**56.** *Unstable Intermediates. Part XXVI.\* Aliphatic Carbonium Ions: Condensation with Acetic Acid.*

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Protonated mesityl oxide and related compounds are characterised by an intense absorption band in the 290 mμ region. Evidence is presented to show that, when solutions of t-butyl alcohol or isobutene in acetic acid are mixed with sulphuric acid, condensation with the solvent occurs slowly to give protonated mesityl oxide. The band at 290 mμ found under these conditions is thus a property neither of trimethyl [1] nor of alkenyl cations.

ATTEMPTS to study saturated carbonium ions such as the t-butyl cation by their ultraviolet absorption spectra have been confused by coincidences. It has been postulated, on apparently reasonable grounds, that an intense band in the 290 mμ region, which is found for solutions of various compounds in sulphuric acid under conditions favouring carbonium ion formation, is characteristic of alkyl cations and, in particular,[1] of the ion $Me_3C^+$. Although this postulate has been much quoted,[2,3] there are many reasons for caution.

Thus, it has been shown that various allylic cations have absorption bands in this region,[4,5] and such ions can well be formed by oxidation of compounds likely to form alkyl cations.[1]

In the work under consideration,[1] substrates were generally introduced into sulphuric acid as dilute solutions in acetic acid, since this technique had been found to be helpful in avoiding side reactions, such as polymerisation, which may otherwise take place during dissolution;[6] under these conditions, it was shown that no sulphur dioxide was produced.[1] If the compounds were directly dissolved in sulphuric acid, an absorption band still appeared in this region, but extinction coefficients were smaller, the bands were broader, and sulphur dioxide was formed. This result seemed to support the view that the role of the acetic acid was indeed to facilitate carbonium ion formation by suppressing side reactions, especially oxidation.

However, results obtained with di-*p*-methoxydiphenylethylene in formic acid, where it was shown conclusively that the blue product was a polyenyl ion formed by condensation with formic acid,[7] made this assumption seem less certain. Also pyrylium salts may be formed by similar processes, but under more vigorous conditions.[8]

Since this work was undertaken, the results of two pertinent studies have been reported. Deno and his co-workers [5a,c,d] have thoroughly identified certain cyclic allylic (alkenyl) cations by means of infrared and nuclear magnetic resonance spectroscopy, cryoscopy, and direct analysis. They postulate [9,5b] that the species formed when t-butyl alcohol reacts with sulphuric acid is a similar ion [possibly (I)] presumably formed according to the equation:

(I)

$$3Me_3C \cdot OH + 10H_2SO_4 \longrightarrow (I) + 2SO_2 + 8HSO_4^- + 7H_3O^+ \qquad (1)$$
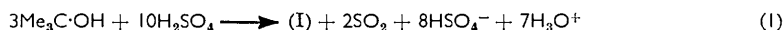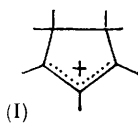
On the other hand, Olah and his co-workers,[10] using, in particular, nuclear magnetic resonance spectroscopy as a probe, have beautifully established that large concentrations of alkyl cations can be formed from tertiary alkyl fluorides and related compounds in

\* Part XXV, Atkins and Symons, *J.*, 1964, 4363.

[1] Rosenbaum and Symons, *Mol. Phys.*, 1960, **3**, 205.

[2] Mason, *Quart. Rev.*, 1961, **15**, 287.

[3] Pryce, *Ann. Rev. Phys. Chem.*, 1960, **11**, 133.

[4] Rosenbaum and Symons, *J.*, 1961, 1.

[5] Deno *et al.*, *J. Amer. Chem. Soc.*, (a) 1962, **84**, 1498; (b) p. 2016; (c) 1963, **85**, 2991; (d) p. 2998.

[6] Grace and Symons, *J.*, 1959, 958.

[7] Cookson, Rosenbaum, and Symons, *Proc. Chem. Soc.*, 1960, 353.

[8] Praill and Whitear, *J.*, 1961, 3573.

[9] Deno, Amer. Chem. Soc., 142nd Meeting, Abs. of Papers, 1962, **142**, 44Q.

