328. *Co-catalysis in Friedel–Crafts Reactions. Part VIII.*[1] *The Visible Chromophores*

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Solutions of n-butenes in ethylene dichloride or methylene chloride rapidly isomerise and polymerise in the presence of large quantities of boron trifluoride and a co-catalyst. They also develop, very much more slowly, visible chromophores with peaks at approximately 380, 475, and 565 mμ; the rate of peak production is accelerated by exposure to air. Similar chromophores are developed, very much more rapidly, when solutions of butene are polymerised in the presence of sulphuric or perchloric acids in the same solvents. In all cases, the colour is discharged on neutralisation and restored by re-acidification, suggesting that the chromophores are ionic in acid solution. Evidence is presented that traces of unsaturated ketones and their acid ions are the chromophores; polyenes and their ions, which may have the necessary physical properties, do not appear to be stable in these solutions. Possible mechanisms of ketone formation are mentioned.

THE previous Paper [1] described the formation of alkenyl ions, with absorption peaks at 304 ± 2 mμ in systems containing butene, polybutene, boron trifluoride, and hydroxylic co-catalysts in ethylene dichloride. At high reagent concentrations (boron trifluoride–cocatalyst complex $\geqslant 0{\cdot}1$M, initial butene approx. 1·0M) the solutions slowly developed visible colours, with peaks at 385 ± 1, 471 ± 4, and 572 ± 3 mμ. The visible spectra closely resembled those obtained by Tauber and Eastham [2] from solutions of butene and mineral acids, and also by Allcock [3] from polybutene and boron trifluoride after exposure to air. This Paper discusses the nature of these visible chromophores.

EXPERIMENTAL AND RESULTS

Ethylene dichloride, *cis*-but-2-ene, boron trifluoride, acetic acid, and methanol were purified as described previously.[4a–c] The first three were manipulated as described by Eastham,[4a] and the co-catalysts were weighed in ampoules sealed under vacuum by the method previously given for acetic acid.[4c] Sulphuric acid was "reagent grade." The ketones were the best quality available, and the simplicity of their absorption spectra in neutral solution indicated a high degree of purity. Hexa 2,4-dien-1-ol, technical grade, distilled at 82·0—82·5°/16 mm., m. p. 18°, $n_D^{22.5}$ 1·4990, $\lambda_{max.}$ 227 mμ ($\varepsilon_{max.}$ 25,400; in MeOH). The physical properties agreed well with the published values,[5] apart from the melting point. Gas chromatography showed

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[1] Part VII, *J.*, 1965, 310.

[2] Tauber and Eastham, *J. Amer. Chem. Soc.*, 1960, **82**, 4888.

[3] Allcock, unpublished results.

[4] (*a*) Eastham, *J. Amer. Chem. Soc.*, 1956, **78**, 6040; (*b*) Clayton and Eastham, *Canad. J. Chem.*, 1961, **39**, 138; (*c*) Clayton and Eastham, *J.*, 1963, 1636.

[5] Shakelford and Schwartzman, *J. Org. Chem.*, 1962, **27**, 1047; Woods, Bolgiano, and Duggan, *J. Amer. Chem. Soc.*, 1955, **77**, 1800.

98% of the substance as a double peak, the minor component being $\leqslant$16%. Probably the two components were geometric isomers.

Solutions containing butene, boron trifluoride, and a co-catalyst (water, acetic acid, or methanol) in ethylene dichloride were prepared as before.[1] The hexadienol and the non-volatile ketones were dissolved in pure ethylene dichloride, and an appropriate quantity of the solution was pipetted into the flask. The solvent was removed, and the reagents and fresh solvent were added, all by distillation *in vacuo*. Ethylene dichloride solutions of the volatile ketones were thoroughly degassed (by consecutive freezing, pumping, and thawing) and the other reagents and more solvent distilled into the flask under vacuum, adjustments being made for the solvent already present. In systems containing both hexadienol and butene, all the organic components were distilled, thawed, mixed, and then re-frozen, before the addition of the boron trifluoride; this prevented initial local high concentrations of the alcohol in the presence of the boron trifluoride. Sulphuric acid was measured from a weight pipette and degassed in the reaction flask, and the other components of the mixture distilled on to it under vacuum. The behaviour of compounds in ethylene dichloride saturated with sulphuric acid was observed by dissolving the compound in ethylene dichloride, measuring the absorption spectrum, adding a few drops of sulphuric acid, shaking the mixture thoroughly, then observing the spectrum of the dichloride layer.

