Iodine Oxidation of Arylacetones in Alkaline Methanol

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The reactions of deoxybenzoin (1) and phenylacetones (2) with iodine have been studied in methanol containing sodium methoxide. The reaction of (1) gives 1.2-dibenzoyl-1.2-diphenylethane (4) (an oxidative coupling product) and benzoin (3) (an epoxidation product) in the ratio 0.2—1.6. The ratio is proportional to the initial concentration of (1). suggesting the intermediacy of α-benzoyl-α-iodotoluene (12). Diphenylacetone afforded only an intramolecular oxidative coupling product, methyl 2.3-diphenylpropionate. The reaction of PhCHMe-$COCH_3$ yields $PhCHMeCO_2Me$ (7) (a halogenoform reaction product). $PhCHMeCH_2CO_2Me$ (5) (a Favorskii reaction product). and a small amount of $PhCMe{=}CHCO_2Me$ (6). The ratio of products (7) and (5) is proportional to the concentration of the remaining I_2 in the alkaline methanol, which implies that the iodination of ketones involves an attack by molecular iodine on the enolate ion. The effect of the ring substituents in PhCHMe-$COCH_3$ on the (7) : (5) ratio (ρ 0.5—0.40: r 0.992) along with the observed position of iodination imply a transition state containing bridged H^+ and I_2 for iodination of the enolate ion of arylacetones.

NUMEROUS papers have been published on the α-halogenation of ketones.[1-10] The reaction in acidic solution proceeds by rate-determining enolisation followed by halogenation with X_2 or X_3^- as shown by the following facts: (i) the rate is first-order in substrate,[1,2] but independent of the nature and concentration of halogen,[1,2] (ii) the reaction slows down upon substitution by α-deuterium,[2] and (iii) the ratio of α- to α′-deuteriation is the same as that of halogenation.[3,4]

However, the detailed mechanism of halogenation of ketones in basic solution is still obscure.[5] The postulated mechanisms are: (i) halogenation of the enolate ion,[2a,6,7] (ii) halogenation of the enol,[2b,5,8,9] and (iii) halogenation of the unenolised ketone.[4] In general, mechanisms (i) and (ii) have been accepted because of the identity of the rates of halogenation and of enolisation.[6,7,10] In fact, the rate of α-deprotonation of ketones have often been measured by following their rates of base catalysed halogenation.[7,10] However, Rappe has recently showed [4] that the ratio of α- to α′-halogenation of butan-2-one is different from their ratio of α- to α′-deuteriation in aqueous alkali, and he suggested two mechanisms which involve the halogenation of unenolised ketone by HOX and OX^-.

Moreover, it is obscure [2a,5] which halogenation species, *i.e.* X_2,[1] X_3^-,[1] HOX,[4,6a,8] and/or OX^-,[4,6b] is most active. We wished to clarify these obscurities and have studied the iodine oxidation of some arylketones in methanol

[1] (*a*) R. P. Bell and K. Yates, *J. Chem. Soc.*, 1962, 1927; (*b*) N. C. Deno and R. Fishbein, *J. Amer. Chem. Soc.*, 1973, **95**, 7445.

[2] (*a*) H. House, 'Modern Synthetic Reactions,' Benjamin, New York, 1972, 2nd edn., p. 463; (*b*) J. March, 'Advanced Organic Chemistry: Reactions, Mechanism, and Structure,' McGraw-Hill, New York, 1968, p. 463.

[3] C. Rappe and W. H. Sachs, *J. Org. Chem.*, 1967, **32**, 4127.

[4] C. Rappe, *Acta Chem. Scand.*, 1966, **20**, 376, 2236; 1967, **21**, 857, 1823; 1968, **22**, 219.

[5] R. C. Fuson and B. A. Bull, *Chem. Rev.*, 1934, **15**, 275.

[6] (*a*) P. D. Bartlett, *J. Amer. Chem. Soc.*, 1934, **56**, 967; (*b*) J. R. Hulett, *J. Chem. Soc.*, 1965, 430.

[7] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell Univ. Press, Ithaca, 1969, 2nd edn., p. 829.

