Reactions of Aryl Ketones and Coumarins with Iodine(III) Tris(trifluoroacetate)

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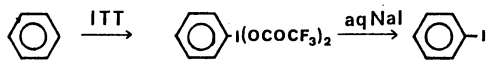
The reaction of acetophenones with iodine(III) tris(trifluoroacetate) yields 3′- and/or 2-iodo derivatives, depending upon the substituent on the aromatic ring and the reaction conditions. The reaction was examined by changing the molar ratio of acetophenone versus the reagent, reaction temperature, and solvent. In similar reactions flavanones and coumarins gave iodo derivatives in which iodine is incorporated at various positions orientated by the oxygen functions. 1,2-Diphenylethanone yields 2-hydroxy-2-(2-iodophenyl)-1-phenylethanone and 1-(2-iodophenyl)-2-phenylethanedione. The reactions of other aromatic ketones such as 9-xanthenone, 9-fluorenone, and anthrone also give iodo derivatives in moderate to good yields. The mechanisms for the iodination at the α-carbon to the carbonyl group have been discussed.

Although several iodination reactions of aromatic hydrocarbons and ketones have been investigated,[1,2] it is still desirable to seek a better method for iodination. The reaction of iodine(III) tris(trifluoroacetate) (ITT), which is readily prepared by the oxidation of iodine with fuming nitric acid in trifluoroacetic anhydride,[3] has been carried out only with a limited number of aromatic substrates such as benzene, toluene, and chlorobenzene by Maletina et al.[4] In Maletina's procedure, iodination products were obtained when a reaction intermediate, bis(trifluoroacetoxy) derivative, was treated with aqueous sodium iodide (Scheme 1).



Scheme 1.

We have studied the reaction for its applicability to a wide variety of compounds. We chose acetophenones, 1,2-diphenylethanone, flavanones, coumarins, 9-xanthenone, 9-fluorenone, and anthrone as the substrate, because they were polyfunctionalized compounds, and some biological activity is expected for their iodination products.[5] At first, the iodination of several acetophenone derivatives **1a—e** was examined in order to understand the dependency of yields on the reaction time, reaction temperature, solvents and substituent effects.

Results

A mixture of acetophenone (**1a**) and ITT in a molar ratio of 1 : 1 was stirred in dichloromethane at 23 °C and the reaction mixture was treated with aqueous sodium iodide, giving 3′-iodoacetophenone (**2a**) in a 41% yield (Table 1, Entry 2). The reaction of **1a** with ITT in a molar ratio of 1 : 2 gave 92% yield of **2a** after 24h (Entry 4). At 0 °C or at the refluxing temperature of dichloromethane, yields of **2a** became lower (Entries 1 and 3). A remarkable change in the products was demonstrated by reaction media. In chloroform, in which ITT is readily soluble, the reaction yielded only 2-iodoacetophenone (**3a**) and 2-hydroxyacetophenone