The absorption spectra were measured in quartz cells with a Carey 14 spectrometer. All the reactions were carried out at room temperature (*ca* 22°).

Product Analyses.—The solutions containing boron trifluoride were neutralised with ammonia which was added, under vacuum, in excess of the boron fluoride and acetic acid. The vessel containing the sulphuric acid system was opened and the acid neutralised with pyridine. The mixtures were washed with water, and the ethylene dichloride solutions were dried ($CaCl_2$). The water-washings of the acetic acid solution (500 ml. at pH 6) were neutralised (pH 7) with sodium hydrogen carbonate, and then extracted 4 times with a total of 150 ml. of ether. The ethereal solution was dried ($CaCl_2$).

The ketones in the neutral ethylene dichloride solutions were estimated shortly after neutralisation, and again 1 day later. The results were the same within experimental error, indicating that the ketones were formed before or during neutralisation. They were estimated as 2,4-dinitrophenylhydrazones by the method described by Lohman,[6] with the exception that they were estimated directly in the neutral ethylene dichloride solution rather than in mineral oil. The method was checked with known ketones dissolved in ethylene dichloride and the net absorbancies were found to be the same as Lohman's. The absorption spectra were measured at 300—500 mμ.

Aromatic compounds were sought in the products by use of their highly coloured charge-transfer complexes with tetracyanoethylene. The reagent (0·05M) was added in ethylene dichloride solution and the resulting absorption spectrum measured. Only increased absorption at wavelengths greater than 400 mμ was considered, because many aliphatic olefins (*e.g.*, hex-1-ene, 2,4,4-trimethylpent-1-ene) absorb at wavelengths between 350 and 400 mμ in the presence of tetracyanoethylene.

The molecular weight of the non-volatile residues (which could not be removed by evacuation, or distilled below 200°/760 mm.) were obtained by cryoscopy in benzene.

Results.—The results reported here were obtained with normal butenes only, because isobutene polymerised rapidly to an insoluble polymer in the catalyst systems used. The mixtures initially contained pure *cis*-but-2-ene but, from results already obtained,[4a,c 7a,b] it was calculated that the normal butenes isomerised within an hour to the equilibrium mixture (75% of *trans*-, 22% of *cis*-but-2-ene, and 3% of but-1-ene) and polymerised within a day to a soluble short-chain polymer in the boron trifluoride–hydroxylic co-catalyst systems; in contrast, the optical density of the solutions increased steadily for at least 50—100 days. The systems containing sulphuric acid as catalyst probably isomerised and polymerised more slowly,[2] but Tauber and Eastham found little variation in the absorption spectra between systems containing pure *cis*-but-2-ene and those containing partly isomerised mixtures. The spectrum of a solution containing initially 0·05M-*cis*-but-2-ene and 0·05M-sulphuric acid varied continuously for 44 days, after which time it contained polymer but no free butene. Thus, the chromophores

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[6] Lohman, *Analyt. Chem.*, 1958, **30**, 972.

[7] (*a*) Allcock and Eastham, *Canad. J. Chem.*, 1963, **41**, 932; (*b*) Clayton, unpublished results.

are probably formed from polybutene rather than from monomeric butene, and the choice of initial isomer is unimportant.

The acid solutions all developed three distinct peaks in the visible spectrum at 383 ± 3, 470 ± 5, and 566 ± 6 mμ, and became opaque below 300 mμ. The optical density at the 383 ± 3 mμ peak was far greater than those at the 470 ± 5 and 566 ± 6 mμ peaks in solutions containing boron trifluoride complexes; this difference was less pronounced in systems containing sulphuric and perchloric acids.

