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## Photolysis of Phenacyl-sulphonium and -ammonium Salts

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Various phenacylsulphonium salts have been photolysed in water and in propan-2-ol-water. Most results can be rationalised in terms of homolytic reaction schemes. Phenacylammonium salts are stable to irradiation in aqueous solution but are photolysed in propan-2-ol-water.

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UNTIL recently there have been few reports on the photolysis of 'onium compounds. The photocyclisations, in water, of  $\alpha$ -dimethylamino- $\alpha$ -phenylacetophenone hydrochloride to give 2-phenylbenzofuran<sup>1</sup> and of 2-bromo-1-phenacylpyridinium bromide to give 7-hydroxybenzo[a]quinolizinium bromide<sup>2</sup> are known, but in both these cases the presence of an extra substituent (Ph or Br) was necessary for the reactions to take place. The photolyses of benzyltriphenylphosphonium chloride in benzene-ethanol, leading to benzyl radicals,3 of anilinium salts (in methanol),<sup>4</sup> of dimethylaniline (in acidic ethanol),5 and of triarylsulphonium salts (in ethanol),<sup>6</sup> leading to aryl radicals, are all thought to occur via charge-transfer mechanisms, which may not operate in aqueous solution. The recent account <sup>7</sup> of the photolysis of phenacyl- and benzyl-sulphonium salts prompts us to report our results.<sup>8</sup>

Photolysis in Aqueous Solution .- Photolysis of dimethylphenacylsulphonium bromide (I) in water for 7 hr. gave the products shown in Scheme 1 together with

 $PhCO\cdot CH_2 \cdot SMe_2 Br - \frac{h\nu}{H_2O} PhCO\cdot CH_2 \cdot CH_2 \cdot COPh$ (II) (28%) (I) For (VIII)-(XI)  $+PhCO\cdot CH_2Br + PhCOMe + PhCO_2H$ (IV) (6%) (V) (0·2%) see Table I) (11)(11%) $+Me_2S + p-BrC_6H_4 \cdot CO \cdot CH_2 \cdot CH_2 \cdot COPh$ (VI) (82%) (VII) (7%) SCHEME 1

much intractable, probably polymeric material.<sup>†</sup> The results are consistent only with a mechanism leading to phenacyl radicals. Further evidence was obtained by photolysis in the presence of vinyl acetate; 9 an increase in the rate of polymerisation of the vinyl acetate occurred. The radicals may arise in several ways:

(A) by homolysis of the C-S bond, leading to phenacyl radicals and a dimethyl sulphide radical cation.<sup>10</sup>

(B) by nucleophilic displacement of the dimethyl sulphide group on an excited phenacylsulphonium ion

 $\dagger$  The results of this experiment, reported in a preliminary communication,<sup>8</sup> have been misquoted by Maycock and Berchtold,<sup>7</sup> who stated that we isolated compound (VII) as the major product (25%)

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<sup>2</sup> A. Fozard and C. K. Bradsher, Tetrahedron Letters, 1966, 3341.

<sup>3</sup> C. E. Griffin and M. L. Kaufmann, Tetrahedron Letters, 1965, 773.

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   <sup>5</sup> (a) C. Pac and H. Sakurai, Tetrahedron Letters, 1968, 1865;
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by bromide ion, leading to excited phenacyl bromide which then undergoes homolysis.

(C) by a charge-transfer mechanism, analogous to that shown by other 'onium salts.<sup>3,4</sup>



Path (C) would be unlikely in dilute aqueous solution and was disproved by irradiation in the presence of a large excess of bromide ion, when no significant change in the rate of reaction or yield of products was apparent. This experiment also rules out path (B), although it

was found that irradiation of a suspension of phenacyl bromide in water led to all the products (except dimethyl sulphide) isolated in the photolysis of the sulphonium salt (I). In path (A), the initial homolysis, to give a phenacyl radical and a dimethyl sulphide

(I) 
$$\longrightarrow$$
 [PhCO·CH<sub>2</sub>·SMe<sub>2</sub>,Br]\*  $\longrightarrow$  PhCO·CH<sub>2</sub>·+ SMe<sub>2</sub> + ·Br  
SCHEME 4

radical cation, should be independent of the anion, although the subsequent electron transfer would depend upon the ease of oxidation of the anion.

Dimethylphenacylsulphonium salts with anions other than bromide were therefore prepared from dimethylsulphonium phenacylide 11 by addition of the appropriate acid. The results of the photolysis of these salts in

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<sup>10</sup> G. Meissner, Angew. Chem. Internat. Edn., 1966, 5, 739.

<sup>11</sup> (a) B. M. Trost, *J. Amer. Chem. Soc.*, 1967, **89**, 138; (b) A. W. Johnson and R. T. Amel, *J. Org. Chem.*, 1969, **34**, 1240; (c) K. W. Ratts and A. W. Yao, *J. Org. Chem.*, 1966, **31**, 1185.

<sup>&</sup>lt;sup>6</sup> J. W. Knapczyk and W. E. McEwen, J. Amer. Chem. Soc., 1969, **91**, 145; J. Org. Chem. 1970, **35**, 2539. <sup>7</sup> A. L. Maycock and G. A. Berchtold, J. Org. Chem., 1970,

water are shown in Table 1. The yields of products isolated in each case were similar, except in the case of the bromide, which is the only salt from which products derived from the anion were isolated. In the photolysis of the chloride (IX) and toluene-p-sulphonate (X) salts,

ative (VII) was detected. Irradiation of *trans*-dibenzoylethylene in aqueous suspension did not give rise to any products obtained from the photolysis of the sulphonium bromide (I).

