

SHORT
COMMUNICATIONS

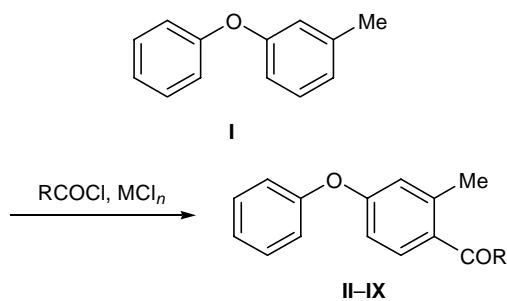
Synthesis of Ketones Containing a Diphenyl Ether Fragment

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In continuation of studies [1, 2] on the synthesis of carbonyl compounds having a diphenyl ether fragment, we effected acylation of *m*-phenoxytoluene (**I**) with carboxylic acid chlorides and obtained ketones **II–IX**. The isolated products contained 90–92% of the main substance. As catalysts we used aluminum chloride, antimony(V) chloride, and tin(IV) chloride. The reactions were carried out in weakly polar solvents (1,2-dichloroethane, methylene chloride), as well as in polar nitrobenzene. The highest selectivity and the greatest yield were achieved using aluminum(III) chloride and methylene chloride.



II, R = CH₃; **III**, R = C₅H₁₁; **IV**, R = C₇H₁₅; **V**, R = C₁₁H₂₃;
VI, R = C₁₅H₃₁; **VII**, R = C₁₇H₃₅; **VIII**, R = C₆H₅; **IX**, R =
m-NO₂C₆H₄; M = Al, *n* = 3; Sb, *n* = 5; Sn, *n* = 4.

Ketones **II–V** and **VIII** are colored liquids, while compounds **VI**, **VII**, and **IX** are crystalline substances. Their structure was confirmed by the IR, ¹H NMR, and mass spectra.

1-(2-Methyl-4-phenoxyphenyl)ethanone (II). A suspension of 11 g (0.08 mol) of AlCl₃ in 50 ml of methylene chloride was cooled to 0°C (ice bath), a mixture of 35 g (0.19 mol) of *m*-phenoxytoluene (**I**) and 5 g (0.06 mol) of acetyl chloride was added dropwise under stirring and cooling, and the mixture was stirred for 1.5–2 h at 3–5°C. It was then poured under stirring into a mixture of ice with concentrated

hydrochloric acid (to decompose the complex formed between the product and AlCl₃) and extracted with methylene chloride. The extract was washed in succession with 10% hydrochloric acid, 10% aqueous Na₂CO₃, and water until neutral reaction, and dried over CaCl₂. The solvent was distilled off, and the residue was subjected to fractional distillation under reduced pressure. Yield 10 g (70%), bp 185–186°C (3 mm). IR spectrum, ν , cm⁻¹: 1600–700 (Ar), 1676 (C=O), 3100–2900 (CH₃). ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 2.4 s (3H, CH₃), 2.5 s (3H, CH₃CO), 6.7–7.95 m (8H, *m*-C₆H₅OC₆H₃). Mass spectrum, m/z (*I*_{rel}, %): 226 (37.1) [M]⁺, 211 (100), 183 (7.1), 168 (5.88), 155 (14.7), 141 (4.71), 128 (10.6), 115 (8.8), 106 (12.4), 91 (10), 77 (37.7), 65 (10.6), 51 (23.5), 43 (21.8), 39 (11.8), 32 (10), 28 (42.4). Ketones **III–IX** were synthesized in a similar way.

1-(2-Methyl-4-phenoxyphenyl)hexan-1-one (III). Yield 6 g (33%), bp 220–222°C (3 mm). IR spectrum, ν , cm⁻¹: 1600–700 (Ar), 1676 (C=O), 3100–2900 (CH₃). Mass spectrum, m/z (*I*_{rel}, %): 282 (11.6) [M]⁺, 267 (7.3), 253 (9.4), 239 (7.3), 225 (21.7), 211 (52.2), 183 (100), 167 (17.4), 155 (23.9), 141 (21.0), 127 (14.5), 115 (15.9), 107 (10.1), 91 (31.9), 77 (31.9), 65 (25.4), 51 (25.4), 40 (26.1).

