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BENZIL AS A BENZOYL GROUP DONOR. BASE-CATALYZED REACTIONS OF BENZIL WITH CYCLIC α-DICARBONYL COMPOUNDS

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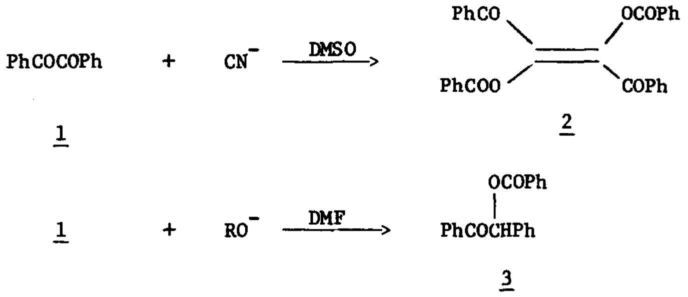
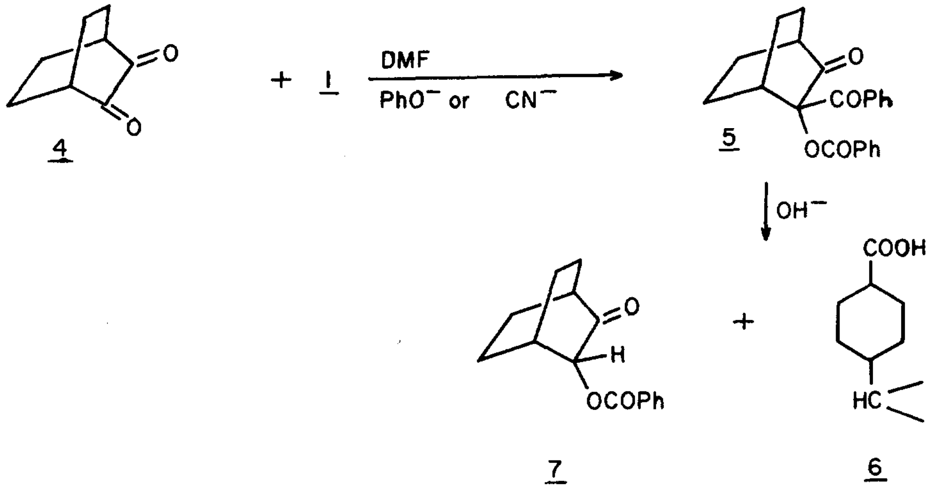
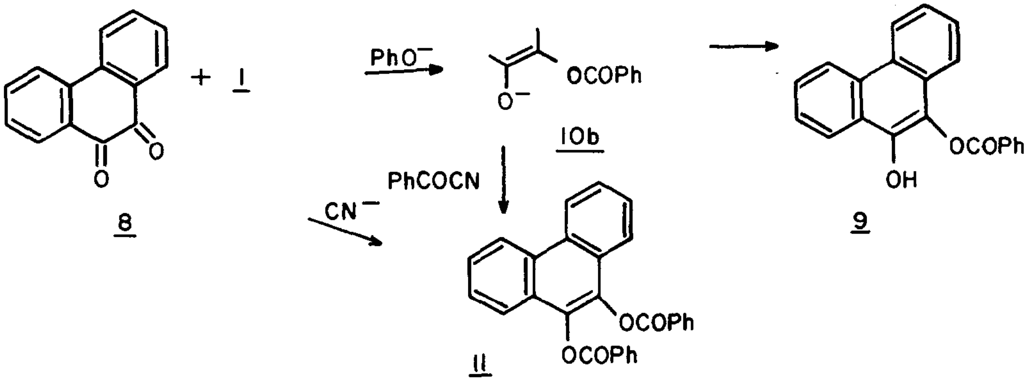
Reports that benzil (1) reacts with cyanide ion[1] in aprotic solvents to give trans-stilbenediol dibenzoate (2) and with various other nucleophiles[2] to give benzoin benzoate (3) suggested that benzil might serve as a donor of benzoyl groups in the presence of suitable acceptors. We report results obtained with cyclic α-dicarbonyl compounds showing that this expectation can be realized in certain cases in a synthetically useful manner.



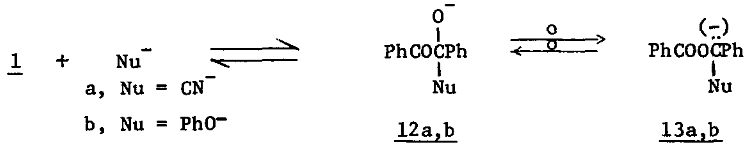
Reaction of an equimolar mixture of benzil and bicyclo[2.2.2]octan-2,3-dione (4) in dry DMF with 20 mole percent of sodium phenoxide for one-half hour at room temperature followed by simple work-up and crystallization from methylene chloride-hexane gave 85% yield of pure benzoate ester[3,4] (5), m.p. 223-4°C, of 2-benzoyl-2-hydroxybicyclo[2.2.2]octan-3-one (5a). Other products were phenyl benzoate and a trace of 3. Similar results were obtained using 50 mole percent of potassium cyanide under the same conditions. These results correspond to addition of the elements of benzil across the double bond of a keto group. The β-diketone 5 underwent competing base catalyzed cleavages as illustrated. It might be noted that compounds such as 5 are available with considerable difficulty since the free alcohol (5a) undergoes extremely facile thermal or base-catalyzed rearrangements[5] to the ester 7.

