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THE PREPARATION OF SOME 4-ORGANOSILICON DERIVATIVES OF 7-HYDROXYCOUMARIN

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Summary

Some organosilicon-substituted ketones have been converted into β-ketoesters, and hence into 4-derivatives of 7-hydroxycoumarin.

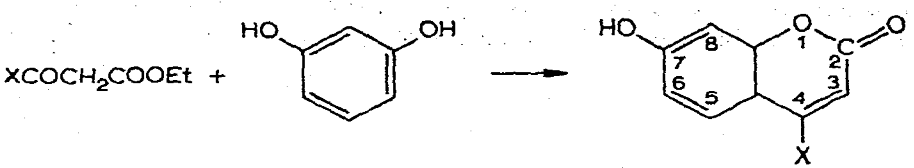
Introduction

As far as we are aware, no organosilicon derivatives of coumarin have been reported previously. We describe below the preparations of some 7-hydroxycoumarin derivatives bearing organosilicon substituents at the 4-position.

Results

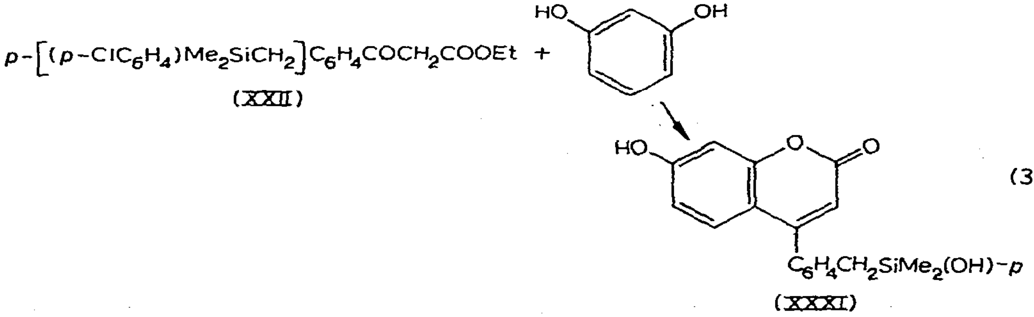
We first synthesized by standard methods the silicon-substituted ketones (I) - (XII) listed in Table 1, and converted them into the corresponding β-ketoesters (XIII) - (XXIV) (see Table 3) by treatment with diethyl carbonate in the presence of sodium hydride in ether, as represented in eqn. (1). These ketoesters were then brought into reaction with resorcinol in the presence of concentrated sulphuric acid. The trimethylsilyl compounds (XIII), (XIV), (XVIII) - (XX), and the tris(p-chlorophenyl)silyl compound (XXI), gave the expected 7-hydroxycoumarins bearing organosilicon substituents in the 4-position, according to eqn. (2). In the case of compound (XVII), the Me_3Si group was cleaved off by the acid during the condensation, and the product isolated was 7-hydroxy-4-phenylcoumarin. With the (p-chlorophenyl)dimethylsilyl compounds, (XXII) - (XXIV), the p-chlorophenyl groups were cleaved from the silicon by the acid to give, in the first case, the corresponding 4-dimethyl(hydroxy)silyl derivative of 7-hydroxycoumarin (XXXI) [eqn. (3)], and in the other two cases, the corresponding disiloxanes [eqn. (4)]. Similar cleavage of the aryl—silicon bonds probably occurred also with the phenyldimethylsilyl derivatives (XV) and (XVI), but pure products were not isolated in these cases.

$$R_3Si\text{-}\!\sim\!\sim\!\sim\text{-}COMe + (EtO)_2CO + NaH \rightarrow R_3Si\text{-}\!\sim\!\sim\!\sim\text{-}COCH_2COOEt \qquad (1)$$

