Reaction of 1,2,4,5-Tetroxan with Antimony Pentachloride or Liquid Sulphur Dioxide: Heterolytic Fission of Carbon–Oxygen or Oxygen–Oxygen Bonds

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The reactions of 11 kinds of tetroxans with antimony pentachloride have been investigated. A mixture of ketone (aldehyde) and ester (carboxylic acid) was obtained, the ratio of which was found to depend on the substituents. In the presence of the catalyst *cis*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxan rearranges to the *trans*-isomer. In the reaction of some tetroxans with liquid sulphur dioxide, a mixture of ester and ketone was obtained in a molar ratio of 1 : 1. Reductive ozonolysis of some alkenes in the presence of 10 mol equiv. of sulphur dioxide in methylene chloride gave the corresponding carbonyl compounds in good yields.

3,3,6,6-TETRA-ALKYL- and 3,6-diaryl-1,2,4,5-tetroxans are well known to be prepared by ozonolysis of tetra-substituted alkenes or the reaction of ketone (aldehyde) with hydrogen peroxide in the presence of acid catalyst.[1] Recently we have found that 3,6-dialkyl derivatives are conveniently prepared by the reactions of ozonides with catalytic amounts of antimony pentachloride or chloro-sulphonic acid.[2,3] The reactions of hydroperoxides[4] and 9,10-dihydro-9,10-epidioxyanthracene derivatives[5] with acid catalysts have been extensively studied, but the only reported reaction of a tetroxan is limited to that

TABLE 1

Reaction of tetroxan with antimony pentachloride

Tetroxan	Proportion of catalyst	Reaction time (min)	Product [%] [a]
(1a)	0.03	120	(2) [74], (3) [71], (1a) [16]
(1a)	0.1	30	(2) [98], (3) [92]
(1a)	0.3	30	(2) [90], (3) [94]
(1b)	0.1	40	(4) [90], (5) [98]
(1c)	0.3	60	(6) [65], (7) [74]
(1d)	0.03	40	(8) [25], (9) [45],[b] (1d) [49]
(1d)	0.1	90	(8) [30], (9) [132] [b]
(1e)	0.03	40	(10) [14], (11) [30],[b] (1e) [72]
(1e)	0.3	40	(10) [22], (11) [136] [b]
(1f)	0.03	40	(12) [6], (13) [11],[b] (1f) [88]
(1f)	0.3	90	(12) [26], (13) [144] [b]
(1g)	6	45	(14) [30], (15) [61]
(1h)	6	45	(16) [54], (17) [90]
(1h)	0.6	15	(16) [10], (17) [90] [c]
(1h)	0.06	30	(17) [4], (1h) [90] [c]
(1i)	6	45	(16) [48], (17) [106]
(1i)	2	30	(17) [69], (1h) [24] [c]
(1i)	0.6	15	(17) [33], (1h) [41] [c]
(1i)	0.06	30	(17) [14], (1h) [30], (1i) [46] [c]
(1j)	6	45	(18) [17], (1j) [78] [d]
(1j)	0.6	30	(18) [8], (1j) [86]
(1k)	6	45	(19) [44] [e]

[a] Yield in mol %. [b] The yield is for the phenyl formate plus the phenol. [c] The yield of (16) was not investigated. [d] The tetroxan (1j) forms with SbCl$_5$ a stable complex, which is highly insoluble in methylene chloride. [e] Much polymeric product was obtained.

of cyclohexanone diperoxide with sulphuric acid in formic acid.[6]

In the light of these results we have studied the reactions of tetroxans with antimony pentachloride or

liquid sulphur dioxide, expecting to clarify the modes of bond fission. In connection with this, ozonolysis of alkenes in the presence of sulphur dioxide has been investigated; sulphur dioxide is known to work as a

TABLE 2

Reaction of tetroxan with liquid sulphur dioxide [a]

Tetroxan	Product (%) [b]
(1a)	(2) [73], (3) [78]
(1b)	(4) [73], (5) [70]
(1c)	(6) [62], (7) [54]
(1d)	(8) [97], (9) [88] [c]
(1f)	(12) [66], (13) [78] [c]

[a] A solution of the tetroxan (1 mmol) in liquid sulphur dioxide (20 ml) was kept at 20 °C for 24 h unless otherwise noted. [b] Yield in mol %. [c] The reaction was performed for 48 h.

reductant,[7,8] but its reaction with ozone is very slow.[9] Sulphur dioxide used as an *in situ* reducing agent, gives carbonyl compounds even in cases where anomalous oxidation would otherwise occur.[10] Hitherto tetra-cyanoethylene[10,11] and pinacolone[11,12] have been used for studies in this area.

