446. *The Salt-forming Characteristics of Doubly- and Singly-linked Elements of the Oxygen Group. Part IV. Oxonium Phosphates of the Carbonyl Group, and Investigations with Derivatives of the Type* $CH_2Ph{\cdot}COR$.

By JOHN W. BAKER and LESLIE HEY.

THE evidence (J., 1931, 307, 314; this vol., p. 1226) for the formation of carbonium-oxonium salts of the type $\left.\overbrace{\mathrm{ArCR{:}OH}}^{\oplus}\right\}\overset{\ominus}{\mathrm{X}}$ was restricted to solutions in sulphuric acid, and to cases where Ar = Ph. The investigation has now been extended to include (*a*) another mineral acid * and (*b*) the corresponding benzyl derivatives (Ar = CH_2Ph) in which the carbonyl group is separated from the phenyl nucleus by a methylene group.

(*a*) The observation that acetophenone and its *p*- and *m*-methyl derivatives unite with syrupy phosphoric acid in the cold to form crystalline additive compounds $ArCOMe,H_3PO_4$ was first made by Klages and Allendorff (*Ber.*, 1898, **31**, 1300), who, however, assigned no structural formulæ to these derivatives, regarding them as loose molecular compounds. In view of the evidence obtained for solutions in sulphuric acid there would seem little doubt that they are actually the pseudo-salts $ArCR(OH){\cdot}O{\cdot}PO_3H_2$, the condition of the carbonyl derivative in phosphoric acid being represented by the equilibria

$$\mathrm{ArCR{:}O + H_3PO_4 \rightleftharpoons ArCR(OH){\cdot}O{\cdot}PO_3H_2 \rightleftharpoons \overbrace{ArCR{:}OH}^{\oplus} + {\cdot}\overset{\ominus}{O}{\cdot}PO_3H_2}$$

Similar crystalline *phosphates* of benzaldehyde and anisaldehyde have now been obtained, the former possessing the minimum, and the latter the maximum, stability of those derivatives which have been obtained crystalline.

No crystalline derivative could be obtained with ethyl benzoate (R = OEt), the other carbonyl derivative previously studied, but evidence of the existence of similar equilibria both with this ester and with ethyl *p*-anisate has been obtained by partition of these esters between ligroin and phosphoric acid. The results are in Table I.

Although the position of equilibrium in these cases is evidently much more in favour of the free carbonyl derivative than it is in sulphuric acid solution, its further displacement in this direction either by dilution or by addition of a common ion (ammonium phosphate) is exactly analogous to that observed in the latter solvent.

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* The author is indebted to Prof. S. Sugden for this suggestion.

The increased stability of the phosphoric acid derivative observed in the case of anisaldehyde is again evident in the case of the corresponding ester, and is in accord with the expected effect of the polar character of the methoxy-group.

TABLE I.

Partition of derivatives of the type Ar·COR between ligroin (b. p. 100—120°) and sulphuric or phosphoric acid at room temperature.

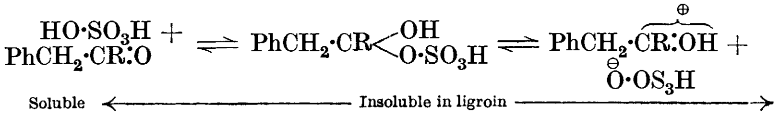
	Proportion of Ar·COR in the ligroin layer, %.			
	R = Me.		R = OEt.	
Conc. of acid, %.	(*a*) Without NH_4 salt.*	(*b*) With NH_4 salt.	(*a*).	(*b*).
Ar = Ph				
98 H_3PO_4	—	—	67·7	95·7
88 H_3PO_4	—	—	99·0	99·0
Ar = *p*-MeO·C_6H_4				
98 H_3PO_4	—	—	15·5	41·8
88 H_3PO_4	—	—	59·8	100·0
Ar = CH_2Ph				
H_2SO_4+5% free SO_3	—	—	3·0	4·1
100 H_2SO_4	—	—	4·0 (5·4)†	6·9 (15·5)
95 H_2SO_4	1·9	3·0	—	—
90 H_2SO_4	2·3	9·2	8·3 (11·7)	81·8 (98·1)
80 H_2SO_4	8·2	86·8	—	—
98 H_3PO_4	9·6	18·0	48·3 (67·7)	91·5 (95·7)
88 H_3PO_4	29·7	56·5	99·1 (99·0)	99·1 (99·0)

* $(NH_4)_2SO_4$ for H_2SO_4; $(NH_4)_2HPO_4$ for H_3PO_4 experiments.