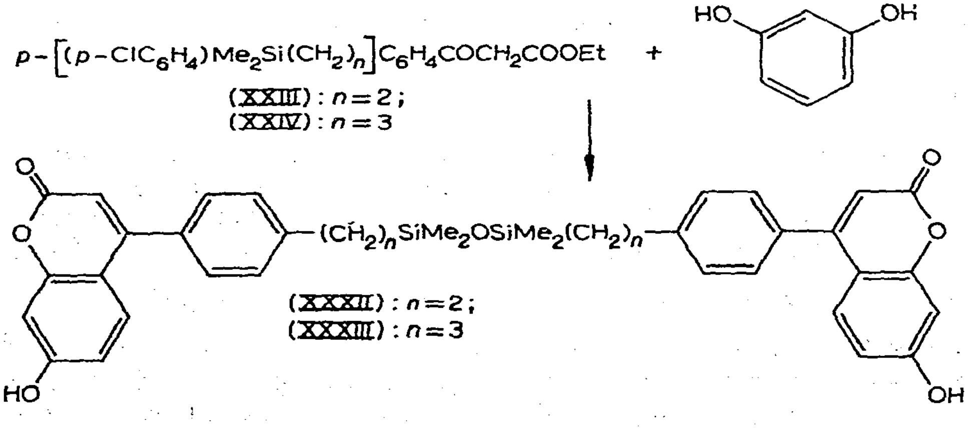


(2)

(XXV): $X = Me_3Si(CH_2)_3$;
(XXVI): $X = Me_3Si(CH_2)_4$;
(XXVII): $X = p\text{-}Me_3SiCH_2C_6H_4$;
(XXVIII): $X = p\text{-}Me_3Si(CH_2)_2C_6H_4$;
(XXIX): $X = p\text{-}Me_3Si(CH_2)_3C_6H_4$;
(XXX): $X = p\text{-}[(p\text{-}ClC_6H_4)_3SiCH_2]C_6H_4$.



(3)



(4)

The possibility of introducing functionality at the silicon atom in the coumarin compounds by treatment of the trimethylsilyl derivatives (XXV) - (XXVII) with 98% sulphuric acid at 50° was briefly investigated. In the case of (XXVII) the volume of gas evolved corresponded to only 34% of that expected for complete cleavage of one Si—Me bond, indicating that substantial cleavage of the Si—$CH_2C_6H_4$ bond had occurred preferentially. In the case of (XXV) and (XXVI), however, the volume of gas corresponded with 80 and 83%, respectively, of that required for cleavage of one Si—Me bond, implying that a reasonable yield of the silanol or siloxane derivative of the 7-hydroxycoumarin could probably be obtained in each case, though no attempt was made to isolate these.

Experimental

General

NMR spectra were recorded on a Varian A60 or T60 instrument, with tetramethylsilane as internal standard; the results are given as δ values in ppm. The IR spectra were recorded on a Perkin—Elmer 237 spectrophotometer, with films in the case of liquids and Nujol mulls in the case of solids. The UV spectra were recorded on a Unicam SP800 spectrophotometer with solutions in 95% ethanol.

The reported molecular weights refer to the parent ion peak as recorded on an AEI MS9 mass spectrometer.

Distillations were carried out with precision-made Vigreux columns, equivalent to ca. 12 theoretical plates. Moisture sensitive compounds (notably chlorosilicon compounds, aluminium chloride, Grignard reagents, and organolithium compounds) were manipulated under dry nitrogen.

5-Trimethylsilylpentan-2-one (I)

(γ-Chloropropyl)dimethylchlorosilane was prepared in 57% yield by treatment of allyl chloride with dimethylchlorosilane in the presence of chloroplatinic acid. A portion of it (25.6 g, 0.17 mol) was refluxed with magnesium turnings (4.8 g, 0.2 g-atom) in ether (150 ml) for 2 h. Anhydrous cadmium chloride (16.5 g, 0.090 mol) was added in portions to the solution with ice-cooling, and the mixture was then allowed to warm to room temperature. Some ether (ca. 80 ml) was distilled off, benzene (200 ml) was added, and the mixture was refluxed for 3 h, then cooled in ice. Acetyl chloride (13.4 g, 0.17 mol) was added dropwise, and the mixture refluxed for 2 h. Treatment with 10% hydrochloric acid, followed by the usual work-up, culminating in fractional distillation at reduced pressure, gave (I) (16.6 g, 62%); details are given in Tables 1 and 2.