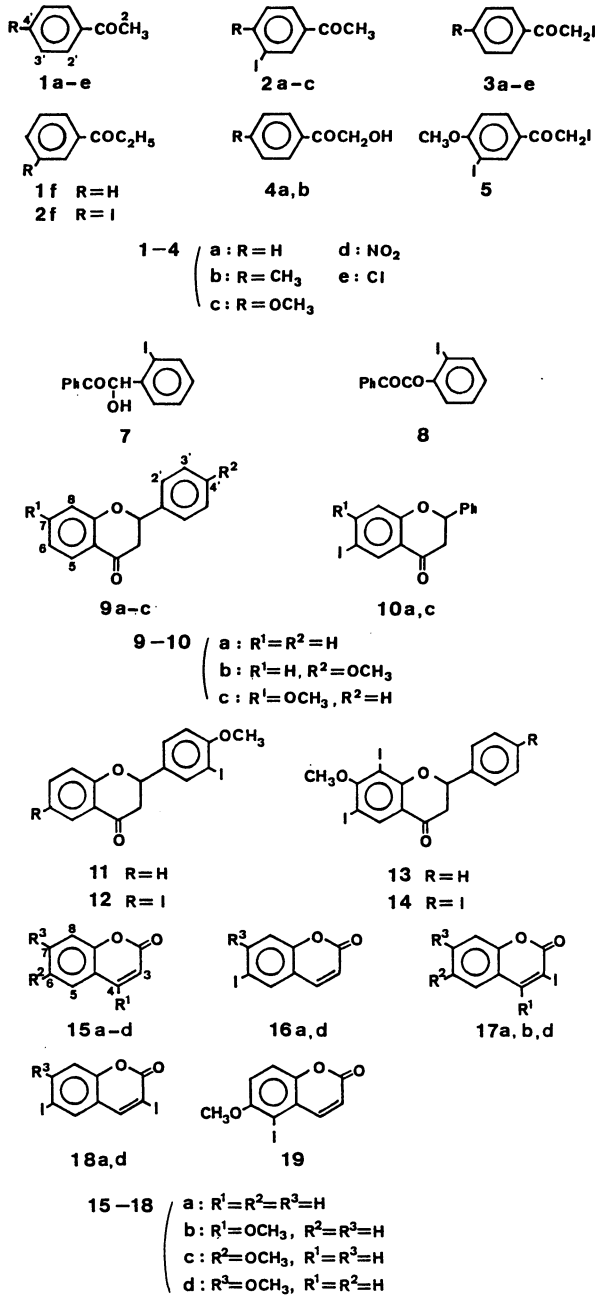


Fig. 1.

Table 1. Reactions of Acetophenones (**1a—e**), Propiophenone (**1f**), and 1,2-Diphenylethanone (**6**) with $I(OCOCF_3)_3$ at Room Temperature

Entry	Substrate	Molar ratio[a]	Solvent	Time / h	Recovery / %	Product (yield/%)[b]
1	**1a**	1:1	CH_2Cl_2	24[c]	70	**2a**[13](10)
2	**1a**	1:1	CH_2Cl_2	12	20	**2a**(41)
3	**1a**	1:1	CH_2Cl_2	6[d]		**2a**(22)
4	**1a**	1:2	CH_2Cl_2	24		**2a**(92)
5	**1a**	1:1	$CHCl_3$	6		**3a**[14](65) **4a**[15](14)
6	**1a**	1:1	CH_3CN	6	18	**3a**(14)
7	**1a**	1:1	CCl_4	8	27	**2a**(16)
8	**1a**	1:2	CCl_4	24		**2a**(32)
9	**1b**	1:1	CH_2Cl_2	7		**2b**[13](85)
10	**1b**	1:1	$CHCl_3$	6	22	**3b**[16](63) **4b**[17](15)
11	**1c**	1:1	CH_2Cl_2	0.5		**2c**[18](97)
12	**1c**	1:1	$CHCl_3$	3	27	**2c**(15) **3c**[19](39) **5**(8)
13	**1d**	1:1	CH_2Cl_2	48	41	**3d**[20](9)
14	**1d**	1:2	$CHCl_3$	7	62	**3d**(36)
15	**1e**	1:2	$CHCl_3$	6	20	**3e**[21](73)
16	**1f**	1:1	CH_2Cl_2	6		**2f**(92)
17	**6**	1:2	CH_2Cl_2	6		**7**(83) **8**(7)

a) Substrate: $I(OCOCF_3)_3$. b) Yields based on the substrate added. c) The reaction at 0 °C. d) The reaction at reflux temperature.

Table 2. Reactions of Flavanones (**9a—c**) and Coumarins (**15a—d**) with $I(OCOCF_3)_3$ in CH_2Cl_2 at Room Temperature

Entry	Substrate	Molar ratio[a]	Time / h	Recovery / %	Product (yield/%)[b]
18	**9a**	1:1	12	34	**10a**[22](43)
19	**9a**	1:1.5	12		**10a**(49)
20	**9b**	1:1.5	2		**11**[23](43) **12**(42)
21	**9c**	1:1.5	6		**10c**(67) **13**(7)
22	**10c**	1:2	12		**14**(93)
23	**15a**	1:1	24	39	**16a**[24](38) **17a**(7)
24	**15a**	1:1.5	24	21	**16a**(55) **17a**(5) **18a**(2)
25	**15a**	1:2	48		**16a**(38) **18a**(38)
26	**15b**	1:1	8		**17b**(88)
27	**15c**	1:1	24	15	**19**(68)
28	**15d**	1:1	24	25	**16d**(43) **17d**(35) **18d**(5)

a) Substrate: $I(OCOCF_3)_3$. b) Yields based on the substrate added.

