1124. *The Dehydration of Aromatic Carbinols by Acids and its Mechanistic Implications*

By A. Gandini and P. H. Plesch

Our study of the interaction of aromatic carbinols with acids showed that a fast, catalytic dehydration is followed by protonation of the resulting olefin. Therefore, no conclusions can be drawn from the fact that the carbonium ions derived from an olefin and from one of its related carbinols are identical.

It has been a common practice in studies on carbonium ions derived from olefins to conduct parallel spectroscopic investigations of the species obtained by dissolving a given olefin and one of the related carbinols in concentrated sulphuric acid. The identity of the two spectra was taken as proof of the presence of carbonium ions in the olefin solution, and it was concluded that other species (such as π-complexes) were not formed. Jordan and Treloar [1] used this argument to show that 1-phenylethyl carbonium ions were formed when styrene was dissolved in 98% sulphuric acid, since the spectrum of this solution was almost identical with that of a solution of 1-phenylethanol in the same medium. An analogous mechanistic interpretation was proposed by Grace and Symons [2] in a study of the spectra of aromatic carbonium ions obtained under similar conditions.

The object of our investigation was to obtain information on the ultraviolet (u.v.) and visible spectra of the carbonium ions derived from the carbinols, $CH_3\cdot CHPhOH$, $CH_3\cdot CPh_2OH$, $CH_2Ph\cdot CPh_2OH$, and $CHPh_2\cdot CPh_2OH$, in the presence of perchloric or sulphuric acid. This information was to be compared with evidence on the direct protonation of the corresponding olefins,[3] on the basis of the considerations expounded above.

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[1] D. O. Jordan and F. E. Treloar, *J.*, 1961, 729.

[2] J. A. Grace and M. C. R. Symons, *J.*, 1959, 958.

[3] A. Gandini, Thesis, Keele, 1964; A. Gandini and P. H. Plesch, *J.*, 1965, 4765, 4826, and unpublished results.

However, it was found that all four carbinols are very rapidly dehydrated by the acid used, and this dehydration forms the subject of this Paper; a preliminary report has been published.[4]

EXPERIMENTAL

Techniques.—All the work involving perchloric acid was carried out in the all-glass high-vacuum spectroscopic device described;[5] 1-cm. silica cells were used in all experiments; the solvent used with perchloric acid was methylene dichloride.

Solutions of the carbinol were made up under vacuum in the device; concentrations were computed from the u.v. spectra recorded before the reactions. The reactions were then started by breaking a phial containing the perchloric acid solution. Scanning could be started 20—30 sec. after the mixing of the reagents.

The experiments involving sulphuric and acetic acid were carried out in glass-stoppered test tubes without special precautions against moisture. A solution of the carbinol in acetic acid was added to a mixture of sulphuric and acetic acid (to minimise heat evolution), and the resulting mixture was quickly poured into a 1-cm. silica cell which was stoppered and placed in the spectrophotometer. About 30 sec. elapsed between the time of mixing and the beginning of the scanning.

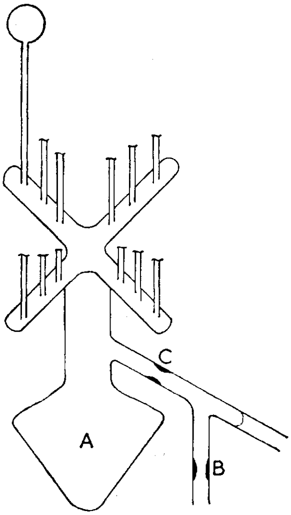

FIGURE 1. The tipping device. Phials of 1—2-ml. capacity are fused to all the vertical tubes

All the reactions described were carried out at room temperature (18—23°). Ultraviolet and visible spectra were taken with an Unicam S.P. 700 spectrophotometer.