RESULTS AND DISCUSSIONS

Tetroxan reactions were performed with antimony pentachloride in methylene chloride or with liquid sulphur dioxide. The results are summarized in Tables 1 and 2.

When the tetroxans (1a—c) were treated with antimony pentachloride, the ester and the ketone were obtained in a molar ratio of 1 : 1. In contrast, the tetroxans (1d—g) gave the ester with a small amount of the aldehyde (ketone). From the tetroxans (1h—k) the carboxylic acid was obtained as the major product. These results suggest that two different paths participate in the above reactions (see Schemes 1 and 2). Scheme 1 illustrates heterolytic C–O bond fission in the first step of the reaction, followed by electron migration and the subsequent rearrangement of a substituent from carbon to oxygen to give equimolar proportions of ketone (aldehyde) and ester (carboxylic acid) oxide. The ester (carboxylic acid) oxide, which is expected to be highly unstable, would be reduced by a reductant such as adventitious water to afford the ester (carboxylic acid).[13] The other path in Scheme 2 is as follows. The first step

involves heterolytic fission of a O–O bond with a concerted rearrangement of a substituent from carbon to oxygen, which is followed by electron migration and subsequent migration of another substituent to oxygen
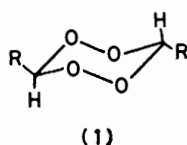
R^1, O—O, R^3 / R^2, O—O, R^4

(1)
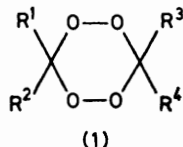
a; R^1 = R^2 = R^3 = R^4 = Ph

b; R^1, R^2 = R^3, R^4 =

c; R^1 = R^3 = Ph, R^2 = R^4 = Me

g; R^1 = R^2 = R^3, R^4 = –[CH$_2$]$_5$–

(1)

(1i) R = PhCO(CH$_2$)$_3$

d; R = p-MeC$_6$H$_4$

e; R = Ph

f; R = p-ClC$_6$H$_4$

h; R = PhCO[CH$_2$]$_3$

j; R = MeCO[CH$_2$]$_3$

k; R = Me[CH$_2$]$_4$
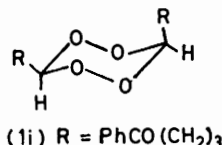
to give 2 mol equiv. of ester.* A further path, however, may be envisaged which yields 2 mol equiv. of ketone from 1 of tetroxan (Scheme 3). The first step involves heterolytic fission of the C–O bond with a concerted

R^{1}COR^2 + R^{4}COR^3
‖
O

R^{4}COR^3 —[O]→ R^{4}C(O)OR^3
‖
O
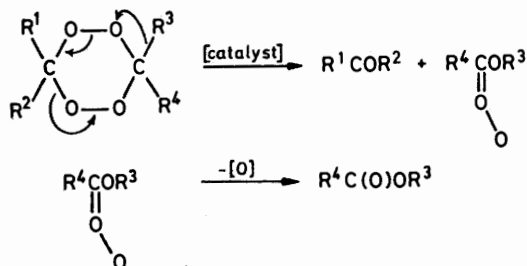
SCHEME 1

migration of an electron, which is followed by ejection of an oxygen molecule (possibly singlet).†

The formation of equimolar proportions of ester and ketone suggests that reaction of the tetroxans (1a—c) proceeds by the mechanism shown in Scheme 1. However, there is a further possibility; two competing modes of decomposition (the processes shown in Schemes 2 and 3) may participate fortuitously to the same extent to give the same mixture of products. The tetroxans (1d—g)

* When the substituent is aryl, this group migrates to the cationic oxygen. In contrast, alkyl is the substituent, the migrating group is hydrogen as will be discussed later.

afforded a mixture of the ester or the aldehyde (the ketone) with preferential formation of the former compound; this suggests that heterolytic O–O bond cleavage competes with C–O bond fission. The tetroxans (1h—k) appear to react in a similar manner. It is thought that the migrating ability of the substituents to the cationic oxygen in the system examined is in the order Ph > H > alkyl, by the fact that (1e) gives selectively phenyl