(**4a**) in a shorter reaction time (Entry 5). In carbon tetrachloride **2a** was again found to be the main product, but in poor yields (Entries 7 and 8). 4′-Methylacetophenone (**1b**) or 4′-methoxyacetophenone (**1c**) in dichloromethane gave the corresponding 3′-iodo derivatives **2b** and **2c** in excellent yields (Entries 9 and 11). On the other hand, 4′-nitroacetophenone (**1d**) yielded 2-iodo-4′-nitroacetophenone (**3d**) in poor yield (Entry 13). Propiophenone (**1f**) gave 3′-iodo derivative **2f** (Entry 16). The reactions of **1b**, **1c**, **1d**, and 4′-chloroacetophenone (**1e**) in chloroform resulted in 2-iodo derivatives **3b**, **3c**, **3d**, and **3e** in moderate to good yields (Entries 10, 12, 14, and 15). In the case of **1c** diiodo compound **5** was also isolated (Entry 12). The reaction of 1,2-diphenylethanone (**6**) with ITT yielded two products, **7** and **8**. The structure of **7** was concluded to be 2-hydroxy-2-(2-iodophenyl)-1-phenylethanone since an AB spin system due to a methine proton and a hydroxy proton appeared at δ 4.50 and 5.20 with J value of 6.0 Hz in the ^{1}H NMR spectrum. One of the doublets at δ 4.50 disappeared upon deutration and the other collapsed to a singlet. The spectral data for **8** indicated that it is an iodine-substituted benzil. The ^{1}H NMR spectrum showed the presence of nine aromatic hydrogen atoms, three of which appeared at a slightly lower field. Therefore, the structure of **8** is assigned to be 1-(2-iodophenyl)-2-phenylethanedione. Benzoin **7** could be oxidized to **8** by iodine in a 73% yield.

Flavanones. The reaction of flavanone (**9a**) yielded 6-iodoflavanone (**10a**) (Table 2, Entry 18). With increasing the amount of the reagent (ITT) the yield of **10a** increased slightly (Entry 19). When 4′-methoxyflavanone (**9b**) was treated with ITT, it gave 3′-iodo (**11**) and 3′,6-diiodo derivative (**12**) (Entry 20). 7-Methoxyflavanone (**9c**) similarly yielded 6-iodo