Materials.—*Perchloric acid*. Anhydrous perchloric acid was prepared in an all-glass apparatus by Eastham and Tauber's method.[6] It was stored at liquid-nitrogen temperature under high vacuum in a microburette (accuracy $\pm 0{\cdot}003$ ml.). The preparation of methylene dichloride solutions was carried out as follows. On a separate vacuum line, a known quantity of the carefully dried solvent was vacuum distilled into flask A of the tipping device (Figure 1). The device was then sealed off at B and fused through a break-seal to the acid line. A known amount of acid was then vacuum distilled on to the frozen solvent and the device sealed off at C. The contents of flask A were allowed to melt and the solution equilibrated; the device was then turned upside down so that the acid solution ran into the phials. The phials were placed in a bath at $-95°$ and sealed off. The content of the phials was determined by the mid-point method.[7]

Very dilute acid solutions could be prepared by a similar procedure. One of the original phials was crushed magnetically under vacuum into methylene dichloride in a side-arm fused

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[4] A. Gandini and P. H. Plesch, *Proc. Chem. Soc.*, 1964, 113.

[5] A. Gandini, P. Giusti, P. H. Plesch, and P. H. Westermann, *Chem. and Ind.*, 1965, 1225.

[6] A. M. Eastham and S. J. Tauber, *J. Amer. Chem. Soc.*, 1960, **82**, 4888.

[7] P. P. Rutherford, *Chem. and Ind.*, 1962, 1614.

on to the tipping device and the new solution was distributed into the phials. We thus prepared phials with an acid content ranging from 5 × 10^{-4} to 3 mmoles.

For phials containing a relatively large quantity of acid, frequent checks were carried out by titration, whilst small quantities of acid were monitored spectroscopically with the device described,[5] by computing the population of triphenylmethyl carbonium ions generated when the phial was crushed into a methylene dichloride solution containing an excess of triphenylmethanol.

The solutions prepared by the present technique and stored at 0° in the dark were found to be stable for at least 2 years.

Acetic acid and sulphuric acid. AnalaR glacial acetic acid and AnalaR 98% sulphuric acid (B.D.H.) were used as supplied.

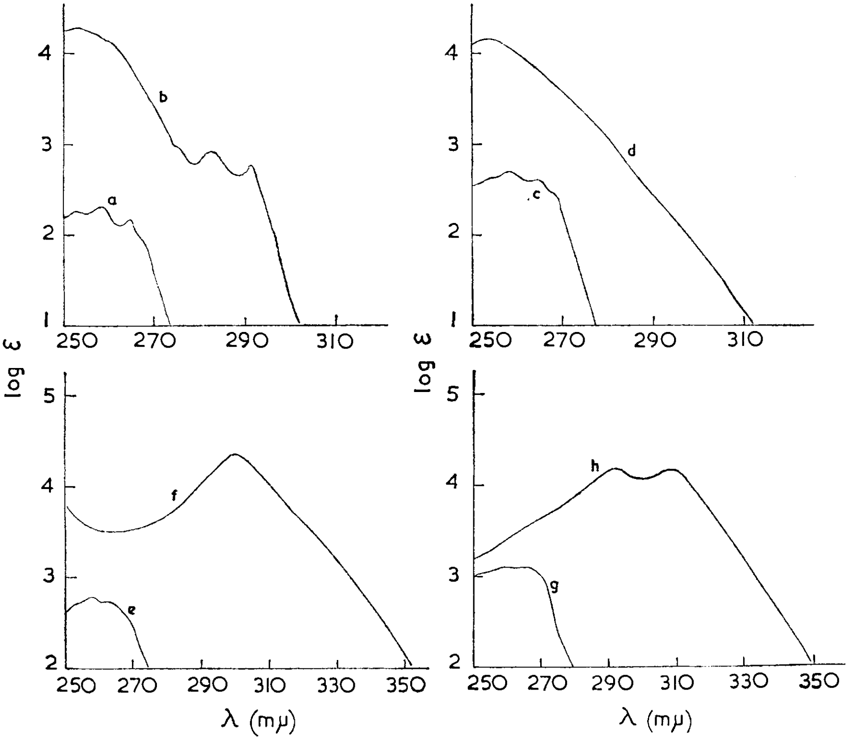

FIGURE 2. Ultraviolet spectra of carbinols and parent olefins. (a) 1-Phenylethanol. (b) Styrene. (c) 1,1-Diphenylethanol. (d) 1,1-Diphenylethylene. (e) 1,1,2-Triphenylethanol. (f) Triphenylethylene. (g) 1,1,2,2-Tetraphenylethanol. (h) Tetraphenylethylene

Methylene dichloride. This was purified, stored, and dosed as described,[8] but phosphorus pentoxide was used as drying agent instead of calcium hydride.