† For comparison the corresponding values for Ph·CO_2Et are given in parentheses.

(*b*) It would be anticipated that the salt-forming power of the carbonyl oxygen in the benzyl derivatives, although of an order comparable with that in the corresponding phenyl derivatives, would possibly be slightly greater than in the latter owing to the inductive (+*I*) effect of the benzyl group $\mathrm{PhCH_2} \longrightarrow \mathrm{CR{:}O}$, which would tend to increase the affinity of the unshared oxygen electrons for a positive charge. This conclusion is supported by the results, summarised in Table I, of partitioning ethyl phenylacetate and benzyl methyl ketone between ligroin and either sulphuric or phosphoric acid of various concentrations.

The close similarity of these results with those obtained for benzaldehyde (J., 1931, 307) and ethyl benzoate (this vol., p. 1226) indicates that the distribution of the entities in the equilibria

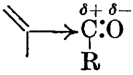


$$\begin{matrix}\mathrm{HO{\cdot}SO_3H} \; + \\ \mathrm{PhCH_2{\cdot}CR{:}O}\end{matrix} \rightleftharpoons \mathrm{PhCH_2{\cdot}CR}<\begin{matrix}\mathrm{OH}\\ \mathrm{O{\cdot}SO_3H}\end{matrix} \rightleftharpoons \mathrm{PhCH_2{\cdot}}\overset{\oplus}{\overbrace{\mathrm{CR{:}OH}}} + \overset{\ominus}{\mathrm{O}}\mathrm{{\cdot}OS_3H}$$

$$\text{Soluble} \longleftarrow \text{Insoluble in ligroin} \longrightarrow$$

is comparable in the phenyl and the benzyl series.

With regard to the effect of the positive charge of the carbonium–oxonium kation on the proportion of *m*-substitution occurring in sulphuric acid solution, important differences in the two series are at once apparent. In the phenyl series the juxtaposition of the fractional dipole $\overset{\delta+\ \delta-}{-\text{C:O}}$ (Baker and Ingold, J., 1927, 832) to the benzene nucleus renders even the neutral molecule largely *m*-directive, so that any increased *m*-substitution arising from the integral positive charge distributed on the kation is necessarily relatively small. In the benzyl series, however, the intercalation of the methylene group exerts a large damping influence on the effect of the fractional dipole, so that, in the neutral condition, benzyl methyl ketone and ethyl phenylacetate are nitrated mainly in the *op*-positions. In sulphuric acid solution, however, the proportion of the integral positive charge which is located on the carbon atom should give rise to a relatively much greater increase in the proportion of *m*-substitution, since the condition of the kation approximates towards that present in the neutral phenylnitromethane molecule. The series giving the % of *m*-substitution (R = Me) and the more detailed results summarised in Table II amply support this conclusion.



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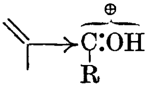

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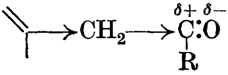

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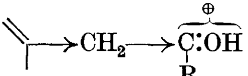

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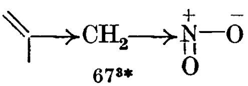

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In the benzyl series the rapid substitution of the *op*-directing neutral molecule (presumably present in equilibrium with the oxonium kation) precludes nitration in the presence of sulphuric acid containing free sulphur trioxide, or even 100% acid, owing to the occurrence of either sulphonation or dinitration as a side-reaction, and this condition limits the concentration of sulphuric acid employed to a maximum of 95%. Since such conditions are conducive to hydrolysis of the salt-form, the degree of *m*-substitution observed for the kation must be regarded as a minimum value. The effect of

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* These figures, together with those for β-phenylnitroethane (13% *m*), indicate that the *m*-directive power of the fractional dipole $\overset{\delta+\ \delta-}{-\text{C:O}}$ is approximately equivalent to that portion of the effect of the integral dipole $\overset{+-}{\text{NO}_2}$ which is transmitted through a saturated CH_2 group.