6-Trimethylsilylhexan-2-one, (II)

From (4-bromo-n-butyl)trimethylsilane, by the organocadmium route described for (I), was obtained (II) (54%); details are given in Tables 1 and 2.

5-(Phenyldimethylsilyl)pentan-2-one, (III)

From (γ-chloropropyl)dimethylphenylsilane, by the organocadmium route described above, was obtained (III) (51%); details are given in Tables 1 and 2.

6-(Phenyldimethylsilyl)hexan-2-one, (IV)

(i). Chlorodimethylphenylsilane (68.2 g, 0.40 mol) was added dropwise with stirring to the Grignard reagent prepared from (4-chlorobutoxy)trimethylsilane (77.2 g, 0.40 mol) and magnesium (9.6 g, 0.40 g-atom) in ether (400 ml). The mixture was refluxed for 4 h, cooled, and treated with dilute hydrochloric

(continued on p. 176)

TABLE 1

PHYSICAL CONSTANTS AND ANALYSES FOR THE KETONES (I)—(XII) [a]

No.	R in RCOMe	Yield (%)	B.p. (°C/mmHg) [or m.p. (°C)]	n_D	Analysis found (calcd.) (%) C	H
(I)	$Me_3Si(CH_2)_3$	62	62/10 [b]	1.4268 (19°) [b]		
(II)	$Me_3Si(CH_2)_4$	54	63/3 [c]	1.4308 (17°) [c]		
(III)	$Me_2PhSi(CH_2)_3$	51	94/*ca.* 0.001	1.4985 (18°)	70.6 (70.9)	9.2 (9.1)
(IV)	$Me_2PhSi(CH_2)_4$	60	95—98/*ca.* 0.001	1.4765 (16°)	71.6 (71.8)	9.2 (9.4)
(V)	p-$Me_3SiC_6H_4$	60	65/0.4 [d]	1.5140 (28°) [d]	68.5 (68.7)	8.2 (8.3)
(VI)	p-$Me_3SiCH_2C_6H_4$	47	67/0.1 [e]	1.5320 (21°)		
(VII)	p-$Me_3Si(CH_2)_2C_6H_4$	61	80/0.2 [f]	1.5152 (20°) [f]		
(VIII)	p-$Me_3Si(CH_2)_3C_6H_4$	74	104/ca. 0.005	1.5080 (20°)	71.9 (71.8)	9.4 (9.4)
(IX)	p-$[(p\text{-}ClC_6H_4)_3SiCH_2]C_6H_4$	61	[127—129]		65.4 (65.4)	4.4 [g] (4.2)
(X)	p-$[(p\text{-}ClC_6H_4)Me_2Si]CH_2C_6H_4$	50	[55—57]		67.6 (67.4)	6.2 [h] (6.3)
(XI)	p-$[(p\text{-}ClC_6H_4)Me_2Si(CH_2)_2]C_6H_4$	64	124/0.001	1.5335 (19°)	68.4 [i] (68.3)	6.8 (6.6)
(XII)	p-$[(p\text{-}ClC_6H_4)Me_2Si(CH_2)_3]C_6H_4$	61		1.5266 (18°)	68.9 (69.0)	6.6 [j] (6.9)

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[a] The parent ion peak corresponded with the correct mol. wt. in each case. [b] Lit. [1], b.p. 71°/13 mmHg; n_D^{25} 1.4231. [c] Lit. [1], b.p. 85°/10 mmHg; n_D^{20} 1.4289. [d] Lit. [2], b.p. 89°/1 mmHg; n_D^{20} 1.5170. [e] Lit. [3], b.p. 140—141°/14 mmHg; n_D^{20} 1.5254. [f] Lit. [3], b.p. 152—154°/11 mmHg; n_D^{20} 1.5270. [g] Cl: found, 21.3; calcd., 21.5%. [h] Cl: found, 11.7; calcd., 11.7%. [i] Cl: found, 11.1; calcd., 11.2%). [j] Cl: found, 10.5; calcd., 10.7%.

