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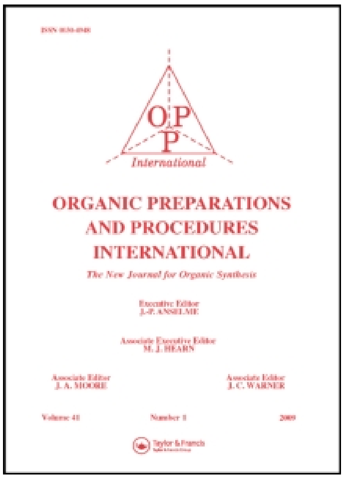

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ALKYLATION AND OXIDATION OF DIARYLACETONITRILES

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ALKYLATION AND OXIDATION
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DIARYLACETONITRILES

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$$\underset{\text{I}}{(C_6H_5)_2CHCN} + Br(CH_2)_3Cl \longrightarrow \underset{\text{III}}{(C_6H_5)_2C(CN)CH_2CH_2CH_2Cl} \qquad (1)$$

$$\underset{\text{II}}{\text{p-Z-}C_6H_4CH(C_6H_5)CN} \xrightarrow{\text{DMSO}} \underset{\text{IV}}{\text{p-Z-}C_6H_4C(O)C_6H_5} \qquad (2)$$

IV a) Z = NO_2
b) Z = OCH_3

Although 2,2-diphenyl-5-chloropentanenitrile was obtained[1] in almost quantitative yield by the alkylation of the sodium salt of diphenylacetonitrile with 1-bromo-3-chloropropane at -78°, recent reports[2,3] suggested a simpler set of conditions might effect the same reaction. We have found that a solution of diphenylacetonitrile in DMSO treated simultaneously with 1-bromo-3-chloropropane and aqueous 50% NaOH at 45° gave a 94% yield of crude product according to reaction (1). Extension of this procedure to the methoxy and nitro substituted diphenylacetonitriles (II) did not give alkylation products but gave oxidation products. The alkylation of (p-nitrophenyl)phenylacetonitrile by typical bases and in common solvents had been unsuccessful. When the present procedure was used, p-nitrobenzophenone was obtained. Eventually, it became evident that the presence of alkylating agent and strong aqueous hydroxide were unnecessary to produce the ketone. Compound II (Z = NO_2) in DMSO with aqueous

K_2CO_3 underwent reaction (2) in 100% yield. A similar oxidation of (p-methoxyphenyl)phenylacetonitrile (II, Z = OCH_3) gave p-methoxybenzophenone (90%).

These results indicate that unsubtituted II undergoes "normal" alkylation with 1-bromo-3-chloropropane but when II contains a substituent (NO_2 or OCH_3) on one of the aryl groups, an oxidation occurs with DMSO acting both as the solvent and oxidizer. Kornblum[4] and his students showed that some alkyl halides lost HX and formed ketones in DMSO at room temperature. The pseudohalogen character of the -C≡N group seems operative in the reactions reported here. The mechanism for the loss of HCN and the formation of the C=O group is probably similar to that proposed by Hunsberger and Tien[5] for the halide cases.

EXPERIMENTAL

2,2-Diphenyl-5-chloropentanenitrile (III). A solution of 4.8 g. (0.025 mole) of diphenylacetonitrile in 25 ml. of DMSO was stirred while 8.4 g. (0.053 mole) of 1-bromo-3-chloropropane and 10 ml. of 50% aqueous NaOH was added simultaneously from separate burets. An additional 20 ml. of DMSO was added to give a homogeneous reaction mixture. During the addition the temperature rose to about 45°. Stirring was continued 7 hrs. longer and the mixture allowed to stand overnight. Addition of water gave a white solid (air-dried) 6.3 g. (94%), mp. 86-91°, lit.[1] mp. 92-93°.

p-Nitrobenzophenone (IVa). To a solution of 1.0 g. (0.004 mole) of (p-nitrophenyl)phenylacetonitrile[6] in 30 ml. of DMSO was added 2.0 g. (0.027 mole) of 1-bromo-3-chloropropane in 20 ml. of DMSO. Then a solution of 1.0 g. (0.007 mole) of potassium carbonate in 1.5 ml. of water was added and the temperature rose to 29°. Stirring was continued overnight at 30-35°. The addition of water gave a solid (air-dried) weighing 1.0 g. (100%), mp. 138-139°. This product was identical in all respects with an authentic sample, mp. 138.5-139.5°, lit.[7] mp. 137-139°, mixture mp. 138-139°, prepared by the chromium trioxide treatment in glacial acetic acid of the same nitrile[7].

p-Methoxybenzophenone (IVb). Prepared by the same procedure without alkyl halide in 90% yield from II (Z = OMe)[8]. A pure sample after recrystallization from hexane melted at 61-61.5°, lit.[9] mp. 61-62.5°.

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