

Stability of Arenide Ions. Cleavage of Unsymmetrical Diaryl Ketones with Potassium t-Butoxide

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Diaryl ketones (RC_6H_4COPh) were cleaved by heating with potassium t-butoxide in the absence of a solvent. After addition of water the products were the two carboxylic acids $RC_6H_4CO_2H$ and $PhCO_2H$, and the two neutral compounds HPh and RPh . The relative proportions of the products indicated the preferred direction of cleavage. It is assumed that the aryl groups were produced as arenide ions, and that the propensity for cleavage is in the same order as the stability of the arenide ions. Substituents R were found to favour cleavage in the order $2-F > 3-F \sim 2-Me > 4-F > 4-CF_3 > H > 3-Me \sim 4-Me > 4-MeO$. Though the actual species undergoing cleavage was $ArAr'C(OBu^t)O^-$ (2) [unlike previous investigations in which the cleaved species was $ArAr'C(OH)O^-$ (1) or $ArAr'C(O^-)_2$ (6)], the results are in accord with previous work.

THE relative stability of substituted arenide ions has been studied previously by two principal methods. One involves measuring relative rates of hydrogen-deuterium or hydrogen-tritium exchange;¹ the other is a competitive method in which a compound or ion containing the system $ArAr'C<$ is treated so as to cause one of the aryl groups to be removed as a carbanion. The arenide ion which is produced to the greater extent is assumed to be the more stable. For example, Bach-

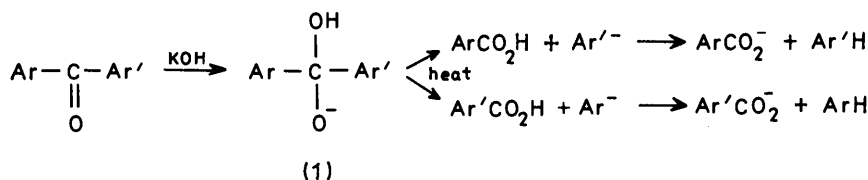
mann² heated unsymmetrical diaryl ketones with an excess of solid potassium hydroxide with the results indicated in Scheme 1. Acidification of the product gave two carboxylic acids, the proportions of which

¹ For example, see (a) G. E. Hall, R. Piccolini, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1955, **77**, 4540; G. E. Hall, E. M. Libby, and E. L. James, *J. Org. Chem.*, 1963, **28**, 311; A. I. Shatenshtein, *Adv. Phys. Org. Chem.*, 1963, **1**, 155; (b) A. I. Shatenshtein and I. O. Shapiro, *Russ. Chem. Rev.*, 1968, **37**, 845.

² W. E. Bachmann, *J. Amer. Chem. Soc.*, 1935, **57**, 737.

corresponded to the extents of cleavage in each of the two possible modes. The same general approach was followed by Lock and Rodiger.³ Swan⁴ showed that better results were obtained if ketone cleavages were carried out by refluxing for several hours with potassium t-butoxide and water (ratio 3 : 1) in a solvent such as

equimolar amount of solid potassium t-butoxide. Water was then added and the products were separated into neutral and acidic fractions; each fraction was analysed separately. The results are shown in Table I. *Mechanism.*—When the reaction is carried out with potassium or sodium hydroxide,^{2,3} the species which



SCHEME 1

ether or benzene. Swan reported that potassium t-butoxide alone did not cause cleavage under these conditions; either water or hydroxide ions also had to be present. Gassman and his co-workers⁵ showed that benzophenone and fluorenone are readily cleaved by room temperature treatment for 2—4 h in 1,2-dimethoxyethane containing potassium t-butoxide and water in

attacks the ketone must be OH⁻, but when Bu^tO⁻ and OH⁻ are both present (as they have to be in a mixture containing Bu^tOK and H₂O with the former in excess) the identity of the attacking species is less obvious. Swan⁴ assumed that the ketone was attacked by Bu^tO⁻, to give the ion (2), and that the purpose of the water was to assist in the conversion of (2) into the products,