R^1, O—O, R^2 / R^2, O—O, R^1 —[catalyst]→ 2 R^{1}C(O)OR^2
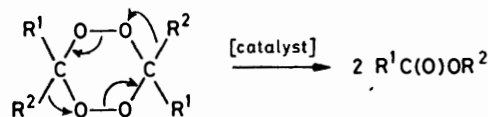
SCHEME 2

formate, and (1m) only affords hexanoic acid. The order is consistent with that found in other systems.[4] In order to investigate the effect of the proportion of the catalyst, the reactions of (1d), (1e), and (1f) with 0.03 or 0.3 mol equiv. of the catalyst were studied; as the proportion of the catalyst was increased, the ratio of the

R^1, O—O, R^3 / R^2, O—O, R^4

↓ [catalyst]

R^{1}COR^2 + R^{3}COR^4 + O$_2$ (possibly singlet)
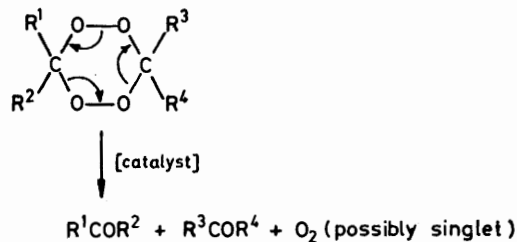
SCHEME 3

ester to the aldehyde was remarkably increased, suggesting that O–O bond cleavage in the first step of the reaction becomes predominant, when the ratio of the catalyst is high. However, the reaction of (1a) with 0.3 mol equiv. of the catalyst afforded a mixture of (2) and (3) in a molar ratio of 1 : 1.

The isomerization of *cis*-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxan (1i) to the *trans*-isomer (1h) was observed in the reaction with 0.06 mol equiv. of catalyst; when the reaction of (1i) was performed for 30 min, (1h) was obtained in a yield of 30% with a 46% of (1i) and a 15% of (17). This result suggests that C–O bond fission
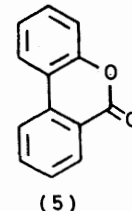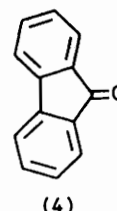
RCOPh

(2) R = Ph

(6) R = Me

RCO$_2$Ph

(3) R = Ph

(7) R = Me

(4)
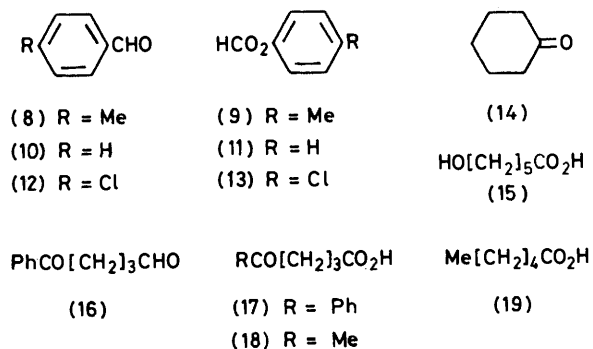
(5)

occurs with the *cis*-tetroxan (1i), followed by rotation of the C–O bond attached to the positive carbon. The subsequent re-formation of the C–O bond affords the *trans*-tetroxan (1h) (Scheme 4). Under the same conditions (1h) was recovered almost quantitatively. The difference in the reactivity between (1h) and (1i) may be
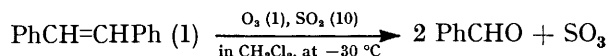
† This mechanism was kindly suggested by one of the referees.

due to the fact that one of 3-benzoylpropyl groups of the cis-tetroxan (1i) occupies the axial position,* compelling (1i) to be less stable because of the steric repulsion between this group and the lone-pair of oxygen, along with easier approach of the catalyst compared with (1h). The
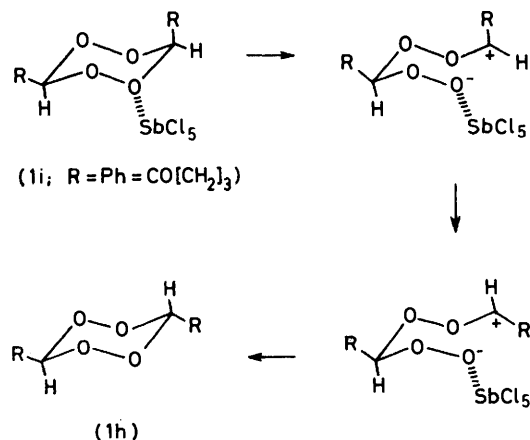