Table 3. Physical, Spectral, and Analytical Data for the New Compounds

Compound	Mp (θ_m/°C) (solvent)	IR/cm^{-1}	^{1}H NMR (δ, J/Hz)	Formula M or C, H (%): Found (Calcd)
2f	Colorless liquid	1688 (>C=O)	1.17 (3H, t, J=7.2, CH_3), 2.91 (2H, q, J=7.2, CH_2), 7.10 (1H, m, H-5′), 7.73 (1H, m, H-4′), 7.88 (1H, m, H-6′), 8.20 1H, m, H-2′)	C_9H_9IO M: 259.9698 (259.9696)
5	115—116 (Ethanol)	1670 (>C=O)	3.93 (3H, s, OCH_3), 4.27 (2H, s, CH_2), 6.87 (1H, d, J=7.8, H-5′), 7.95 (1H, dd, J=7.8, 1.8, H-6′), 8.39 (1H, d, J=1.8, H-2′)	$C_9H_8I_2O_2$ C: 27.17 (26.89) H: 2.11 (2.01)
7	113.2—114.2 (Ethanol)	1678 (>C=O) 3460 (OH) 3620 (OH)	4.50 (1H, d, J=6.0, OH), 6.20 (1H, d, J=6.0, CH), 6.9—7.5 (6H, m, ar. H), 7.8—8.0 (3H, m, ar. H)	$C_{14}H_{11}IO_2$ C: 49.64 (49.73) H: 3.25 (3.28)
8	Yellow liquid	1679 (>C=O)	7.0—7.8 (6H, m, H-3′—H-5′, H-3″—H-5″), 7.8—8.3 (3H, m, H-6′, H-2″, H-6″)	$C_{14}H_9IO_2$ M: 335.9649 (335.9649)
10c	112—113 (Ethanol)	1676 (>C=O)	2.85 (1H, dd, J=16.2, 5.4, HCH), 2.98 (1H, dd, J=16.2, 11.4, HCH), 3.82 (3H, s, OCH_3), 5.46 (1H, dd, J=5.4, 11.4, CH), 6.36 (1H, s, H-8), 7.34 (5H, s, Ph), 8.19 (1H, s, H-5)	$C_{16}H_{13}IO_3$ C: 50.38 (50.55) H: 3.42 (3.45)
12	180—182 (Benzene-hexane)	1691 (>C=O)	2.84 (1H, dd, J=16.8, 6.0, HCH), 2.97 (1H, dd, J=16.8, 10.8, HCH), 3.90 (3H, s, OCH_3), 5.34 (1H, dd, J=6.0, 10.8, CH), 6.79 (1H, d, J=8.4, H-8 or H-5′), 6.82 (1H, d, J=8.4, H-5′ or H-8), 7.39 (1H, dd, J=8.4, 1.8, H-6′), 7.73 (1H, dd, J=8.4, 1.8, H-7), 7.87 (1H, d, J=1.8, H-2′), 8.16 (1H, d, J=1.8, H-5)	$C_{16}H_{12}I_2O_3$ C: 38.24 (37.95) H: 2.49 (2.39)
13	120—121 (Ethanol)	1690 (>C=O)	2.93 (1H, m, J=16.0, 4.0, HCH), 3.01 (1H, m, J=16.0, 12.0, HCH), 3.89 (3H, s, OCH_3), 5.52 (1H, q, CH), 8.20 (1H, s, H-8)	$C_{16}H_{12}I_2O_3$ C: 37.69 (37.97) H: 2.37 (2.39)
14	174.5—175.5 (Ethanol)	1705 (>C=O)	2.95 (2H, d, J=8, CH_2), 3.85 (3H, s, OCH_3), 5.50 (1H, t, J=8, CH), 7.1—7.9 (4H, m, ar. H), 8.20 (1H, s, H-5)	$C_{16}H_{11}I_3O_3$ C: 30.50 (30.41) H: 1.75 (1.80)
16d	194—195 (Ethanol)	1730 (>C=O)	3.95 (3H, s, OCH_3), 6.23 (1H, d, J=8.4, H-3), 6.72 (1H, s, H-8), 7.55 (1H, d, J=8.4, H-4), 7.85 (1H, s, H-5)	$C_{10}H_7IO_3$ M: 301.9453 (301.9439)
17a	88—89 (Ethanol)	1728 (>C=O)	7.1—7.7 (4H, m, ar. H), 8.31 (1H, s, H-4)	$C_9H_5IO_2$ C: 39.83 (39.73) H: 1.82 (1.85)
17b	89—90 (Ethanol)	1717 (>C=O)	4.14 (3H, s, OCH_3), 7.1—7.9 (4H, m, ar. H)	$C_{10}H_7IO_3$ C: 39.75 (39.76) H: 2.33 (2.34)
17d	153—154 (Ethanol)	1721 (>C=O)	3.90 (3H, s, OCH_3), 6.79 (1H, d, J=1.8, H-8), 6.87 (1H, dd, J=1.8, 8.4, H-6), 7.36 (1H, d, J=8.4, H-5), 8.28 (1H, s, H-4)	$C_{10}H_7IO_3$ C: 39.60 (39.76) H: 2.28 (2.34)
18a	151—152 (Ethanol)	1736 (>C=O)	7.01 (1H, m, H-8), 7.8—8.0 (2H, m, H-5, H-7), 8.34 (1H, s, H-4)	$C_9H_4I_2O_3$ C: 27.23 (27.16) H: 1.00 (1.01)
18d	251—252 (Ethanol)	1731 (>C=O)	3.94 (3H, s, OCH_3), 6.73 (1H, s, H-8), 7.77 (1H, s, H-5), 8.16 (1H, s, H-4)	$C_{10}H_6I_2O_3$ C: 28.22 (28.07) H: 1.43 (1.41)
19	140—141 (Ethanol)	1722 (>C=O)	3.93 (3H, m, OCH_3), 6.40 (1H, d, J=10.2, H-3), 7.05 (1H, d, J=9.6, H-8), 7.25 (1H, d, J=9.6, H-7), 7.96 (1H, d, J=10.2, H-4)	$C_{10}H_7IO_3$ C: 39.90 (39.76) H: 2.44 (2.34)

derivative **10c** and 6,8-diiodo derivative **13** (Entry 21). The repeated iodination of **10c** with ITT gave 4′,6,8-triiodo-7-methoxyflavanone (**14**) (Entry 22).