1-*Phenylethanol.* This compound (B.D.H.) was fractionated under high vacuum and thereafter stored under its own vapour pressure at room temperature; $n_D^{25} = 1{\cdot}5328$ (lit.,[9] $n_D^{20} = 1{\cdot}5395$); its spectrum is given in Figure 2a and in the Table.

Ultraviolet spectra of the four carbinols used (in methylene dichloride)

Compound	$\lambda_{max.}$ (mμ) ($10^{-2}\varepsilon$)			
1-Phenylethanol	253 (1·71)	258 (1·84)	265 (1·33)	(267 (~0·9)
1,1-Diphenylethanol	254 (4·07)	258 (4·85)	265 (4·00)	(268) (~2·9)
1,1,2-Triphenylethanol	253 (4·30)	258 (5·85)	264 (4·70)	(267) (~3·1)
1,1,2,2-Tetraphenylethanol		259 (12·5)	264 (12·5)	269 (8·30)

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[8] W. R. Longworth, P. H. Plesch, and M. Rigbi, *J.*, 1958, 451.

[9] " Chemistry of Carbon Compounds," ed. H. E. Rodd, Elsevier Publishing Co., Amsterdam, 1956, vol. IIIB.

1,1-*Diphenylethanol.* The commercial product (Kodak) was used without further purification; 81° (lit.,[9] 81°); the spectrum (Figure 2c, Table) agreed well with that published.[10]

1,1,2-*Triphenylethanol.* This compound was synthesised by Carter and Hey's method,[11] and recrystallised twice from light petroleum. After prolonged vacuum drying it melted at 91° (lit.,[11] 88—90°); its spectrum is given in Figure 2e and the Table.

1,1,2,2-*Tetraphenylethanol.* This compound was prepared by Banchetti's method.[12] It was washed with light petroleum and recrystallised once from cyclohexanol and once from methylene dichloride. It formed white needles, m. p. 239—240° (lit.,[12] 238—239°); the spectrum is given in Figure 2g and the Table.

As can be seen from Figure 2, the olefins under consideration have absorption bands at wavelengths where the corresponding carbinols do not absorb at all. Thus, the computation of the olefin concentration from the first spectrum scanned after the mixing of the reagents was easy and unambiguous. Good agreement was always found between the initial quantity of carbinol and the corresponding quantity of olefin produced from it by the dehydration reaction.

RESULTS

Perchloric Acid.—Reaction with 1-*phenylethanol.* When solutions of 1-phenylethanol (3—5 × 10^{-4}M) were treated with a large excess of perchloric acid (3—6 × 10^{-2}M), a yellow colour was produced, which deepened in the first minute or two after the mixing. A single peak was found in the visible region at 428—429 mμ; the rate of increase in optical density at this wavelength was recorded in two experiments and was found to be first-order overall, in good agreement with the corresponding rate of protonation found for the reaction between styrene and perchloric acid.[3] Owing to the large excess of perchloric acid, secondary reactions played an important part in this system; after having reached a maximum value, D_{428} remained constant for a few minutes, then started to decrease slowly, whilst a strong absorption band developed at *ca.* 250 mμ. However, it was possible to compute the molar extinction coefficient at the absorption maximum, $\varepsilon_{428} = (4{\cdot}0 \pm 0{\cdot}1) \times 10^3$, on the assumption that all the carbinol had been converted into the 1-phenylethyl carbonium ion. Three runs were carried out with this system.