[10] Olah, Tolgyesi, Moffatt, Bastein, and Baker, *J. Amer. Chem. Soc.*, 1963, **85**, 1328.

antimony pentafluoride. Their results are consistent and represent the first unambiguous physical evidence for these intermediates. Of significance to the present work is the fact that all ions other than methyl appear to have an absorption band in the 300 mμ region. The extinction coefficients are low (between 500 and 1000) compared with that for the species formed in sulphuric acetic acid (up to 6000). The workers concerned are confident that this absorption is not due to impurities,[11] and that the only species likely to be responsible for the absorption are alkyl cations.

Thus Deno's re-interpretation[9] cannot account for results reported by Rosenbaum and Symons,[1] since sulphur dioxide is a necessary product. Olah's results[10] agree qualitatively with the earlier conclusions,[1] but there is a major discrepancy in the magnitude of the extinction coefficients. The aim of the present work was to investigate any possible role of acetic acid in these reactions.

## EXPERIMENTAL

*Materials.*—98% sulphuric acid was AnalaR material. 100% acid was prepared by addition to this of redistilled dilute oleum to give minimum conductivity.[12] Acetic acid was glacial AnalaR material. Dimethyl sulphate (B.D.H.) was dried over anhydrous potassium carbonate, refluxed over roasted calcium oxide under reduced pressure, and distilled[13] through a Vigreux column under 80—90°/10—15 mm. (7·5% yield); in a 1 cm. cell, this distillate was transparent to 41,000 cm.$^{-1}$ and had $\bar{v}_{max.}$ 46,400 cm.$^{-1}$ (O.D. 1·24), $\bar{v}_{min.}$ 49,800 cm.$^{-1}$ (O.D. 0·72). This spectrum contrasts with that previously reported,[14] in which a peak at about 36,800 cm.$^{-1}$ and a minimum at 40,000 cm.$^{-1}$ were probably due to dissolved sulphur dioxide, which is a known impurity. The bulk of the material distilled above 110°/10 mm. and appeared to be dimethyl pyrosulphate.[15] In view of the low yield, commercial dimethyl sulphate was, for most purposes, neutralised with anhydrous potassium carbonate and stored over calcium oxide. Methylene chloride (May and Baker) and carbon tetrachloride (AnalaR) were shaken three times with sulphuric acid, once with dilute aqueous sodium carbonate and three times with water, and were dried over sodium sulphate.

Butyl alcohols (B.D.H.) were refluxed over anhydrous calcium sulphate and fractionally distilled. Their purity was established by measurement of their refractive indexes, and that of t-butyl alcohol by its m. p. after being degassed by repeated fusion and resolidification under reduced pressure. Di-isobutene (B.D.H.), t-butyl chloride (B.D.H.), and t-butyl acetate were shaken with anhydrous potassium carbonate and distilled. Mesityl oxide was distilled. Isobutene was prepared by the dehydration of t-butyl alcohol catalysed by Zeo-Karb 225[16] or oxalic acid dihydrate.[17] It was passed over calcium chloride granules and condensed in a cold trap; the vapour was withdrawn from the warming trap through a stopple into a Hamilton gas-tight syringe. 2,3-Dimethyl-2-butene was A.P.I. standard of 99·90 ± 0·05% purity. Other solutes were used as received, but their purity, and that of the above, were further checked by vapour phase chromatography.

*Preparation of Solutions in Sulphuric Acid.*—Solutions for conductometry were prepared by direct addition of the solutes to 100% sulphuric acid in the cell. Dilute solutions (*ca.* 10$^{-3}$ M) for spectrophotometry were prepared as follows: (i) by direct and rapid addition of sulphuric acid to the solute placed in a graduated flask; (ii) by passing the solute through an argon vapour-phase chromatograph and extracting it from the emerging dilute gaseous solution by passing this through sulphuric acid; (iii) by extraction with carbon tetrachloride; (iv) by rapid addition of sulphuric acid to a dilute solution of the solute in glacial acetic acid, with shaking; (v) by dropwise addition during 60—90 sec. of a dilute solution of the solute in glacial acetic acid to rapidly stirred and cooled sulphuric acid; (vi) by adding a dilute solution of the solute in dimethyl sulphate to rapidly stirred and cooled sulphuric acid.