TABLE I
Cleavage of diaryl ketones (RC₆H₄·COPh) with potassium t-butoxide

R	Time of heating (h)	Highest reflux temp (°C)	Initial no. of moles	Re-covered ketone (%)	PhH (%)	PhR (%)	Total PhR + PhH (%)	RC ₆ H ₄ ·CO ₂ H (%)	PhCO ₂ H (%)	Total acidic products (%)	Other products
H	3.5	145	0.050 0	42	24		24		26	26	3.6% Ph ₃ C·OH 13% Ph(2-MeC ₆ H ₄)CHOH
2-Me	3	100	0.030 0	44	2.1	12	14	1.9	13	15	
3-Me	3.3	102	0.020 0	13	31	13	44	22	17	39	<i>a</i>
4-Me	2	107	0.030 0	15	28	6.9	35	14	11	25	<i>a</i>
4-MeO	3	108	0.025 0	38	10	6.2	16	10	5.1	15	<i>b</i>
2-F	3	138	0.010 0	26	0.6	21	22	0	15	15	<i>c</i>
3-F	3	170	0.010 0	16	5.0	38	43	5.7	24	30	<i>d</i>
4-F	3	130	0.010 0	17	2.5	7.5	10	0.5	3.3	3.8	<i>e</i>
4-CF ₃	3	139	0.005 0	62	3.7	9.8	13.5	4.2	8.0	12	<i>f</i>
4-NO ₂	3	115	0.020 0	42	0	0	0	0	<i>g</i>	<i>g</i>	Complex mixture

^a Two unidentified products in very small amounts, probably triarylmethanols. ^b *p*-Benzylanisole and an unidentified product. ^c *o*-*t*-Butoxybenzophenone and an unidentified compound. ^d *m*-*t*-Butoxybenzophenone and an unidentified compound. ^e *p*-*t*-Butoxybenzophenone. ^f Two unidentified products in very small amounts. ^g Benzoic acid identified but the amount not determined.

the molar ratio (Bu^tOK : H₂O : ArCOAr') 10 : 3 : 1. This molar ratio has been used by two groups to study the direction of competitive cleavages.⁶ Hodge and his co-workers^{6a,b} carried out their experiments in 1,2-dimethoxyethane either at room temperature or at reflux temperature; Hausigk^{6c} used refluxing anisole.

We have discovered that diaryl ketones can be cleaved with potassium t-butoxide alone, without the presence of water or hydroxide ions, if the ketone is heated with the solid t-butoxide in the absence of solvent.

RESULTS AND DISCUSSION

Benzophenone and nine monosubstituted benzophenones were cleaved by heating for 2—3 h with an

³ G. Lock and E. Rodiger, *Ber.*, 1939, **72B**, 861.

⁴ G. A. Swan, *J. Chem. Soc.*, 1948, 1408.

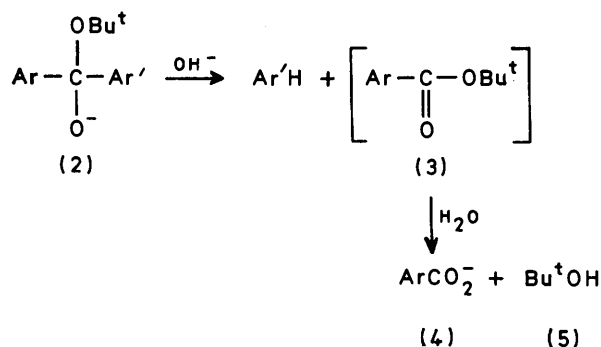
⁵ P. B. Gassman, J. T. Lumb, and F. V. Zalar, *J. Amer. Chem. Soc.*, 1967, **89**, 946.

by way of the *t*-butyl ester (3). However, Gassman and his co-workers⁵ ruled out this mechanism by showing that the ketone (3; Ar = Ph), independently prepared and subjected to the reaction conditions, was converted into (4) and (5) more slowly than was benzophenone. They suggested a mechanism in which the attacking species is OH⁻ rather than Bu^tO⁻. The function of the Bu^tO⁻ would then be either to remove a proton from (1) to give the dianion (6) [which would be cleaved more readily than (1)], or to make the OH⁻ more soluble in the solvent.