1-(2-Methyl-4-phenoxyphenyl)octan-1-one (IV). Yield 11 g (59%), bp 228–229°C (3 mm). IR spectrum, ν , cm⁻¹: 1600–700 (Ar), 1684 (C=O), 3100–2900 (CH₃). Mass spectrum, m/z (*I*_{rel}, %): 310 (14.7) [M]⁺, 281 (4.7), 267 (5.3), 253 (21.3), 239 (12), 225 (70.7), 211 (100), 183 (58.7), 167 (30.7), 155 (44.7), 141 (31.3), 127 (24.7), 115 (18), 107 (24), 91 (56), 77 (88.7), 65 (57.3), 57 (36.7), 51 (77.3), 40 (80).

1-(2-Methyl-4-phenoxyphenyl)dodecan-1-one (V). Yield 8 g (34%), bp 240–245°C (3 mm). IR spectrum, ν , cm⁻¹: 1600–700 (Ar), 1680 (C=O), 3100–2900 (CH₃). Mass spectrum, m/z (*I*_{rel}, %): 366 (5.3) [M]⁺, 351 (5.9), 337 (5.9), 309 (5.9), 281 (5.3), 267 (7.2).

253 (7.9), 239 (10.5), 225 (32.9), 211 (88.2), 196 (25.7), 183 (32.2), 167 (23.7), 153 (29), 139 (25.7), 127 (23), 115 (24.3), 93 (30.9), 91 (27), 77 (5.9), 65 (26.3), 52 (38.2), 43 (74.3), 40 (100).

1-(2-Methyl-4-phenoxyphenyl)hexadecan-1-one (VI). Yield 8 g (31%), bp 261–263°C (3 mm), mp 30–31°C. IR spectrum, ν , cm^{-1} : 1600–700 (Ar), 1680 (C=O), 3100–2900 (CH_3). Mass spectrum, m/z (I_{rel} , %): 422 (6.8) [M]⁺, 281 (33.1), 267 (100), 253 (16.5), 239 (34.6), 225 (65.4), 204 (11.3), 191 (18.1), 174 (12.8), 162 (24.8), 147 (12), 132 (18.1), 127 (24.8), 105 (19.6), 93 (27.1), 91 (25.6), 77 (39.9), 71 (15.8), 65 (32.3), 57 (43.6), 65 (33.1).

1-(2-Methyl-4-phenoxyphenyl)octadecan-1-one (VII). Yield 6 g (22%), bp 280–282°C (3 mm), mp 49–50°C. IR spectrum, ν , cm^{-1} : 1600–700 (Ar), 1684 (C=O), 3100–2900 (CH_3). Mass spectrum, m/z (I_{rel} , %): 271 (11.3), 267 (18.9), 253 (45.9), 239 (15.7), 211 (17.6), 196 (18.2), 183 (50.9), 167 (44), 153 (32.1), 139 (52.8), 127 (27), 115 (39), 93 (41.5), 91 (30.2), 77 (50.9), 65 (39), 52 (56.6), 40 (100).

2-Methyl-4-phenoxybenzophenone (VIII). Yield 14 g (80%), bp 240–245°C (3 mm). IR spectrum, ν , cm^{-1} : 1600–700 (Ar), 1660 (C=O), 3100–2900 (CH_3). Mass spectrum, m/z (I_{rel} , %): 288 (100) [M]⁺, 273 (9.9),

211 (36.3), 196 (23.4), 183 (30.4), 168 (9.9), 155 (12.9), 141 (9.9), 128 (9.9), 115 (10.5), 105 (25.2), 91 (13.5), 77 (35.1), 65 (10.5), 51 (14.6), 39 (12.3).

2-Methyl-3'-nitro-4-phenoxybenzophenone (IX). Yield 10 g (51%), mp 81–82°C. IR spectrum, ν , cm^{-1} : 1600–700 (Ar), 1664 (C=O), 3100–2900 (CH_3). ¹H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 2.35 s (3H, CH_3), 6.8–8.6 m (8H, $m\text{-C}_6\text{H}_5\text{OC}_6\text{H}_3$). Mass spectrum, m/z (I_{rel} , %): 333 (93.3) [M]⁺, 318 (42.2), 287 (40), 211 (100), 183 (13.3), 169 (16.7), 150 (24.4), 127 (15.6), 114 (12.2), 105 (33.3), 91 (13.3), 77 (46.7), 65 (12.2), 51 (22.2).

The IR spectra were recorded on a Specord M-82 spectrometer from samples dispersed in mineral oil. The ¹H NMR spectra were obtained on a Bruker WM-250 instrument at 250 MHz. The mass spectra were run on a Variant MAT-111 spectrometer.

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