Coumarins. The reaction of coumarin (**15a**) with ITT yielded 6-iodo (**16a**) and 3-iodocoumarin (**17a**) (Entry 23). The ^{1}H NMR spectrum of **16a** showed an AB quartet with a J value of 9.6 Hz due to H-3 and H-4, and three aromatic hydrogen atoms. The

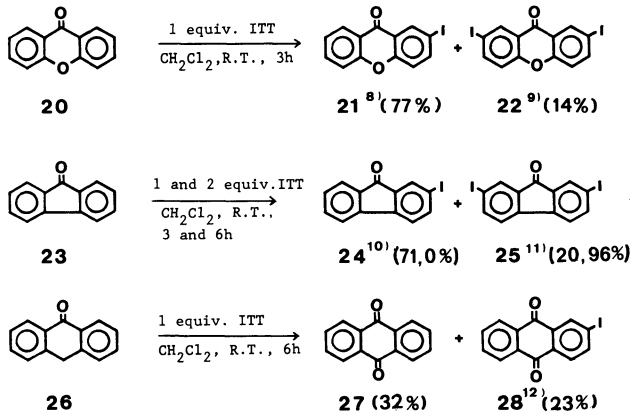
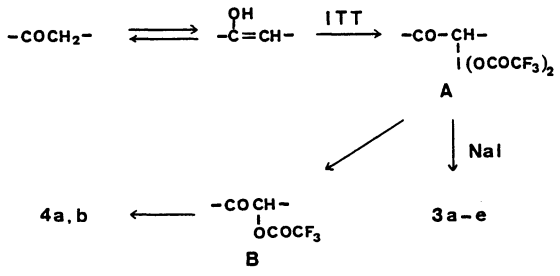
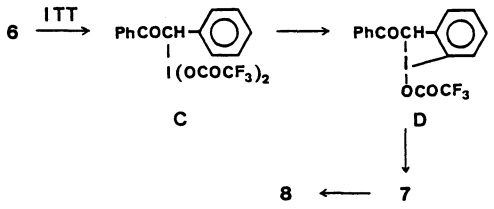


Fig. 2.



Scheme 2.



Scheme 3.

^{1}H NMR spectrum of **17a** exhibited a multiplet at the aromatic region corresponding to four hydrogen atoms, H-5—H-8, and a singlet at δ 8.31, indicating the presence of H-4. 3,6-Diiodocoumarin (**18a**) was obtained in a reaction at a molar ratio of 1 : 1.5 and the yield increased remarkably in the reaction at a molar ratio of 1 : 2 (Entries 24 and 25). Introduction of a methoxy group at the C-4 yielded 3-iodo derivative **17b** as the sole product in the reaction of **15b** (Entry 26), while that of a methoxy group at the C-6 in **15c** changes the site of the reaction to the C-5. A methoxy group at the C-7 in **15d** activated the C-3 as well as the C-6, giving **16d**, **17d**, and **18d** (Entry 28).

Other Aromatic Ketones. The reactions of 9-xanthenone (**20**), 9-fluorenone (**23**), and anthrone (**26**) with ITT in dichloromethane were examined and it was found that **20** and **23** gave monoiodo and diiodo derivatives, respectively, and **26** gave anthraquinone (**27**) and 2-iodoanthraquinone (**28**) in moderate yields (Fig. 2).