In view of the results obtained by Anderson and

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Photolysis of PhCO·CH<sub>2</sub>· $\overset{+}{S}Me_2$  X<sup>-</sup> (5 mmoles) in water (400 ml.)

		Time of photolysis	Recovered	Me <sub>s</sub> S ø	PhCO·CH <sub>a</sub> ·CH <sub>a</sub> ·COPh ¢	PhCOMe a	Polvmer ª	Other products <sup>a</sup>
x		(hr.)	salt (%)	(%)	(%)	(%)	(%)	· · · · · · · · · · · · · · · · · · ·
Br-	<b>(I</b> )	7	9	82	28	6	20	(III) (11%), (VII) (7%), (V) $(0.2\%)$
Br-	(I) Þ	7	5	82	27	8	20	(III)(12.5%), (VII)(9%)
NO3-	(VIÌI)	4.5	$^{2}$	<b>78</b>	44.5	10	35	
Cl-	(IX)	6	3	88	51.5	10	<b>27</b>	
OTs-	$(\mathbf{X})$	$2 \cdot 5$	12	<b>78</b>	$52 \cdot 4$	11	25	
HSO4-	(XI)	2	13	83	47	9	20	

<sup>a</sup> Yields based on starting material reacted. <sup>b</sup> Sodium bromide (2.45 g., 24 mmoles) added.

phenacyl chloride and phenacyl toluene-p-sulphonate were shown to be absent by t.l.c. This difference is probably due to the differing ease of oxidation of the anions, bromide ion being more readily oxidised to a bromine atom, which can then react with a phenacyl radical. Concomitant with the non-production of  $\omega$ -substituted acetophenones, the salts (VIII)—(XI) gave enhanced yields of dimer and appeared to react faster. The yield of product derived from phenacyl radical and the yield of dimethyl sulphide were the same for each Reese <sup>12</sup> for the photolysis of substituted phenacyl chlorides ( $XC_6H_4$ ·CO·CH<sub>2</sub>Cl) in ethanol, when phenylacetic esters were obtained as products for X = OH or OMe, the effect of substituents in the aromatic ring on the photolysis of phenacylsulphonium salts was investigated. The results are shown in Table 2. The *p*-bromosalt (XII) gave *p*-bromophenacyl bromide as the major product, other than dimethyl sulphide, and little polymer was formed. The corresponding toluene-*p*-sulphonate (XIII), however, behaved very similarly to the unsub-

### TABLE 2

# Photolysis of p-XC<sub>6</sub>H<sub>4</sub>·CO·CH<sub>2</sub>·SMe<sub>2</sub>Y<sup>-</sup> (5 mmoles) in water (400 ml.) Products: (A) p-XC<sub>6</sub>H<sub>4</sub>·CO·CH<sub>2</sub>Y, (B) p-XC<sub>6</sub>H<sub>4</sub>·COMe, (C) (p-XC<sub>6</sub>H<sub>4</sub>·CO·CH<sub>2</sub>)<sub>2</sub>, (D) p-XC<sub>6</sub>H<sub>4</sub>·CO·CH<sub>2</sub>·OH, and (E) p-XC<sub>6</sub>H<sub>4</sub>·CO<sub>2</sub>H.

Compound	x	۰Y	Time of photolysis (hr.)	Unchanged salt (%)	(A) (%)	(B) (%)	(C) (%)	(D) (%)	(E) (%)	$\frac{Me_2S}{(\%)}$	Polymer (%)
(I) <i>a</i>	н	$\mathbf{Br}$	7	9	11	5	<b>28</b>	0	0	82	20
(XÌI) •	$\mathbf{Br}$	$\mathbf{Br}$	4.5	<b>25</b>	61	3	13	<b>2</b>	0	100	4
(XIII)	$\mathbf{Br}$	OTs	$2 \cdot 5$	9	0	6	51	1	0	82	10
(XIV) «	OMe	$\mathbf{Br}$	4	9	6	14	36	10	5	b	15
(XIX) °	$\mathbf{Ph}$	$\mathbf{Br}$	6.5	35	1.5	19	3	0	0	b	е
(XIX) ª	$\mathbf{Ph}$	$\mathbf{Br}$	5	27	4.5	31	7	0	0	b	е

• These results are each an average for two or more experiments under identical conditions. • The estimated yield of dimethyl sulphide by titration gave values > 100%. • Water (600 ml.) used because of the low solubility of (XIX). • A solution of compound (XIX) (2.5 mmoles) in water (400 ml.) was irradiated through a quartz filter. • A large amount of polymer was formed.

salt, indicating that they decompose by the same mechanism. Only mechanism (A) accounts satisfactorily for these results. The formation of the *p*-bromodibenzoylethane (VII) from the bromide (I) probably occurs by radical substitution of 1,2-dibenzoylethane (II), although we did not isolate the corresponding ortho- and meta-isomers. It might be expected that bromination  $\alpha$  to the carbonyl group would be preferred, but 1,2-dibenzoyl-1-bromoethane was shown to be absent from the products. Photolysis of an aqueous suspension of 1,2-dibenzoyl-1-bromoethane gave mainly trans-dibenzoylethylene, which was not detected in the products of photolysis of compound (I). A small amount of dibenzoylethane (II) was isolated but no *p*-bromo-derivstituted salt (X), the major product being the substituted 1,2-dibenzoylethane. Although a radical mechanism must operate for compound (XIII), the different results for compound (XII) indicate that an alternative mechanism, perhaps an excited  $S_N 2$  displacement by Br<sup>-</sup> may occur in this case.

