Reactions of Phenacyl Bromide with Nickel Carbonyl

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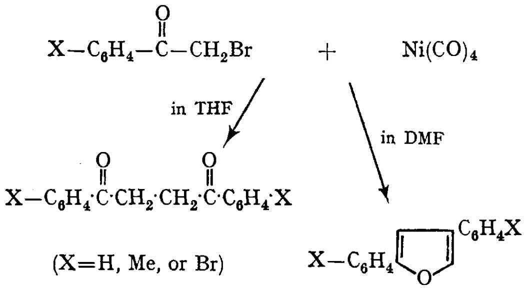
WE report a new type of reaction of nickel carbonyl with *p*-substituted phenacyl bromides and a remarkable solvent effect. A mixture of phenacyl bromide (5·0 g., 0·025 mole) and nickel carbonyl (4·5 g., 0·03 mole) in *NN*-dimethylformamide (DMF) (50 ml.) was stirred at room temperature in an argon atmosphere for 10 hr. Carbon monoxide was evolved in the course of the reaction. The reaction mixture was then partitioned with water and ether, and the ether layer was washed with water and dried over anhydrous magnesium sulphate. After removal of the ether, the residue was recrystallized from ethanol to give a product of m.p. 111° (1·1 g.). The compound showed no carbonyl absorption band in its infrared spectrum and was confirmed to be 2,4-diphenylfuran (lit.,[1] m.p. 111°, 40% yield based on the halide) by the following data: n.m.r. (in CCl_4): τ 3·25 (singlet, 1H at C-3), 2·4 ∼ 2·9 (11H, ten aromatic protons on the phenyl groups at C-2 and C-4 and a proton at C-5).

On the other hand, when the same reaction was carried out in tetrahydrofuran (THF) at 50° for 10 hr., the compound obtained was 1,2-dibenzoylethane, (0·8 g, 28% yield), m.p. 145° (lit.,[2] m.p. 145°; no depression in melting point was observed when the product was admixed with an authentic sample), and no furan compounds were obtained.

The reactions were also carried out with *p*-methyl- and *p*-bromo-phenacyl bromide, and a similar solvent effect was observed.



Physical and spectra data of the compounds obtained from the reactions between *p*-methyl- or *p*-bromo-phenacyl bromide and a slight excess of nickel carbonyl in tetrahydrofuran at 40° or in *NN*-dimethylformamide at room temperature are as follows:

1,4-Di-(*p*-tolyl)butane-1,4-dione (15% yield): m.p. 159—160° (lit.,[3] m.p. 159°).

2,4-Di-(*p*-tolyl)furan (50% yield): m.p. 129—130°; n.m.r. (in CCl_4): τ 7·71 (singlet, 6H on two methyl groups), 3·23 (singlet, 1H at C-3), 2·5 ∼ 3·0 (9H, eight aromatic protons and a proton at C-5).

1,4-Di-(*p*-bromophenyl)butane-1,4-dione (45% yield): m.p. 180—181° (lit.,[4] m.p. 182°). 2,4-Di-(*p*-bromophenyl)furan (92% yield); n.m.r. (in $CDCl_3$): τ 3·08 (singlet, 1H at C-3), 2·3 ∼ 2·6 (9H, eight aromatic protons and a proton at C-5). All the products described gave satisfactory elemental analyses and molecular weights (vapour-pressure osmometry).

The results of application of this method to other bromoacetyl compounds and a suggested reaction mechanism will be described in a forthcoming paper.

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[1] R. C. Fuson, C. L. Fleming, and R. Johnson, *J. Amer. Chem. Soc.*, 1938, **60**, 1994.
[2] J. B. Conant and R. E. Lutz, *J. Amer. Chem. Soc.*, 1923, **45**, 1303.
[3] A. Claus, *Ber.*, 1877, **20**, 1377.
[4] W. J. Hale and L. Thorp, *J. Amer. Chem. Soc.*, 1913, **35**, 273.