

Iodination of Dibenzoylmethanes with Iodine-Peracetic Acid

By Iwao Urasaki,* Department of Industrial Chemistry, Numazu Technical College, Ooka, Numazu, Japan
Yoshiro Ogata, Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

The reaction of dibenzoylmethane (enol content *ca.* 97%) with iodine-peracetic acid gave dibenzoyliodomethane (keto form) in >90% yield. However, no di-iodo-derivative was obtained by using an excess of reagent. Some *p*-substituted dibenzoylmethanes were also iodinated by this method in fairly high yields. However, 1,1-dibenzoyl-ethane (keto form) was stable to the reagent. This high reactivity of enols together with some kinetic results suggest that the mechanism may be similar to that of the iodoacetoxylation of propene. Dibenzoyliodomethane was also obtained in good yield by the reaction of dibenzoylmethane with iodine-iodic acid, which also gave a di-iodo-derivative in high yield when used in excess.

We have reported previously^{1,2} that olefins and acetylenes are iodoacetoxylation by iodine-peracetic acid. Thus, propene gave 2-iodo-1-methylethyl acetate in *ca.* 80% yield,¹ and diphenylacetylene gave *trans*- α -acetoxy- β -iodostilbene (*ca.* 70%) together with benzil.²

We were interested in the reaction of β -diketones with iodine-peracetic acid in the light of the olefinic properties of the enol forms of these compounds, and now report that dibenzoylmethanes are easily iodinated to give dibenzoyliodomethanes in high yield. In contrast to chlorination or bromination,³ the iodination of β -diketones with elemental iodine is a slow reaction, analogous to aromatic halogenation.⁴ Some methods of obtaining dibenzoyliodomethanes have been reported. Thus, when the sodium salt of dibenzoylmethane was treated with iodine in ether, dibenzoyliodomethane was obtained as a by-product (*ca.* 3%).⁵ Keller prepared dibenzoyliodomethane from dibenzoylbromomethane by the action of sodium iodide.^{3c} Recently, dibenzoylmethane has been iodinated by iodic or periodic acid to give mono- (43–50%) and also di-iodo-derivatives (19–20%).⁶ However, the yields in these iodinations are not as high as ours. The present paper describes the results of iodination of dibenzoylmethanes with iodine-peracetic acid and with iodine-iodic acid, which also gave high yields of mono- and di-iodo-derivatives.

RESULTS AND DISCUSSION

Treatment of dibenzoylmethane (Ic) (enol content in acetic acid *ca.* 97% by n.m.r.) with iodine-peracetic acid in acetic acid at 40° for 3 h gave >90% yield of dibenzoyliodomethane (IIc), identified by i.r. and n.m.r. spectra, determination of iodine content, and m.p. The enol content of (IIc) was virtually zero in deuteriochloroform (no n.m.r. signal for enolic OH). Fatiadi reports that a signal at δ 6.97 for (IIc) is that of the enolic α -proton ($-\text{CH}=\text{C}<$).⁶ However, we consider that this signal should be assigned to the α -proton of the keto-form ($-\text{CO}\cdot\text{CHI}\cdot\text{CO}-$), although it is very close to the signal (δ 6.82) for the enolic α -proton of (Ic) ($-\text{CH}=\text{C}<$).

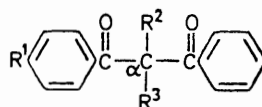
On extraction of a solution of (IIc) in an organic sol-

¹ Y. Ogata and K. Aoki, *J. Org. Chem.*, 1966, **31**, 1625.

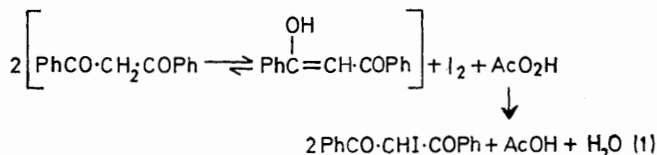
² Y. Ogata and I. Urasaki, *J. Org. Chem.*, 1971, **36**, 2164.

³ (a) R. de Neufville and H. v. Pechmann, *Ber.*, 1890, **23**, 3375; (b) R. Altschul and P. D. Bartlett, *J. Org. Chem.*, 1940, **5**, 623; (c) H. Keller and H. v. Halban, *Helv. Chim. Acta*, 1944, **27**, 1253.

vent with aqueous acidic potassium iodide, (IIc) was converted into (Ic), with liberation of molecular iodine.