Irradiation of p-methoxyphenacyldimethylsulphonium bromide (XIV) led to the substituted 1,2-dibenzoylethane (XV) as the major product (36%), but a small amount of a rearrangement product, p-methoxyphenylacetic acid (XVI) (5%) besides p-methoxyphenacyl alcohol (XVII) (10%) was formed. Whereas compound (XV) must arise from a homolytic process, the formation <sup>12</sup> J. C. Anderson and C. B. Reese, *Tetrahedron Letters*, 1962, 1. of the acid (XVI) and the alcohol (XVII) is best explained by a heterolytic mechanism, the p-methoxy-group stabilising the resultant cation.

Hill<sup>13</sup> and Nozaki<sup>14</sup> have found, in contrast to the foregoing results and those of Anderson,<sup>12</sup> that photolysis of p-methoxyphenacyl p-tolyl sulphide and p-methoxyphenacyl methyl sulphoxide in alcoholic solution led only to p-methoxyacetophenone. In the former case





p-tolyl disulphide was also obtained, indicating that a homolytic mechanism operated. It therefore seems likely that photolysis of p-methoxyphenacyl compounds  $(Me \cdot C_6 H_4 \cdot CO \cdot CH_2 X)$  leads exclusively to p-methoxyphenacyl radicals when X = SR or S-OMe but can lead to p-methoxyphenacyl carbonium ions, besides radicals, when good leaving groups ( $X = \overline{S}Me_2$  or Cl) are present.

Photolysis of p-phenylphenacylsulphonium bromide (XIX) in water gave p-phenylacetophenone as the major identified product. It is difficult to account for this; possibly the p-phenyl group may destabilise the resultant phenacyl radical and thus enhance its reactivity to hydrogen atoms or electron donors, thereby reducing dimerisation. Alternatively, it may undergo a cyclic ' type II' mechanism, similar to that postulated for the photolysis of phenacyl sulphides, 9c, 15 ethers, 16 and amines,<sup>17</sup> although it is difficult to see how the p-phenyl group should favour this reaction. Further evidence

<sup>13</sup> J. Hill, unpublished results, reported at a conference on organic photochemistry, University of Salford, July 1968. These results are also quoted by E. Block in *Quart. Reports* Sulphur Chem., 1969, **4** (4). <sup>14</sup> T. Shirafuji, J. Yamamoto, and H. Nozaki, Tetrahedron Letters, 1969, 4097.

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for some anomalous behaviour of salts (XIV) and (XIX) was apparent from the fact that we were unable to obtain accurate estimates of the yield of dimethyl sulphide in these cases, since the oxidation method of determination gave values greater than theoretical, indicating that other volatile reductant(s) accompanied the sulphide.

Substituents in the aromatic ring of phenyl ketones are known to cause a change in the lowest excited state from  $n-\pi^*$  to  $\pi-\pi^*$ ,<sup>18</sup> although in some cases the  $\pi-\pi^*$ state may be moderately reactive because it retains some  $n-\pi^*$  character.<sup>19</sup> To ascertain whether a change in excited state caused a change in the mechanism of decomposition of the substituted phenacylsulphonium salts, dimethyl- $\alpha$ - and - $\beta$ -naphthoylmethylsulphonium bromides [(XX) and (XXI)], which should have lowest excited states of  $\pi - \pi^*$  character, were irradiated. Little decomposition had occurred, however, after 7 hr., and much starting material was recovered. The nature of the excited state apparently has a considerable effect on the rate of the photochemical reaction of sulphonium salts. Photolysis of the tetrafluoroborate analogues of compounds (I) and (XXI) in methanol is reported to give the corresponding methyl ketones, but the naphthalene salt apparently reacted appreciably slower.<sup>7</sup>



When trimethylphenacylammonium bromide and phenacylpyridinium bromide were irradiated in aqueous solution, no decomposition of the salts occurred. Irradiation of the ammonium salt with use of a quartz filter sleeve instead of Pyrex also failed to cause decomposition. These results are consistent with the higher bond strength of C-N as compared with C-S,<sup>20</sup> and the generally higher reactivity of sulphonium compounds when compared with ammonium compounds.<sup>21</sup>

Photolysis in Aqueous Propan-2-ol.-When the sulphonium salt (I) was irradiated in propan-2-ol-water (9:1), only acetophenone (7.5%) and its further reduction products, a mixture of  $(\pm)$ - and meso-acetophenone pinacols (65%), were isolated. Trimethylphenacylammonium bromide (XXII) reacted readily in aqueous propan-2-ol (19:1), undergoing cleavage of the C-N

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 <sup>18</sup> (a) D. R. Kearns and W. A. Case, J. Amer. Chem. Soc., 1966, 88, 5087; (b) E. J. Baum, J. K. S. Wan, and J. N. Pitts, jun., J. Amer. Chem. Soc., 1966, 88, 2652; (c) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. L. Dusenbery, J. Amer. Chem. Soc., 1967, 89, 5466.
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<sup>20</sup> T. L. Cottrell, 'The Strengths of Chemical Bonds,' Butterworths, 1958.