Solutes were generally dispensed with a Hamilton Microliter syringe.

[11] Olah, personal communication.
[12] Arotsky and Symons, *Trans. Faraday Soc.*, 1960, **56**, 1426.
[13] Cf. Beilstein's " Handbuch der Organischen Chemie," Vol. EII, 1, p. 272.
[14] Lorenz and Samuel, *Z. phys. Chem.*, 1931, **14**, B, 228.
[15] Machinskaya, Belov, and Usov, *Zhur. obshchei Khim.*, 1947, **17**, 2295.
[16] Sussman, *Ind. Eng. Chem.*, 1946, **38**, 1230.
[17] Hurd and Spence, *J. Amer. Chem. Soc.*, 1929, **51**, 3562.

The proton magnetic resonance spectra of concentrated solutions of the solutes in glacial acetic acid, measured periodically with a Varian A60 spectrometer, were found to be unchanged; the solutions were therefore regarded as stable.

Spectra could be obtained within 2 min. of preparation only when methods (i), (iv), (v), and (vi) were used.

Method (iii) was an improvement on extraction from hexane [1] and cyclohexane [6] which, even after prolonged purification by shaking with sulphuric acid, still resulted in the appearance of rapidly growing absorption bands in the 33,000 cm.$^{-1}$ region in the acid, which would have masked those due to the products from any solute.

The most intense absorptions at 35,200 cm.$^{-1}$ were obtained by method (iv) by using 98% sulphuric acid, and 8% v/v acetic acid to give a solute concentration of 0·4 mM. Greater or smaller concentrations of acetic acid gave lower apparent extinction coefficients. If the concentration of the solute was considerably increased, or that of the acetic acid considerably decreased, the band was shifted to lower wavenumbers and, in the limit, to 33,200 cm.$^{-1}$ reached in the absence of acetic acid.

*Spectrophotometry.*—A Unicam S.P. 700 recording spectrophotometer with linear recording of optical density was used. Silica cells of such path-lengths to give optical densities in the range 0·2—1·0 were selected.

*Analysis of Solutions.*—The sulphuric acid solutions to be analysed (5 ml.) were added dropwise to 5N-sodium hydroxide (37 ml.) which was stirred and cooled internally and externally with ice. The pH was brought to about 4 and the spectra were recorded against appropriate reference solutions. A portion of each aqueous solution was extracted with hexane (B.D.H. special for spectroscopy) for spectrophotometry. The remainder was then extracted with just a little more ether than was necessary to saturate it. These extracts were carefully concentrated, and portions (10—20 $\mu$ l.) were analysed by vapour-phase chromatography.

*Conductometry.*—Resistance of solutions in stoppered Pyrex cells of accurately known cell constant (*ca.* 15) kept in a thermostat at 25 $\pm$ 0·005° were measured with a Wayne-Kerr Universal Bridge of type B.221. Because of the heat of mixing, reliable results could not be obtained within 30 min. of preparation. Measurements were made over periods of at least 48 hr. The concentration of solvent anions was estimated from the previously measured specific conductance of potassium sulphate at various concentrations in 100% sulphuric acid. At intervals, a portion of the solution was withdrawn and diluted for spectrophotometry. In another series of measurements, potassium sulphate was added initially and [HSO$_4^-$] determined from the conductance. The weighed solute was added and the conductance redetermined after 24 hr. to give the new [HSO$_4^-$]. The ratio of the increase in [HSO$_4^-$] to the solute concentration was then calculated.

## RESULTS

Results are summarised in Tables 1—4 and pertinent spectra are given in the Figure.

*Effect of Varying the Method of Dissolution.*—Our earlier work [1] was based entirely upon the principle [6] that dissolution *via* dilute solutions in acetic acid would avoid unwanted side reactions such as polymerisation or oxidation. This is only effective provided that protonation of the relevant alkene is rapid and complete. If in the solvent used there is an appreciable equilibrium concentration of unprotonated alkene, then both polymerisation and oxidation may nevertheless occur. The present results are in accord with Deno's conclusion [9] that such processes occur in sulphuric acid, but only in the absence of acetic acid. Thus, similar results were obtained by procedures (i), (ii), and (iii).