[8] C. F. Cullis and M. H. Haschmi, *J. Chem. Soc.*, 1956, 2512; 1957, 1548, 3080.

[9] F. Straus and R. Kühnell, *Ber.*, 1933, **66**, 1834.

[10] (*a*) A. C. Knipe and B. G. Cox, *J.C.S. Perkin II*, 1973, 1391; (*b*) A. Lapworth, *J. Chem. Soc.*, 1904, **85**, 30; (*c*) A. M. van Arendonk and M. E. Cupery, *J. Amer. Chem. Soc.*, 1931, **53**, 3184.

containing sodium methoxide. Since these reactions are very fast, direct measurement of rates is difficult. Further, the rate only gives information on the primary rate-determining deprotonation step, but nothing on subsequent steps.

Hence, we attempted to study the mechanisms by means of product determination. Alkaline methanol was selected as a solvent to simplify the system by excluding HOI and OI^- and to obtain a homogeneous solution, so that the reactivities of molecular iodine (I_2), methyl hypoiodite (MeOI), and iodide ion (I_3^-) could be compared.

RESULTS

Reaction of Deoxybenzoin and αα'-Diphenylacetone with Iodine.—The reactions were conducted by two methods. (A) A methanolic solution (15 ml) of iodine was dropped slowly (during 15 min) into a mixture of ketones and sodium methoxide in methanol. This method suppresses the further oxidation (an attack of iodine on iodinated compounds leading to iodoform) because of the deficiency of iodine.

(B) A methanolic solution of substrate was added at once to a methanolic mixture of sodium methoxide and iodine which was present in large excess to the equivalent amount of substrate. This method affords an almost constant concentration of reagents during the reaction, and also some further oxidation products (halogenoform reaction products).

The reaction of deoxybenzoin (1) with iodine by method (A) at 0—25° gave benzoin (3) together with 1,2-dibenzoyl-1,2-diphenylethane (± and *meso*) (4) and a small amount of methyl benzoate (a halogenoform reaction product) which was obtained in various yields depending on the rate of addition of iodine.

$$\underset{(1)}{PhCH_2COPh} \xrightarrow{I_2\text{–}MeONa} \underset{(3)}{PhCH(OH)COPh} + \underset{(4)}{PhCH(COPh)CH(COPh)Ph} + PhCO_2Me$$

The ratio of products [(4) : (3)] at 25° was measured by means of g.l.c.; Table 1 shows that the ratio is proportional to the initial concentration of (1). On the other hand, the

$$(4) : (3) = k_1[(1)]_0 \qquad (1)$$

treatment of (1) by method (B) at 25° afforded only methyl benzoate in quantitative yield.

TABLE 1

Product ratios in the reaction of deoxybenzoin with iodine at 25° in alkaline methanol [a]

		Yields of products (%)			
$[(1)]_0$/M	$[NaOMe]_0$/M	$PhCO_2Me$ [b]	PhCH(OH)COPh	$(PhCHCOPh)_2$	$\frac{(PhCHCOPh)_2}{PhCH(OH)COPh}$
0.0071	2.00	Trace	99	Trace	0
0.04	2.00	12	70	18	0.257
0.12	2.00	4	65	31	0.477
0.20	2.00	3	48	49	1.021
0.32	2.00	2	37	61	1.647
0.20	1.00	7	46	47	1.001
0.20	1.50	3	49	48	0.979
0.01 [c]	0.10			99 [d]	

[a] A solution of iodine (0.5M; 20 ml) was dropped slowly to a 20 ml solution of the reaction mixture [method (A), see text]. The yield of methyl benzoate varies with the dropping rate of iodine. [c] $(PhCH_2)_2C{=}O$. [d] $PhCH_2CHPhCO_2Me$.

