β-Dianils from Reaction of Trimethylaluminium with Benzanilides

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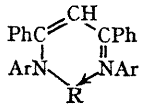
IN view of recent interest in *β*-dianils as chelating ligands,[1] we report a new preparation of the dianils of dibenzoylmethane. Substituted benzanilides PhCO·NHAr react with trimethylaluminium at room temperature with evolution of methane and formation of the dimethylaluminium derivative (I; R = $\mathrm{OAlMe_2}$), which is dimeric.[2] When an excess of trimethylaluminium is used at elevated temperature, reaction proceeds further, presumably by formation of the substituted acetophenone anil (I; R = Me) and subsequent condensation with (I; R = $\mathrm{OAlMe_2}$), to give an aluminium derivative of the dianil (II; R = H). Hydrolysis gives the free dianil in good yield. In some instances (I; R = Me) is obtained as a minor by-product.

For example, trimethylaluminium (3·52 g., 49 mmole) was heated under reflux with benzanilide (3·50 g., 17·7 mmole) in ethylbenzene (30 ml.) under nitrogen for 18 hr. The orange solution was then poured into water, and extracted with chloroform. The chloroform extract was washed with 1N-hydrochloric acid and sodium hydrogen carbonate solution, then evaporated to dryness. The residue was chromatographed from alumina. Benzene eluted yellow 1,3,*N*-triphenyl-3-phenyliminopropeneamine (II; R = H, Ar = Ph) (2·69 g., 81% yield), m.p. 215—216°. Other dianils have been prepared similarly by reaction in toluene: (II; R = H, Ar = $\mathrm{C_6H_4}$-Cl-*m*), m.p. 155—157°; (II; R = H, Ar = $\mathrm{C_6H_4}$-Cl-*p*), m.p. 186—187·5°; II; R = H, Ar = $\mathrm{C_6H_4}$-Me-*m*), m.p. 147—148·5°; and (II; R = H, Ar = $\mathrm{C_6H_4}$-OMe-*p*), m.p. 158—160°.

Ph·CR:NAr (I)



(II)

The unsubstituted dianil (II; R = H; Ar = Ph) reacts with trimethylaluminium and with triphenylaluminium to give the aluminium derivatives (II; R = $\mathrm{AlMe_2}$, Ar = Ph), m.p. 184—186°, and (II; R = $\mathrm{AlPh_2}$, Ar = Ph), m.p. 226—228°, which are monomeric in boiling benzene. Transition metal derivatives of the dianils have also been prepared.

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