TABLE 2

CHARACTERISTIC IR AND NMR PEAKS FOR THE KETONES (I)—(XII)

Compound	IR(cm^{-1})[a]			NMR[δ(ppm)][b]			
	C=O	C_6H_4	SiMe	MeSi[c]	CH_2	MeCO[c]	Aryl-H
(I)	1725—1730		1255, 840	0.04	0.50(m), 1.57(m), 2.42(t)	2.07	
(II)	1730		1255, 840	0.02	0.57(m), 1.47(m), 2.38(t)	2.07	
(III)	1715		1250, 830	−0.20	0.34(m), 1.00(m), 2.24(t)	2.37	6.84(m)
(IV)	1718		1252, 835	−0.11	0.66(m), 1.03(m), 1.83(t)	2.50	7.00(m)
(V)	1690	1600, 820	1250, 845	0.08		2.26	7.50(q)
(VI)	1695	1610	1255, 855	0.05	2.25(s)	2.48	7.45(q)
(VII)	1695	1615	1255, 840	0.05	0.88(m), 2.70(t)	2.48	7.54(q)
(VIII)	1695	1618, 825[d]	1228, 840		0.54(m), 1.65(m), 2.70(t)	2.49	7.58(q)
(IX)	1682				2.37(s)	2.36	7.11(m)
(X)	1680	1610, 815[d]	1255, 850	−0.13	2.38(s)	2.52	7.30(m)
(XI)	1680	1605, 795[d]	1255, 840	−0.16	0.67(m), 2.33(t)	2.08	7.00(m)
(XII)	1680	1605, 795[d]	1268, 1250, 830	−0.12	0.33(m), 1.46(m), 2.43(t)	2.23	7.26(m)

[a] Liquid films except for (IX) and (X) (Nujol mull). [b] Neat samples except for (IX) and (X) (10% $CHCl_3$ solution). [c] Singlets. [d] *p*-Substitution.

TABLE 3

YIELDS, PHYSICAL CONSTANTS AND ANALYSES FOR THE KETOESTERS (XIII)–(XXIV) [a]

No.	R in $RCOCH_2COOEt$	Yield (%)	B.p. (°C/mmHg) [or m.p. (°C)]	n_D	Analysis found (calcd.) (%)	
					C	H
(XIII)	$Me_3Si(CH_2)_3$	60	88–90/0.6	1.4420 (18°)	57.6 (57.4)	9.7 (9.6)
(XIV)	$Me_3Si(CH_2)_4$	50	88/0.5	1.4428 (19°)	59.3 (59.0)	9.9 (9.8)
(XV)	$Me_2PhSi(CH_2)_3$	70		1.5056 (18°)	65.8 (65.7)	8.4 (8.3)
(XVI)	$Me_2PhSi(CH_2)_4$	75		1.5038 (19°)	66.7 (66.6)	8.5 (8.5)
(XVII)	p-$Me_3SiC_6H_4$	67	90–95/ca. 0.005	1.5184 (20°)	63.6 (63.6)	7.4 (7.6)
(XVIII)	p-$Me_3SiCH_2C_6H_4$	68	100/ca. 0.01	1.5260 (21°)	64.6 (64.7)	7.7 (7.9)
(XIX)	p-$Me_3Si(CH_2)_2C_6H_4$	75	132/0.2	1.5180 (18°)	65.7 (65.7)	8.3 (8.2)
(XX)	p-$Me_3Si(CH_2)_3C_6H_4$	67	146/ca. 0.002	1.5120 (20°)	66.4 (66.6)	8.7 (8.5)
(XXI)	p-$[(p\text{-}ClC_6H_4)_3SiCH_2]C_6H_4$	62	[145–147]		63.3 (63.4)	4.5 [b] (4.4)
(XXII)	p-$[(p\text{-}ClC_6H_4)Me_2SiCH_2]C_6H_4$	56		1.5635 (19°)	64.1 (64.1)	6.3 (6.1)
(XXIII)	p-$[(p\text{-}ClC_6H_4)Me_2Si(CH_2)_2]C_6H_4$	58		1.5460 (19°)	64.6 (64.9)	6.2 [c] (6.4)
(XXIV)	p-$[(p\text{-}ClC_6H_4)Me_2Si(CH_2)_3]C_6H_4$	60		1.5305 (16°)	65.6 (65.5)	6.9 [d] (6.7)