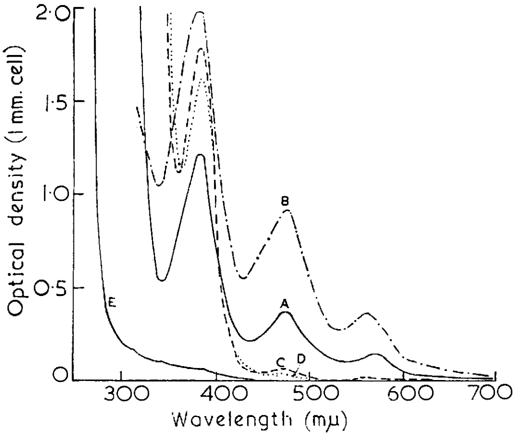
On neutralisation, the solutions became pale yellow and their spectra contained three peaks or shoulders in the ultraviolet region, and no light was transmitted below 270—300 mμ. The visible peaks reappeared instantaneously on re-acidification, indicating that the chromophores survived both neutralisation and the water-washing used to remove the original acid. Table 1 shows the position of the peaks in many acid and neutral solutions, and the Figure typical absorption spectra in such solutions.

TABLE 1

The peak maxima in acid and neutral solutions and the relative rate of growth of the 383 ± 3 mμ acid peak

	Initial concn. (mole l.$^{-1}$)				
Acid	Acid	*cis*-But-2-ene	Acid peaks $\lambda_{max.}$ (mμ)	Neutral peaks (or shoulders) $\lambda_{max.}$ (mμ)	Relative rate
$HClO_4$ ¶	0·06	0·6	380, 475, 560	—	17,000
H_2SO_4 ‡	0·05	0·05	382, 472, 570	310, 340, 380	4100
FSO_3H *	0·07	0·55	380, 475, 560	—	190
$BF_3–CH_3·CO_2H$ + air †	0·5	0·7	385, 475, 570	—	100
BF_3 + RF *	0·04	0·04 (fluoride)	380, 465	—	19
$BF_3–H_2O$	0·04	1·0	385, 467, 570	341, 380	11
$BF_3–CH_3·CO_2H$	0·5	1·0	386, 472, 572	365, 341, 385	2
$BF_3–CH_3·OH$	0·4	1·0	386, 475, 575	355, 335, 385	1

¶ Ref. 2. ‡ Heterogeneous reaction, therefore rate somewhat uncertain. * Ref. 8 (RF = fluorohexane). † Reaction contained in a tightly stoppered 250 ml. conical flask.



Typical absorption spectra developed by butene and acids in ethylene dichloride.

A, ——— H_2SO_4, 16 days; *B*, –·–·–$HClO_4$, 10 min.; *C*, – – – – BF_3CH_3COOH, 30 days; *D*, ···· BF_3H_2O, 50 days; *E*, ———, a solution initially containing H_2SO_4, after pyridine neutralisation and water washing. The concentrations are given in Table 1, the 380 mμ peak is declining in A.

The visible peaks formed much more rapidly in sulphuric and perchloric acids than in systems containing boron trifluoride and co-catalysts. To illustrate this difference, the rates of formation of the peaks at 383 ± 3 mμ are compared in Table 1, where " relative rate " = $\{t_{MeOH}[BF_3\text{–}MeOH][butene]_{MeOH}\}/\{t_{acid}\ [acid]\ [butene]_{acid}\}$, where " acid " is the mineral acid or boron trifluoride complex under consideration; the subscripts MeOH and " acid " indicate the conditions applying in the individual systems, and t is the time taken for the optical density of the 383 ± 3 mμ peak to reach a value of $1·96_{(1\ cm.)}$. The comparison is only approximate,

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[8] Chapman, unpublished results; Woolhouse, unpublished results.

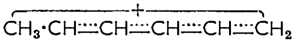
because the true rate of peak formation may depend on higher powers of [acid] and [butene] than the first; if this is so, the difference in rate between the mineral acids and the boron trifluoride complexes is even more pronounced.

The optical densities at 383 ± 3 and 470 ± 5 mμ increased at constant rates for periods of up to 120 days in solutions containing boron trifluoride and a co-catalyst; the densities at 566 ± 6 mμ were too small to be measured accurately. In mixtures containing sulphuric acid, the optical densities reached maxima and then declined; for example, a mixture containing 0·05M-sulphuric acid and 1·0M-*cis*-but-2-ene rapidly became bright yellow, but became virtually colourless after a few days. In these mixtures, the three major peaks grew and declined independently, indicating that the systems contained several chromophores. Similar results were obtained by Tauber and Eastham.[2]

The close similarity of the peak maxima shown in Table 1 indicated that all the systems developed similar chromophores, which did not, therefore, incorporate the individual catalysts in the chromophore system itself. The behaviour of the systems indicated that the chromophores did not absorb above 400 mμ in neutral solution, but on addition of acid instantly became visibly coloured, and that this change was reversible. It seemed reasonable to suppose that the absorption spectrum of each chromophore contained one major peak in acid solution; that the chromophores were moderately stable in acid solution and, if somewhat reactive, that they reacted to form colourless products.