- | | |
|---|---|
| (Ia) R ¹ = MeO, R ² = R ³ = H | (IIa) R ¹ = MeO, R ² = H, R ³ = I |
| (Ib) R ¹ = Me, R ² = R ³ = H | (IIb) R ¹ = Me, R ² = H, R ³ = I |
| (Ic) R ¹ = R ² = R ³ = H | (IIc) R ¹ = R ² = H, R ³ = I |
| (Id) R ¹ = Cl, R ² = R ³ = H | (IIId) R ¹ = Cl, R ² = H, R ³ = I |
| (Ie) R ¹ = NO ₂ , R ² = R ³ = H | (IIe) R ¹ = NO ₂ , R ² = H, R ³ = I |
| (If) R ¹ = R ² = H, R ³ = Me | (III) R ¹ = H, R ² = R ³ = I |



This indicates that the iodine atom in (IIc) is highly positive.^{3b} By using this reaction [equation (2)], the iodine



content in α -iodo-derivatives (II) can be determined by simple iodometry, as described in the Experimental section. Table I shows good agreement between found and required values.

In contrast to Fatiadi's iodination,⁶ the reaction of (Ic) with an excess of iodine-peracetic acid gave no di-iodo-derivative (III).

The results of similar iodinations for *p*- and α -substituted dibenzoylmethanes (Ia–f) are listed in Table I, which shows that relatively 'mild' *para*-substituents (Me or Cl) have little effect upon the yields. However, compounds having 'powerful' *para*-substituents (MeO or NO₂) gave poorer yields, and products were not isolated; yields in these cases were deduced from the iodine content of the reaction mixture. These results may be due to low reactivity of the substrates or instability of the products, and the reactions are now being examined in more detail.

⁴ Y. Ogata and K. Nakajima, *Tetrahedron*, 1964, **20**, 43.

⁵ R. D. Abell, *J. Chem. Soc.*, 1912, **101**, 989, 997.

⁶ A. J. Fatiadi, *Chem. Comm.*, 1970, 11.

The α -methyl-derivative (If) was found to be essentially unreactive. This phenomenon together with our failure to obtain the di-iodo-derivative (III) suggests that the keto forms of these compounds are not iodinated by iodine-peracetic acid, since, whereas the *p*-substituted dibenzoylmethanes (Ia—e) mostly exist in the enol form, α -substituted derivatives [(If) and/or (IIc)] exist as the keto form in deuteriochloroform (Table 1). However, steric hindrance by the α -substituent cannot be neglected.

seems to be high, on the basis of n.m.r. data in deuteriochloroform; *i.e.* the enolic α -proton in (Ic) (β -hydroxy-chalcone) resonates at δ 6.82 ($-\text{CH}=\text{C}<$), at much higher field than the corresponding α -proton of chalcone [δ *ca.* 7.4 ($-\text{CH}=\text{CH}\cdot\text{CO}-$), hidden by the Ph multiplet].

From these facts, the illustrated Scheme 1 is suggested for the iodination of (Ic) by iodine-peracetic acid. As shown (IV), and reported by Bratan *et al.*,⁷ the enolic hydroxy-hydrogen atom in (Ic) is centrally located

TABLE 1
Iodination of dibenzoylmethanes (Ia—f) with iodine-peracetic acid in acetic acid at 40° for 3 h^a

Substituent	Substrate		Product				
		Enol content (%) ^b		Yield (%)	M.p. (°C)	Iodine content (%)	
						Found	Required
<i>p</i> -MeO	(Ia)	95	(IIa) ^c	(50—62) ^d			
<i>p</i> -Me	(Ib)	96	(IIb)	80	126—127	34.5	34.9
H	(Ic)	97	(IIc)	92	108	36.1	36.3
<i>p</i> -Cl	(Id)	98	(IId)	88	96—97	32.7	33.0
<i>p</i> -NO ₂	(Ie)	100	(IIe) ^c	(39—48) ^d			
α -Me	(If)	0					

^a Initial concentration of the substrate 0.1M; iodine and peracetic acid 0.05M. ^b Calculated from the intensity ratio of the n.m.r. peak for the enolic α -proton at δ *ca.* 6.7—6.9 ($-\text{CH}=\text{C}<$) to that for the α -protons of the keto form at δ *ca.* 4.4—4.6 ($\text{CO}\cdot\text{CH}_2\cdot\text{CO}$) in deuteriochloroform. ^c Not isolated. ^d Deduced from the iodine content of the reaction mixture.