TABLE 2

Product ratios of the reaction of α-methyl-α-phenylacetone (2b) with iodine in alkaline methanol at 40° [a]

		Yields of products (%)			$\frac{PhCHMeCH_2CO_2Me}{PhCHMeCO_2Me}$	
$10^{-3}[I_2]_t$/M	$10^{-3}[NaOMe]_t$/M	$PhCHMeCO_2Me$	$PhCHMeCH_2CO_2Me$	$PhCMe{=}CHCO_2Me$		Slope [b]/l mol^{-1}
322	322	69.6	21.7	8.7	0.312	
322	419	46.4	47.8	5.8	1.03	
322	516	25.5	63.4	11.1	2.49	14.3
322	644	18.8	71.4	9.8	3.79	
322	966	9.4	82.7	7.9	8.82	
161	210	26.4	63.9	9.7	2.42	
161	258	18.5	74.4	7.1	4.02	
161	322	9.3	85.1	5.6	9.19	51.2
161	419	7.3	87.1	5.6	12.0	
161	516	4.0	89.1	6.9	22.4	
96.6	129	17.3	79.5	3.2	4.61	
96.6	162	10.2	86.9	2.9	8.50	
96.6	194	5.6	90.7	3.7	16.2	152
96.6	258	3.8	92.3	3.9	24.5	
96.6	322	2.4	95.2	2.4	39.7	

[a] The methanolic (2a) (0.1M; 1 ml) was added to 30 ml of the solution of iodine and sodium methoxide at 40°, and the mixture was stirred for 15 min. [b] This value is proportional to $[I_2]_t^{-2}$.

αα'-Diphenylacetone gave methyl 2,3-diphenylpropionate quantitatively at 25° (see Table 1).

$$PhCH_2COCH_2Ph \xrightarrow{I_2\text{–}MeONa} PhCH_2CH(Ph)CO_2Me$$

Reaction of Arylacetones (2).—The reaction of α-methyl-α-phenylacetone (2b) by method (A) yielded methyl 3-phenylbutanoate (5) and methyl 3-phenylbut-2-enoate (6) at 25° (see Scheme 6). However, when (2b) was added to the iodine solution [method (B)] at −30 to 0°, methyl

2-phenylpropionate (7) and iodoform were obtained quantitatively, while the reaction by method (B) at 40° gave

$PhCHRCOCH_3$ (2)	$PhCHMeCH_2CO_2Me$ (5)	$PhCH_2CH_2CO_2Me$ (8)
a; R = H	$PhCMe{=}CHCO_2Me$	$PhCH{=}CHCO_2Me$
b; R = CH_3	(6)	(9)
	$PhCHMeCO_2Me$ (7)	$PhCH(OH)COCH_3$ (10)

(7), (5), and a small amount of (6) (Scheme 6). The ratio of products (7) : (5) at 40° was measured by means of g.l.c. and is listed in Table 2. These data show that the ratio is expressed as in equation (2). Here, [ ]$_t$ denotes the concentration of the total amount of added reagents.

$$(7) : (5) = k_2[I_2]_t^2/([MeONa] - [I_2]_t) \quad (2)$$

The reaction of phenylacetone (2a) by method (A) at 0° yielded methyl 3-phenylpropionate (8), methyl cinnamate (9), and 1-hydroxy-1-phenylacetone (10), while methyl benzoate was obtained by method (B) at 0° (see Scheme 5).

Substituent Effects.—The product ratios (7) : (5) for the reactions of some ring-substituted α-methyl-α-phenylacetones (2b) by method (B) at 40° were measured and the calculated constants (k_2) in equation (2) are listed in Table 3. A plot of log k_2 against Hammett σ values gave a ρ value of −0.40 (r 0.992).

TABLE 3

Effect of substituents on k_2 in equation (2) [a] for the reaction of $XC_6H_4CHMeCOCH_3$ with iodine in alkaline methanol at 40°

X	k_2/l mol^{-1} s^{-1}
p-Me	1.74
m-Me	1.58
H	1.41
p-Cl	1.15
m-Cl	1.05

$$\frac{ArCHMeCO_2Me}{ArCHMeCH_2CO_2Me} = k_2 \frac{[I_2]_t^2}{([NaOMe]_t - [I_2]_t)}$$

