38.3° (760 mm.). The possible small amount of unsymmetrical methylethylethylene which may have been present would not have an appreciable effect on the results. Previous constants,[4] *viz.*, K_D 2165 and K_O 0.00613, are lower than those obtained here.

Cyclohexene was purified by distilling the Eastman Kodak Co. material from sodium in an atmosphere of nitrogen, b. p. 82.1–82.2° (uncor.). It gave a negative test for peroxide on adding potassium iodide, dilute sulfuric acid, and starch. Previous constants,[4] *viz.*, K_D 4305 and K_O 0.0184, are lower than those obtained here.

Carbon tetrachloride solutions approximately 1 N in trimethylethylene and cyclohexene were analyzed by bromine absorption. For making up large volumes of the mixtures the proper volume of each to give the desired composition was forced into an especially calibrated pipet[5] by nitrogen, then delivered into a suitable flask filled with nitrogen. The contents were well mixed. Each mixture was used as soon as possible after being made to avoid any change in composition resulting from evaporation.

Distributions.—All distributions were carried out in a thermostat at 25.00 ± 0.05° in an all-glass apparatus equipped with a mercury-sealed stirrer. In the distributions with water and with 1 N potassium nitrate the volume of the aqueous phase was 100 to 125 ml. and of the organic phase, 10 to 15 ml. With 1 N silver nitrate, these were 50 to 75 ml., and 10 to 15 ml., respectively. After stirring for fifteen minutes in the thermostat, the contents were allowed to stand for one hour, which was sufficient time for the phases to become perfectly clear. Samples were removed by forcing the liquid with nitrogen into calibrated pipets of the type used previously.[5] The carbon tetrachloride sample was 5 ml., and the aqueous sample 150 ml., except when silver ion was present; then 10 to 25 ml. was sufficient.

Analysis.—This was carried out as described previously.

Summary

The distribution constants of mixtures of cyclohexene and trimethylethylene between carbon tetrachloride and water (K_W), and between carbon tetrachloride and 1 N potassium nitrate solution (K_D), were determined. Also the argentation constants K_O and K_E were determined. K_W and K_O of the mixtures agree well with the calculated values while K_D and K_E are lower. This is attributed to the fact that in aqueous salt solutions one olefin increases the solubility of the other.

The composition of a mixture of trimethylethylene and cyclohexene, and probably of a mixture of any two olefins may be evaluated empirically from the distribution constant of the mixture between carbon tetrachloride and water, inert salt solution, or silver nitrate solution.

PASADENA, CALIFORNIA RECEIVED OCTOBER 19, 1942

---

[3] J. F. Norris and G. Thomson, THIS JOURNAL, **53**, 3114 (1931).

[4] S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938).

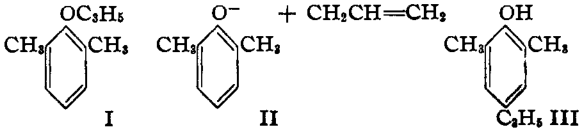
[5] W. F. Eberz and H. J. Lucas, *ibid.*, **56**, 1230 (1934).

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

The Thermal Decomposition of Quaternary Ammonium Phenolates, with Reference to the Claisen Rearrangement

BY D. STANLEY TARBELL AND JAMES R. VAUGHAN, JR.

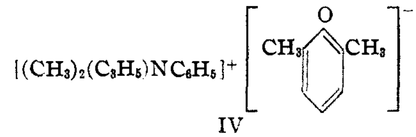
In the rearrangement of allyl aryl ethers such as I to the para position, one of the possible mechanisms involves a dissociation of the ether into a positive allyl ion and a negative phenolate ion as in II. This would be followed by a recombination in the para position, with a shift of a hydrogen atom, to yield the rearrangement product III.[1] It occurred to us that information about these ions as intermediates in the rearrangement might be obtained by a study of allyldimethylphenylammonium phenolates, such as IV. This quaternary ammonium compound



I II III

---

[1] For a summary of the evidence, *cf.* (a) Tarbell and Kincaid, THIS JOURNAL, **62**, 728 (1940); (b) Tarbell, *Chem. Rev.*, **27**, 495 (1940).



IV

when decomposed should yield the ions II. If the rearrangement of I actually involves these ions, the product of the decomposition should be 2,6-dimethyl-4-allylphenol III. The results of the present work indicate that the ions II probably are not the intermediates.