<sup>21</sup> G. L. Walcott, M.Sc. Thesis, University of London, 1965.

bond, leading to acetophenone and also giving the reduction product (XXIII) (19%). In view of the stability of compound (XXII) to irradiation in aqueous solution and the absence of dibenzoylethane in the products, it is unlikely that initial C-N homolysis occurs. The most likely mechanism of formation of the products is by initial abstraction of the  $\alpha$ -hydrogen atom of propan-2-ol, leading to the semipinacol radical ion (XXIV), which



SCHEME 6

can then either decompose to acetophenone \* or abstract another hydrogen atom from propan-2-ol. Dimerisation of the radical ion (XXIV) to give the diol (XXV) would be unfavourable because it necessitates the close proximity of two positively charged 'onium groups. The sulphonium salt (I) probably also reacts by this mechanism, the semipinacol radical ion analogous to (XXIV) undergoing ready cleavage of the C-S bond, which is significantly weaker than the C-N bond, rather than abstracting another hydrogen to give a reduced salt. The absence of dibenzoylethane indicates that the homolysis observed in aqueous solution does not occur in the aqueous propan-2-ol: this suggestion is supported

\* Semipinacol radicals derived from 2-phenoxyacetophenones have been shown to yield acetophenone exclusively.<sup>22</sup>

by results from the photolysis of diphenacylammonium salts (see later).

The photolysis of dimethyldiphenacylammonium bromide (XXVI) was investigated to see whether the close proximity of the carbonyl groups would cause formation of the cyclic pinacol (XXVII) or products derived from Photolysis in propan-2-ol-water (19:1), however, it. led only to products of cleavage of the C-N bond, *i.e.* acetophenone (46%), 1-2-dibenzoylethane (16%), and phenacyldimethylamine hydrobromide (90%). Although the expected photoreduction did not occur, these results are of interest since dibenzoylethane (II) was isolated when two phenacyl groups were incorporated in the ammonium salt, whereas when only one phenacyl group was present, dibenzoylethane was absent from the products. The possibility that this product might be formed by an intramolecular rearrangement was tested by irradiating the unsymmetrical salt (XXVIII). The products were bis-p-bromobenzoylethane (3%), p-bromoacetophenone (25%), and phenacyldimethylamine hydrobromide (66%), but no p-bromodibenzoylethane (VII) was detected, and the intramolecular rearrangement reaction path was thus eliminated. The diphenacyl salts (XXVI) and (XXVIII) appear to decompose by a homolytic mechanism leading to phenacyl and p-bromophenacyl radicals, respectively, which give rise to the dimers. This result rules out the direct homolysis of the sulphonium salt (I) to phenacyl radicals in aqueous propan-2-ol, since this should also give 1,2-dibenzovlethane, which was not detected (see before).

In agreement with the results of Maycock and Berchtold,<sup>7</sup> we have found that irradiation of benzyldimethylsulphonium bromide in water formed benzyl alcohol (56%), bibenzyl (34%), benzyl bromide (1%), and a trace of toluene. Although bibenzyl presumably arose by dimerisation of benzyl radicals, benzyl alcohol is more likely to be formed from the benzyl carbonium ion. It has been stated <sup>7</sup> that whereas benzyl salts undergo photochemical homolysis and heterolysis, phenacyl salts appear to undergo homolysis only. An important factor opposing heterolysis in the latter case is that in the resulting phenacyl carbonium ion, the benzoyl group cannot effectively delocalise the charge. Strongly electron-releasing groups may facilitate the heterolysis through formation of the spiro-intermediate (XVIII).<sup>12</sup>

### EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 237 spectrophotometer for Nujol mulls or thin films. U.v. spectra were recorded with a Unicam SP 800 spectrophotometer; n.m.r. spectra with a JEOL C60H instrument, and mass spectra with an A.E.I. MS 902 instrument. G.l.c. was carried out with a Varian Aerograph A90P model (10% Ucon 2000 on Chromosorb W column). M.p.s were recorded with a Kofler hot-stage apparatus. Merck silica gel HF<sub>254</sub> was used for t.l.c. and preparative layer chromatography (p.l.c.). For p.l.c., plates ( $40 \times 20$  cm.) coated with a 1 mm. layer of silica gel were used, with benzene or

<sup>22</sup> Y. Saburi, T. Yoshimoto, and K. Minami, J. Chem. Soc. Japan, Pure Chem. Sect., 1969, **90**, 587 and previous papers.

benzene-ethyl acetate as eluant. The bands were located under a u.v. lamp.

In all photochemical experiments, ' dark' reactions were carried out. However, no decomposition of any of the compounds occurred and starting materials were recovered in all cases. Unless spectral details are given, products were identified by comparison (i.r. spectrum, t.l.c., m.p.) with samples prepared by standard methods.

Phenacyl Bromides and a-Bromoacetonaphthones.-Substituted acetophenones and acetonaphthones were brominated by the method of Schevchuk.23

Phenacyl Alcohols.-The phenacyl bromides were converted into the acetates, which were hydrolysed with barium carbonate 24 or dilute sulphuric acid.25

Phenacyl Toluene-p-sulphonate.-Silver toluene-p-sulphonate  $(0.5 \text{ g}.)^{26}$  and phenacyl bromide (0.4 g.) were each dissolved in the minimum quantity of acetonitrile, and the solutions were mixed and heated to 50°. The precipitate of silver bromide was filtered off and washed with acetone, the washings being combined with the filtrate and evaporated. The resultant solid was dissolved in acetone, filtered to remove excess of silver toluenesulphonate, and evaporated. The product (0.2 g., 30%) had m.p.  $95^{\circ}$  (from light petroleum) (Found: C, 61·45; H, 5·15; S, 10·85. C<sub>15</sub>H<sub>13</sub>SO<sub>4</sub> requires C, 62·05; H, 4·85; S, 11·05%),  $\nu_{max}$ . 1720 cm.<sup>-1</sup> (C=O),  $\tau$  (CDCl<sub>3</sub>) 2.5 (9H, m), 4.76 (2H, s), and 7.57 (3H, s).

p-Bromophenacyl Toluene-p-sulphonate. This was prepared according to the foregoing procedure in 60% yield; m.p. 129° (lit.,<sup>27</sup> 127.5-129°).