(8) R = Me
(10) R = H
(12) R = Cl

(9) R = Me
(11) R = H
(13) R = Cl

(14)

$HO[CH_2]_5CO_2H$
(15)

PhCO$[CH_2]_3$CHO
(16)

RCO$[CH_2]_3CO_2H$
(17) R = Ph
(18) R = Me

Me$[CH_2]_4CO_2H$
(19)

reaction of (1h) and (1i) with 6 mol equiv. of catalyst gave the mixture of (16) and (17) in good yields.

Solutions of the tetroxans (1a—f) in liquid sulphur dioxide when kept at 20 °C for an appropriate time gave mixtures of ketone (the aldehyde) and ester in equimolar proportions. In Scheme 1 sulphur dioxide, a reductant,[7,8] is expected to reduce the ester oxide immediately, thus favouring this path. This possibility was investigated by the reductive ozonolysis of alkenes in the presence of 10 mol equiv. of sulphur dioxide (Table 3). In these reactions sulphur dioxide is considered to reduce

$$PhCH=CHPh \ (1) \xrightarrow[\text{in CH}_2\text{Cl}_2, \text{ at } -30\,°C]{O_3\ (1),\ SO_2\ (10)} 2\ PhCHO + SO_3$$

(1i; R = Ph = CO$[CH_2]_3$)

(1h)

SCHEME 4

the Criegee zwitterion,[11,12] to afford the carbonyl compounds. Thus, it is reasonable to consider that the ester oxide, if formed, would be reduced spontaneously in liquid sulphur dioxide. In the reductive ozonolysis the yield of aldehyde was lower than that of ketone, as a result of the aldehyde reacting with the excess of sulphur

* The tetroxan (1e) is known to exist as a chair form, in which bulkier substituents occupy the equatorial positions.[14] The conformation of tetra-substituted tetroxan was also confirmed to be a chair form in solution at least at room temperature.[15]

dioxide or sulphur trioxide to form polymeric products. However, this procedure is advantageous in some respects compared with the use of tetracyanoethylene or pinacolone as a reducing agent since sulphur dioxide is inexpensive and sulphur trioxide is easy to remove.

EXPERIMENTAL

Tetroxans (1a) (m.p. 206—207 °C), (1b) (m.p. 203—204 °C),[17] (1c) (m.p. 182—183 °C),[18] (1d) (m.p. 230—231 °C),[19] (1e) (m.p. 202—203 °C),[20] (1f) (m.p. 236.5—237.5 °C),[19] and (1g) (m.p. 127—128 °C)[20] were prepared according to reported methods, and purified by recrystallization. trans-3,6-Bis(3-benzoylpropyl)-1,2,4,5-tetroxan (1 h) (m.p. 147—148 °C), cis-3,6-bis(3-benzoylpropyl)-1,2,4,5-tetroxan (1i) (m.p. 106—107 °C), trans-3,6-bis(4-oxopentyl)-1,2,4,5-tetroxan (1j) (m.p. 79.5—81.0 °C), and trans-3,6-dipentyl-1,2,4,5-tetroxan (1j) (m.p. 33—34 °C) were prepared by literature methods [2,3] and purified by recrystallization. The configuration of the tetroxan was assigned

TABLE 3

Ozonolysis of alkene in the presence of sulphur dioxide [a]

Alkene	Product [%] [b]
Tetraphenylethylene	(2) [190]
trans-Stilbene	(10) [130]
1-Phenylcyclopentene	(16) [55]
2,3-Diphenylinden-1-one	o-Benzoylbenzil [91]
2,3-Diphenyl-1-methyl-indene	o-(1-Benzoylethyl)benzophenone [95]

[a] Ozonolysis was performed at −30 °C in the presence of 10 mol equiv. of sulphur dioxide. [b] Yield in mol %.

on the basis of its n.m.r. spectrum;[2,3] the chemical shift of H-3 was same with that of H-6 in the trans-tetroxan (1d—f, h, k). In contrast, the signal for the equatorial proton of the cis-tetroxan (1i) is at δ 5.47 br (s) and the axial proton at δ 5.68 (t).