[1] Baker and Moffit, J., 1931, 314. [2] This communication. [3] Baker, J., 1929, 2257.

addition of ammonium sulphate in both the nitration and the partition experiments is exactly similar in magnitude and type to that discussed in previous papers.

TABLE II.

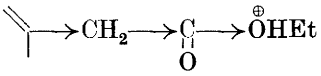
Nitration of derivatives of the type $CH_2Ph{\cdot}COR$ under various conditions. (Nitric acid, *d* 1·53.)

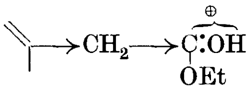
	Conc. of H_2SO_4, %.	Mean proportion of *m*-isomeride formed, %. (Error ± 1—2%.)	
		(*a*) Without $(NH_4)_2SO_4$.	(*b*) With $(NH_4)_2SO_4$.
R = Me	90	28·6	19·9
	85	23·7	21·4
	80	18·3	18·9
	0	18·1	—
	98 *	19·2	—
R = OEt	100	30·8	—
	90	25·0	18·2
	80	16·9	(*ca.* 21)
	0	11 †	—

* H_3PO_4 used.

† Baker and Ingold, J., 1927, 832; Flürscheim and Holmes, J., 1928, 1607.

The results obtained with ethyl phenylacetate also throw light on one other aspect of the problem. It has already been noticed (Part III) that, in the case of the carbethoxy-group, the possibility of oxonium-salt formation on the singly-linked oxygen $\left.\mathrm{O{:}C{\cdot}\overset{\oplus}{O}HEt}\right\}\overset{\ominus}{\mathrm{X}}$, cannot be theoretically excluded. In such a case there exists no electronic mechanism (such as is present when the carbonyl group is involved) whereby the positive charge can be transferred to the β-carbon atom, and its directive influence could only be transmitted to the benzene nucleus by induction through two intervening carbon atoms.





The data relating to the nitration of β-phenylnitroethane (13% *m*; Baker and Wilson, J., 1927, 842) and β-phenylethylammonium salts (19% *m*; Goss, Hanhart, and Ingold, *ibid.*, p. 250) indicate that under such conditions the increase in *m*-substitution would be exceedingly small. Actually, however, it is found that on nitration of ethyl phenylacetate in sulphuric acid solution the proportion (25%) and also the increase (14%) in the proportion (relative to nitric acid alone) of the *m*-nitro-isomeride formed is approximately the same as that given by benzyl methyl ketone (29% and 11%, respectively). Hence it appears that at least the major portion of the effect must be due to salt-formation on the doubly-linked oxygen of the carbonyl group.

EXPERIMENTAL.

Materials.—The $CH_2Ph{\cdot}COMe$, purified by conversion into its $NaHSO_3$ derivative, steam distillation, and fractionation, had b. p. 94°/11 mm. Its p-*nitrophenylhydrazone*, cryst. from AcOH, had m. p. 143° (Found : C, 66·2; H, 5·6. $C_{15}H_{15}O_2N_3$ requires C, 66·9; H, 5·7%). The $CH_2Ph{\cdot}CO_2Et$ was purified by fractional distillation and had b. p. 227°/760 mm.

The ligroin was B.D.H. A.R. petroleum, b. p. 100—120°, free from aromatic hydrocarbons. A.R. H_3PO_4 (88% by titration) was converted into approx. 100% H_3PO_4 by dissolution of P_2O_5, the excess being filtered off through glass wool (Found by titration : H_3PO_4, sample I, 97·8%; sample II, 98·0%).

Preparation of Crystalline H_3PO_4 *Salts.*—A.R. 88% H_3PO_4 was added to an excess of the carbonyl compound, and the whole cooled in ice (when necessary) until crystn. occurred. The crystals were washed with ligroin (b. p. 40—60°), crystallised from the pure liquid carbonyl compound, which helped to remove free H_3PO_4, washed with ligroin, drained, and kept in a vac. desiccator for *ca.* 1 hr. : a weighed amount was then decomp. with H_2O, and the P estimated as $Mg_2P_2O_7$. Thus were obtained the *phosphates* of PhCHO (Found : P, 17·7. C_7H_6O,H_3PO_4 requires P, 15·2%) and *p*-$MeO{\cdot}C_6H_4{\cdot}COMe$, m. p. 82° (Found : P, 13·7. $C_8H_8O_2,H_3PO_4$ requires P, 13·3%). The PhCHO compound was

TABLE III.