With these limitations in mind, compounds that represented possible products were tested either in boron trifluoride co-catalyst solutions prepared under vacuum, or in ethylene dichloride saturated with sulphuric acid, *i.e.*, conditions under which butene–polybutene solutions gave visible peaks. The results were as follows: n-butenes, 2,4,4-trimethypent-1-ene, 2,5-dimethylhexa-2,4-diene and polybutene developed peaks as described above and in reference 1; hexa-2,4-dienol, which should give some dienyl ion (*A*) polymerised rapidly; linear polyenes were not available; acetaldehyde, acetone, biacetyl, acetophenone, diethyl ether, anisole, diphenyl ether, allyl ethyl ether, acetic acid, the butyl acetates, and cymene gave visually colourless solutions; vinyl acetate and the vinyl ethers gave complex spectra which varied rapidly with time;[9] furan, benzaldehyde, and *p*-benzoquinone charred in the presence of sulphuric acid giving indeterminate spectra; *trans*-stilbene, triphenylethylene, benzophenone, and 1,3-diphenylpropene developed visible peaks slowly at 420—430 mμ in the presence of sulphuric acid, but were not closely studied; unsaturated conjugated ketones (mesityl oxide, β-ionone, etc.) behaved in the manner desired, as described below.

(*A*)



$$\overbrace{\mathrm{CH_3{\cdot}CH{\cdots}CH{\cdots}CH{\cdots}CH{\cdots}CH_2}}^{+}$$

The ultraviolet spectra in neutral solution of the unsaturated ketones had one sharp absorption band. On addition of acid, this band disappeared partially or entirely and a new peak appeared at a longer wavelength, usually in the visible spectrum. This colour could be discharged by neutralisation (*e.g.*, with sodium carbonate) and regenerated by addition of sulphuric acid. Some ketones (*e.g.*, β-ionone) were not entirely stable in acid solution, but reacted to form completely colourless products, and the loss of visible colour in acid solution was paralleled by a reduction in the amount of ketone that could be recovered on neutralisation.

Table 2 lists the absorption spectra of ketones in ethylene dichloride both alone and in the presence of a large excess of the boron trifluoride–acetic acid complex; in the latter solutions, the spectra of the neutral ketones vanished entirely. An indication of the stability of the protonated ketones is also given in Table 2, as the percentage of the initial protonated ketone remaining after 18 hr., calculated from the optical density change in that time.

The 2,4-dinitrophenylhydrazones of the ketones had broad adsorption bands with peak maxima between 344 and 401 mμ; these maxima increased by *ca.* 6—7 mμ with each olefinic conjugated double bond, and by 20 mμ with each conjugated benzene ring. The long-wavelength " tail " of the peak varied markedly with both aliphatic unsaturation and the presence of aromatic rings, and a guide to the type of ketone present could be found in the density ratio (D.R.), which was defined as D.R. = optical density at 350 mμ/optical density at 460 mμ.

The values of $\lambda_{\max.}$, $\varepsilon_{\max.}$, and D.R. for the 2,4-dinitrophenylhydrazones of several ketones are listed in Table 2.

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[9] Latremouille, Merrall, and Eastham, *J. Amer. Chem. Soc.*, 1960, **82**, 120.

Traces of unsaturated ketones appear to have little effect upon a large excess of butene and boron trifluoride–acetic acid complex, and *vice versa*. β-Ionone, mesityl oxide, and 4-*p*-methoxyphenylbut-3-en-2-one were added separately, in trace quantities 4—5 × 10^{-4}M, to systems containing 1·0M-butene and 0·5M-complex in ethylene dichloride. All three became protonated immediately. The optical density of β-ionone diminished at approximately the same rate in the presence or absence of butene; the spectrum of the protonated mesityl oxide ($\lambda_{max.}$ = 280 mμ) was obscured by the rapid growth of the ultraviolet spectrum of the reacting butene/polybutene system, but neither ketone affected the rate of formation of the normal visible chromophores from polybutene. The protonated aromatic ketone reacted slowly to form traces of new peaks at 535 mμ and 600 mμ. The normal chromophores (at 386, 472, and 572 mμ) appeared at a somewhat accelerated rate and finally obscured all the other peaks in the system.