Quaternary ammonium bases derived from dimethylaniline and alkyl halides or alkyl arylsulfonates have been used to alkylate phenols in the presence of alkali[2]; this procedure is particularly useful in the preparation of codeine from morphine. The behavior of quaternary allylammonium salts such as IV, however, does not seem to have been studied.

An aqueous solution of IV was prepared by adding 2,6-dimethylphenol to a solution of allyldimethylphenylammonium hydroxide. When steam distilled, IV decomposed to give, in high yield, allyl 2,6-dimethylphenyl ether I and dimethylaniline. Both compounds were characterized by the preparation of suitable solid derivatives, and 2,6-dimethylphenol was not observed among the products. When IV was prepared in anhydrous *n*-propanol by the action of allyldimethylphenylammonium bromide on potassium 2,6-dimethylphenolate, a crystalline solid was isolated after removal of the solvent at room temperature. The product was extremely hygroscopic, and decomposed rapidly on standing; good analytical values for carbon and hydrogen were not obtained, due to its unfavorable properties, but on gentle heating at reduced pressure the compound yielded I and dimethylaniline. A sample of IV was obtained with a lower m. p., which seemed to contain more water of crystallization.

These experiments indicate that the ions II combine to give the ether I instead of its rearrangement product III, and suggest that the Claisen rearrangement does not go through the ions. It might be argued that the behavior of ions formed during the Claisen rearrangement at fairly high temperatures may be different from their behavior at the lower temperatures of the decomposition of the quaternary ammonium compounds. However, the activation energy for the combination of the ions must be quite low, and the reaction they undergo should be the same, regardless of whether they were produced at 150 or 50°.

The decomposition of the allyldimethylphenylammonium ion of IV should be a unimolecular process, according to the considerations of Ingold,[3] with the formation of dimethylaniline and a positive allyl ion as the rate-determining step. The allyl ion would then combine with the phenolate ion very rapidly to form the ether. This mechanism would give an opportunity for the allyl and phenolate ions to unite to form the allylphenol, but this is obviously not the favored mode of reaction.

Reactions were also carried out between allyldimethylphenylammonium hydroxide and phenol, as well as *p*-cresol, under several conditions. In no case was any carbon-alkylation observed when the quaternary ammonium phenolate was decomposed; the allyl ether was formed instead of the allylphenol.

The neutralization reaction between the quaternary hydroxide and phenol or *p*-cresol in aqueous solution did not seem to be complete; about 65% of the phenol or cresol was recovered unchanged unless excess sodium hydroxide was added to the solution.

Experimental

Allyldimethylphenylammonium bromide was prepared[4] in quantitative yield by mixing purified allyl bromide and dimethylaniline in equimolar amounts in dry ethyl acetate. The mixture on standing several days over calcium chloride in a vacuum desiccator deposited the product as large plates, m. p. 125–126°.

Allyldimethylphenylammonium 2,6-Dimethylphenolate: in Aqueous Solution.—The quaternary ammonium hydroxide was prepared from 24.2 g. of allyldimethylphenylammonium bromide in 300 cc. of water by treatment with a molar equivalent of freshly prepared silver oxide. The mixture was stirred until no bromide ion remained in solution, and the precipitated silver bromide was then removed by filtration. To the clear aqueous solution was added 12.2 g. of 2,6-dimethylphenol, which dissolved readily. Sodium hydroxide (2.0 g.) was added to the solution to prevent unreacted phenol from distilling, and the quaternary ammonium phenolate was decomposed by distilling the solution at atmospheric pressure. Dimethylaniline was obtained (11.1 g., 92%), and was identified through the picrate, m. p. and mixed m. p. 160–163°. Allyl 2,6-dimethylphenyl ether (12.2 g., 77%) was obtained as the other product,[5] n^{23}_{D} 1.5061. It was further

---

(2) C. F. Boehringer and Sons, German Patent 247,180 (*C. A.*, **6**, 2497 (1912)); Rodionow, *Bull. soc. chim.*, **39**, 305 (1926); **45**, 109 (1929); Hla Baw, *Quart. J. Indian Chem. Soc.*, **3**, 101 (1926) (*C. A.*, **20**, 3695 (1926)), studied the action of benzyldimethylphenylammonium chloride on phenols.

(3) Hughes, Ingold and Patel, *J. Chem. Soc.*, 526 (1933).

(4) Snyder and Speck, This Journal, **61**, 2896 (1939).