We conclude that acetic acid modifies the reaction, not because it prevents these complications as was previously supposed,[1] but because it reacts with the solute at a rate comparable with that of oxidation. Nevertheless the speed, manner, and temperature of mixing influence the structure of the $\alpha\beta$-unsaturated ketone produced. Thus, for example, mesityl oxide was obtained from t-butyl alcohol only when procedure (v)was used. Without the special precautions of this procedure, the $\alpha\beta$-unsaturated carbonyl compounds formed [Table 3, procedure (iv)] had spectra that differed from that of mesityl oxide, and they had relatively high molecular weights. Also, alkenes reacted more rapidly than alcohols when procedure (iv) was used as was originally observed,[1] and in contrast with the new results obtained by procedure (v).

High yields of $\alpha\beta$-unsaturated ketones unaccompanied by dienes were obtained only in the presence of a large excess of acetic acid.

TABLE 1.

Moles of solvent anions formed per mole of solute in 100% sulphuric acid at 25° estimated conductometrically.

| Solute | Concn. $(10^{-2}M)$ | Number of anions at | | | Spectrum (24 hr.) | |
|---|---|---|---|---|---|---|
| | | ½ hr. | 2 hr. | 24 hr. | $\bar{\nu}_{max.}$ $(10^3$ cm.$^{-1})$ | $\varepsilon$ (cm.$^2$ mole$^{-1}$) |
| Bu$^t$OH | 2·12 | 1·9 | 2·0 | 2·5 | 33·3 | 2100 |
| ,, | 4·93 | 1·8$_5$ | 2·0 | 2·5 | — | — |
| ,, | 6·06 | 2·3 | 2·8 | 3·0 | — | — |
| ,, | 8·41 | 2·1 | 2·7 | 3·0 | — | — |
| ,, | 9·41 | 1·9 | 2·4 | 2·7 | 33·4 | 2000 |
| ,, | 11·42 | 1·7$_5$ | 2·5 | 2·8 | — | — |
| ,, | 13·8 | 1·8 | 2·3 | 2·8 | — | — |
| ,, | 20·6 | 1·3 | 1·9 | 2·6 | 33·3 | 2000 |
| Average | | | | 2·7 * | | |
| 1-Me-cyclohexan-1-ol | 9·96 | 2·1 | 2·4 | 2·7$_5$ | 30·1, 31·3 | 4250 / 4150 |
| ,, ,, | 18·23 | 1·7 | 2·2 | 2·6 | 29·9, 31·3 infl. | 4600 |
| Average | | | | 2·7 | | |
| Bu$^t$Cl | 9·18 | 1·1 | 1·2 | 1·3$_5$ † | 33·4 | 1800 |
| Di-isobutene | 6·74 | 2·1 | 2·6 | 3·1 | 33·6 | 3700 |
| ,, | 7·18 | 2·4 | 2·9 | 3·4 | 33·2 | 3750 |
| ,, | 8·89 | 1·9$_5$ | 2·1 | 3·4 | 33·3 | 3650 |
| Average | | | | 3·3 ‡ | | |

* 2·7 is expected for the formation of (I). This value was unchanged by the presence of potassium sulphate up to a concentration of 0·3M in another series of experiments. † 1·7 is expected for the process: $3C_4H_9Cl + 7H_2SO_4 \longrightarrow C_{12}H_{20},H^+$ (I) $+ 2SO_2 + 4H_3O^+ + 3HCl + 5HSO_4^-$. ‡ 3·3 is expected for the process: $3C_8H_{16} + 14H_2SO_4 \longrightarrow 2C_{12}H_{20},H^+$ (I) $+ 4SO_2 + 8H_3O^+ + 10HSO_4^-$.
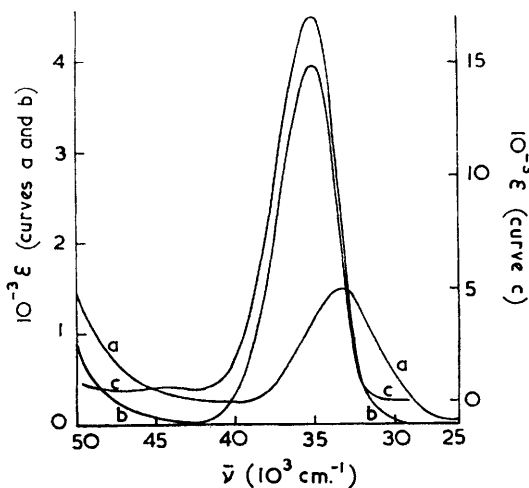
TABLE 2.