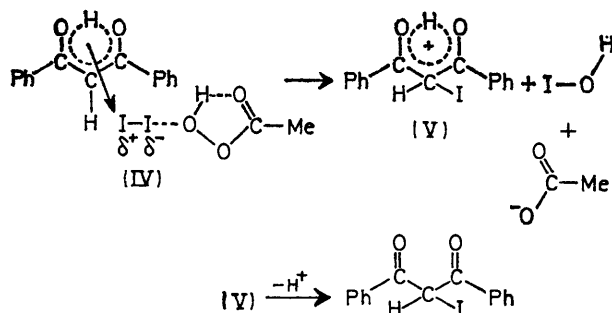
TABLE 2
Iodination of dibenzoylmethane (Ic) with iodine-iodic acid in aqueous acetic acid

(Ic) (mmol)	I ₂ (mmol)	HIO ₃ (mmol)	AcOH (ml)	H ₂ O (ml)	Temp. (°C)	t/h	Product	Yield (%)
20	10	4	90	10	50	2	(IIc)	75
10	10	8	60	8	70	1	(III)	80

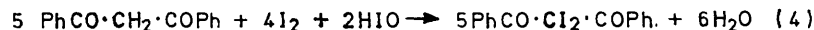
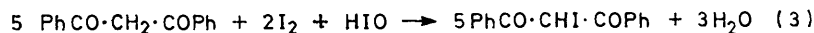
As to the rate of the iodination, preliminary experiments revealed that the reaction of (Ic) with iodine-peracetic acid was very fast and of the third order [k (30°)

between the oxygen atoms. More detailed kinetic and mechanistic studies are in progress.

Iodination of Dibenzoylmethane with Iodine-Iodic Acid.—According to Fatiadi's report,⁶ dibenzoyliodomethane was also obtained by the reaction of dibenzoylmethane with periodic acid (43—46%) and/or with iodic acid (50%). Further, he obtained the di-iodo-derivative (III) by the reaction of dibenzoylmethane with an excess of periodic acid (19—20%). In the light of a report that aromatic compounds are iodinated by iodine-iodic acid,⁸ we treated dibenzoylmethane with iodine-iodic acid in aqueous acetic acid and obtained good yields of (IIc) and (III) (Table 2). The results suggest that the reactions proceed with the approximate stoichiometries shown in equations (3) and (4). Particularly remarkable is the ready formation of (III) in such a high yield, whereas this product could not be obtained by iodination of (Ic) with



ca. 4.2 l² mol⁻² s⁻¹], as in the case of the iodoacetoxylation of propene ¹ [k (30°) *ca.* 5 l² mol⁻² s⁻¹]. Accordingly, the



mechanism of iodination of (Ic) by iodine-peracetic acid may be similar to that of the iodoacetoxylation of propene, for which a rate-determining attack of peracetic acid on the olefin-iodine π -complex is suggested.¹ In fact, the electron density of a double bond in enolic (Ic)

iodine-peracetic acid. These facts suggest that the mechanisms of the two iodinations are different.

Thus dibenzoyliodomethane (IIc) can be produced in good yield by iodination of dibenzoylmethane with either iodine-peracetic acid or iodine-iodic acid. The former reaction is to be preferred for the synthesis of (IIc) because of the lack of contamination with the di-iodo-derivative (III).

⁷ S. Bratan and F. Strobusch, *Ber.*, 1972, **105**, 2284.

⁸ H. O. Wirth, O. Königstein, and W. Kern, *Annalen*, 1960, **634**, 84.