DISCUSSION

Oxidative Coupling of Deoxybenzoin and αα′-Diphenylacetone.—The reaction of deoxybenzoin (1) with iodine in methanol gives (4), as reported.[11] As shown in Scheme 1,[12a] the intermediacy of the iodide (12) in this reaction is supported by the formation of a by-product, benzoin (3). In view of the ready oxidation of this benzoin to benzil in the solution,[13a] the absence of benzil in the products implies that benzoin is not a direct product but is derived only from the methoxyoxiran (13),[13b] which gives benzoin as a result of pouring the product into water. The oxiran (13) is formed by methanolysis of (12).[13b] The rate of formation of benzoin (3) is close to that of (13) and is given by equation (7). Here, $k_7 = k_5$ or $k_5'k_5/k_{-5}$.

$$d[(3)]/dt = d[(13)]/dt = k_7[(12)][MeO^-] \quad (7)$$

Application of the mechanism postulated for the oxidative coupling of benzyl cyanide [12a,d] to the formation of (4) leads to Scheme 2. Scheme 2 leads to the

$$(11) + (12) \xrightarrow{k_8} (4) + I^- \quad (8)$$

SCHEME 2

rate expression (9), if equation (8) is rate determining.

$$d[(4)]/dt = k_8[(11)][(12)] = k_8K_3[(12)][MeO^-][(1)] \quad (9)$$

Since the ratio (4) : (3) (*i.e.*, the ratio of oxidative coupling to epoxidation) approximates to d[(4)]/d[(3)] in the early stages of the reaction, equation (10) is obtained from equations (7) and (9). The validity of

$$(4) : (3) \simeq d[(4)]/d([(3)] = k_8K_3[(1)]/k_7 \quad (10)$$

equation (10) was determined as in the case of equation (1), *i.e.*, an increase in the concentration of ketone (1) results in an increase of the ratio (4) (oxidative coupling) : (3) (epoxidation). In the case of diphenylacetone which bears two adjacent unsolvated methylene groups the initial concentration is high. As stated in the Results section, αα′-diphenylacetone gives quantitatively methyl 2,3-diphenylpropionate (a Favorskii product), but no hydroxylated product corresponding to equations (5) and (6). The Favorskii reaction has been reported to involve an intramolecular S_N2 reaction of an α-carbanion

SCHEME 1

[11] E. Knoevenagel, *Ber.*, 1888, **21**, 1355.

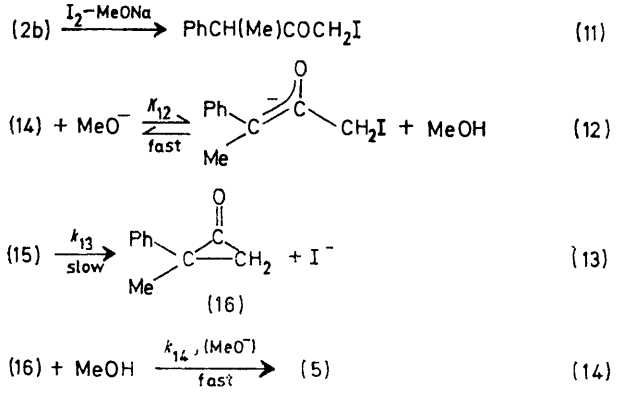
[12] (*a*) Y. Ogata and K. Nagura, *J. Org. Chem.*, 1974, **39**, 394; (*b*) G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, 1968, **90**, 347; (*c*) H. Feuer, J. Doty, and J. P. Lawrence, *J. Org. Chem.*, 1973, **38**, 417; (*d*) K. G. Shipp and L. A. Kaplan, *ibid.*, 1966, **31**, 857.

[13] (*a*) B. B. Corson and R. W. McAllister, *J. Amer. Chem. Soc.*, 1929, **51**, 2822; (*b*) F. G. Bordwell and J. Almy, *J. Org. Chem.*, 1973, **38**, 575.

as in Scheme 2.[14] A radical mechanism [12b-d] cannot explain equation (1).