Under similar reaction conditions, one equivalent of sodium phenoxide was required for complete reaction of an equimolar mixture of 1 and 9,10-phenanthrenequinone (8); the product, obtained in 87% yield, was the monobenzoate[6] (9) of 9,10-phenanthrenediol in addition to phenyl benzoate. Chemical applications of 9 have been described[7]. When benzoyl cyanide was added at the end of the usual reaction time and the solution allowed to stand for an additional one-half hour at room temperature, the dibenzoate[8] (11) was obtained. The latter compound was also isolated in 70% yield from reaction of 1 and 8 with 50 mole percent of potassium cyanide in DMF at room temperature.





Trisler et al[1,2] have proposed that the reaction 1→2 proceeds via addition of cyanide ion to 1 to give 12a which then rearranges to the so-called "active aldehyde intermediate" 13a. Addition of 13a to 1 followed by further rearrangement (analogous to 12a→13a) and elimination of cyanide ion yields 2. The conversion 1→3 was suggested to proceed similarly via 2 (involving participation of cyanide ion present in trace amounts in DMF[9]) followed by phenoxide (or other base) catalyzed cleavage of 2 to give 3 and phenyl benzoate. According to this



$$\underline{1} + \mathrm{Nu}^- \rightleftharpoons \mathrm{PhCO}\overset{\mathrm{O}^-}{\underset{\mathrm{Nu}}{\mathrm{C}}}\mathrm{Ph} \xrightleftharpoons[o]{o} \mathrm{PhCOO}\overset{(\ddot{-})}{\underset{\mathrm{Nu}}{\mathrm{C}}}\mathrm{Ph}$$

a, Nu = CN^-

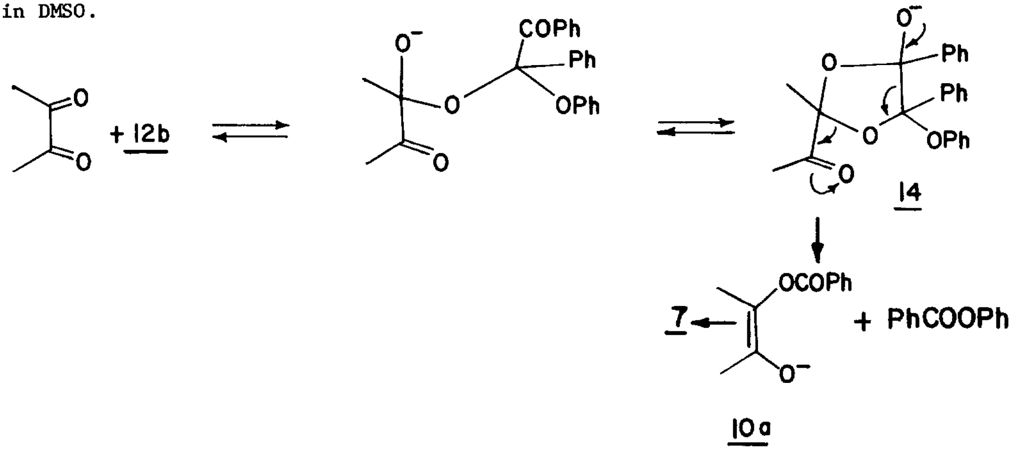
b, Nu = PhO^-

12a,b

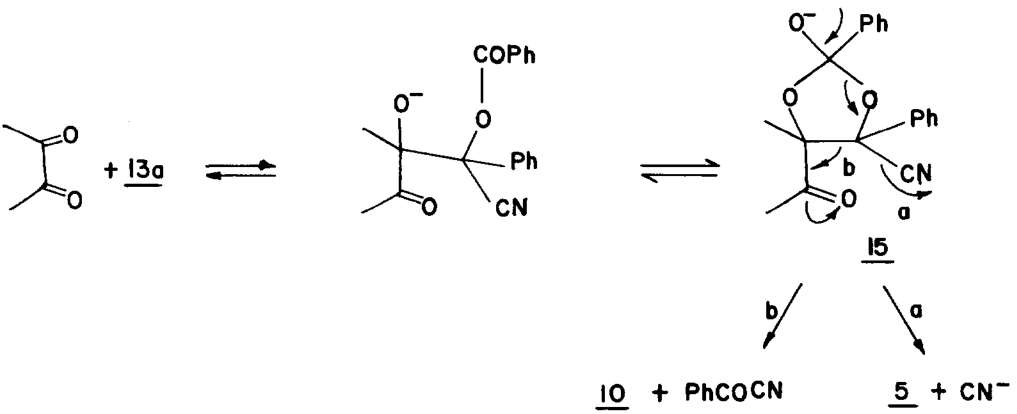
13a,b

proposal, none of the bonds originally joining carbonyl groups in the two molecules of benzil which form 2 remain intact in contrast to the results obtained in the present work.

