A CONVENIENT METHOD FOR THE PREPARATION OF AROMATIC α-DIKETONES

JERRY HIGGINS AND JOE F. JONES
Illinois State University, Normal, Illinois

ABSTRACT. — A convenient method has been developed for the preparation of aromatic α-diketones from α-halo aromatic ketones and pyridine-N-oxide. Desyl chloride (**1**) and phenylglyoxalybenzil (**4**) were prepared in 50% and 70% yields, respectively.

A new synthesis of glyoxals and α-diketones has recently been described (Kornblum, et al. 1966). This synthesis involves the reaction of *a*-halo ketones with nitrate to produce the organo nitrate esters followed by the elimination of nitrite with a weak base such as sodium acetate. Benzil was obtained in 95% yield from desyl bromide and yields of various glyoxals ranged from 82-90%. A similar method which has been used to form aromatic aldehydes from the reaction of benzyl halides and pyridine-N-oxide has been reported in the literature (Feely et al. 1957). In this particular reaction pyridine-N-oxide is used as the nucleophile for producing benzyloxypyridinium bromide from benzyl bromide. This salt is then treated with dilute sodium hydroxide to produce benzaldehyde by the abstraction of a proton from the benzyl carbon and the elimination of pyridine. Yields of benzaldehyde and aromatic dialdehydes ranged from 80-95%. The chemical requirements for reactions of this type are that a nucleophile capable of displacing reactive halides is used and that this nucleophile possesses a good leaving group with the elimination of a proton in the formation of the carbonyl group.

The method we would like to report in this communication is a combination of the procedures used by Feely and Kornblum. Our modified method uses aromatic α-halo ketones as in Kornblum's method and pyridine-N-oxide as in Feely's method.

EXPERIMENTAL

Preparation of Benzil(2). — Equal molar quantities of desyl chloride and pyridine-N-oxide were refluxed for three hours in acetonitrile. An equal molar quantity of sodium acetate was then added, and the reaction mixture was refluxed for an additional three hours. After removal of two-thirds of the acetonitrile, the reaction mixture was poured into water and the product collected by filtration. Recrystallization from methanol gave 50% yield of benzil melting at 91-94°C (reported m.p. 95°).

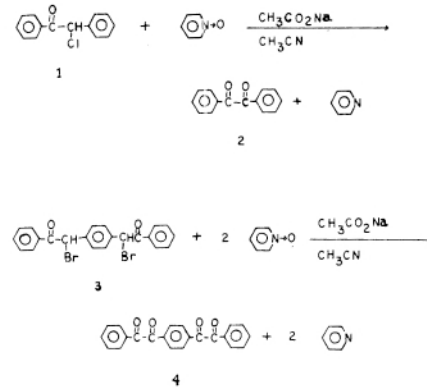

FIGURE 1. Scheme for Synthesis of α-diketones.

Preparation of α α′-dibenzoyl-α, α′- dibromo-*p*-xylene (3).—to 150 ml of glacial acetic acid was added 11.6 g (0.037 moles) of α, α′-dibenzoyl-*p*-xylene (Wrasidlo and Augl, 1969). After dissolving the compound, 12.5 g (0.078 moles) of bromine was added dropwise to the warm reaction solution. The product was collected by filtration and washed three times with 100 ml portions of water. The yield of crude product was 15 g (86%). After recrystallization from carbon tetrachloride, 10.9 g (62%) of pure product, m.p. 179-180°C, was obtained. Calcd. for $C_{22}H_{18}Br_2O_2$: C, 55.94%; H, 3.42%; Br, 33.85%. Found: C, 55.83%; H, 3.21%; Br, 34.00%.

Preparation of phenylglyoxalylbenzil(4).

—To 200 ml acetonitrile were added 25.0 g (0.053 mole) of α, α'-dibenzoyl-α, α'-dibromo-*p*-xylene and 12.0 g (0.126 mole) pyridine-N-oxide. The reaction solution was refluxed for three hours and then 12.0 g of anhydrous sodium acetate was added to the hot solution. After refluxing for an additional three hours, about two-thirds of the acetonitrile was removed and the remaining residue added to 300 ml of water. The aqueous mixture was stirred for 30 minutes. The product was filtered off and then dried *in vacuo*. Recrystallization from methanol gave 12.3 g (0.036 mole) (70%) of product melting at 124-126°C. Reported m. p. 126°C (Oliarinso, et al. 1963).

Results and Discussion

Benzil and phenylglyoxalylbenzil can be prepared easily and conveniently by the reaction of pyridine-N-oxide with aromatic α-halo ketones in acetontirile solvent (Scheme 1). Other solvents such as alcohols, cyclic ethers, diols, N,N-dimethylacetamide were also used as solvents in the present procedure, and the yields were similar to those in acetonitrile solvent. Since this appears to be a general reaction, we are presently expanding this procedure to the preparation of glyoxals and other α-diketones.

Literature Cited

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