Dibenzoylethylenes. A Friedel-Crafts reaction of benzene with fumaroyl chloride (method of Lutz 28) gave the transisomer, irradiation of which in ethanol<sup>29</sup> gave the cisisomer.

1,2-Dibenzoylethane (II).-trans-Dibenzoylethylene was reduced with tin(II) chloride according to the method of Bailey.30

1,2-Dibenzoyl-1-bromoethane.-1,2-Dibenzoylethane was treated with bromine (1 mol.) in acetic acid solution.<sup>31</sup>

1,2-Dibenzoyl-1,2-dibromoethane.—Bromine (1.6 g., 10 mmoles) was added to a solution of 1,2-dibenzoylethane (1.19 g., 5 mmoles) in acetic acid (200 ml.) at  $40^{\circ}$ . When the solution had become decolourised, water (500 ml.) was added, and the product was extracted into chloroform. The extracts were washed with water, dried, and evaporated, and the resultant solid was recrystallised from propan-2-ol; m.p. 179-182° (lit.,<sup>32</sup> 179-182°).

p-Methoxyphenylacetic Acid (XVI).-The acid was prepared by a Willgerodt reaction from p-methoxyacetophenone in 25% yield, m.p. 77-79° (lit.,<sup>33</sup> 83-84°).

Acetophenone Pinacol.<sup>34</sup>—A solution of acetophenone (25 g.) in propan-2-ol (400 ml.) was irradiated for 20 hr. and then evaporated to give an oil which crystallised slowly. Re-

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<sup>31</sup> C. Paal and H. Schulze, Ber., 1902, 35, 168.

crystallisation from light petroleum gave the  $(\pm)$ -acetophenone pinacol, m.p. 125° (5 g., 20%) (lit., 35 122-123°). The mother liquors were evaporated and the residue was crystallised from cyclohexane to give the meso-isomer, m.p. 116° (7 g., 28%) (lit.,<sup>35</sup> 117-118°).

Sulphonium Bromides. The appropriate  $\alpha$ -bromo-ketone (0.25 mole) was dissolved in chloroform, a slight excess of dimethyl sulphide (16 g., 0.27 mole) was added, and the mixture was set aside overnight at room temperature. The sulphonium bromide was filtered off and recrystallized from ethanol or propan-2-ol. Yields were usually 80-90%. The following were prepared: dimethylphenacylsulphonium bromide (I), m.p. 149° (lit., 36 148°); p-bromophenacyldimethylsulphonium bromide (XII), m.p. 133° (lit.,<sup>37</sup> 134-135°); dimethyl-p-phenylphenacyl bromide (XIX), m.p. 147-148° (lit., 38 148°); p-methoxyphenacyldimethylsulphonium bromide (XIV), m.p. 127-128° (Found: C, 45.3; H, 5.05; Br, 27.3. C<sub>11</sub>H<sub>15</sub>BrO<sub>2</sub>S requires C, 45.3; H, 5.2; Br, 27.4%);dimethyl-a-naphthoylmethylsulphonium bromide (XX), m.p. 123-124° (Found: C, 53.9; H, 4.75; Br, 25.7.  $C_{14}H_{15}BrOS$  requires C, 54.0; H, 4.85; Br, 25.7%); dimethyl-\beta-naphthoylmethylsulphonium bromide (XXI), m.p. 128-129° (Found: C, 52.4; H, 5.15; Br, 24.3. C<sub>14</sub>H<sub>15</sub>-BrOS, H<sub>2</sub>O requires C, 52·3; H, 5·2; Br, 24·2%).

Conversion of Sulphonium Bromides into Salts of Other Anions.—The sulphonium bromide was converted into the phenacylide in quantitative yield by treatment with aqueous sodium hydroxide.<sup>11</sup> To a solution of the ylide in chloroform, 1 equiv. of the appropriate acid (HX) was added, together with enough propan-2-ol to make the solution homogeneous. Crystals of the sulphonium salt were deposited in quantitative yield. The following salts were prepared: dimethylphenacylsulphonium chloride (IX), m.p. 139-140° (lit.,<sup>39</sup>139°); dimethylphenacylsulphonium nitrate (VIII) m.p. 123-124° (Found: C, 49.3; H, 5.6; N, 5.55; S, 13.0. C<sub>10</sub>H<sub>13</sub>NO<sub>4</sub>S requires C, 49·3; H, 5·4; N, 5·75; S, 13·2%); dimethylphenacylsulphonium hydrogen sulphate (XI), m.p. 128-129° (Found: C, 43.3; H, 4.9; S, 22.9. C10H14O5S2 requires C, 43.4; H, 5.05; S, 23.1%); dimethylphenacylsulphonium toluene-p-sulphonate (X), m.p. 194-195° (Found: C, 57.8; H, 5.65; S, 17.8.  $C_{17}H_{20}O_4S_2$  requires C, 57.9; H, 5.7; S, 18.2%); p-bromophenacyldimethylsulphonium toluene-p-sulphonate (XIII), m.p. 158-160°. (Found: C, 47.35; H, 4.35; Br, 18.6. C<sub>17</sub>H<sub>19</sub>BrO<sub>4</sub>S<sub>2</sub> requires C, 47.3; H, 4.45; Br, 18.5%).