[a] The parent ion peak in the mass spectrum corresponded to the calcd. mol. wt. in each case. [b] Cl: found, 18.6; calcd., 18.8%. [c] Cl: found, 9.0; calcd., 9.1%. [d] Cl: found, 8.7; calcd., 8.8%.

TABLE 4

CHARACTERISTIC IR AND NMR PEAKS FOR THE KETOESTERS (XIII)—(XXIV)

Compound	IR(cm^{-1}) [a]				NMR[δ(ppm)] [b]					
	C=O (Ester)	C=O (Keto)	C_6H_4	SiMe	MeSi [c]	$Si(CH_2)_n$	OCH_2CH_3 [d]	$COCH_2CO$ [c]	OCH_2CH_3 [e]	Aryl-H
(XIII)	1755	1728		1255, 840	0.22	0.72(m), 2.73(t)	1.48	3.51	4.35	
(XIV)	1755	1730		1255, 840	0.14	0.66(m), 2.66(t)	1.40	3.50	4.29	
(XV)	1745	1715		1250, 830	−0.16	0.90(m), 1.76(m), 2.36(t)	1.34	3.42	4.62	7.46(m)
(XVI)	1740	1715		1250, 830	−0.16	0.56(m), 1.78(m), 2.34(t)	1.12	3.48	4.34	7.28(m)
(XVII)	1750	1695	1625, 1600	1250, 840	0.25		1.22	3.82	4.12	7.68(q)
(XVIII)	1750	1695	1610	1255, 855	0.00	2.13(s)	1.18	3.82	4.12	7.41(q)
(XIX)	1755	1695	1615	1255, 845	0.19	1.00(t), 2.82(t)	1.40	4.00	4.16	7.63(q)
(XX)	1750	1695	1615, 805 [f]	1235, 840	0.06	0.58(m), 1.73(m), 2.70(t)	1.22	3.94	4.16	7.60(q)
(XXI)	1740	1680	812 [f]			2.84(s)	1.21	3.97	4.05	7.20(m)
(XXII)	1750	1690	1610, 815 [f]	1265, 840	−0.13	2.21(s)	1.31	3.91	4.23	7.50(m)
(XXIII)	1750	1690	1605, 800 [f]	1255, 840	−0.16	0.83(t), 2.66(t)	1.15	3.86	4.10	7.50(m)
(XXIV)	1740	1682	1605, 790 [f]	1250, 830	−0.17	0.68(m), 1.74(m), 2.68(m)	1.17	3.91	4.04	7.58(m)

[a] Liquid films, except for (XXI) (Nujol mull). [b] Neat samples except for (XV), (XVI), (XXI–XXIV) (10% CCl_4 solution). [c] Singlets. [d] Triplets. [e] Quartets. [f] p-Substitution.

acid. The usual work up gave (4-hydroxybutyl)dimethylphenylsilane (nc) (50.1 g, 60%), 92°/ca. 0.002 mmHg, n_D^{20} 1.5110. (Found: C, 69.4; H, 9.6%; mol.wt. 208. $C_{12}H_{20}OSi$ calcd.: C, 69.2; H, 9.6%; mol.wt. 208.) IR (liquid film), ν(O—H), 3337 s(br); ν(Si—Me), 1248 s(sh), 830 s cm^{-1}. NMR (neat), HO δ 4.23 (s); Ph, 7.26(m); CH, 3.43(t), 1.42(m), 0.66(m); Me_2Si, 0.16(s) ppm.