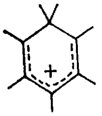
TABLE 2

The acid and neutral spectra of ketones and the spectra of their 2,4-dinitrophenylhydrazones

Ketone	$\lambda_{max.}$ (mμ) Neutral	$\lambda_{max.}$ (mμ) Acid	$10^{-3}\varepsilon_{max.}$ Acid	% remaining after 18 hr.	2,4-Dinitrophenylhydrazone $\lambda_{max.}$	2,4-Dinitrophenylhydrazone $10^{-3}\varepsilon_{max.}$	2,4-Dinitrophenylhydrazone D.R.
$Me_2C\!:\!CHCOMe$	240	280	15	100	351	21·5	11
MeCOEt	—	—	—	—	344	22·9	16·5
A.CH:CHCOMe *	245	375	15·5	67	—	—	—
B.CH:CHCOMe *	294	380	30	43	357	28·7	6
PhCO:CH·COMe	285	345	22	92·5	363	31·4	4·6
p-$MeO\cdot C_6H_4\cdot CH\!:\!CH\cdot COMe$	315	423	30	100	385	35·2	3·7
PhCH:CH·COPh	310	370	—	—	382	38·1	3·0
$Ph\cdot[CH\!:\!CH]_2\cdot COPh$	340	485	33	98	394	43·9	1·5
$(PhCH\!:\!CH)_2\cdot CO$	340	445	30	80 †	—	—	—
$(Ph[CH\cdot CH]_2)_2CO$	370	530	50	85	401	45·5	3

A = 2,6,6-trimethylcyclohex-2-enyl; B = 2,6,6-trimethylcyclohex-1-enyl.

* The chromophores from α- and β-ionone react very rapidly making their exact extinction coefficients difficult to obtain. The optical density of α-ionone solutions at 375 mμ first rises, probably during the formation of conjugated β-ionone, then declines. The optical densities of β-ionone solutions decay continuously from the initial values. The ionones may self-condense to form aromatic compounds. † This is the percentage remaining after 66 hr.



(*B*)

The Behaviour of Dienyl Ions. Cyclic dienyl ions, of type (*B*) have been reported in hydrochloric acid solutions and also in hydrogen fluoride–boron trifluoride mixtures.[10] The absorption maxima of the ions are found at approximately 400 mμ and their $\varepsilon_{max.}$ values vary from 5 × 10^3 to 20 × 10^3. Linear dienyl ions might display similar properties, and it is possible that they may be formed in traces from polybutene by hydride transfer. However, experiments with hexadienol in the presence of large quantities of butene, which are described below, suggest that dienyl ions are very unstable in the catalyst systems used, and polymerise rapidly to form weakly coloured products, which would not contribute appreciably to the final visible spectra of the systems.

Hexa-2,4-dienol, which ought to product some dienyl ions (*A*) polymerised rapidly in these systems, even at a concentration of 10^{-3}M; the resulting solution had a broad spectrum with weak peaks at 310 and 380 mμ ($\varepsilon_{max.}$ 830 and 860 with respect to the initial alcohol concentration). This behaviour is similar to that of butadiene in similar systems.[1] However, alkenyl ions with terminal alkyl groups were stable in Friedel–Crafts catalyst solutions, and butadiene reacted with excess of butene to form these ions.[1] A similar reaction was sought with hexa-2,4-dienol.

Hexa-2,4-dienol (0·6—1·5 × 10^{-3}M), when mixed with *cis*-but-2-ene (0·5M) and boron trifluoride–acetic acid (0·1M) in ethylene dichloride solution, immediately developed an intense yellow colour, the absorption spectrum of which contained one sharp major peak, $\lambda_{max.}$ 420 mμ ($\varepsilon_{max.}$ *ca.* 10^4 with respect to the initial alcohol concentration). By analogy with the reaction of the butenyl ion with butene and, having regard to the physical characteristics of the cyclic dienyl