General Procedure for the Reaction of Tetroxans with Antimony Pentachloride in Methylene Chloride.—To a solution of the tetroxan (1 mmol) in methylene chloride (40 ml) was added an appropriate amount of antimony pentachloride in methylene chloride (20 ml) in one portion at 20 °C. After the appropriate reaction time, the mixture was poured into ice-cold aqueous potassium hydroxide, and extracted with ether. After acidification of the aqueous solution with hydrochloric acid, the acid products were extracted with diethyl ether. Products were isolated by column chromatography on silica gel and characterized by comparing physical data with those of authentic samples.

Reaction of Compounds (1a), (1b), or (1c) with SbCl₅.—A mixture of (1b) (82 mg, 0.21 mmol) and SbCl₅ (0.02 mmol) in methylene chloride (30 ml) was kept at 20 °C for 40 min. After work-up the solution of the crude products and potassium hydroxide in ethanol was refluxed for 2 h. From the neutral layer fluorenone (4) (34 mg, 90%) was obtained; m.p. 84 °C (from ethanol). From the acid layer was isolated benzocoumarin (5) (40 mg, 98%); m.p. 91—92 °C (lit.,[21] 93 °C), ν_max. 1 735 cm⁻¹, m/e 196.

The reaction of (1a) (150 mg, 0.38 mmol) gave a mixture of benzophenone (2) and phenyl benzoate (3), which were separated by column chromatography on silica gel (elution with benzene–ether, 10 : 1). The first fraction contained (3) (69 mg, 92%), m.p. 70 °C (from ethanol). The second fraction contained (2) (72 mg, 98%).

When a solution of (1c) (408 mg, 1.5 mmol) in methylene

chloride (40 ml) was treated with $SbCl_5$ (150 mg, 0.5 mmol) for 1 h, a mixture of phenyl acetate (7) and acetophenone (6) was obtained. By column chromatography on silica gel (elution with benzene–ether, 10 : 1), (7) (150 mg, 74%) [$v_{max.}$ 1 760 cm^{-1}, δ 2.28 (3 H, s)] and (6) (130 mg, 65%) were isolated.

Reaction of Compounds (1d), (1e), *or* (1f) *with* $SbCl_5$.—A mixture of (1d) (317 mg, 1.17 mmol) and $SbCl_5$ (0.12 mmol) in methylene chloride (60 ml) was kept at 20 °C for 90 min. After work-up the neutral products were isolated by column chromatography on silica gel (elution with benzene–ether, 10 : 1). The first fraction contained *p*-tolyl formate (9) (95 mg, 59%); $v_{max.}$ 1 735, 1 190, and 1 110 cm^{-1}.[22] The second fraction contained *p*-tolualdehyde (8) (42 mg, 30%). As an acid product *p*-cresol was isolated in pure state (73%).

The reaction of (1e) or (1f) was performed as above. The i.r. spectra of phenyl formate (11) [$v_{max.}$ 1 700, 1 190, and 1 100 cm^{-1}] and *p*-chlorophenyl formate (13) [$v_{max.}$ 1 745, 1 205, and 1 095 cm^{-1}] were identical with those of authentic samples.[22]

Reaction of trans-3,6-*Bis*(3-*benzoylpropyl*)-1,2,4,5-*tetroxan* (1h) *with* $SbCl_5$.—To a solution of (1h) (192 mg, 0.5 mmol) in methylene chloride (40 ml) was added $SbCl_5$ (3 mmol) in methylene chloride (20 ml) in one portion, and the reaction was continued with stirring for a further 45 min. From the neutral layer 4-benzoylbutyraldehyde (16) (42 mg, 48%) was isolated by column chromatography on silica gel (elution with benzene–ether, 5 : 1); $v_{max.}$ 1 725 and 1 685 cm^{-1}. The aldehyde was oxidized by potassium permanganate to 4-benzoylbutanoic acid (17),[23] m.p. 125—126 °C (lit.,[23] 125—126 °C). As an acid product (17) was isolated in pure state (90%).