When the carbinol (5 × 10^{-4}—2 × 10^{-3}M) was made to react with a slight excess of perchloric acid, by the time the first spectrum was taken an equivalent amount of styrene had been formed; the solution then turned faint yellow and its visible spectrum showed the presence of a broad peak centred at about 425 mμ. The styrene formed polymerised to a mixture of oligomers, as shown by the u.v. spectra frequently scanned, and by a spectrum of the material recovered after the end of the reaction. Two runs were performed under these conditions.

Finally, when the carbinol ($\approx 10^{-3}$M) was treated with small quantities of perchloric acid ($\approx 10^{-4}$M), dehydration to styrene was so fast as to be complete by the time the first spectrum was recorded. Polymerisation of the olefin followed the dehydration, but no absorption in the visible region of the spectrum could be detected under these conditions. Two runs were carried out on this system.

1,1-*Diphenylethanol.* Small quantities of perchloric acid (to give solutions approximately 10^{-4}M) were found to dehydrate rapidly (*i.e.*, within 20—30 sec.) five or ten times their amount of 1,1-diphenylethanol to 1,1-diphenylethylene. Two runs were carried out on this system.

1,1,2-*Triphenylethanol.* Two reactions were carried out with this carbinol under the conditions reported for 1,1-diphenylethanol. Again, by the time the scanning was started, all the carbinol had been dehydrated to triphenylethylene.

1,1,2,2-*Tetraphenylethanol.* Four experiments were carried out with this carbinol. The acid was 1—3 × 10^{-4}M and the ratios [carbinol]/[acid] were 0·7, 2·0, 3·5, and 7. In the first run, after the fast dehydration of the alcohol to tetraphenylethylene, a small peak slowly developed at 491 mμ; its origin will be discussed elsewhere.[3] The other three runs produced a rapid dehydration to the olefin, the reaction being complete before the scanning of the first spectrum. No colour developed in the solutions over about 24 hr.

Sulphuric Acid and 1,1,2-*Triphenylethanol.*—Several reactions were carried out between these two compounds in glacial acetic acid by the procedure described above. Addition of sulphuric acid to 10^{-5}—10^{-4}M-solutions of the carbinol, to form solutions 1—6M in sulphuric

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[10] P. Ramart-Lucas and J. Hoch, *Bull. Soc. chim. France*, 1935, **2**, 1376.

[11] P. R. Carter and P. H. Hey, *J.*, 1948, 150.

[12] A. Banchetti, *Gazzetta*, 1942, **72**, 74.

acid, resulted in a rapid and complete dehydration of the carbinol to triphenylethylene; no carbonium ions were subsequently formed, and these solutions remained colourless for about 24 hr., after which time they still exhibitied the same u.v. spectrum of the olefin. At sulphuric acid concentrations between 6 and 9M, the carbinol was again dehydrated to less than 30 sec., but the triphenylethylene formed was then slowly protonated, and the solution turned yellow-green.[2]

The visible spectrum of these solutions had two peaks: one at 430 mμ due to the carbonium ion [13] $CH_2Ph{\cdot}CPh_2^+$, the other at 660 mμ; the appearance of an absorption band around 600 mμ is typical for solutions of 1,1-diphenylethylene [2,14,15] and triphenylethylene [3] in weakly acidic media, but the origin of this band has not yet been fully elucidated. When the concentration of sulphuric acid exceeded 9M, it was almost impossible to record a spectrum of the olefin, for its protonation was then very rapid. Since the colour formation in these reactions always *followed* the dehydration, and was therefore due to some reaction between the olefin and the acid, the detailed description of these experiments and the discussion of the results will form the subject of another Paper.

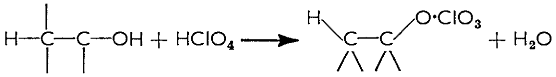
Acetic acid and 1,1,2-*Triphenylethanol*.—Solutions of 1,1,2-triphenylethanol in glacial acetic acid (5×10^{-4}—5×10^{-2}M) although apparently stable for a few days, were checked after several months' storage in stoppered bottles in the dark. Their spectra showed the presence of triphenylethylene. A $5{\cdot}1 \times 10^{-4}$M-solution was tested ten months after its preparation and showed that 50% of the carbinol had been converted into the corresponding olefin.