Spectrophotometry of dilute solutions not containing acetic acid.

| Solute | Method | Time (min.) after prepar. | $\bar{\nu}_{max.}$ $(10^3$ cm.$^{-1})$ | $\varepsilon$ (cm.$^2$ mole$^{-1}$) | $\Delta\bar{\nu}_{\frac{1}{2}}$ $(10^3$ cm.$^{-1})$ |
|---|---|---|---|---|---|
| Bu$^t$OH | (i) | 5—120 | 33·2 | 1600 | 5·5 |
| | | | 50·5 | 1750 | — |
| ,, | (i) * | 32 | 33·2 | 1400 | 5·0 |
| | | | 52·3 | 1300 | — |
| | | 24 hr. | 33·3 | 1700 | 5·2 |
| | | | 52·3 | 2500 | — |
| ,, | (i) † | 5—240 | 33·4 | 1400 | 4·9 |
| | | | >51 | >2100 | — |
| ,, | (i) ‡ | 2·5 | 33·2 | 1650 | 5·3 |
| | | 120 | 33·2 | 2000 | 5·2 |
| | | | 50·1 | 3000 | — |
| ,, | (ii) | 15 | 33·2 | 1200 | 5·6 |
| ,, | (iii) | ¼—360 | 33·6 | 1250 | 5·3 |
| ,, | (vi) | 2 | 31·9 | 500 | 5·0 |
| | | 16 | 33·3 | 700 | 5·5 |
| | | 180 | 33·6 | 800 | 5·3 |
| Bu$^t$Cl | (i) | 5 | 33·2 § | 800 | 5·5 |
| ,, | (i) † | 7·5—30 | 33·2 § | 1400 | *ca.* 5·2 |
| Bu$^t$OAc | (i) | 5 | 33·4 | 850 | *ca.* 5·5 |
| ,, | (i) † | 5—30 | 33·2 | 1300 | 5·1 |
| Bu$^i$OH | (i) | 5 | 33·3 | 800 | 5·5 |
| | | 24 hr. | 33·8 | 1250 | 5·8 |
| ,, | (i) † | | 33·4 | 1000 | 5·1 |
| Di-isobutene | (i) or (ii) | 10 | 33·3 | 1500 | 5·7 |
| CMe$_2$Et·OH | (i) | 5 | 33·0 | 850 | 5·0 |
| | | 15 | 33·2 | 1050 | 5·2 |
| | | 6—24 hr. | 33·6 | 1400 | 5·2 |
| 2,4,6-Me$_3$-pyrylium ClO$_4^-$ ... | (i) | | 43·7 | 4100 | 3·9 |
| | | | 35·3 | 10,200 | 3·1 |
| Mesityl oxide | (ii) | | 35·1 | ~9500 | 4·2 |
| Mesityl oxide + Bu$^t$OH | (i) | 120 | 34·8 | 16,000 + 700 | 4·8 |

Unless otherwise stated, solutions prepared in 98% sulphuric acid were *ca.* 0·3—1·5mM.

* 21 mM. † 100% sulphuric acid. ‡ 42mM in 100% sulphuric acid. § 33·6 × 10$^3$ cm.$^{-1}$ at 24 hr.

Absorption spectra of (a) t-butyl alcohol in 98% sulphuric acid prepared by method (ii); (b) t-butyl alcohol and acetic acid in 98% sulphuric acid prepared by method (v); (c) mesityl oxide in sulphuric–acetic acid.