EXPERIMENTAL

Materials.—*para*-Substituted dibenzoylmethanes (Ia—e) were prepared by the action of sodium methoxide on the corresponding *para*-substituted chalcone dibromides in methanol,⁹ and recrystallised from 95% ethanol (except for the *p*-nitro-derivative which was recrystallised from carbon tetrachloride). Yields and m.p.s were as follows: *p*-MeO (Ia), 60%, m.p. 129° (lit.,¹⁰ 130—131°); *p*-Me (Ib), 78%, m.p. 84—85° (lit.,¹¹ 84—85°); H (Ic), 70%, m.p. 77.5° (lit.,⁹ 77—78°); *p*-Cl (Id), 75%, m.p. 88° (lit.,¹² 89°); *p*-NO₂ (Ie), 69%, m.p. 160—161° (lit.,¹³ 160°). *para*-Substituted chalcone dibromides were prepared by the addition of bromine to the corresponding *para*-substituted chalcones in carbon tetrachloride,⁹ except for the *p*-nitro-derivative for which chloroform was used as solvent. The products were washed with hot ethanol. Yields and m.p.s were as follows: *p*-MeO, 71%, m.p. 140° (lit.,¹⁰ 139—140°); *p*-Me, 55%, m.p. 152—155° (lit.,¹⁴ 159°); H, 89%, m.p. 159—160° (lit.,¹⁵ 159—160°); *p*-Cl, 88%, m.p. 183° (lit.,¹² 178—180°); *p*-NO₂, 70%, m.p. 150—151° (lit.,¹³ 151°). *para*-Substituted chalcones were prepared by condensation of the corresponding *para*-substituted benzaldehydes with acetophenone,¹⁶ and recrystallised from ethanol except for the *p*-nitro-derivative which was recrystallised from chloroform. Yields and m.p.s were as follows: *p*-MeO, 91%, m.p. 75° (lit.,¹⁰ 77—78°); *p*-Me, 91%, m.p. 96.5° (lit.,¹⁴ 96.5°); H, 93%, m.p. 56° (lit.,¹⁶ 55—57°); *p*-Cl, 88%, m.p. 115° (lit.,¹⁷ 115—116°); *p*-NO₂, 53%, m.p. 164° (lit.,¹⁸ 164.5°).

1,1-Dibenzoylthane (If) was prepared (92%) by the reaction of the sodium salt of dibenzoylmethane (Ic) with methyl iodide in acetone;¹⁹ m.p. 84.5—85° (from light petroleum) (lit.,²⁰ 84—85°). The sodium salt of (Ic) was prepared (ca. 100%) by the reaction of sodium methoxide with (Ic) in methanol.

Peracetic acid (ca. 1.8M) in acetic acid was prepared by the reaction of acetic anhydride (473 g) with 35% hydrogen peroxide (100 g) in the presence of a catalytic amount of sulphuric acid (1 ml).²¹ The solution was distilled under reduced pressure, and the fraction boiling at 40—43° and 44 mmHg (ca. 2M-peracetic acid) was collected. Iodic acid was prepared by adding 2M-peracetic acid (50 ml, 100 mmol) in acetic acid to a solution of iodine (10 mmol) in acetic acid (50 ml) at 50° during 3 h. After 1 day at room temperature the precipitate was filtered off, washed with petroleum, and dried; yield 92%. Acetic acid for kinetic studies was purified by rectification; b.p. 118—118.5°. A guaranteed grade of commercial iodine was used for kinetic studies without further purification.

Iodination of Dibenzoylmethanes (Ib—d) with Iodine-Peracetic Acid.—A 2.0M-solution (2.5 ml) of peracetic acid (5 mmol) was added to a stirred solution of (Ic) (10 mmol) and iodine (5 mmol) in acetic acid (97 ml). The mixture was kept at 40° for 3 h, then diluted with a ca. two-fold volume of water, filtered, washed with water, and dried. The dibenzoyliodomethane (IIc) obtained (m.p. 107—108°, yield 92%) was recrystallised from light petroleum; m.p. 108° (lit.,⁶ 108—109°) (Found: I, 36.1. Calc. for C₁₅H₁₁IO₂: I,

⁹ C. F. H. Allen, R. D. Abell, and J. B. Normington, *Org. Synth.*, 1941, Coll. vol. I, p. 205.

¹⁰ F. J. Pond and A. S. Shoffstall, *J. Amer. Chem. Soc.*, 1900, **22**, 658.

¹¹ C. Weygand, E. Bauer, H. Günther, and W. Heynemann, *Annalen*, 1927, **459**, 99, 113.

¹² S. Bodforss, *Ber.*, 1918, **51**, 214.

¹³ H. Wieland, *Ber.*, 1904, **37**, 1148.

¹⁴ V. Hanzlik and Al. Bianchi, *Ber.*, 1899, **32**, 2282, 2283.

36.3%); ν_{\max} (KBr) 550 (Cl), 1660 and 1690 (CO), and 3000—3070 cm⁻¹ (C₆H₅); δ (CDCl₃) 6.97 (1H, s, CO-CHI-CO), and 7.16—8.12 (10H, m, Ph) [no C(OH)=CI signal at δ ca. 17]. These data indicate that (IIc) is almost completely in the keto form.