Trimethylphenacylammonium bromide (XXII) was prepared from trimethylamine and phenacyl bromide in 70% yield; m.p. 213-214° (lit.,40 207°).

Phenacylpyridinium bromide was prepared from pyridine and phenacyl bromide in 85% yield; m.p. 198-200° (lit.,41  $199-200^{\circ}$ ).

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<sup>37</sup> T. Hashimoto, H. Kitano, and K. Fukui, J. Chem. Soc. Japan, 1968, 89, 83. <sup>38</sup> R. W. Bost and H. C. Schulze, J. Amer. Chem. Soc., 1942,

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40 H. Bohme and W. Krause, Chem. Ber., 1951, 84, 170.

<sup>41</sup> J. W. Baker, J. Chem. Soc., 1932, 1148.

Dimethyl(phenacyl)amine Hydrobromide.-Phenacyl bromide (10 g., 50 mmoles) was dissolved in ether and cooled in ice, and dimethylamine (4.5 g., 100 mmoles) was added. The precipitate of dimethylamine hydrobromide was filtered off, and the ether solution was extracted with hydrobromic acid. The acid extracts were neutralised and extracted with ether. The ether extract was dried and evaporated to give dimethyl(phenacyl)amine (7 g., 85%). This was converted into the hydrobromide with 40% hydrobromic acid; m.p. 191-193° (lit.,42 182-183°).

Dimethyldiphenacylammonium Bromide (XXVI).—A mixture of phenacyl bromide (8.5 g.) and dimethyl(phenacyl)amine (7 g.) in ethanol-ether (1:3; 100 ml.) was left at room temperature for 24 hr. and diluted with ether. The precipitate was crystallised from propan-2-ol; m.p. 127-128° (Found: C, 59.4; H, 5.7. C<sub>17</sub>H<sub>20</sub>BrNO<sub>2</sub> requires C, 59.6; H, 5.7%).

p-Bromophenacyldimethyl(phenacyl)ammonium Bromide (XXVIII).-This was prepared by the foregoing method from dimethyl(phenacyl)amine and p-bromophenacyl bromide in 87% yield; m.p. 193-194° (ethanol-water) (lit.,43 194°).

β-Hydroxyphenethyltrimethylammonium Bromide (XXIII). —The salt was prepared by reduction of trimethylphenacylammonium bromide with excess of sodium borohydride in ethanol; m.p. 228° (lit.,44 228°).

General Procedure for the Irradiation of 'Onium Salts in Water.---A solution of the salt (5 mmoles) in water (400 ml.) was deoxygenated by bubbling nitrogen through for 0.5 hr., then irradiated with a 70 W Hanau high-pressure lamp, surrounded by a Pyrex cooling jacket. Products were precipitated from solution during the reaction and a thin film was deposited on the cooling jacket, reducing the efficiency of the lamp. The film was removed by washing with acetone at half-hourly intervals. The extent of reaction was followed by the decrease in pH, the change in u.v. absorbance of the aqueous solution, and t.l.c. of the acetone washings. After most of the 'onium salt had reacted, the solution was centrifuged and filtered, the solid thus obtained being combined with the acetone washings. This mixture was evaporated and separated by p.l.c.

The aqueous solution was extracted with chloroform and ether, and the dried extracts were evaporated and chromatographed separately. The u.v. spectrum of the residual aqueous solution (after all the organic solvents had been removed), indicated the quantity of unchanged 'onium salt. The aqueous solution was evaporated at  $<40^{\circ}$  to ensure that no other salt product was present.

The quantity of dimethyl sulphide evolved during the reaction was estimated by passing the nitrogen stream through standardised potassium permanganate solution, followed by back-titration with oxalate. Control experiments showed that this method was accurate to  $\pm 1\%$ , provided that dimethyl sulphide was the only volatile product. In preliminary experiments the dimethyl sulphide was estimated by passing the nitrogen stream through 3% mercury(II) chloride solution, when a precipitate of a complex, m.p. 160° (alcohol), was obtained (lit.,45 m.p. 158°). It was found, however, that this method could not be used to estimate the yield of dimethyl sulphide accurately.

<sup>44</sup> W. E. Truce and J. A. Sims, J. Org. Chem., 1957, 22, 762.
<sup>45</sup> F. Challenger, 'Aspects of the Organic Chemistry of Sulphur,' Butterworths, 1959, p. 18.

Photolysis of Dimethylphenacylsulphonium Salts (I) and (VIII)-(XI).-The salts were irradiated according to the general procedure; the yields of products isolated are shown in Table 1. All the products except (VII) were identified by comparison with authentic samples (i.r. spectrum, t.l.c., m.p., or m.p. of a suitable derivative). Compound (VII) was identified by its spectral properties as 1-benzoyl-2-p-bromobenzoylethane, m.p. 115° (ether-light petroleum) (lit.,46 m.p. 108-110°) (Found: C, 60.8; H, 3.95. Calc. for C<sub>16</sub>H<sub>13</sub>BrO<sub>2</sub>: C, 60.6; H, 4.1%), v<sub>max</sub>. 1675s (C=O), 1660s (C=O), 1575m (Ar), 840m (p-BrC<sub>6</sub>H<sub>4</sub>), 793m, 742s, and 683m (Ph) cm.<sup>-1</sup>, m/e 316 and 318 (90%,  $M^+$ ), 183 and 185 (97%,  $BrC_6H_4$ ·CO<sup>+</sup>), and 105 (100%,  $C_6H_5CO^+$ ),  $\tau$ (Me<sub>2</sub>CO) 1.9-2.6 (9H, A<sub>2</sub>B<sub>2</sub> system overlapping a multiplet) and 6.5 (4H, s).