### TABLE 3.

Spectrophotometry of dilute solutions containing acetic acid.

| Solute | Method | Time (min.) to reach 67% final intensity | $\bar{v}_{max.}$ ($10^3$ cm.$^{-1}$) | $\varepsilon$ (cm.$^2$ mole$^{-1}$) | $\Delta\bar{v}_{\frac{1}{2}}$ ($10^3$ cm.$^{-1}$) |
|---|---|---|---|---|---|
| Mesityl oxide ............... | (iv), (v) | Invariant | 35·2 | 16,500 | 4·3 |
| *Class A* | | | | | |
| Bu$^t$OH ..................... | (iv) † | 5—15 | 34·8—35·2 | 4600 | 4·3—5·2 |
| ,, ................... | (v) | 22 | 35·2 | 5200 * | 4·4 |
| Bu$^t$Cl ....................... | (iv) † | 5 | 35·2 | 4300 | 4·4 |
| Bu$^t$OAc ..................... | (iv) † | 7 | 35·1 | 4600 | 4·4 |
| Bu$^i$OH ..................... | (iv) † | 25 | 35·2 | 6400 | 4·4 |
| Isobutene ................. | (v) | 11 | 35·0 | 3600 * | 4·3 |
| Di-isobutene .............. | (iv) | <3 | 34·7 | 6800 | 5·4 |
| ,, .............. | (v) | 25 | 35·0 | 5600 | 4·9 |
| *Class B* | | | | | |
| Oct-1- + 1-2-ene ........ | (v) | ~120 | 34·0 | 4000 | 5·8 |
| (CMe$_2$·)$_2$ .................... | (iv) | <5 | 34·0 | 3200 | 5·1 |
| ,, .................... | (v) | ~30 | 33·9 | 2500 | 5·6 |

Unless otherwise stated, solutions were prepared in 98% sulphuric acid and were 0·3—1·5 mM.

* Very little absorption in the 50,000 cm.$^{-1}$ region, indicating negligible formation of SO$_2$.   † 100% sulphuric acid gave broader and less intense bands at the same frequency.

### TABLE 4.

Analysis of recovered products.

| Solutes | Method of dissoln. | $\bar{v}_{max.}$ ($10^3$ cm.$^{-1}$) water | hexane | V.P.C. retention time (min.) * |
|---|---|---|---|---|
| Mesityl oxide .................. | (i), (v) | 41·2 | 43·4 | 45 |
| *Class A* (AcOH) | | | | |
| Bu$^t$OH ..................... | (v) | 41·1 | 43·5 | 46 |
| Isobutene ................. | (v) | 40·7 | 43·3 | 46 |
| Di-isobutene .............. | (v) | 40·8 | 43·0 | 46 |
| Bu$^t$OH ..................... | (iv) | 40·4 | 42·6 | † |
| Bu$^i$OH ..................... | (iv) ‡ | 40·4 | 42·0 | † |
| *Class B* (HOAc) | | | | |
| Oct-1-ene ................. | (v) | 40·2 | 42·2 | — |
| Oct-2-ene ................. | (v) | 40·2 | 42·2 | — |
| (CMe$_2$·)$_2$ .................... | (v) | 40·3 | 41·6 | — |
| *No* AcOH | | | | |
| Bu$^t$OH ..................... | (i) | 40·7 | 41·3 | 17 § |

* On 5% w/w dinonyl phthalate, flow rate 11 ml./min., unless otherwise stated.   † Nothing emerged from the V.P.C.   ‡ In 100% sulphuric acid.   § On 20% w/w dinonyl phthalate, flow rate 18 ml./min., products not identified; Bu$^t$OH has retention time of 14·5 min.