Discussion

The reaction of ITT with simple aromatic compounds has been reported by Maletina et al.[4] Our study revealed that the electron-donating groups, such as methyl and methoxy groups in acetophenones, enhance the reactivity as shown in Entries 9 and 11. The electron-withdrawing substituents, such as the nitro group, deactivate the aromatic ring and, thus, the reaction occurs at the α-carbon atom to the carbonyl group. The reaction at the aromatic ring can be interpreted as an electrophilic aromatic substitution[4] as shown in Scheme 1. The reaction of acetophenone (**1a**) with ITT in chloroform showed quite different products from those in dichloromethane. 2-Hydroxyacetophenone (**4a**) was obtained along with **3a** and the reaction took much shorter time. A mechanism for the iodination of acetophenone (**1a**) at the C-2 is depicted in Scheme 2. A keto-enol equilibrium and the subsequent addition of ITT to the double bond gave an alkyliodine(III) intermediate **A** which is then decomposed to **3a—e** and **4a,b** during work-up with aqueous sodium iodide. It may be also possible that in the reaction the intermediate **A** could partially be converted to 2-(trifluoroacetoxy)acetophenone (**B**), which may give rise to **4a** during the work-up. In fact, the analogue of **B** prepared from 2-bromoacetophenone with sodium trifluoroacetate was readily hydrolyzed on TLC to give **4a**. It should be noted that iodine is incorporated regiospecifically into the ortho-position in benzyl moiety and a hydroxyl group is introduced onto the methylene group in the reaction of **6** with ITT in dichloromethane. The formation of **7** could be accounted for by modifying the mechanism which has been described for the reaction of acetophenones with ITT in chloroform (as shown in Scheme 3). The reaction intermediate **C** may form an iodine(III)-containing cyclic compound **D** which could be decomposed during work-up to give **7**. The oxidation of benzoin to benzil has precedence.[6]

The orientation in the reaction of coumarins with ITT is quite similar to the orientation in the nitration and the sulfonation of coumarin (**15a**) in which the aromatic ring and the pyrone ring undergo the electrophilic aromatic substitution.[7] The reaction of 4-methoxycoumarin (**15b**) and 7-methoxycoumarin (**15d**) with ITT yielded 3-iodo derivatives **17b** and **17d** that are expected from the consideration of the electron-donating effect of the methoxy group. The reaction of 9-xanthenone (**20**) and 9-fluorenone (**23**) gave 2-iodo derivatives as the major product and diiodo derivatives. These iodo derivatives have been previously prepared by various methods.[8-12] However, the ease of operation in the iodination with ITT made the latter better for the preparation of these compounds. The formation of 2-iodoanthracene (**28**) deserves comments. Anthraquinone (**27**) could not give **28** on treatment with ITT. It therefore follows that anthrone (**26**) was iodinated at the 2-position and then oxidized to **28**.

Conclusion

The reaction of ITT proved to be useful for the iodination of aromatic ketones, particularly for those activated by oxygen functions. The fact that **10c** gave triiodo derivative **14** would also indicate the synthetic utility of the reaction for the preparation of periodinated aromatic compounds. The regiospecific iodination that was observed in the reaction of **6** may suggest that iodine could be incorporated at the ortho-position of a vinyl group in aromatic substrates.

Experimental

Measurements. All the ^{1}H NMR spectra were taken in deuteriochloroform solutions with a Hitachi Perkin-Elmer R-24 NMR spectrometer (60 MHz) with tetramethylsilane as the internal standard. The IR spectra were measured in chloroform solutions on a JASCO A-102 IR spectrometer. The MS sperctra were obtained with a JMS-O1SG-2 and a JMS DX300 instrument. The melting points were determined with a Yanagimoto micromelting point apparatus and were not corrected. The HPLC analysis were performed on an ALTEX model 330/110A/153 isocratic liquid chromatograph equipped with an UNSIL Pack 5C18 250A column, eluting with methanol or 80% aqueous methanol.

Materials. Iodine(III) tris(trifluoroacetate),[3] 4′-methoxyacetophenone[25](**1c**), 1,2-diphenylethanone[26] (**6**), flavanone[27] (**9a**), 4′-methoxyflavanone[28] (**9b**), 7-methoxyflavanone[29] (**9c**), 4-methoxycoumarin[30] (**15b**), 6-methoxycoumarin[31] (**15c**), and 7-methoxycoumarin[32] (**15d**) were prepared by the methods described in the literature. The other 4′-substituted acetophenones **1b**, **d**, and **e**, propiophenone (**1f**), coumarin (**15a**), 9-xanthenone (**20**), 9-fluorenone (**23**), and anthrone (**26**) were purchased from Wako Pure chemical Industries, Ltd. Acetophenone (**1a**) was commercially available from Katayama chemical Industries, Ltd.