Reaction of cis-3,6-*Bis*(3-*benzoylpropyl*)-1,2,4,5-*tetroxan* (1i) *with* $SbCl_5$.—A mixture of (1i) (192 mg, 0.5 mmol) and $SbCl_5$ (0.03 mmol) in methylene chloride (60 ml) was kept at 20 °C for 30 min. Trituration of the neutral products with ether gave (1h) (58 mg, 30%), m.p. 147—148 °C. By column chromatography of the mother liquors on silica gel (elution with benzene–ether, 10 : 1) (1i) was isolated in a yield of 46% (88 mg), m.p. 106—107 °C. As an acid product (17) was isolated in 14% yield (13 mg).

Reaction of trans-3,6-*Bis*(4-*oxopentyl*)-1,2,4,5-*tetroxan* (1j) *with* $SbCl_5$.—To a solution of (1j) (236 mg, 1 mmol) in methylene chloride (40 ml) was added $SbCl_5$ (6 mmol) in methylene chloride (20 ml) in one portion. A solid precipitated immediately, which did not redissolve during the reaction. After 45 min the solution was poured into aqueous potassium hydroxide. By column chromatography on silica gel (elution with benzene–ether, 10 : 1) (1j) was recovered in 78% yield, m.p. 79—80 °C. As an acid product 5-oxohexanoic acid was isolated (20 mg, 17%); $v_{max.}$ 1 720 cm^{-1}, δ 1.88 (2 H, q, *J* 7.5 Hz), 2.14 (3 H, s), 2.40 (2 H, t, *J* 7.5 Hz), and 2.52 (2 H, t, *J* 7.5 Hz).

Reaction of trans-3,6-*Dipentyl*-1,2,4,5-*tetroxan* (1k) *with* $SbCl_5$.—A mixture of (1k) (232 mg, 1 mmol) and $SbCl_5$ (6 mmol) in methylene chloride (60 ml) was kept at 20 °C for 45 min. As an acid product hexanoic acid (19) was obtained in a yield of 44%. Polymeric products, which could not be characterized, were obtained from the neutral layer.

Reaction of 7,8,15,16-*Tetraoxadispiro*[5.2.5.2]*hexadecane* (1g) *with* $SbCl_5$.—A mixture of (1g) (300 mg, 0.76 mmol) and $SbCl_5$ (4.6 mmol) in methylene chloride (60 ml) was kept at 20 °C for 45 min. From the neutral layer cyclohexanone (14) (42 mg, 30%) was isolated by column chromatography on silica gel (elution with benzene–ether, 5 : 1). As an acid

product 6-hydroxyhexanoic acid (15) was obtained (96 mg, 61%).

General Procedure for the Reaction of the Tetroxan with Liquid Sulphur Dioxide.—Into a high-pressure vessel containing the tetroxan (1 mmol), sulphur dioxide (20 ml) was distilled at -70 °C. The vessel was allowed to warm to 20 °C, and the reaction was continued for the appropriate time. After conventional work-up the products were isolated and characterized as above.

Ozonolysis in the Presence of Sulphur Dioxide.—Ozonolysis were carried out using Nippon Ozone Model O-1-2 ozonator. In a flask fitted with a magnetic stirrer bar, a gas inlet tube, and a solid-CO_2 condenser equipped with calcium chloride tube, were placed the alkene (1 mmol) and sulphur dioxide (10 mmol) in methylene chloride (30 ml). The flask was kept in a solid CO_2–methanol bath at -30 °C during the reaction. After passage of a slow stream of ozone (1 mol equiv.) into the mixture it was poured into ice-cold aqueous potassium hydroxide, and extracted with ether. By column chromatography on silica gel the carbonyl compounds were isolated.

Treatment of 2,3-diphenylinden-1-one [24] afforded *o*-benzoylbenzil (91%), m.p. 94 °C (from methanol) (lit.,[25] 94 °C), $v_{max.}$ 1 680 and 1 630 cm^{-1}. The reaction of 2,3-diphenyl-1-methylindene,[26] followed by column chromatography on silica gel (elution with benzene–ether, 10 : 1), gave *o*-(1-benzoylethyl)benzophenone in 95% yield, m.p. 107 °C (from methanol) (Found: C, 84.05; H, 5.5. $C_{22}H_{18}$-O_2 requires C, 84.05; H, 5.77), $v_{max.}$ 1 680 and 1 660 cm^{-1}; δ 1.48 (3 H, d, *J* 7.0 Hz) and 5.10 (1 H, q, *J* 7.0 Hz).

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