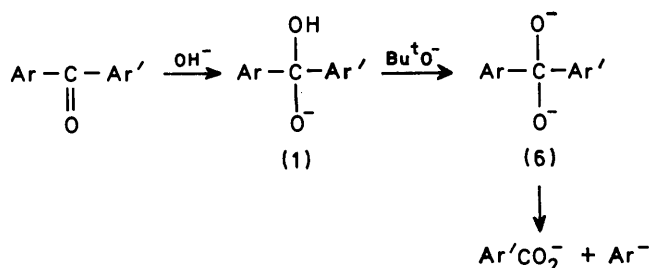
Thus in all previous cleavages with OH⁻ or Bu^tO⁻, the attacking species was OH⁻, and the species which underwent the actual cleavage was (1) or (6). In the

⁶ (a) D. G. Davies, M. Derenberg, and P. Hodge, *J. Chem. Soc. (C)*, 1971, 455; (b) D. G. Davies and P. Hodge, *Chem. Comm.*, 1968, 953; (c) D. Hausigk, *Chem. Ber.*, 1971, **104**, 2637.

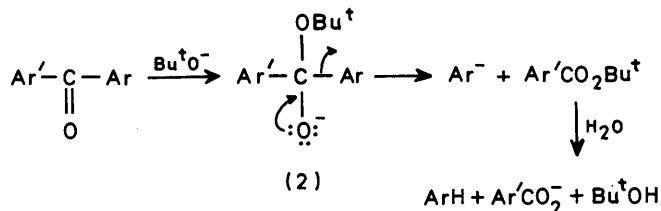
present work, however, there is no source of OH^- , so that the attacking species must be Bu^tO^- and the



species undergoing cleavage is (2). The mechanism may be pictured as in Scheme 2.



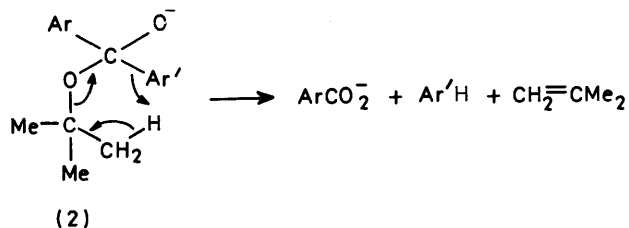
Despite the fact that a different species is undergoing cleavage, the results of competitive experiments are



SCHEME 2

similar to those previously reported, as will be shown in the next section.

An alternative mechanism for the cleavage of (2) has been suggested,^{7,8} involving a six-membered transition state but no arenide ion (Scheme 3). However, this



SCHEME 3

mechanism cannot account for the formation of triaryl-methanols, mentioned below.

⁷ G. W. Kenner, M. J. T. Robinson, C. M. B. Taylor, and B. R. Webster, *J. Chem. Soc.*, 1962, 1756.

Direction of Cleavage.—In all the previous work cited the investigators determined the relative extents of cleavage by analysing the carboxylic acid products only. The other products (ArH and $\text{Ar}'\text{H}$) were not analysed quantitatively, though in some cases their presence was established. We analysed both the carboxylic acid and the neutral fractions, with the results shown in Table 1. Ideally, in each case the yield of HPh should equal the yield of $\text{RC}_6\text{H}_4\cdot\text{CO}_2\text{H}$, and the yield of PhR should equal the yield of PhCO_2H (after allowance for side products). In most cases, the actual results are not far from this, though discrepancies do exist. We feel that the ratios determined from the carboxylic acid mixtures are more accurate than those determined from the neutral fractions, except for the cases of the three monofluoro-ketones, where analysis of the carboxylic acid fractions proved troublesome.