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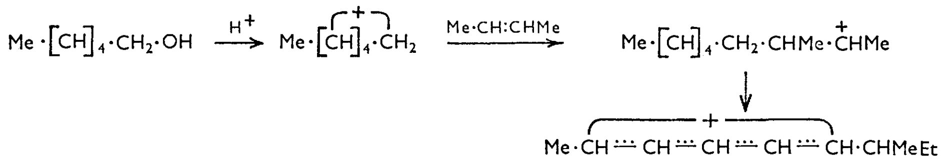
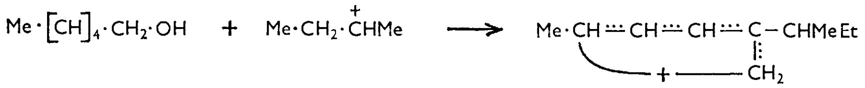
[10] Deno, *J. Amer. Chem. Soc.*, 1962, **84**, 1498, and ref. 9 of that Paper.

ions, it is reasonable to suggest that hexadienol is rapidly and almost quantitatively transformed into alkenyl ions by the reactions of the following types



or (less probably)



However, the chromophore proved to be very unstable; the optical density decreased, following the first-order rate law, and the half-life was 12—13 min. in the above solutions. The peak at 420 mμ vanished within an hour and a weak peak at 380 mμ ($\varepsilon_{\text{max.}} < 1{,}000$ with respect to the initial alcohol concentration) was visible. This peak was very similar to that obtained in polymerised solutions of sorbic alcohol, suggesting that the unstable diene had reacted to form a weakly coloured polymer.

Reaction Products.[1]—The reactions of butene with various catalysts in ethylene dichloride were followed spectroscopically for 2—4 months, the solutions were then neutralised, and the products examined.

Distillation of portions of the neutral ethylene dichloride solutions obtained from reactions initially containing boron trifluoride with water, methanol, or acetic acid as co-catalysts showed that 96, 92, and 81%, respectively, of the initial weight of butene could be recovered as non-volatile residues (b. p. >200°/760 min.); in sulphuric acid catalyst, the figure dropped to 66%. None of the solutions contained any volatile product. The molecular weights of the residues indicated that they were polymers containing, on average, 4—7 butene molecules (see Table 3). Distillation of a portion of the ether extract from the system initially containing acetic acid provided about 6% of the butene as volatile compounds (b. p. 110—118°) which were probably impure butyl acetates, and 2% more as non-volatile residue.

TABLE 3

The products of the reactions

Acid	[Acid] (mole l.$^{-1}$)	[Butene] (mole l.$^{-1}$)	Reaction time (days)	ΣOD	ΣDNPH	D.R. (DNPH)	10^3 [Ketone] (mole l.$^{-1}$)	% Butene as polymer	Mol. wt. of polymer
BF_3–CH_3·COOH	0·5	1·0	118	64	68	7	1·4—3·4	83	253
BF_3–CH_3·OH ...	0·4	1·0	66	12·3	16·4	5·4	0·3—0·8	92	410
BF_3–H_2O.........	0·04	1·0	50	11·7	10·5	5·0	0·2—0·5	96	408
H_2SO_4	0·05 *	0·05	44	7·5	30	4·8	0·6—1·5	66	297

* The reaction involving sulphuric acid was heterogeneous, and the density of the visible spectra did not increase after 15 days.

The very low recovery of butene as non-volatile residue from the mixture containing sulphuric acid was probably due to the formation of butyl esters of sulphuric acid, which would be removed from the dichloride layer in the washing process; no effort was made to recover them. Tauber and Eastham,[2] report the formation of esters in similar solutions containing perchloric acid.

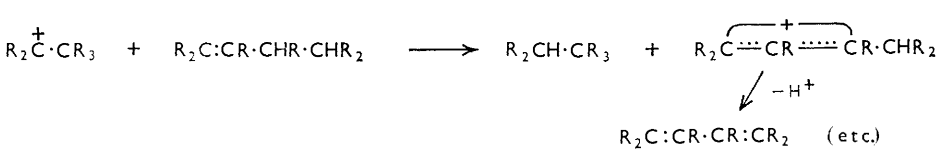
The product solutions were tested with tetracyanoethylene solution, and all failed to produce the broad, smooth peaks indicative of charge-transfer complexes. This showed that no appreciable quantity of alkylated aromatics was formed, since calibration experiments indicated that aromatics equivalent to not more than 5% of the initial butene (in the systems containing boron trifluoride) would be detected in this way.

No ketones were found in the ether extract obtained from the washings of the system containing acetic acid, which suggested that ketones of low molecular weight were not final products of the mixtures.