Relation between Favorskii and Halogenoform Reactions with α-Methyl-α-phenylacetone (2b).—As reported by Bordwell, a probable mechanism is shown in Scheme 3 for α-methyl-α-phenylacetone (2b), which involves the intermediate (14). The preferential iodination of CH_3 is discussed later.

At higher concentration of halogen, further halogenation produces a halogenoform reaction (Scheme 6). Compound (7) may be formed from (14) by further iodination (*i.e.*, halogenoform reaction) (Scheme 4). In these basic



SCHEME 3

solutions, iodine is converted into methyl hypoiodite (MeOI) by equilibrium (15). Hence, the concentration

$$I_2 + MeO^- \overset{K}{\rightleftharpoons} MeOI + I^- \qquad (15)$$

of the remaining molecular iodine * is very low [15a,b] and can be estimated by equation (16),[16] where [ ]$_t$ denotes

$$[I_2] = \frac{1}{K_{15}}\frac{[MeOI][I^-]}{[MeO^-]} = \frac{1}{K_{15}}\frac{[I_2]_t^2}{[MeONa]_t - [I_2]_t} \qquad (16)$$

the total concentration of added reagents. Since the total added sodium methoxide and iodine are in large excess over the amount of substrate (2b) and since the concentration of (14) is small and constant in the steady state, equation (2) is reduced to (17) by using equation

$$(7) : (5) \simeq d[(7)]/d[(5)] = k_2K_{15}[I_2] \qquad (17)$$

(16). On the other hand, the rate of formation of (5) should be expressed as equation (18) according to

$$d[(5)]/dt = k_{13}K_{12}[(14)][MeO^-] \qquad (18)$$

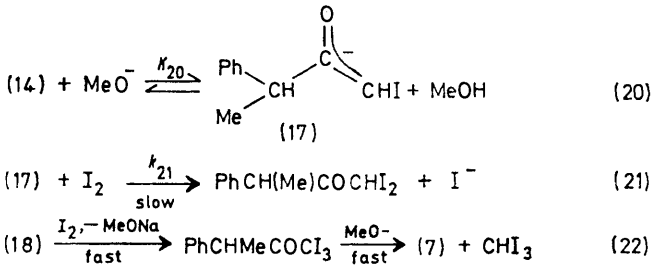
* The concentration of I_3^- (in $I_2 + I^- \overset{K}{\rightleftharpoons} I_3^-$) should be lower because the equilibrium constant of above reaction is very small ($K = 16$) [1,15] and the concentration of I_2 is very low.

[14] Some examples for these mechanistic studies are (*a*) F. G. Bordwell and J. G. Strong, *J. Org. Chem.*, 1973, **38**, 579 and previous papers; (*b*) M. Charpentier-Morize, M. Mayer, and M. B. Tchoubar, *Bull. Soc. chim. France*, 1965, 529; (*c*) E. W. Galson, *J. Amer. Chem. Soc.*, 1969, **91**, 3951; (*d*) H. O. House and W. F. Gilmore, *ibid.*, 1961, **83**, 3980; (*e*) H. O. House and G. A. Frank, *J. Org. Chem.*, 1965, **30**, 2948.

Scheme 3. Consequently, equation (19) is derived, which agrees with Scheme 4 as shown below.

$$d[(7)]/dt = k_2k_{13}K_{15}K_{12}[(14)][MeO^-][I_2] \qquad (19)$$

Therefore a molecule of (14), I_2, and MeO^- should participate in the rate-determining step for the iodination of (14). This can be explained only by Scheme 4.



SCHEME 4

If equation (21) determines the rate, the overall rate should be expressed as equation (23), which is consistent

$$d[(7)]/dt = k_{21}K_{20}[(14)][MeO^-][I_2] \qquad (23)$$

with (19). It seems curious that step (21) determines the rate, since the enolisation step is generally rate determining in acid-catalysed halogenation of ketones.[1] But in highly basic solutions, the concentration of molecular halogen is so low that equation (21) (halogenation) determines the rate. In fact, the rate is also dependent on the halogen concentration for acid-catalysed halogenation with dilute halogen.[1] Further, it has been reported that the halogenation rates of acetone [6a] and acetophenone [6b] are dependent on the halogen at high basicity in the order: $I_2 > Br_2 > Cl_2$.