Photolysis of Dimethylphenacylsulphonium Bromide (I) in the Presence of Vinyl Acetate.-- A solution of the salt (I) (1.305 g., 5 mmoles) and vinyl acetate (30 ml.) in water (400 ml.) was stirred vigorously by bubbling nitrogen through and irradiated in the usual manner. After 2 hr. the cooling jacket had become coated with a layer of white polymer. Irradiation of vinyl acetate alone, under the same conditions, gave only a small amount of polymer.

Photolysis of Phenacyl Bromide (III) in Water.-A solution of phenacyl bromide (0.76 g.) in methanol (5 ml.) was poured into water (400 ml.) and the methanol was removed with a rotary evaporator, leaving the phenacyl bromide suspended in water. The suspension was irradiated in the usual way for 4 hr., the products were extracted into chloroform, and the extracts were dried and evaporated. The resultant solid was chromatographed to give phenacyl bromide (54 mg.), a mixture of 1,2-dibenzoylethane and 1-benzoyl-2-p-bromobenzoylethane (18 mg.), 1,2-dibenzoylethane (74 mg.), acetophenone (57 mg.), and some polymer (35 mg.).

Photolysis of 1,2-Dibenzoyl-1-bromoethane in Water. This substance (0.79 g., 2.5 mmoles) was suspended in water (600 ml.) and irradiated for 3.5 hr. The products were extracted into chloroform and chromatographed to give a mixture of diastereoisomeric 1,2-dibenzoyl-1,2-dibromoethanes (60 mg.), from which one isomer, m.p. 181-182° (20 mg.) was obtained by crystallisation from light petroleum-benzene: this was identical with an authentic sample (lit.,<sup>32</sup> 179-182°). Other products were unchanged 1,2-dibenzoyl-1-bromoethane (100 mg.), trans-dibenzoylethylene (204 mg.), 1,2-dibenzoylethane (10 mg.), and a compound (21 mg.), m.p. 257-259°, tentatively identified as cis-anticis-1,2,3,4-tetrabenzoylcyclobutane (lit.,47 259-261°), on the basis of its i.r. spectrum, which was identical with that reported by Griffin.47 The mass spectrum showed a molecular ion at 472 and fragmentation patterns consistent with the structure.

Photolysis of trans-Dibenzoylethylene in Water .--- A suspension of trans-dibenzoylethylene (0.295 g., 1.25 mmole) in water (400 ml.) was irradiated for 3 hr. The products were extracted into chloroform and the extract was dried and evaporated. The resultant solid was chromatographed to give trans-dibenzoylethylene (105 mg.), cis-dibenzoylethylene (70 mg.), and an unidentified oil (25 mg.).

Photolysis of p-Substituted Phenacylsulphonium Salts (XII)-(XIV) and (XIX).-These salts were irradiated according to the general procedure: the results are given in Table 2. All the compounds except the substituted 1,2-di-

<sup>42</sup> T. Nakano, Chem. and Pharm. Bull. (Japan), 1954, 2, 321. <sup>43</sup> W. Heffe and F. Krohnke, Chem. Ber., 1956, 89, 822.

 <sup>&</sup>lt;sup>46</sup> C.-K. Dien and R. E. Lutz, J. Org. Chem., 1956, 21, 1492.
 <sup>47</sup> G. W. Griffin, R. B. Hager, and D. F. Veber, J. Amer. Chem. Soc., 1962, 84, 1008.

benzoylethanes were identified by comparison with samples prepared by standard methods. The substituted 1,2-dibenzoylethanes were identified spectroscopically:

1,2-Bis-(p-bromobenzoyl)ethane, m.p. 186—187° (from propan-2-ol) (lit.,<sup>48</sup> 182—183°),  $\nu_{\rm max}$  1672s (C=O) 852s, and 788s (p-BrC<sub>6</sub>H<sub>4</sub>) cm.<sup>-1</sup>, *m/e* 394, 396, and 398 (ratio 1:2:1,  $M^+$ ), 211 and 213 (7%, BrC<sub>6</sub>H<sub>4</sub>·CO·CH<sub>2</sub>·CH<sub>2</sub><sup>+</sup>), 183 and 185 (100%, BrC<sub>6</sub>H<sub>4</sub>·CO<sup>+</sup>), and 155 and 157 (BrC<sub>6</sub>H<sub>4</sub><sup>+</sup>).

1,2-Bis-(*p*-methoxybenzoyl)ethane (XV), m.p. 154—156° (from ethyl acetate) (lit.,<sup>49</sup> 154°),  $\nu_{max}$  1681s (C=O), 1671s (C=O), 852m, and 838s (*p*-CH<sub>3</sub>·O·C<sub>6</sub>H<sub>4</sub>) cm.<sup>-1</sup>,  $\tau$  (CDCl<sub>3</sub>) 6·61 (4H, s), 6·12 (6H, s), 3·04 (4H, d), and 1·95 (4H, d),<sup>50</sup> m/e 298 (7%, M<sup>+</sup>) and 135 (100%, CH<sub>3</sub>·O·C<sub>6</sub>H<sub>4</sub>·CO<sup>+</sup>).