Table 2 shows a comparison of cleavage ratios from our work with earlier results. Previous investigators had found that when 3- and 4-substituted aryl groups were compared with the unsubstituted phenyl group, the direction of cleavage was that expected from the field effect of the substituent, *e.g.* electron-withdrawing groups were seen to stabilize arenide ions. Our results do not deviate from the pattern. For the 3-Me, 4-Me, and 4-MeO substituents our ratios are similar to those reported earlier. The 3-F, 4-F, and 4-CF₃-substituted phenyl groups, reported here for the first time, are removed more readily than the phenyl group, as predicted. However, the 2-substituted groups do not follow the above pattern. It had been shown previously (Table 2) that 2-MeO and -Cl-substituted phenyl groups are removed much more readily than the phenyl group (ratios were 99 : 1 or higher). We now add the 2-F group to this list. All these results are in accord with the electron-withdrawing field effects of these substituents. However, the 2-Me group, which should cause the substituted group to be removed less readily than the phenyl group, does not do so. Our results, in accord with previous work, show that the *o*-tolyl group is removed much more readily. A steric explanation has been advanced for this case,^{6a} and it is likely that steric effects are also at least partially responsible for the cases of 2-MeO, 2-Cl, and 2-F, though it has been shown⁹ that 2-halogenoarene ions are particularly stable even in cases where steric effects are absent. The 2-CO₂⁻ group is another electron-donating group which causes a high degree of cleavage.^{6a}

Our attempts to cleave 4-nitrobenzophenone did not give useful results (Table 1). As previously reported for this compound⁴ and for its 2-nitro- and 3-nitro-isomers,³ an intractable mixture of products resulted, in which only benzoic acid was detected. No benzene, nitrobenzene, or 4-nitrobenzoic acid was found.

From our work alone, it is possible to arrange the substituents in the following approximate order, based on their ability to cause cleavage: 2-F > 3-F ~ 2-Me >

⁸ G. Rawson and H. Wynberg, *Rec. Trav. chim.*, 1971, **90**, 46.

⁹ J. F. Bunnett, *Accounts Chem. Res.*, 1972, **5**, 139.

4-F > 4-CF₃ > H > 3-Me ~ 4-Me > 4-MeO. Combining our results with those of the previous investigators, we obtain the approximate order shown in Table 3. The order of substituents in the 3- and 4-positions follows the order of σ values fairly closely, except for 4-CF₃. The following order of carbanion stabilities obtained

fluorobenzophenones, a large amount of the product (more than half in each case) was the *t*-butyl ether (7) formed by nucleophilic displacement. This is not unexpected, since the PhCO group is a good activating group for nucleophilic aromatic substitution, and F is a very good leaving group.¹¹ The failure to detect phenyl

TABLE 2
Cleavage ratios from this work and previous investigations

R	Ratio		Ref.	R	Ratio		Ref.	R	Ratio		Ref.	
	Ph	RC ₆ H ₄			Ph	RC ₆ H ₄			Ph	RC ₆ H ₄		
2-Me	13	87	This work	2-MeO	59	41	<i>b</i>	2-Cl	<0.5	>99.5	<i>a</i>	
	20	80	<i>a</i>		58	42	<i>c</i>		0	100	<i>b</i>	
	15	85	<i>b</i>		<0.5	>99.5	<i>a</i>		3-Cl	5	95	<i>a</i>
	18	82	<i>c</i>		37	63	<i>a</i>		6	94	<i>b</i>	
3-Me	56	44	This work	4-MeO	66	34	This work	4-Cl	21	79	<i>a, b</i>	
	61	39	<i>a</i>		57	43	<i>a</i>		4-CF ₃	33	67	This work
	51	49	<i>b</i>		53	47	<i>d</i>		2-CO ₂ ⁻	6	94	<i>a</i> ^e
	52	48	<i>c</i>		<3	>97	This work		4-CO ₂ ⁻	72	28	<i>a</i> ^e
4-Me	56	44	This work	3-F	12	88	This work	4-Ph	39	61	<i>a</i>	
	57	43	<i>a</i>	4-F	25	75	This work		51	49	<i>c</i>	