Partition of derivatives of the type Ar·COR between ligroin and H_2SO_4 or H_3PO_4 at room temp.

Ligroin = 20 c.c. $H_2SO_4(H_3PO_4)$ = 5 c.c. NH_4 salt = 2 g.

Data relating to ligroin layer.

Conc. of acid, %.	Ar·COR taken, g.	G. of *p*-nitrophenylhydrazone in 10 c.c.		C.c. of 0·4420*N*·KOH for ester in 10 c.c.		G. of Ar·COR in 20 c.c.	
		(*a*) Without NH_4 salt.	(*b*) With NH_4 salt.	(*a*).	(*b*).	(*a*).	(*b*).
R = Me (Ar = CH_2Ph)							
95	0·5018	0·0098	0·0151	—	—	0·0098	0·0151
90	0·4798	0·0107	0·0439	—	—	0·0107	0·0439
80	0·4750	0·0389	0·4121	—	—	0·0389	0·4121
98*	0·4948	0·0474	0·0892	—	—	0·0474	0·0892
88*	0·4782	0·1452	0·2700	—	—	0·1452	0·2700
R = OEt (Ar = CH_2Ph)							
H_2SO_4 + 5% SO_3	1·2120	—	—	0·25	0·34	0·0362	0·0493
100	1·1964	—	—	0·33	0·57	0·0478	0·0826
90	1·2232	—	—	0·35	6·90	0·1015	1·000
98*	0·9256	—	—	3·10	5·86	0·4482	0·8482
88*	0·9390	—	—	6·43	6·43	0·9312	0·9312
R = OEt (Ar = Ph)							
98*	1·0713	—	—	5·47	7·73	0·7255	1·0260
88*	1·0713	—	—	8·01	8·01	1·0606	1·0606
R = OEt (Ar = *p*-$MeO{\cdot}C_6H_4$)							
98*	1·0880	—	—	1·06	2·86	0·1686	0·4551
88*	1·0880	—	—	4·38	6·84	0·6970	1·0880

* H_3PO_4 used.

very unstable and lost PhCHO during isolation. The phosphates of PhCOMe (Found: P, 15·3. Calc.: P, 14·2%) and p-C_6H_4Me·COMe (Found: P, 14·0. Calc.: P, 13·4%) were similarly prepared (cf. Klages and Allendorff, *loc. cit.*).

Partition Experiments.—These were carried out as previously described. The proportion of ketone in the ligroin layer was determined gravimetrically as its p-nitrophenylhydrazone (cf. PhCHO; J., 1931, 307) and the ester by quant. hydrolysis with 0·442N-KOH in EtOH (cf. $PhCO_2Et$; this vol., p. 1226). The results are in Table III, from which those in Table I are derived.

Nitration Experiments.—(a) *In* H_2SO_4. The CO-derivative was run with mechanical stirring into the nitrating medium at −10° to −15° during ½ hr., and the mixture stirred in the freezing mixture for a further hr. while the temp. rose to −5°. It was then poured on ice and an excess of $KHCO_3$ and worked up as usual. The bulk of the material not obtained as neutral mononitrated derivative was accounted for by the acid products formed by oxidation during nitration.

(b) *In* H_3PO_4. A solution of 3·335 g. of CH_2Ph·COMe in 36·8 g. of 98% H_3PO_4 was run into 15 g. of HNO_3 (d 1·53) containing a little P_2O_5 at 0° to −5°. After 1½ hr. the mixture was worked up as in the H_2SO_4 cases. The quant. result obtained, however, is not reliable, since some cryst. material separated from the neutral nitration product. This, after draining on porous porcelain and crystn. from EtOH, had m. p. 106° (? 2 : 6-dinitro-isomeride). The nitration results are in Table IV.

TABLE IV.