Substituent Effects.—The effect of ring-substituents on k_2 affords a Hammett ρ value of −0.40. Combining equations (19) and (23) gives (24). Consequently,

$$k_2 = k_{21}K_{20}/K_{15}k_{13}K_{12} \qquad (24)$$

equation (25) applies. Since K_{15} is independent of the

$$\log(k_2) = \log(k_{21}K_{20}) - \log(k_{13}K_{12}) - \log(K_{15}) \qquad (25)$$

substituent, the substituent effects can be expressed in terms of a modified Hammett equation (26).[13b] Thus

$$\log(k_2)_{rel} = \rho\sigma = (\rho_H - \rho_F)\sigma \qquad (26)$$

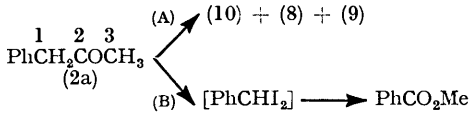
$\rho = \rho_H - \rho_F$ where ρ_H and ρ_F refer to the Hammett reaction constants for halogenation of (14) [formation of (7)] and a Favorskii reaction [formation of (5)], respectively. The ρ value for the Favorskii reaction of (14) (ρ_F) is unknown as yet, but it may be between −2 and −3, since the ρ value for the Favorskii reaction of $ArCH_2COCH_2Cl$ is −2.93.[13b] If so, ρ_H shows that an attack of molecular iodine on the enolate ion (17) [step (21)] is favoured by the presence of electron-releasing substituents and the effect is fairly large in spite of the

[15] (*a*) A. Skrabal, *Monatsh*, 1911, **32**, 167 (*Chem. Abs.*, 1911, **5**, 2591); (*b*) C. H. Li, *J. Amer. Chem. Soc.*, 1947, **64**, 1147.

[16] Y. Ogata and K. Nagura, *J.C.S. Perkin II*, 1974, 1089.

one-atom separation of the reaction site from the substituent. The reason for this will be discussed later.

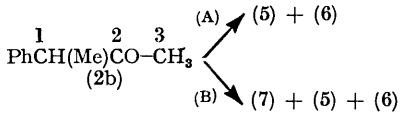
Direction of Iodination of Phenylacetones (2a *and* b).—The reaction of phenylacetone (2a) by method (A) at 0° gives 1-hydroxy-1-phenylacetone (10) together with other products [(8) and (9)] but no 3-hydroxylated product. This is due to iodination of (2a) at the 1-position because of the higher acidity of 1-position bearing an electron-attracting phenyl group. On the other hand, the reaction of (2a) by method (B) at 0° gives only methyl benzoate, a halogenation product at the 1-position.



SCHEME 5

In contrast, α-phenyl-α-methylacetone (2b) gives by method (B) at below 0° only methyl propionate (7) *via* 3-iodination but no product *via* 1-iodination.

Increasing the temperature increases the yields of other products [(5) and (6)], but these by-products are also formed *via* 3-iodination because of the formation of (5) and (6) by method (A) (insufficient iodine) at lower temperatures.