(5) Ref. 1a gives n^{25}_{D} 1.5048 for this compound.

identified by rearrangement to 2,6-dimethyl-4-allyl phenol, $n^{24}D$ 1.5376; the reported value for this compound[1a] is $n^{25}D$ 1.5370.

In *n*-Propanol Solution.—To a solution prepared from 1.17 g. of potassium and 15 cc. of *n*-propanol was added 3.06 g. of 2,6-dimethylphenol and a second solution containing 6.05 g. of allyldimethylphenylammonium bromide in 10 cc. of *n*-propanol. The precipitated potassium bromide (2.98 g., 100%) was removed by filtration and about 20 cc. of the solvent was evaporated from the filtrate at low pressure. The resulting oil was diluted with 500 cc. of dry ether and the product allowed to precipitate slowly as the ether was evaporated under diminished pressure. The white crystals of allyldimethylphenylammonium 2,6-dimethylphenolate, yield 3.95 g. (55%), were highly hygroscopic, soluble in polar solvents only and could not be recrystallized successfully. The freshly prepared crystals melted with decomposition at 85–87° but the m. p. fell rapidly after standing for several hours at room temperature. When heated at 60–85°, under 2 mm. pressure, the compound yielded dimethylaniline (74%) and allyl 2,6-dimethylphenyl ether (69%) as distillate; they were identified through the m. p. of the picrate and through the refractive index, respectively.

Anal.[6] Calcd. for $C_{19}H_{25}NO{\cdot}H_2O$: C, 75.8; H, 9.0. Found: C, 76.4; H, 9.1.

The ether filtrate from the preceding preparation deposited 1.80 g. (25%) of additional product when agitated with a stream of damp air. The second product had a lower m. p. than the first one, 68–70°, but likewise gave dimethylaniline and allyl 2,6-dimethylphenyl ether on decomposition. Water analysis by the method of Smith and Bryant[7] using acetyl chloride showed the compound to be a trihydrate rather than a monohydrate.

Anal.[6] Calcd. for $C_{19}H_{25}NO{\cdot}3H_2O$: C, 67.6; H, 9.3; H_2O, 16.0. Found: C, 66.8; H, 9.3; H_2O, 15.9.

In carrying out the water analyses, account was taken of the fact that one mole of acetyl chloride was consumed by the acetylation of the 2,6-dimethylphenolate ion, without the production of any acid. The formation of 2,6-dimethylphenyl acetate in the analysis mixture was confirmed by isolation, followed by hydrolysis of the liquid acetate to 2,6-dimethylphenol, m. p. 46–48°.

Allyldimethylphenylammonium Phenolate.—Allyldimethylphenylammonium hydroxide was prepared using silver oxide as above from 24.2 g. of the quaternary ammonium bromide. Silver bromide was obtained in 97% yield, and to the clear filtered solution were added 9.4 g. of phenol and 2.8 g. of sodium hydroxide. The quaternary ammonium phenolate could not be isolated from the solution, but when the solution was distilled as described above, dimethylaniline (90%), allyl phenyl ether (58%) and phenol (39%) were obtained. When the sodium hydroxide was omitted in this preparation, 63% of the phenol was recovered unchanged, and a correspondingly smaller amount of allyl phenyl ether was isolated. The same procedure applied to *p*-cresol yielded dimethylaniline (81%) and allyl *p*-tolyl ether (80%).

With Silver Phenolate.—Silver phenolate was prepared by adding 25.5 g. of silver nitrate to a mixture of 14.1 g. of phenol and 6.0 g. of sodium hydroxide in aqueous solution. The precipitated silver phenolate was removed and treated with an aqueous solution of 21.2 g. of allyldimethylphenylammonium bromide. The silver bromide which formed and the unreacted silver phenolate were removed by filtration, and an aliquot portion of the solution was decomposed by the usual procedure. Allyl phenyl ether (59%), dimethylaniline (81%) and phenol (19%) were obtained.

Summary

Allyldimethylphenylammonium 2,6-dimethylphenolate has been prepared and isolated in two hydrated forms. It decomposes to yield dimethylaniline and allyl 2,6-dimethylphenyl ether. The corresponding compounds from phenol and *p*-cresol also yield the allyl ethers on decomposition. This indicates that the Claisen rearrangement does not take place by cleavage of the ether into allyl and phenolate ions, followed by recombination of the ions to form the allylphenol.

ROCHESTER, NEW YORK RECEIVED NOVEMBER 18, 1942

---

[6] Analyses by R. W. King.

[7] Smith and Bryant, THIS JOURNAL, **57**, 841 (1935).