

A Convenient and Practical Preparation of Dibenzoylmethane

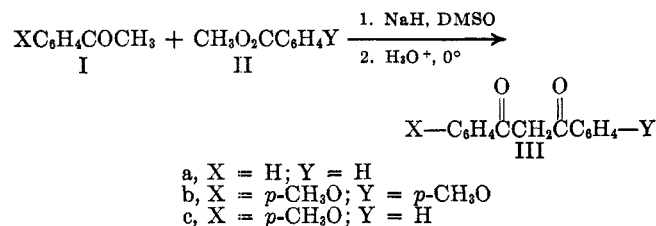
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In 1962, Bloomfield reported the preparation of some symmetrical aliphatic 1,3-diketones by the sodium hydride catalyzed acylation of the methyl ketones with the corresponding methyl esters in dimethyl sulfoxide (DMSO).¹ However, the experimental manipulations entailed the use of oil-free sodium hydride and the utilization of a drybox and oven-baked apparatus.

The reported methods for the preparation of dibenzoylmethane² all involve one or more undesirable features such as complicated procedures, long reaction time, and not readily available or easily handled reagents. We have been able to improve and greatly simplify the procedure of Bloomfield. Dibenzoylmethane has been obtained in 77% yield in less than 3 hr from acetophenone and methyl benzoate. The use of dimethyl sulfoxide as solvent and of sodium hydride (NaH) coupled with very careful temperature control during the various operations account for the success of the reaction. Similarly, bis(*p*-anisoyl)methane (IIIb) and 1-phenyl-3-(*p*-anisyl)-1,3-propanedione (IIIc) were obtained in 87 and 76% yields, respectively.



Experimental Section

Dibenzoylmethane.—To a 1-l. three-necked round-bottom flask, equipped with a mechanical stirrer, a condenser to which was attached a drying tube, a thermometer, and an addition funnel, was added 10.0 g (0.25 mole) of a 60% suspension of sodium hydride in mineral oil. The flask was cooled in an ice-salt bath and 150 ml of dimethyl sulfoxide (dried over molecular sieves) was added. The cooling bath was removed and the mixture was stirred at ambient temperature for 30 min. The temperature was then lowered to 18° and 34.0 g (0.25 mole) of methyl benzoate was added while the temperature was kept below 20°. The temperature was allowed to drop to 8–10° and 18.0 g (0.15 mole) of acetophenone was added at such a rate that the temperature did not rise above 15°. Upon completion of the addition, the bath was removed, the reaction mixture was stirred until no more rise in temperature was noted and warmed to 30° if necessary. The dark reaction mixture was poured slowly in a very thin stream into 500 g of cracked ice containing 10 ml of 85% phosphoric acid with constant stirring. The pre-

cipitate was filtered on a large Büchner funnel and washed thoroughly with water. To the wet cake suspended in about 200 ml of water was added a solution of bromine water until the odor of sulfur compounds was not noticeable. The pale yellow solid was recrystallized from boiling 95% ethanol. The product was filtered and washed with 50 ml of cold cyclohexane. The yield of pale yellow crystals of dibenzoylmethane amounted to 25.9 g (77%), mp 76–77°.

Application of the same procedure, with the exception that a solution of the solid reagents in dimethyl sulfoxide was used when necessary, gave bis(*p*-anisoyl)methane and 1-phenyl-3-(*p*-anisyl)-1,3-propanedione in 87 and 76% yields, respectively.

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Cleavage of β -Ketonic Esters by the Action of Metal Iodides. II. The Action of Hydrated Sodium and Calcium Iodides on Acetoacetic Ester and Its α -Methylated Derivatives

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In our previous paper,¹ it has been shown that the use of hydroxylic solvents facilitates the reaction between β -ketonic esters and metal iodides. It was thought that the use of hydrated metal iodides might produce a similar effect. Thus acetoacetic ester when heated with hydrated sodium iodide or calcium iodide at 150–160° readily underwent cleavage with the production of acetone in yields of 56 and 61%, respectively. The cleavage of mono- and dimethylacetoacetic esters occurred less effectively when sodium iodide was used. However, cleavage of mono- and dimethylacetoacetic esters proved more efficient when calcium iodide was employed. This new procedure has simplified the reaction by dispensing with solvent, by causing a faster reaction, and by furnishing a better yield of ketone in most cases.

The reaction of acetoacetic ester with hydrated sodium iodide took place vigorously, with the yield of acetone attaining 56%, in contrast with the yield of 32% resulting from the reaction of the same ester with anhydrous sodium iodide under optimum conditions. The reactions of mono- and dimethylacetoacetic esters with hydrated sodium iodide were much less vigorous and became sluggish within the span of a few hours. Much of the unreacted esters was recovered, and the yields of the corresponding ketones were even smaller than those resulting from the reactions in which the anhydrous salt was used in the absence of hydroxylic solvent.

As was expected, the use of hydrated calcium iodide in place of hydrated sodium iodide brought about far more vigorous reactions irrespective of whether the β -ketonic ester was α -methylated or not. The yields

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(2) C. F. H. Allen, R. D. Abell, and J. B. Normington in "Organic Syntheses," Coll. Vol. I, Gilman, H., and Blatt, A. H., Ed., John Wiley and Sons, Inc., New York, N. Y., 1932, p 205; A. Magnani and S. M. McElvain in Coll. Vol. III, Horning, E. C., Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 251; G. R. Zellars and R. Levine, *J. Org. Chem.*, **13**, 160 (1948); A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 3723 (1953).

(3) Careful control of the temperature is essential!

(1) D. Y. Chang, C.-F. Yam, S.-Y. Chan, S. H. Lee, and H.-C. Lee, *J. Org. Chem.*, **31**, 3267 (1966).