Reaction of Iodine(III) Tris(trifluoroacetate). The general procedure for the reaction of ITT was follows. To a solution of a substrate (1 mmol) in a solvent (20 cm^3), iodine(III) tris(trifluoroacetate) (1—2 mmol as shown in Tables 1 and 2, and in Fig. 2) was added under an atmosphere of nitrogen. The solution was stirred with the undissolved ITT at 23 °C. A high-pressure liquid chromatographic analysis was performed on aliquots which were withdrawn periodically from the reaction mixture with the aid of a pipet. There appeared several peaks due to the substrate and products in the chromatogram. When one of the product peaks became maximum (the time is shown in the Tables 1 and 2, and in Fig. 2), the reaction mixture was treated with 20% aqueous sodium iodide solution (20 cm^3) with stirring for 30 min and extracted with dichloromethane or chloroform. The organic layer was washed with a saturated sodium hydrogencarbonate solution, 5% sodium thiosulfonate solution, and water. The solvent was removed under reduced pressure. The products were separated on TLC with benzene or chloroform as the developing solvent. The yields on reasonably pure products are summarized in Tables 1 and 2, and in Fig. 2. Analytical samples were further purified by distillation or recrystallization. The known compounds were identified by comparing them with spectral data and/or the melting points found in the literature. The physical, spectral, and analytical data for the new compounds are listed in Table 3.

A Typical Procedure for the Reaction of Acetophenone (1a) with ITT. To a solution of **1a** (1 mmol) in calcium chloride-dried chloroform (20 cm^3) was added iodine(III) tris(trifluoroacetate) (1 mmol) under an atmosphere of nitrogen. The solution was stirred for 6h at 23 °C. After adding 20% aqueous sodium iodide solution (20 cm^3), the mixture was stirred for 30 min. The chloroform layer was washed with a saturated sodium hydrogencarbonate solution, 5% aqueous sodium thiosulfonate solution, and water. After the removal of the chloroform, the resulting liquid was fractionated on a silica-gel plate eluting with benzene, giving **3a** and **4a** in yields shown in Table 1 (Entry 5). 2-Iodoacetophenone (**3a**): Light-brown liquid;[14] IR ($CHCl_3$) ν/cm^{-1}=3012, 1676, 1600, 1581, 1492, 1449, 1418, 1316, 1303, 1271, 1181, 1169, 1004, 983, 697; ^{1}H NMR ($CDCl_3$) δ=4.32 (2H, s), 7.3—7.6 (3H, m), 7.8—8.0 (2H, m); MS *m/z* (rel intensity) 246 (55, M$^+$), 141 (6), 127 (23), 105 (100), 77 (51). 2-Hydroxyacetophenone (**4a**): Colorless needles; mp 85—86 °C (sublimed) (lit,[15] mp 86—87 °C); IR ($CHCl_3$) ν/cm^{-1}=3484, 3012, 1597, 1448, 1285, 1202, 1091, 972, 661; ^{1}H NMR ($CDCl_3$) δ=3.7 (1H, br. s), 4.90 (2H, s), 7.3—7.7 (3H, m), 7.8—8.1 (2H, m); MS *m/z* (rel intensity) 136 (6, M$^+$), 105 (100), 77 (55).

2-(Trifluoroacetoxy)acetophenone (B). A mixture of 2-bromoacetophenone (2.0 g), sodium trifluoroacetate (1.36 g), and 2-butanone (20 cm^3) was heated under reflux for 24 h. After the removal of the 2-butanone under reduced pressure, the resulting semisolid was extracted with chloroform. The chloroform solution evaporated to give a light-brown liquid (2.1 g, 90%). IR ($CHCl_3$) ν/cm^{-1}=1685 (>C=O) and 1783 ($OCOCF_3$); ^{1}H NMR ($CDCl_3$) δ=4.88 (2H, s, -OCH_2-) and 7.3—8.0 (5H, m, Ph). **B** could not be purified and was hydrolyzed to give **4a** on a silica-gel plate eluting with benzene.

Oxidation of 2-Hydroxy-2-(2-iodophenyl)-1-phenylethanone (7) with Iodine. A mixture of **7** (100 mg), sodium methoxide which prepared by dissolving metallic sodium (13.6 mg) in methanol (5 cm^3), and iodine (150 mg) was heated under reflux for 30 min. After the removal of the methanol, the resulting mixture was triturated with water and then extracted with benzene. The benzene solution evaporated and the product was purified on a silica-gel plate with chloroform as developing solvent, giving light-yellow liquid (72.4 mg, 73%). The IR and ^{1}H NMR spectra were identical with those of **8** obtained by the ITT oxidation of **6**.

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