Compounds (Ib and d) were iodinated in the same way, giving the corresponding α -iodo-derivatives [(IIb), 80%; (IIc), 88%]. *Benzoyl(iodo)-(p-toluoyl)methane* (IIb) had m.p. 126—127° (from light petroleum) (Found: I, 34.5. C₁₆H₁₃IO₂ requires I, 34.9%); δ (CDCl₃) 2.30 (3H, s, *p*-Me), 6.93 (1H, s, CO-CHI-CO), and 7.06—8.10 (9H, m, Ph and C₆H₄). *Benzoyl-(p-chlorobenzoyl)iodomethane* (IIc) had m.p. 96—97° (from light petroleum) (Found: I, 32.7. C₁₅H₁₀ClIO₂ requires I, 33.0%); δ (CDCl₃) 6.92 (1H, s, CO-CHI-CO) and 7.20—8.05 (9H, m, Ph and C₆H₄).

Determination of Iodine Content in Dibenzoyliodomethanes (II).—The sample (30—50 mg) was dissolved in chloroform (ca. 5 ml) to which water (ca. 30 ml), aqueous 0.3N-potassium iodide (5 ml), and aqueous 10N-sulphuric acid (1 ml) were added, and the liberated iodine was titrated with aqueous 0.01N-sodium thiosulphate.

Kinetics.—The rate of consumption of peracetic acid was measured as follows. Solutions in acetic acid of (Ic) (0.4M; 5 ml) and iodine (0.05M; 20 ml) were mixed in a flask containing acetic acid (24.5 ml), and kept at 30° to reach temperature equilibrium. A 2.0M-solution (0.5 ml) of peracetic acid in acetic acid at 30° was quickly added to start the reaction; thus the initial concentrations were 0.04M for (Ic) and 0.02M for iodine and peracetic acid. Samples (5 ml) were pipetted out at appropriate intervals and placed in a separatory funnel containing benzene (25 ml) and water (50 ml). The funnel was shaken and the layers were separated. The benzene layer was washed with water (2 × 10 ml) and the content of peracetic acid in the combined aqueous layer was measured iodometrically by titration with aqueous 0.01N-sodium thiosulphate.

Iodination of Dibenzoylmethane (Ic) with Iodine-Iodic Acid.—An aqueous solution (10 ml) of iodic acid (4 mmol) was added dropwise to a stirred solution of (Ic) (20 mmol) and iodine (10 mmol) in acetic acid (90 ml) at 50° during ca. 10 min. The solution was kept at 50° for 2 h, then worked up as in the iodination by iodine-peracetic acid, giving a 75% yield of (IIc), m.p. and mixed m.p. 108°.

Preparation of Dibenzoyldi-iodomethane (III).—An aqueous solution (8 ml) of iodic acid (8 mmol) was dropped into a stirred solution (60 ml) of (Ic) (10 mmol) and iodine (10 mmol) in acetic acid at 70° during ca. 10 min, and the solution was kept at 70°. A yellow precipitate soon began to separate. After 1 h, the mixture was cooled to room temperature, and the precipitate was filtered off, washed with methanol, and dried. The product (III) was pure; yield 80%, m.p. 155° (lit.,⁶ 152—153°).

We thank K. Endo and H. Yamada for aid in performing the experiments.

[5/024 Received, 7th January, 1975]

¹⁵ E. Lutz, D. F. Hinkley, and R. H. Jordan, *J. Amer. Chem. Soc.*, 1951, **73**, 4647, 4651.

¹⁶ E. P. Kohler and H. M. Chadwell, *Org. Synth.*, 1941, Coll. vol. I, p. 78.

¹⁷ W. Dilthey, L. Neuhaus, E. Reis, and W. Schommer, *J. prakt. Chem.*, 1930, **124**, 81, 126.

¹⁸ C. Weygand and F. Schächer, *Ber.*, 1935, **68**, 227, 234.

¹⁹ C. Weygand, *Ber.*, 1928, **61**, 687.

²⁰ J. Marshall, *J. Chem. Soc.*, 1915, **107**, 509, 518.

²¹ Y. Ogata and I. Urasaki, *J. Chem. Soc. (C)*, 1970, 1689.