(ii). Phosphorus tribromide (32.5 g, 0.12 mol) was added dropwise with stirring to (4-hydroxybutyl)trimethylphenylsilane (49.9 g, 0.24 mol) at 0°. The mixture was subsequently kept at 80° for 1 h, then cooled, and added to ice-water. The organic layer was separated, washed with 10% aqueous sodium carbonate then with water, dried ($CaCl_2$), and fractionated to give (4-bromobutyl)dimethylphenylsilane (nc) (39 g, 60%), b.p. 94°/ca. 0.001 mmHg, n_D^{21} 1.5184. (Found: C, 53.1; H, 7.0; Br, 29.5%; mol.wt. 271. $C_{12}H_{19}BrSi$ calcd.: C, 53.1; H, 7.0; Br, 29.5%; mol. wt. 271.) IR (liquid film): ν(Si—Me) 1250 s(sh), 535 s(br) cm^{-1}. NMR (neat): Me_2Si, δ 0.12 (s); CH_2, 3.0(t), 1.33 (m), 0.50 (m); Ph, 7.16 (m) ppm.

(iii). By the organocadmium route described above, (4-bromobutyl)dimethylphenylsilane was converted into (IV) in 54% yield; details are given in Tables 1 and 2.

p-Trimethylsilylacetophenone (V)

Anhydrous aluminium chloride (10 g, 0.15 mol) was stirred at 0° with anhydrous dichloromethane (100 ml), and acetyl chloride (7.9 g, 0.10 mol) was added dropwise with stirring during 2 h. The mixture was filtered through glass wool, and the clear solution was added dropwise to a stirred solution of *p*-bis(trimethylsilyl)benzene (22.2 g, 0.10 mol) in dichloromethane (100 ml) at 0°. The mixture was subsequently allowed to warm up, then stirred for 3 h at room temperature, and added to crushed ice. The organic layer was separated,

TABLE 5

YIELDS, PHYSICAL CONSTANTS, AND ANALYSES FOR THE 7-HYDROXYCOUMARIN DERIVATIVES (XXV)—(XXXIII) [a]

Compound	Yield (%)	M.p. (°C)	Recryst. solvent	Analysis found (calcd.) (%)	
				C	H
(XXV)	64	155—156 [b]	MeOH		
(XXVI)	44	102—104	MeOH	66.1 (66.2)	7.6 (7.6)
(XXVII)	50	182—183 [b]	MeOH	70.2 (70.4)	7.3 (6.2)
(XXVIII)	59	188—190	EtOH—MeOH	70.8 (71.0)	6.6 (6.5)
(XXIX)	54	180—182	EtOH	71.5 (71.6)	6.9 (6.8)
(XXX)	65	244—246	EtOH	66.8 (66.5)	3.9[c] (3.8)
(XXXI)	40	250—253	EtOH	66.3 (66.3)	5.5 (5.5)
(XXXII)	62	198—200	EtOH	68.9 (68.9)	5.6 (5.7)
(XXXIII)	43	170	EtOH	69.3 (69.5)	6.2 (6.1)

[a] The parent peak in the mass spectrum corresponded with the calcd. mol. wt. in each case. [b] Pale yellow. [c] Cl: found, 17.2; calcd., 17.4%.

TABLE 6

CHARACTERISTIC IR AND NMR PEAKS FOR THE 7-HYDROXY COUMARIN DERIVATIVES

Compound	IR(cm^{-1})[a]				NMR[δ(ppm)][b]				
	OH	C=O	C_6H_4	MeSi	MeSi[c]	CH[d]	CH_2	Aryl-H[d]	OH[c]
(XXV)	3250	1690	1600	1240, 840	−0.17	5.90	0.43(m), 1.50(m), 2.56(m)	7.03	10.32
(XXVI)	3160	1700	1600	1250, 840	−0.17	5.90	0.40(m), 1.40(m), 2.59(m)	7.07	10.39
(XXVII)	3140	1700	1605	1245, 860	−0.07	5.97	2.08(s)	6.92	10.38
(XXVIII)	3080	1690	1590	1250, 845	−0.16	5.84	0.67(s), 2.50(t)	6.84	10.39
(XXIX)	3150	1700	1600	1250, 850	−0.17	5.90	0.46(m), 1.46(m), 2.49(m)	6.90	10.42
(XXX)	3200	1695	1605			5.84	2.95(s)	6.90	10.32
(XXXI)	3150	1700		1250, 850	−0.07	5.90	2.07(s)	6.90	10.58[e]
(XXXII)	3150	1680		1250, 840[f]	−0.13	5.90	0.45(t), 2.83(t)	7.07	10.58