Nitration No.	CH_2Ph·COR taken, g.	HNO_3 (d 1·53), g.	H_2SO_4, g.	Conc. of H_2SO_4, %.	Am_2SO_4 added, g.	Product, g.	
						Neut.	Acid.
R = Me							
1	2·946	3	60	90	0	2·554	1·181
2	3·026	3	60	90	0	2·881	0·802
3	3·623	3	60	90	0	3·476	—
4	3·085	3	60	90	12	2·843	0·791
5	3·213	3	60	90	12	3·104	0·494
6	3·788	3	60	90	12	3·631	—
7	4·062	3	70	85	0	4·288	—
8	4·174	3	70	85	12	4·884	—
9	3·883	3	70	80	0	4·358	—
10	3·911	3	70	80	12	4·123	—
11	2·688	25	0	0	0	3·499	—
12	5·024	50	0	0	0	6·592	—
13	3·335	15	36·8*	98*	0	3·798	—
R = OEt							
14	4·907	1·9	30	100	0	6·120	—
15	3·977	3	60	90	0	4·955	—
16	3·989	3	60	90	12	4·532	—
17	3·072	2·3	45	80	0	3·550	—
18	2·997	2·3	45	80	9	2·738	—

* H_3PO_4 used.

Determination of the Isomerides.—This was effected by oxidation to the mixed nitrobenzoic acids, which were determined by Flürscheim and Holmes's method (J., 1928, 448) in the usual manner. In the case of CH_2Ph·COMe optimum oxidation yields were obtained by employing 3% $KMnO_4$ in neutral solution (CO_2 stream) in a bath at 130°. Details are summarised in Table V.

TABLE V.

Nitration No.	Neut. prodt. oxid., g.	Acids.		Recovered.			Composition of acids, $R\cdot CO_2H$, mols. %. R =			Nitro-isomerides, %.	
		obt.	sep.	$C_6H_5\cdot CO_2H$.	$C_6H_2Br_3\cdot NH_2$.	$C_6HBr_3{<}^{NH_2}_{CO_2H}$.	C_6H_5.	$NO_2\cdot C_6H_4$. *op.*	*m.*	*op.*	*m.*
1	1·750	1·324	0·573	0·068	0·530	0·265	19·7	55·7	24·6	69·4	30·6
2	1·969	1·445	0·712	0·047	0·737	0·354	10·8	62·6	26·6	70·2	29·8
3	1·596	1·124	0·659	0·080	0·683	0·277	19·7	58·0	22·3	72·3	27·7
	1·156	0·890	0·666	0·055	0·675	0·272	14·0	63·4	22·6	73·7	26·3
4	1·703	1·324	0·610	0·003	0·820	0·269	7·8	71·5	20·7	77·4	22·6
5	1·827	1·383	0·715	0·031	1·006	0·256	6·4	76·4	17·2	81·6	18·4
6	1·600	1·190	0·624	0·040	0·834	0·234	9·4	72·6	18·0	80·2	19·8
	1·201	0·925	0·622	0·019	0·869	0·228	4·6	77·5	17·9	81·2	18·8
7	2·022	1·624	0·621	0·027	0·671	0·236	7·7	70·4	21·9	76·3	23·7
8	2·456	1·717*	0·658	0·085	0·832	0·257	17·9	64·5	17·6	78·6	21·4
9	1·912	1·336	0·638	0·025	0·878	0·222	5·9	76·9	17·2	81·7	18·3
10	2·442	1·594	0·613	0·090	0·629	0·166	23·9	61·7	14·4	81·1	18·9
11	1·711	1·150	0·612	0·015	0·881	0·215	3·6	79·3	17·1	82·3	17·7
12	1·830	1·342	0·608	0·016	0·809	0·215	4·1	77·7	18·2	81·0	19·0
	3·033	2·186*	0·602	0·014	0·825	0·200	3·6	79·4	17·0	82·4	17·6
13	2·990	1·650	0·626	0·039	0·835	0·222	9·3	73·4	17·3	80·8	19·2
14	2·220	1·189	0·609	0·041	0·751	0·378	9·3	62·8	27·9	69·2	30·8
15	3·063	1·516	0·673	0·014	0·861	0·337	3·2	71·9	24·9	74·3	25·7
			0·607	0·007	0·810	0·294	1·7	74·4	23·9	75·7	24·3
16	3·000	1·883	0·676	0·014	1·009	0·244	3·0	79·9	17·1	82·5	17·5
			0·655	0·006	0·907	0·238	1·4	80·0	18·6	81·2	18·8
17	2·273	1·621	0·645	0·015	0·963	0·222	3·4	80·3	16·3	83·1	16·9
18	2·335	1·607	0·648	0·385	0·189	0·058	81·2	14·7	4·1	78·5	21·5

* Mechanical loss.

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