By analogy with the mechanism proposed by Wenkert and Mekler[10] for the reaction of benzil with ammonia, we suggest that the reactive species in phenoxide catalyzed reactions is the anion 12b formed by reversible addition of phenoxide ion to 1. Addition of 12b to cyclic dione followed by formation of the cyclic intermediate 14 and fragmentation, as illustrated below, results in formation of the anion (10) of enediol monoester. The anion (10a) derived from 4 would be sufficiently reactive to undergo C-acylation with phenyl benzoate (or benzoyl cyanide) thus forming product and regenerating phenoxide (or cyanide) ion. The more stabilized anion (10b) formed in the phenanthrene system could undergo O-acylation with benzoyl cyanide but not with phenyl benzoate. A very similar mechanism has recently been suggested by Kawasaki and Ogata[11] to account for the results observed in reaction of unsymmetrical benzils with cyanide ion in DMSO.



The proposal above provides a unifying mechanism for all the reactions involved but we cannot rule out a variation of the original Trisler proposal, at least for the cyanide catalyzed reactions[12]. As illustrated below, addition of 13a to dione can be followed by formation of cyclic intermediate 15. Two possible fragmentations of 15 can be envisaged: (1) by path a in which elimination of cyanide leads directly to products of type 5 or: (2) via path b in



which benzoyl cyanide and enediolate monoester (10) are formed. Competition between these two paths will depend on the species involved thus providing an explanation for the different results observed in reactions of benzil with 4 and with 8.

The considerable steric requirements of the intermediates proposed above provide a rationalization for the failure of camphorquinone and 1,1,4,4-tetramethyltetralin-2,3-dione to undergo similar reactions; only products derived from reaction of benzil with itself (2 and 3) were observed.

References and Notes

1) (a) J. C. Trisler and J. L. Frye, *J. Org. Chem.*, **30**, 306 (1965). (b) J. P. Kuebrich and R. L. Schowen, *J. Am. Chem. Soc.*, **93**, 1220 (1971).

2) (a) J. C. Trisler, J. D. Cheng, and B. F. Freasier, *J. Org. Chem.*, **35**, 2693 (1970).
   (b) B. Lachmann, H. Steinmaus, and H. W. Wanzlick, *Tetrahedron*, **27**, 4085 (1971).
   (c) J. C. Trisler, B. F. Freasier, and S.-M. Wu, *Tetrahedron Lett.*, 687 (1974).
   (d) W. C. Reardon, J. E. Wilson, and J. C. Trisler, *J. Org. Chem.*, **39**, 1596 (1974) and references contained therein.

3) Satisfactory analytical data were obtained for new compounds.

4) IR, ν_{max}(KBr) 1742, 1722, 1670 cm^{-1}; UV, λ_{max}(CH_3OH) 235 nm (22,800), sh 280 (2250); NMR, ($CDCl_3$) δ 7.9-8.3 (m, 4H), 7.3-7.7 (m, 6H), 2.93 (1H), 2.55 (1H), 1.6-2.8 (m, 8H); M^+ 348.1397.

5) M. B. Rubin and S. Inbar, unpublished results.

6) R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 238 (1953).

7) M. B. Rubin and P. Zwitkowits, *J. Org. Chem.*, **29**, 2362 (1964).

8) A. Benrath and A. von Meyer, *J. Prakt. Chem.*, **89**, 258 (1914).

9) In the present work, identical results were obtained using commercial DMF (Fluka AG) or DMF purified by the procedure of Trisler et al[2c]; no reaction was observed when mixtures of benzil and BOD or benzil and PQ were allowed to stand in solution of commercial DMF. The purported cyanide ion impurity in commercial DMF[2c] does not appear to be involved.

10) E. Wenkert and A. B. Mekler, *J. Am. Chem. Soc.*, **78**, 2213 (1956).

11) A. Kawasaki and Y. Ogata, *J. Org. Chem.*, **42**, 2506 (1977).

12) Rearrangement 12→13 should be much less favorable with phenoxide than with cyanide. It might also be noted that rapid reversible addition of nucleophile to 4 or 8 undoubtedly occurs but does not result in subsequent chemical reaction.

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