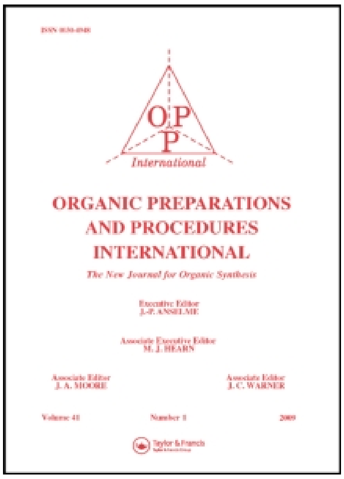

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DIPHENACYL ETHER

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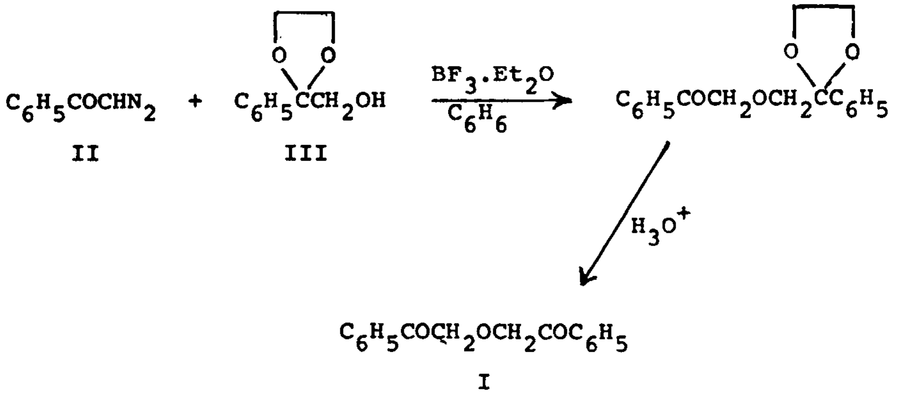

There has been a single previous reference[1] to the preparation of diphenacyl ether (I). Reaction of phenacyl bromide with silver oxide in boiling toluene was reported to give a product, m.p. 117-118°, assigned structure I. However, on repetition of this procedure we obtained a product, m.p. 118-119°, that was shown to be phenacyl benzoate (IV) by direct comparison with an authentic sample.[2,3]

$C_6H_5COCH_2OCOC_6H_5$
IV

We have prepared diphenacyl ether (I) by reaction of α-diazoacetophenone (II) with the ethylene ketal of phenacyl alcohol (III),[4] in the presence of boron trifluoride etherate, followed by aqueous acid hydrolysis. The product, m.p. 70-

71°, is assigned structure I on the basis of its elemental composition and p.m.r. spectrum (see Experimental). Its i.r. spectrum, $\lambda_{max}^{CCl_4}$ 5.85, 5.89 (sh) μ, indicates that in solution in carbon tetrachloride it exists predominantly in a conformation in which dipole-dipole interactions raise the carbonyl stretching frequency relative to that of acetophenone ($\lambda_{max}^{CCl_4}$ 5.91 μ).[5] Its mass spectrum (70 eV; direct insertion) shows no molecular ion peak, but includes a weak peak corresponding to $[M-C_6H_5CO]^+$; the base peak corresponds to $C_6H_5CO^+$.

EXPERIMENTAL

Reaction of Phenacyl Bromide with Silver Oxide. Phenacyl bromide (2.00 g) and silver oxide (3.05 g) were added to toluene (30 ml), and the mixture was boiled under reflux for 24 h. The reaction mixture was filtered, and the filtrate was stripped of solvent under reduced pressure to give a pale yellow oil, which slowly crystallized. The product was purified by chromatography on silica gel; elution with 15-20% ether-petroleum ether gave phenacyl benzoate (IV) as pale yellow prisms, m.p. 118-119°; $\lambda_{max}^{CCl_4}$ 5.77, 5.85 μ; δ^{CDCl_3} 5.58 (s, 2 H), 7.3-7.7 (m, 6 H), 7.9-8.3 (m, 4 H); m/e 240 (0.3), 118 (14), 105 (100), 77 (36). The m.p. was not depressed on admixture with an authentic sample of IV,[2] m.p. 118-119° (lit.[6] m.p. 118-120°); the i.r. and p.m.r. spectra of the two samples were identical. No significant amounts of other products could be detected in the chromatography fractions.

Phenacyl Alcohol Ethylene Ketal (III). A solution of phenacyl alcohol (2.40 g), ethylene glycol (2.40 g) and *p*-toluenesulfonic acid (0.05 g) in benzene (200 ml) was boiled under reflux for 2.5 h; water was removed by means of a Dean-Stark trap. The solution was cooled, washed with dilute aqueous sodium carbonate, dried over anhydrous sodium sulfate, and stripped of solvent under reduced pressure. The crystalline residue was recrystallized from cyclohexane to give III (2.00 g, 63%) as colorless needles, m.p. 102-103°; $\lambda_{max}^{CCl_4}$ 2.88, 2.95 (sh)μ; δ^{CDCl_3} 2.32 (br s, 1 H), 3.75 (s, 2 H), 3.90 (m, 2 H), 4.12 (m, 2 H), 7.3-7.6 (m, 5 H).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71. Found: C, 66.88; H, 6.66.

Diphenacyl Ether (I). Freshly prepared boron trifluoride etherate (0.20 ml) was added to a stirred solution of III (1.85 g) in anhydrous benzene (20 ml). Solid α-diazoacetophenone (II) (0.90 g) was added to the stirred solution in small portions, the evolution of nitrogen being allowed to subside between additions. After addition was complete and no further nitrogen was evolved, the solution was stripped of solvent under reduced pressure. The oily residue was dissolved in 80% aqueous dioxane (50 ml) containing p-toluenesulfonic acid (0.30 g), and the solution was boiled under reflux for 6 h. The mixture was poured into excess dilute aqueous sodium bicarbonate, and the resulting aqueous solution was extracted with ether. The ethereal extract was washed several times with water, dried over anhydrous magnesium sulfate, and stripped of solvent under reduced pressure to give a pale yellow oil, which slowly crystallized. Several recrystallizations from cyclohexane yielded I as long colorless needles (0.70 g, 45% based on α-diazoacetophenone), m.p. 70-71°; $\lambda_{max}^{CCl_4}$ 5.85, 5.89 (sh) μ; δ^{CDCl_3} 4.97 (s, 4 H), 7.3-7.7 (m, 6 H), 7.85-8.1 (m, 4 H); m/e 149 (3.5), 136 (6), 122 (8.5), 105 (100), 77 (98), 51 (24).

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.49; H, 5.77.

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3. The reported elemental analytical data[1] do not distinguish between I and IV. Found: C, 75.5; H, 5.1. Calcd. for $C_{16}H_{14}O_3$ (I): C, 75.57; H, 5.55. Calcd. for $C_{15}H_{12}O_3$ (IV): C, 74.99; H, 5.03.
4. Use of phenacyl alcohol rather than its ketal III gave low yields of I, which could not readily be separated from other reaction products.
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