[a] Liquid films. [b] 10% Solutions in DMSO. [c] Singlets. The resonances for the HO proton in phenol (XXXIII), 7-hydroxycoumarone (XXXIV) and 4-methyl-7-hydroxycoumarone (XXXV) appeared at δ 9.35, 10.49, and 10.35 ppm respectively under similar conditions. Other resonances were at 7.12(m) for (XXXIII); 7.20(m), 6.29(d), and 7.91(d) for (XXXIV), and 7.15(m), 6.11(s), and 2.37(s) for (XXXV). [d] Multiplets. [e] SiOH at 3.23(s). [f] Si—O—Si at 1060 cm^{-1}.

TABLE 7

MAIN UV PEAKS IN 95% EtOH FOR THE 7-HYDROXYCOUMARIN DERIVATIVES (XXV)—(XXXIII)

Compound	λ_{max}(nm)	Compound	λ_{max}(nm)
(XXV)	253, 325	(XXX)	230, 260, 292, 332
(XXVI)	254, 325	(XXXI)	295, 315, 330
(XXVII)	230, 260, 329	(XXXII)	262, 282, 332
(XXVIII)	236, 256, 283, 331	(XXXIII)	262, 280, 332
(XXIX)	235, 282, 331		

washed, dried (Na_2SO_4), and fractionated to give *p*-trimethylsilylacetophenone (11.6 g, 60%); details are given in Tables 1 and 2.

Ketones (VI) - (XII)

In a typical procedure, the 1/1 aluminium chloride—acetyl chloride complex in methylene chloride (200 ml) was prepared, and treated with benzyltrimethylsilane, as described in the preceding experiment. Work-up as before gave (VI) (47%); details are given in Tables 1 and 2.

The same method was used for ketones (VII) - (XII); details are given in Tables 1 and 2.

β-Ketoesters (XIII) - (XXIV)

In a typical procedure, sodium hydride (0.20 mol of a 50% suspension in paraffin oil) was freed from oil by washing with light petroleum followed by ether. The hydride was stirred with ether (150 ml) at room temperature, and diethyl carbonate (11.8 g, 0.10 mol) was added, followed by the ketone (I) (7.9 g, 0.10 mol) in ether (50 ml). The mixture was refluxed for 30 h, then cooled, and added with stirring to crushed ice, along with 2 *M* hydrochloric acid to maintain the system neutral to litmus. The aqueous system was then slightly acidified, and the organic layer was separated and combined with ether extracts of the water layer. The extracts were washed, dried (Na_2SO_4), and fractionated to give (XIII) (6.6 g, 60%); details of the product are given in Tables 3 and 4.

Similar procedure with the appropriate ketones (II) - (XII) gave the β-ketoesters listed in Table 3; further details are given in Table 4.

Preparation of 7-hydroxycoumarin derivatives (XXV) - (XXXIII)

Concentrated sulphuric acid (10 ml) was added to a stirred, ice-cooled mixture of resorcinol (0.050 mol) and one of the ketoesters (XIII) - (XXIV). The deep-red mixture was kept at 0° for 24 h, then added to crushed ice. The resulting heavy oil was washed thoroughly with water by decantation and the residue was then stirred with a little light petroleum. The resulting solid was recrystallized from methanol or ethanol (see Table 5). Details of the products are given in Tables 5 - 7.

From ketoester (XVII) the product was 7-hydroxy-4-phenylcoumarin, m.p. and mixed m.p., 238 - 239°. (The same result was obtained when zinc chloride was used as catalyst in place of sulphuric acid.) The ketoesters (XV) and (XVI) reacted very exothermically, and with vigorous gas evolution, to give dark red oils which could not be recrystallized.

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