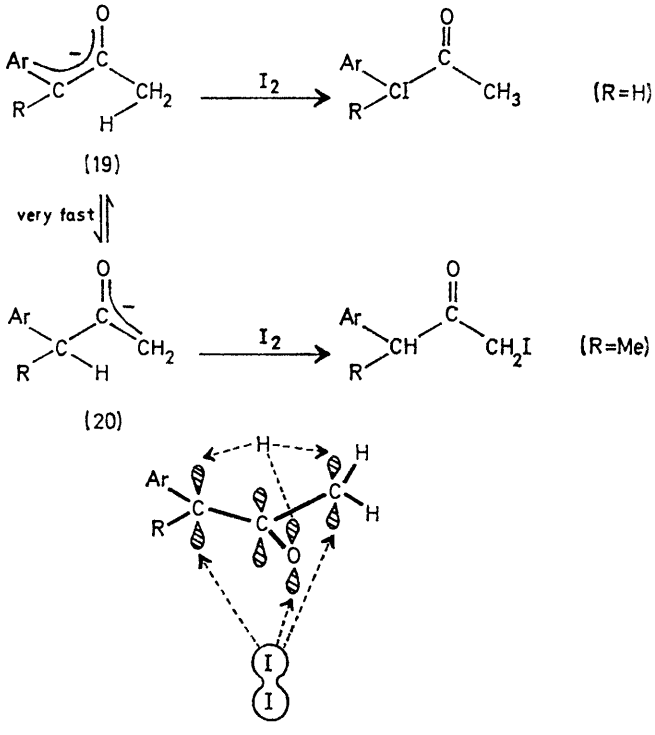
SCHEME 6

The 3-iodination of (2b) is in contrast to the 1-iodination of (2a). Taft's σ_I values [17] are 0.10 for Ph, 0 for H, and −0.05 for Me, predicting the higher acidity of 1-H compared with that of 3-H for (2b).

It has been said that the position of halogenation is determined by the acidity of the methylene protons of ketones.[6,9] However, there are other factors which determine the direction of halogenation. In fact, there is a discrepancy between the directions of halogenation and deuterium exchange in highly basic media,[3,4] but good agreement is observed in acidic media, where the mechanism involves rate-determining enolisation.[1]

The different direction for the iodination of arylacetones (Schemes 5 and 6) suggests a mobile equilibrium between enolate ions (19) and (20), which are then iodinated [3,7] as shown in Scheme 7. The transition state (21) with a bridged proton is postulated for iodination by analogy with Bordwell's mechanism for the Favorskii reaction.[13a]

The direction of protonation (deuteriation) of the enolate ion is decided only by the structure of the anions (19) and (20), but the position of halogenation is determined by several factors such as the acidity or stability of (19) and (20), the steric effect (due to the bulky halogen atom), and/or the product stability. This transition state, in which the orbitals of O and C overlap



SCHEME 7

and transmit the electronic effect of aryl, can explain the large ρ_H in spite of the separation of the aromatic ring from the reaction site for (14).

EXPERIMENTAL

Materials.—Deoxybenzoin (1) was of guaranteed grade and used without further purification. Dibenzylketone had b.p. 290—292° at 1.2 mmHg (lit.,[18] 320° at 3 mmHg). *m*-Chloro-, *m*-methyl-, and unsubstituted -phenylacetones (2a) were prepared by sulphuric acid-catalysed hydrolysis and decarboxylation of α-acetyl-α-arylacetonitriles.[19] Substituents and b.p.s are as follows: unsubstituted, 62—63° at 2 mmHg (lit.,[19a] 109—112° at 24 mmHg); *p*-Cl, 88—90° at 2 mmHg (lit.,[20] 85—86° at 1 mmHg); *m*-Cl, 97—99° at 5 mmHg (lit.,[21a] 89—92° at 2 mmHg); *m*-Me, 74—75° at 2 mmHg (lit.,[21b] 118—119° at 18 mmHg); *p*-Me, 75—77° at 2 mmHg (lit.,[21c] 109—110° at 12 mmHg). For substituted 3-phenylbutan-2-ones (2b),[22] substituents, b.p.s, and analytical data for new compounds are as follows: unsubstituted, 93—95° at 15 mmHg (lit.,[22] 103—106° at

[17] M. Charton, *J. Org. Chem.*, 1964, **29**, 1222.
[18] C. D. Hurd and C. L. Thomas, *J. Amer. Chem. Soc.*, 1936, **58**, 1240.
[19] (*a*) P. L. Julian and J. J. Oliver, 'Organic Syntheses,' Wiley, New York, Coll. Vol. I, 1943, p. 391; (*b*) P. L. Julian, J. J. Oliver, R. H. Kimball, A. B. Pike, and G. D. Tefferson, *ibid.*, p. 487.
[20] T. M. Patrick, jun., E. T. McBee, and H. B. Hass, *J. Amer. Chem. Soc.*, 1946, **68**, 1135.
[21] (*a*) K. Binovic, S. Vrancea, D. Grandet, J. M. Lebourg, and R. Porquet, *Chim. Theor.*, 1968, **3**, 313 (*Chem. Abs.*, 1969, **70**, 87171y); (*b*) H. Boit, 'Beilstein Handbuch der Organischen Chemie III,' 1968, vol. 7, p. 1093; (*c*) L. Ruzicka and L. Ehman, *Helv. Chim. Acta*, 1932, **15**, 140.
[22] C. M. Suter and A. W. Weston, *J. Amer. Chem. Soc.*, 1942, **64**, 533.