Ketones were detected in every ethylene dichloride solution, and the density ratios (defined for Table 2) of their 2,4-dinitrophenylhydrazones (DNPH) suggested that the ketones were aliphatic and contained on average slightly more than two olefinic bonds conjugated with the carbonyl bond. The optical density of the DNPH that would be developed by each undiluted product solution in a 1-cm. cell (ΣDNPH) was compared with the sum of the final optical densities (ΣOD) recorded in the acid solutions in a similar cell. The possible range of molarity of the total ketone concentration in the solution was calculated on the assumption that the average extinction coefficient of the 2,4-dinitrophenyl hydrazones lay between 20,000 and 50,000. This is given as the " ketone concentration " in Table 3.

DISCUSSION

The final optical densities of the acid solutions, and the major products obtained from them (Table 3) indicate that, in the presence of Friedel–Crafts catalysts, the chromophores are minor components in solutions that contain *cis*-but-2-ene initially, and polybutene and esters finally. The present evidence suggests that the chromophores are conjugated unsaturated ketones. Polyenes may form cations with absorption bands in the visible spectrum, but do not appear to be stable in the presence of Friedel–Crafts catalysts and butene. Also, if the colours were formed from polyenes of varying chain length, the mechanism of formation would depend on hydride acceptance by carbonium ions causing the unsaturation of some molecules to increase, *e.g.*,



The number of carbonium ions, and hence the rate of reaction, would increase with increasing hydrogen-donor properties of the acids ($-H_0$). Gillespie[11] quotes the following $-H_0$ values: HSO$_3$F 12·8, BF$_3$–H$_2$O 11·4, H$_2$SO$_4$ 11·0, and HF 10·2 (thus, BF$_3$ + HF may be stronger than H$_2$SO$_4$); HSO$_3$F is the strongest acid known. The rate of peak formation varies widely (Table 1) and does not follow this order; the very high rates of growth in solutions containing perchloric and sulphuric acid suggest that oxygen may be necessary for peak formation (fluorosulphonic acid is not a powerful oxidising agent). In support of this hypothesis, it was noted that the oxygen present in a tightly stoppered flask (*ca.* 230 ml. of air) was enough to increase the rate of colour formation 50-fold in a solution (20 ml.) containing 0·7M-butene and 0·5M-boron trifluoride–acetic acid complex.

Tauber and Eastham,[2] and Allcock,[3] examined the infrared spectra of their coloured solutions and found absorption corresponding to the carbonyl group. The coloured solutions analysed in the present work all contained ketones, and were shown to be reasonably stable in the presence of excess of butene and boron trifluoride complex.

The absence of large quantities of aromatic compounds in the products, coupled with the density ratios obtained for their 2,4-dinitrophenylhydrazones suggested that the ketones were aliphatic with conjugated chains of varying length, whose general formula was $R\cdot[CR'{:}CR']_n\cdot COR$, where R is any alkyl group and R′ either an alkyl group or a hydrogen atom. Such ketones of this type with $n > 2$ are not commercially obtainable, but available evidence suggests that the longer-chain compounds may have the desired absorption spectra in acid and neutral solutions. Thomas and Branch[12] studied the aromatic ketones $Ph\cdot[CH{:}CH]_n\cdot COPh$, where $n = 1$—6, and found that the positions of the absorption maxima increase approximately linearly with *n*, and may be described by the equations $\lambda_{\max.}$ (in mμ) $= 288 + 27n$ for neutral solutions and $\lambda_{\max.}$ (in mμ) $= 328 + 66n$ for acid solutions. The aliphatic ketones $CH_3\cdot[CH{:}CH]_n\cdot CO\cdot CH_3$, where $n = 1$—4, give absorption

[11] Gillespie in " Friedel–Crafts and Related Reactions," ed. Olah, Interscience, 1963, vol. I, ch. III.