1,4-Bis(p-biphenyl)-butane-1,4-dione, m.p. 260°,  $\nu_{ma}$  1670s (C=O), 1595m (Ar), 840s, and 760s (p-C<sub>6</sub>H<sub>5</sub>·C<sub>6</sub>H<sub>4</sub>) cm.<sup>-1</sup>, m/e 390 (15·2%, M<sup>+</sup>), 209 (8·7%, p-C<sub>6</sub>H<sub>5</sub>·C<sub>6</sub>H<sub>4</sub>·CO·CH<sub>2</sub>·CH<sub>2</sub><sup>+</sup>) and 181 (100%, C<sub>6</sub>H<sub>5</sub>·C<sub>6</sub>H<sub>4</sub>·CO<sup>+</sup>).

Photolysis of Dimethyl- $\alpha$ -naphthoylmethylsulphonium Bromide (XX).—A solution of compound (XX) (1.555 g., 5 mmoles) in water (420 ml.) was irradiated for 7 hr., during which time the u.v. absorbance (at 329 nm.) decreased by only 10%. Extraction with chloroform and ether, followed by evaporation of the dried extracts, gave material (100 mg.) which was shown by t.l.c. to contain at least eight components. The quantity of starting material remaining in the aqueous solution was calculated from u.v. measurements to be 1.19 g. (77%). When the experiment was repeated with a quartz cooling jacket instead of Pyrex, the rate of photolysis was unchanged.

Photolysis of Dimethyl- $\beta$ -naphthoylmethylsulphonium Bromide (XXI).—Photolysis of a solution of compound (XXI) (1.61 g.) in water (500 ml.) for 7 hr. gave only 70 mg. of a complex mixture of products. Evaporation of the aqueous solution gave starting material (1.45 g., 90%).

Photolysis of Dimethylphenacylsulphonium Bromide (I) in Aqueous Propan-2-ol.—A solution of compound (I) (1.305 g., 5 mmoles) in propan-2-ol-water (9:1; 400 ml.) was irradiated for 3.5 hr. Evaporation of the solvent and t.l.c. of the product showed the presence of acetophenone and acetophenone pinacols, but 1,2-dibenzoylethane and 1-phenylethanol were absent. Chromatography of the product gave acetophenone (46 mg., 7.5%) and a mixture of acetophenone pinacols (392 mg., 65%), separated by fractional crystallisation into the racemate, m.p. 125° (light petroleum), and the meso-isomer, m.p. 116° (cyclohexane) (lit.,<sup>25</sup> 122.3° and 117—118°).

Photolysis of Trimethylphenacylammonium Bromide (XXII) in Aqueous Propan-2-ol.—A solution of compound (XXII) (1.295 g., 5 mmoles) in propan-2-ol-water (19:1; 400 ml.) was irradiated for 3 hr. The solvent was evaporated off to give a white solid, which was partitioned between chloroform and water. The aqueous solution was evaporated to give a white solid, which was vacuum-

sublimed (160° at 0.02 mm. Hg) to give trimethylamine hydrobromide (535 mg., 77%). The residue from the sublimation was recrystallised from propan-2-ol to give  $\beta$ -hydroxyphenethyltrimethylammonium bromide (XXIII), m.p. 228° (240 mg., 19%). The chloroform solution was chromatographed to give acetophenone (19 mg., 4%) and a mixture of acetophenone pinacols (243 mg., 49%).

Photolysis of Dimethyldiphenacylammonium Bromide in Aqueous Propan-2-ol.—A solution of compound (XXVI) in propan-2-ol-water (19:1; 400 ml.) was irradiated for 4.5 hr. The solvent was evaporated off and the product was partitioned between chloroform and water. The aqueous solution was evaporated to give dimethyl(phenacyl)amine hydrobromide, m.p. 191—193° (1.12 g., 90%). The chloroform solution was dried and evaporated and the product was chromatographed to give 1,2-dibenzoylethane (94 mg., 16%) and acetophenone (280 mg., 46%).

Photolysis of p-Bromophenacyldimethyl(phenacyl)ammonium Bromide (XXVIII) in Aqueous Propan-2-ol.—A solution of compound (XXVIII) (2·20 g., 5 mmoles) in propan-2-ol-water (1:1; 600 ml.) was irradiated for 2·5 hr. The solvent was evaporated off and the product was partitioned between chloroform and water. Evaporation of the aqueous solution gave a solid (1·40 g.) which was shown to be a mixture of compound (XXVIII) and dimethyl(phenacyl)amine hydrobromide by i.r. spectroscopy. Recrystallisation from propan-2-ol gave the latter salt (0·8 g., 66%). The chloroform solution was shown by chromatography to contain a mixture of p-bromoacetophenone (250 mg., 25%) and 1,2-bis-(p-bromobenzoyl)ethane (30 mg., 3%). Neither 1,2-dibenzoylethane nor 1-benzoyl-2-p-bromobenzoylethane was present.

Photolysis of Benzyldimethylsulphonium Bromide in Water. -A solution of the salt (2.34 g., 10 mmoles) in water (400 ml.) was irradiated in the usual manner. No decomposition occurred during the first hour: the u.v. spectrum of the solution remained unchanged. Acetone (5 ml.) was added as sensitiser and the mixture was irradiated for 4 hr., during which dimethyl sulphide was given off and a precipitate was deposited. The products were extracted into ether and the extract was dried and evaporated to give an oil (0.185 g.), whose i.r. spectrum showed that it was mainly benzyl alcohol. G.l.c. showed that the oil was a mixture of benzyl bromide, benzyl alcohol, and bibenzyl in the ratio 1:30:17.5, with a trace of toluene present. The aqueous solution contained a large amount of unchanged starting material. The photochemical reaction also proceeded in the absence of acetone when a quartz cooling jacket was used instead of Pyrex.

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 <sup>49</sup> E. Buchta and G. Schaeffer, Annalen, 1955, **597**, 129.