^a Ref. 6a. ^b Ref. 3; the figures from the original paper have been converted to a basis of 100%. ^c Ref. 2. ^d Ref. 4. ^e These figures include a statistical correction, to allow for the fact that cleavage of a substrate molecule can give rise to two molecules of benzoic acid.

from hydrogen-deuterium and hydrogen-tritium exchange is drawn from the work of Hall, Roberts, Shatenshtein, and their co-workers:^{1a} 2-F > 4-CF₃ > 3-F ~ 2-MeO > 4-F > 4-Ph > 3-MeO ~ 4-MeO ~ 4-Me ~ 2-Me ~ 3-Me. The two orders are fairly similar,

TABLE 3

Groups arranged in approximate descending order of ability to cause cleavage; and σ values of *m*- and *p*-substituents

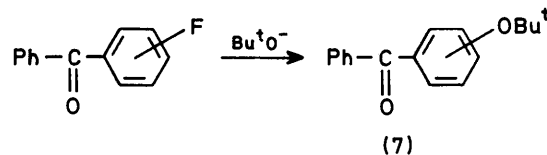
Group	σ^a	Group	σ^a
2-F, 2-Cl, 2-MeO		3-MeO	0.12
3-Cl	0.37	4-Ph	-0.01
2-CO ₂ ⁻		H	0
3-F	0.34	3-Me	-0.07
2-Me		4-Me	-0.17
4-Cl	0.23	4-MeO	-0.27
4-F	0.06	4-CO ₂ ⁻	-0.1
4-CF ₃	0.54		

^a From ref. 10.

except for the positions of the 2-Me and 2-MeO groups, supporting the idea that the large extents of cleavage in these cases are caused by steric factors (which are absent in the hydrogen exchange reactions).

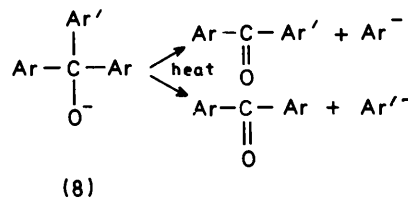
Side Products.—A number of side products were isolated or detected, most of them clearly understandable on the basis of previous work. In the reaction between benzophenone and potassium *t*-butoxide, 3.6% of the product was triphenylmethanol, formed by attack of benzenide ion on benzophenone or *t*-butyl benzoate. This product had been identified in previous cleavages of benzophenone.^{3,4,6a} Similarly, cleavage of 3- and 4-methylbenzophenones each gave rise to small amounts of two unidentified products with long retention times (similar to that of triphenylmethanol), probably also triarylmethanols. In the cleavages of the three mono-

t-butyl ether among the products indicated that (7), once formed, was not cleaved under these conditions. In the reaction of 2-methylbenzophenone an important side product (13%) was phenyl-(*o*-tolyl)methanol. It



had previously been shown (*e.g.* ref. 4) that alkoxides could reduce diaryl ketones, though ethoxides and isopropoxides are better for this purpose than *t*-butoxides. An unexpected side-product was *p*-benzylanisole, isolated from the reaction of *p*-methoxybenzophenone.

Cleavage of Salts of Triarylmethanols.—When heated, sodium triphenylmethanide is cleaved to give benzophenone and benzenide ion.¹² It occurred to us that a salt (8) of an unsymmetrical triarylmethanide could be



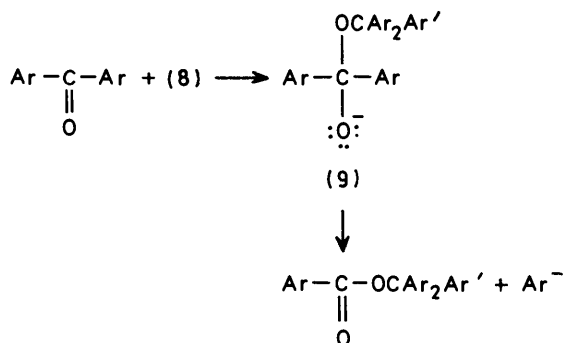
cleaved in either of two directions, and that this would be another way of determining the relative stability of arenide ions. Diphenyl-(*o*-, *m*-, and *p*-tolyl)methanol were cleaved in this way. The results were qualitatively similar to those obtained by cleaving the three methylbenzophenones. In the cases of the *m*- and *p*-tolyl derivatives it was the phenyl group which was

¹⁰ M. Charton, *Chem. Technol.*, 1975, 245.