[12] Thomas and Branch, *J. Amer. Chem. Soc.*, 1953, **75**, 4793.

peaks in ethanol[13] whose maxima approximate to the equation $\lambda_{\text{max.}} = 178 + 44n$. Therefore ketones of the formula $R{\cdot}[CR'{:}CR']_n{\cdot}COR$ are unlikely to give absorption spectra in neutral solution with peak maxima at wavelengths greater than 400 mμ, where $n = 1$—4. $R_2C{:}CH{\cdot}CMe{:}OH^+$ and $R_2C{:}CR{\cdot}CH{:}CH{\cdot}CMe{:}OH^+$ (as exemplified by mesityl oxide and β-ionine in solutions of boron trifluoride–acetic acid complex) absorb at 280 and 380 mμ; they are the first two compounds in a series $R{\cdot}[CR'{:}CR']CR{:}OH^+$, and the equation for the series may be $\lambda_{\text{max.}}$ (in mμ) $\simeq 190 + 95n$. If so, the absorption maxima of the protonated ketones would approximate to 285, 380, 475, and 570 mμ, which are very close to the peak maxima observed for the solutions listed in Table 1.

The optical density at the peak at 383 ± 3 mμ, where $n = 2$, was much greater than those at the peaks at longer wavelength in solutions containing boron trifluoride and a co-catalyst. Also the D.R. value indicated that the average unsaturation in these systems approximated to two olefinic double bonds per molecule. This value of the D.R. suggests that mono-unsaturated ketones (whose peaks at approximately 285 mμ would be obscured) were not present in significant quantities in the final system. If this were so, a rough correspondence between the ΣOD and ΣDNPH (Table 3) could be expected, since the extinction coefficients for protonated ketones are 1—5×10^4 and those of the DNPH's are 2—4×10^4 (Table 2). This correspondence exists in the three solutions containing boron trifluoride (Table 3). It was noted that the ketones in the mixture containing sulphuric acid tended to concentrate in the acid droplets; these would enter the ethylene dichloride solution in the neutralisation process and thus ΣDNPH was expected (and found) to be greater than ΣOD of the ethylene dichloride solution saturated with acid.

The Formation of the Ketones.—In oxidising acids, alcohol intermediates and ketones are probably formed by direct reduction of the acids; such reactions are often found when olefins are added to sulphuric acid.[14] The relatively low rate of reaction in the presence of fluorosulphonic acid reflects its poor oxidising qualities. In air, the formation of ketones may take place through peroxide intermediates. Allcock[3] found hydroperoxides gave colours very rapidly with boron trifluoride in ethylene dichloride. The formation of coloured compounds in butene–boron trifluoride–co-catalyst systems may involve the intermediate formation of traces of alcohols from carbonium ions and the OH group of the catalyst. These would normally be dehydrated to an olefin, but may occasionally react with another carbonium ion by hydride transfer, forming a saturated hydrocarbon and the acid ion from a ketone,

$$R_2CH{\cdot}OH + R_3C^+ \longrightarrow R_2C{:}\overset{+}{O}H + R_3CH$$

Such reactions are extremely rapid,[15] and can probably take place even with the minute concentrations of the reactants present in these systems.

The systems containing 1-fluorohexane and boron trifluoride apparently contained no oxygen, but the reactions to form the visible peaks were slow and accompanied by some etching of glass flasks, indicating that the reaction

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

was taking place. The reactions in these systems would then parallel those in other boron trifluoride systems.

When formed, the ketones may be destroyed by olefin addition to, or sulphonation or esterification of, their double bonds, or by condensation of the ketone group to give olefins.

Thus, the present evidence suggests that in systems containing butene, polybutene, and esters with Friedel–Crafts catalysts in inert solvents, the visible colours are formed from traces of unsaturated conjugated aliphatic ketones. These are in all probability a highly complex mixture of the general formula $R{\cdot}[CR'{:}CR']_n{\cdot}COR$, where R is any alkyl

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[13] " Organic Electronic Spectral Data," ed. Phillips and Nachod, Interscience, 1958—1959, Vol. IV.
[14] Gillespie, *Quart. Rev.*, 1954, **8**, 40.
[15] Deno, Peterson, and Saines, *Chem. Rev.*, 1960, **60**, 7.

group, R′ is an alkyl group or hydrogen atom, and $n = 2$—4. The precise identities of R and R′ are unlikely to affect the wavelengths of the peak maxima appreciably.[16] The exact composition of the mixture depends on the relative stabilities of the ketones and their precursors, which in turn will be dependent on the alkyl groups, and it is doubtful whether any useful information could be gleaned from the difficult analysis of such a mixture.

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[16] See *e.g.*, Gillam and Stern, " An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Arnold Ltd., London, 1947, 2nd edn., ch. 7, p. 107.