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SHORT COMMUNICATIONS

Radical Anion Addition of Metal Ketyls Derived from Benzophenone and 4-Phenylbenzophenone to Carbon Dioxide

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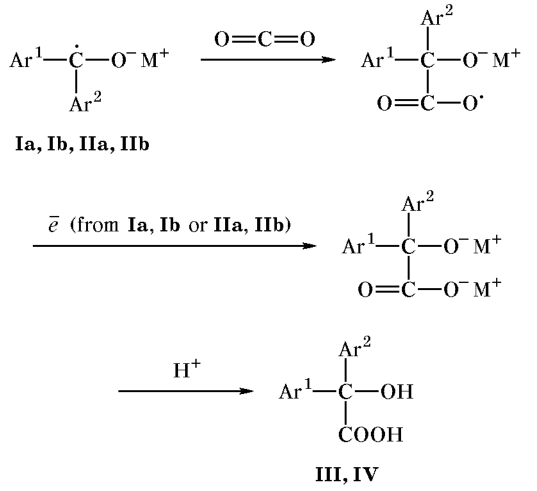
We have found that metal ketyls are capable of not only participating in radical anion substitution [1, 2] and cycloadditions reactions [3] but also adding to carbon dioxide. The reactions of lithium and sodium diphenylketyls and phenyl-4-biphenylylketyls **I** and **II** with carbon dioxide in a solvating solvent (tetrahydrofuran) resulted in formation of the corresponding salts of benzilic acid and hydroxy(phenyl)-4-biphenylylacetic acid **III** and **IV**.



I, $Ar^1 = Ar^2 = C_6H_5$; **II**, $Ar^1 = C_6H_5$, $Ar^2 = 4\text{-}C_6H_5C_6H_4$; M = Li (**a**), Na (**b**).

High concentration of radical anions and homogeneity of the medium increase the probability of collisions of electron-rich radical anion species with electron-deficient carbon atom of carbon dioxide. The absence among the products of oxalic acid which could be formed via reductive dimerization of carbon dioxide indicates that the process follows mainly the radical anion addition path. The revealed reaction offers new possibilities for a simple synthesis of aromatic α-hydroxy acids having various groups at the α-carbon atom (e.g., acid **IV**) via radical anion reductive carboxylation of ketones.

Benzilic acid (III). A suspension of 0.58 g (25 mmol) of sodium (cut in fine pieces) in 20 ml of anhydrous THF was added under purified nitrogen to a solution of 4.6 g (25 mmol) of benzophenone in 30 ml of anhydrous THF. The reaction flask was tightly capped, and the mixture was stirred on a magnetic stirrer until the metal dissolved completely. Carbon dioxide was passed over a period of 1 h through the resulting solution of sodium diphenylketyl (**Ib**). The originally blue mixture turned yellow–green and warmed up. After 24, the mixture was diluted with water and repeatedly extracted with diethyl ether. The first extract was evaporated by half, and the precipitate of benzopinacolone, mp 184–185°C (published data [4]: mp 185–186°C), was filtered off. The mother liquor and the other extracts were combined and evaporated to obtain an oily mixture of benzophenone and benzopinacolone, which was treated with 1:1 pentane–hexane. Benzophenone, 1.1 g (24%), was separated, and benzopinacolone was isolated from the residue. The overall yield of benzopinacolone was 2.3 g (50%). The aqueous phase was acidified to pH 1 and extracted with benzene to isolate benzilic acid (**III**). Yield 1 g (18%), mp 148–149°C (from water; published data [4]: mp 150°C).

The reaction of lithium diphenylketyl with carbon dioxide was performed in a similar way. Yield of acid **III** 46%, and of benzophenone, 49%.

α-Hydroxy(phenyl)-4-biphenylylacetic acid (IV). Sodium phenyl-4-biphenylylketyl (**IIb**) was prepared from 6.5 g (25 mmol) of 4-phenylbenzophenone and 0.58 g (25 mmol) of sodium in 70 ml of anhydrous tetrahydrofuran, following the procedure described above for ketyl **Ib**. Carbon dioxide was passed over a period of 1 h through the resulting yellow solution of **IIb**. The reaction was accompanied by heat evolution, and the mixture thickened and turned light brown (from green). After 24 h, the mixture was diluted with water, and the precipitate of 4-phenylbenzophenone was filtered off. The filtrate was extracted with benzene to isolate an additional amount of 4-phenylbenzophenone; overall yield 4.35 (67%), mp 98–100°C (from ethanol) (published data [4]: mp 102°C). The aqueous phase was acidified to pH 1. The precipitate of α-hydroxy(phenyl)-4-biphenylylacetic acid, 1.7 g, was separated, and an additional amount of **IV** (0.3 g) was isolated by extraction of the filtrate with benzene. Overall yield 26%. mp 171–172°C (from 50% ethanol; published data [5]: mp 168–170°C). By carboxylation of lithium derivative **IIa** we obtained 17% of acid **IV** and 74% of 4-phenylbenzophenone.

The products were identified by comparing with authentic samples (no depression of the melting point was observed on mixing) and by paper chromatography using 1-butanol–ethanol–water (4 : 5 : 1) as eluent and Bromophenol Blue in alcoholic NaOH as developer (for acids). Using the same procedure, the absence of oxalic acid in aqueous solutions was established.

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