¹¹ J. March, 'Advanced Organic Chemistry,' McGraw-Hill, New York, 1968, pp. 495-498.

¹² H. D. Zook, J. March, and D. F. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 1617.

removed preferentially (after correction for the fact that these alcohols contain two phenyl groups); with the *o*-tolyl compound, it was the *o*-tolyl group which was removed to a greater extent. However, the method did not prove satisfactory for quantitative estimations, because some of the ketone, once formed, suffered further attack by unchanged alkoxide (*e.g.* Scheme 4), and the



SCHEME 4

resulting ion (9) was cleaved again. In each case the total yield of benzene and toluene was considerably greater than the total yield of ketone, making it impossible to tell how much of the benzene and toluene recovered in each case had come from cleavage of the original alcoholate, and how much from cleavage of the ketone.

EXPERIMENTAL

3-Fluorobenzophenone was synthesized by the method of Buu-Hoï *et al.*¹³ Benzophenone was obtained from the J. T. Baker Chemical Company, 3-methyl and 4-methoxybenzophenone from Pfaltz and Bauer, Inc., and 4-tri-

fluoromethylbenzophenone from PCR, Inc. All other ketones were obtained from the Aldrich Chemical Company, Inc.

General Procedure for the Base-induced Cleavage of Diaryl Ketones.—Equimolar quantities of solid diaryl ketone and potassium *t*-butoxide were mixed without a solvent and heated to over 100 °C. In all cases a slow reflux was soon noticed. The external heating was maintained for several hours (see Table 1), and the mixture allowed to cool to 40 °C. Water (*ca.* 10 ml) and an equal volume of chloroform were added, and the mixture was transferred to a separatory funnel. After rinsing and washing, the chloroform layer was quantitatively analysed (g.l.c.) for neutral components. The strongly basic aqueous layer was acidified with hydrochloric acid. The acidic products, which separated either as solids or oils, were extracted with benzene and chloroform. The combined extracts were washed, dried (MgSO₄), and evaporated. The residue was weighed and analysed by g.l.c. In the cases of the fluoro-benzophenones and trifluoromethylbenzophenone the acidic products were converted into their methyl esters with diazomethane before g.l.c.

Cleavage of Triarylmethanols.—The three diphenyl(*tolyl*)-methanols [prepared (by E. F. Martin) by the method of Acree¹⁴] (0.004 00 mol each) were partially converted into their salts with sodium amide (0.001 30 mol), and cleaved according to the method of Zook *et al.*¹² The products were analysed by g.l.c.

*Phenyl-(*o*-tolyl)methanol.*—To *o*-methylbenzophenone (4.90 g) in ethanol (25 ml), cooled to 15 °C, a slurry of sodium borohydride (0.42 g) in ethanol (10 ml) was added over 3 min. After 1 h stirring, addition of water (120 ml) and dilute hydrochloric acid (10 ml) gave the alcohol (4.7 g), m.p. 89–92° (lit.,¹⁵ 91°).

p-Benzylanisole was prepared by the method of Goldschmidt and Larson.¹⁶

[6/1517 Received, 3rd August, 1976]

¹³ N. P. Buu-Hoï, E. Lescot, jun., and N. D. Xuong, *J. Org. Chem.*, 1957, **22**, 1057.

¹⁶ H. Goldschmidt and H. Larsen, *Z. phys. Chem.*, 1904, **48**, 424.

¹³ N. P. Buu-Hoï, E. Lescot, jun., and N. D. Xuong, *J. Org. Chem.*, 1957, **22**, 1057.

¹⁴ S. F. Acree, *Ber.*, 1904, **37**, 990.