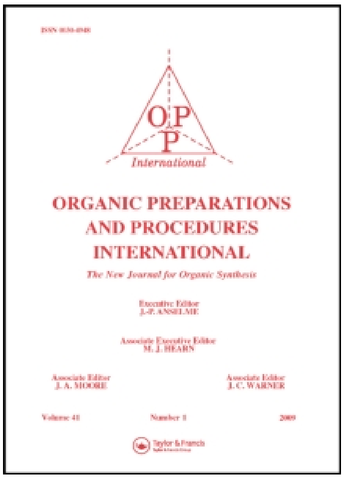

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N-BENZOYLBENZILIMINE

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N-BENZOYLBENZILIMINE

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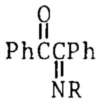
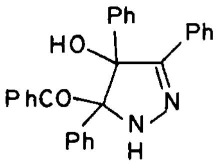
The conversion of phenanthraquinone to its monoimine by reaction with ammonia has been reported.[1] Although the reaction of benzil with ammonia gives products that may be formed via benzilimine (I), the latter has not been isolated.[2] We wished to generate the anion of I in connection with our study of the reaction of benzil monoazine with sodium methoxide, where we have entertained the possibility that the phototropic product II is formed via dimerization of the anion of I.[3] To this end we have prepared N-benzoylbenzilimine (III) as a possible precursor of this anion.



$\mathrm{Ph}\overset{\overset{\displaystyle O}{\|}}{C}\underset{\underset{\displaystyle NR}{\|}}{C}\mathrm{Ph}$

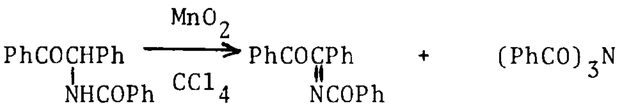
I, R = H

III, R = PhCO



II

Oxidation of N-desylbenzamide (IV)[4] in carbon tetrachloride with active manganese dioxide gave two crystalline products in addition to benzil and benzamide. One of these $C_{21}H_{15}NO_2$, is the desired benzilimine derivative III. Its i.r. spectrum shows bands at 5.97, 6.08, and 6.12 μ, but no band in the N-H stretching region; its p.m.r. spectrum shows signals in the δ 7-8 region only. Hydrolysis occurred on attempted chromatography to give benzil and benzamide; hydrolysis with hydrochloric acid gave benzil and benzoic acid. Treatment of III with sodium methoxide followed by aqueous work-up failed to give II; however formation of the anion of I must occur only to a minor extent, if at all, since the major products were benzil and benzamide, and only a small amount of methyl benzoate was formed.



$$\underset{\mathrm{NHCOPh}}{\mathrm{PhCOCHPh}} \xrightarrow[\mathrm{CCl_4}]{\mathrm{MnO_2}} \underset{\mathrm{NCOPh}}{\mathrm{PhCOCPh}} + (\mathrm{PhCO})_3\mathrm{N}$$

IV III V

The other product from IV, $C_{21}H_{15}NO_3$, was also formed by further treatment of III with active manganese dioxide. It was shown to be tribenzamide (V) by comparison with an authentic sample.[5] Its formation finds analogy in the observation of Padwa[6] that N-arylbenzilimines are oxidized to N-aryldibenzamides by peracids.

EXPERIMENTAL

N-Desylbenzamide (IV).- N-Desylbenzamide was prepared in 95% yield by the method of Davidson, Weiss, and Jelling;[4] mp. 141-142°, lit.[4] mp. 141°; $\lambda_{max}(CCl_4)$ 2.91, 6.00 μ; δ ($CDCl_3$) 6.78 (d, J = 8 Hz, 1 H; s, 1 H after D_2O treatment), 7.50 (m, 12 H; m, 11 H after D_2O treatment), 7.95 (m, 4H).

N-Benzoylbenzilimine (III).- A solution of N-desylbenzamide (9.90 g.) in carbon tetrachloride (400 ml.) was stirred with "active" manganese dioxide[7] for 98 hr. Filtration through sintered glass and concentration of the filtrate to 100 ml. gave tribenzamide (V) as a white solid (400 mg., 8%). This was recrystallized several times from ether and indentified by mixture mp. and i.r. and n.m.r. spectral comparison with an authentic sample;[5] mp. 212-213°, lit.[5] mp. 211.5-212°; $\lambda_{max}(CHCl_3)$ 5.87 μ; λ_{max}(MeOH) 245 nm (log ε 4.44); δ ($CDCl_3$) 7.53 (m, 9 H), 7.92 (m, 6 H).

Anal. Calcd. for $C_{21}H_{15}NO_3$: C, 76.57; H, 4.59; N, 4.25. Found: C, 76.27; H, 4.64; N, 4.21.

Further concentration of the reaction solution to 20 ml. and cooling gave N-benzoylbenzilimine as a crystalline solid, mp. 109-111°; this was recrystallized four times from carbon tetrachloride to give material,mp. 110.5-111.5°; $\lambda_{max}(CCl_4)$ 5.97, 6.08, 6.12 μ; λ_{max}(n-C_6H_{14}) 252 nm (log ε 4.46); δ ($CDCl_3$) 7.42 (m, 9 H), 7.80 (m, 6 H).

Anal. Calcd. for $C_{21}H_{15}NO_2$: C, 80.49; H, 4.83; N, 4.47. Found: C, 80.24; H, 4.78; N, 4.42.

The yield of N-benzoylbenzilimine was 20-40%; the wide variation may be attributed to variation in the activity of the manganese dioxide.

Hydrolysis of III.- A solution of III (114 mg.) in dioxane (1 ml.) and conc. hydrochloric acid (1 ml.) was boiled under reflux for 2 hr. The solvents were removed under reduced pressure and the residue was taken up in ether. The ethereal solution was extracted with aqueous 5% sodium bicarbonate, and the extract was acidified to pH 2 and extracted with ether to give benzoic acid. The original ethereal solution gave benzil.

Oxidation of III. A solution of III (79 mg.) in carbon tetrachloride (10 ml.) was stirred with "active" manganese dioxide[7] for 120 hr. Filtration through sintered glass and evaporation gave a yellow oil that on trituration with carbon tetrachloride gave tribenzamide (5 mg.).

Reaction of IV with Sodium Methoxide.- Compound IV (798 mg.) was added to a mixture of sodium methoxide (250 mg.) and dry tetrahydrofuran (75 ml.), and the mixture was boiled under reflux for 26 hr. under nitrogen. No color change was observed. The reaction mixture was poured into water (150 ml.) and partitioned into neutral and acidic fractions. The neutral fraction contained benzamide (130 mg.), mp. 125-126°, lit.[8] mp. 130°, methyl benzoate (44 mg.), bp. 120° (55 mm.), lit.[8] bp. 199.2°, and benzil (300 mg.), mp. 93-94° after crystallization from 95% ethanol, lit.[8] mp. 95°. The acidic fraction yielded benzoic acid, mp. 121-122° after sublimation, lit.[8] mp. 122.4°.

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