DISCUSSION

The above results concerning the dehydrating action of perchloric, sulphuric, and acetic acid upon the carbinols, is of considerable importance for the problems of carbonium-ion preparation. The arguments based upon the similarity of spectra obtained from acidic media containing an olefin and the corresponding carbinol, seem now untenable. In both cases one is in fact dealing ultimately with the same system (olefin + acid), and it is now obvious that similar results would be obtained.

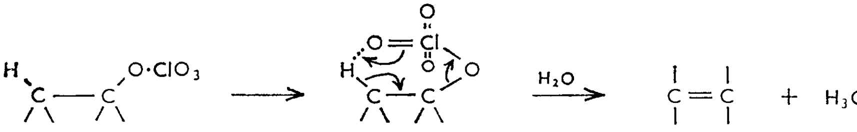
It is especially noteworthy that when the quantity of water liberated by the dehydration was greater than that of the acid, *i.e.*, when the ratio [carbinol]/[acid] exceeded unity, no carbonium ions were produced; this shows the high sensitivity of this species to even small quantities of water. Since the dehydration promoted by perchloric acid is truly catalytic, and proceeds to completion even when the ratio [carbinol]/[acid] = 10, we cannot accept the carbonium-ion mechanism proposed by La Vonne [16] for the dehydration in the systems 1,1,2-triphenyl- and 1,1,2,2-tetraphenyl-ethanol–acetic acid–perchloric acid.

Both La Vonne's and our results can be interpreted on the basis of a series of reactions involving ester molecules rather than carbonium ions, as shown below. The reactions will be written for perchloric acid, on the understanding that they apply equally well to sulphuric or acetic acid. The carbinol reacts with the acid to give the ester:



$$H{-}C{-}C{-}OH + HClO_4 \longrightarrow \underset{H}{}C{-}C{\cdot}O{\cdot}ClO_3 + H_2O$$

(When the reaction is carried out in acetic acid, as in La Vonne's work, the perchloric acid is present in the form of the ternary complex $2CH_3CO_2H,HClO_4$.[17]) The ester then undergoes a cyclic *cis*-elimination with formation of the olefin and the acid hydrate:



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[13] V. Gold and F. L. Tye, *J.*, 1952, 2172.

[14] A. G. Evans, N. Jones, P. M. S. Jones, and J. H. Thomas, *J.*, 1956, 2757.

[15] H. P. Leftin and W. K. Hall, *J. Phys. Chem.*, 1962, **66**, 1457.

[16] H. La Vonne, Ph.D. Thesis, University of St. Louis, 1957 (*Diss. Abs.*, 1958, **18**, 389).

[17] M. Usanovich and T. Sumarokova, *J. Gen. Chem.* (*U.S.S.R.*), 1947, **17**, 1415.

The acid hydrate can interact with more carbinol and thus it can catalyse further its dehydration to olefin, through the same set of reactions. There is a close similarity of mechanism between these reactions and those involved in the preparation of olefins by the Chugaev *cis*-elimination method.[18]

In view of the fact that the carbonium-ion mechanism is incompatible with our results, as discussed above, our interpretation involving an ester seems to be the most reasonable alternative. Moreover, this is supported by the evidence we have obtained for the existence of perchlorate esters, which will be presented elsewhere.[3]

Jordan and Treloar[1] have suggested that 1-phenylethanol reacts with concentrated sulphuric acid to give an oxonium ion. In our study of the interaction of this carbinol with excess of perchloric acid, no evidence for the formation of such ions could be found. As will be shown elsewhere,[3] our results concerning the protonation of styrene indicated that in both instances 1-phenylethyl carbonium ions are formed, and that the water produced by the dehydration of the carbinol is sequestered by the excess of acid present in the system, with formation of $HClO_4 \cdot H_2O$.

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[18] L. A. Chugaev, *Ber.*, 1899, **32**, 3332.