22 mmHg); *p*-Cl, 100—101° at 1.2 mmHg (lit.,[21a] 112—113° at 1.5 mmHg); *m*-Cl, 93—94° at 1.5 mmHg (lit.,[21a] 110—112° at 2.5 mmHg); *m*-Me, 80—82° at 2 mmHg (Found: C, 81.2; H, 8.95; O, 9.85. $C_{11}H_{14}O$ requires C, 81.45; H, 8.7; O, 9.85%); *p*-Me, 85—87° at 2 mmHg (Found: C, 81.55; H, 8.6; O, 9.85%).

Products.—The reaction of the ketones with iodine was carried out by two methods (A) and (B). The reaction mixture was extracted with benzene and washed with aqueous $Na_2S_2O_3$ and then water. The extracts were chromatographed on a 1 × 50 cm column of silica gel, and eluted with benzene. All isolated products were identified by comparison with the corresponding authentic sample in their g.l.c., i.r., and/or n.m.r. peaks.

A Hitachi K-53 gas chromatograph equipped with a flame ionisation detector was used with a 1.5 m × 3 mm column packed with PEG 20M (10%) on Celite 545, DEGS (13%) on Chromosorb W, and/or SE-30 (3%) on Chromosorb W. A Perkin-Elmer grating i.r. spectrophotometer model 337 and a JEOL C60HL n.m.r. spectrophotometer were used.

The reaction of deoxybenzoin gave benzoin, (±)- and *meso*-1,2-dibenzoyl-1,2-diphenylethane, and methyl benzoate [method (A) at 25°] Benzoin (3) had m.p. 125—127° (lit.,[23] 129°) with i.r. spectrum and g.l.c. retention times consistent with those of the authentic sample. (±)-1,2-Dibenzyl-1,2-diphenylethane had m.p. 250—254° (lit.,[11] 254—255°). *meso*-1,2-Dibenzoyl-1,2-diphenylethane had m.p. 160—165° (lit.,[11] 160—161°). Methyl benzoate had an i.r. spectrum and g.l.c. retention times consistent with those of the authentic sample. Reaction by method (B) of deoxybenzoin (1) gave only methyl benzoate in quantitative yield.

The reaction of diphenylacetone with iodine by methods (A) and (B) gave methyl 2,3-diphenylpropionate in a quantitative yield.

The reaction [method (B)] of phenylacetone (2a) gave methyl benzoate at 0°. The same reaction by method (A) gave methyl 3-phenylpropionate, methyl cinnamate, and 1-hydroxy-1-phenylacetone.

The reaction [method (A) at 25°] of 3-phenylbutan-2-one (2b) gave methyl 3-phenylbutanoate and methyl 3-phenylbut-2-enoate. On the other hand, the reaction by method (B) at $<0°$ of (2b) gave methyl 2-phenylpropionate (7).

Products Ratios.—Deoxybenzoin (1) and sodium methoxide were mixed in methanol and thermostatted at 25°. A methanolic solution of iodine thermostatted at 25° was dropped slowly during 15 min into the solution which was stirred vigorously under nitrogen. After completion of the reaction, the mixture was treated as stated above, and the yields of products were measured by means of g.l.c. (SE-30).

Iodine and sodium methoxide were mixed in methanol and thermostatted at 40°. Methanolic 3-phenylbutan-2-one (2b) was added, and the mixture was stirred for 15 min. The yields of products were measured by means of g.l.c. (PEG 20M).

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