*The Identity of the Product.*—In the foregoing, we have for convenience assumed that the product of reaction between t-butyl alcohol and acetic acid is mesityl oxide. This identification rests on the following evidence: (*a*) Mesityl oxide in sulphuric acid has $\bar{\nu}_{max.}$ 35,200 cm.$^{-1}$, $\Delta\bar{\nu}_{\frac{1}{2}}$ 4300 cm.$^{-1}$, $\varepsilon$ 16,000. The spectral band of solutions of t-butyl alcohol prepared under optimum conditions has $\bar{\nu}_{max.}$ 35,200 cm.$^{-1}$ and $\Delta\bar{\nu}_{\frac{1}{2}}$ 4300 cm.$^{-1}$. The apparent molar extinction coefficient and its rate of increase are markedly dependent on concentration, but values as high as 5200 have been observed. (*b*) The spectra in various solvents of the products of neutralization are identical with those of mesityl oxide. The marked shifts of the band when the solvent is changed are characteristic of $\alpha\beta$-unsaturated ketones and differentiate them from conjugated dienes that absorb in the same region. The concentration of recovered $\alpha\beta$-unsaturated ketone inferred from the optical density of these aqueous solutions agreed well with that inferred from the optical density of the solutions in sulphuric acid. (*c*) Vapour-phase chromatography of the concentrated ethereal extract of the product of neutralization demonstrated the presence of a compound of retention time identical with that of mesityl oxide.
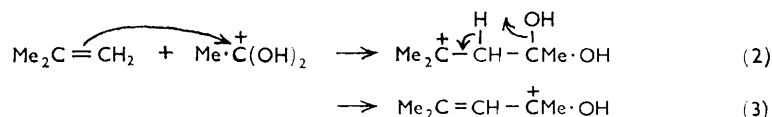
The solutions did not contain detectable concentrations of the 2,4,6-trimethylpyrylium ion known to be formed under more vigorous conditions,[8] since the optical spectrum of this ion in sulphuric acid has $\bar{\nu}_{max.}$ 43,700 and 35,300 cm.$^{-1}$, the high-energy band being near a minimum in the spectra of our solutions.

*Other Solutes.*—Compounds of Class A (Tables 3 and 4), which are all sources of isobutene, gave results similar to those obtained from t-butyl alcohol. Those of Class B in the presence of an excess of acetic acid also gave protonated $\alpha\beta$-unsaturated ketones, as shown by their optical spectra and the spectra of the recovered materials in selected neutral solvents (Table 4). However, application of Woodward's rules [18] suggests that the common product from oct-1-ene and oct-2-ene is a $\beta\beta$-disubstituted $\alpha\beta$-unsaturated ketone (cf. mesityl oxide) although an $\alpha\beta$-disubstituted product would be expected.

We have confirmed the previous observation [1] that, in the presence of an excess of acetic acid, di-isobutene gives anomalously high extinctions in sulphuric acid. This was also true of the spectra of the recovered product shown by vapour-phase chromatography to be mesityl oxide, suggesting that depolymerisation to isobutene was extensive.[1] Indeed, it seems likely that dimerization and even polymerization are reversible under our conditions and that di-isobutene should give the same products as isobutene itself. The observation that the extinction coefficient of the band at 35,200 cm.$^{-1}$ increases with dilution is in accord with this.

## DISCUSSION

*Reaction with Acetic Acid.*—The following discussion is based on the conclusion that $\alpha\beta$-unsaturated ketones are the major products of reaction when experimental procedures (iv) and (v) are used. Reactions such as the following are thought to occur:

$$Me_2C = CH_2 \ + \ Me \cdot \overset{+}{C}(OH)_2 \ \longrightarrow \ Me_2\overset{+}{C} \cdot CH - \overset{H}{\underset{}{\overset{\vert}{C}}} Me \cdot OH \qquad (2)$$

$$\longrightarrow \ Me_2C = CH - \overset{+}{C}Me \cdot OH \qquad (3)$$

We stress that this supersedes the earlier conclusions that alkyl [1] or alkenyl [5b,9] cations are the absorbing species.

However, our spectral and conductometric results for solutions prepared by direct dissolution of t-butyl alcohol, though inconclusive in themselves, are nevertheless in reasonable accord with the postulate of Deno *et al.*[9] Thus the number of $HSO_4^-$ ions per alcohol molecule required by equation (1) is 2·67, and our results give 2·7 $\pm$ 0·2. Since one carbonium ion is formed from three alcohol molecules, the apparent maximum extinction coefficient, if conversion were complete, is about 5000, which is well within the range expected for the ion (I).

*Spectra of Alkyl Cations.*—In view of these conclusions, the postulate that alkyl cations

[18] Cf. Evans and Gillam, *J.*, 1941, 815.

in sulphuric acid also absorb in this region might be considered redundant. Nevertheless, despite objections,[9] we still consider that there are sound reasons for retaining this postulate This will be discussed later.

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