A Convenient and Practical Preparation of Dibenzoylmethane

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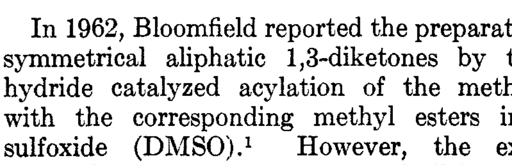
In 1962, Bloomfield reported the preparation of some symmetrical aliphatic 1,3-diketones by the sodium hydride catalyzed acylation of the methyl ketones with the corresponding methyl esters in dimethyl sulfoxide (DMSO).[1] However, the experimental manipulations entailed the use of oil-free sodium hydride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

The reported methods for the preparation of dibenzoylmethane[2] 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.



$$\underset{\text{I}}{XC_6H_4COCH_3} + \underset{\text{II}}{CH_3O_2CC_6H_4Y} \xrightarrow[\text{2. } H_3O^+,\ 0^\circ]{\text{1. NaH, DMSO}} \underset{\text{III}}{X—C_6H_4\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}C_6H_4—Y}$$

a, $X = H; Y = H$
b, $X = p\text{-}CH_3O; Y = p\text{-}CH_3O$
c, $X = p\text{-}CH_3O; Y = H$

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°*.[3] 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 precipitate 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.

Registry No.—III, 120-46-7.

Acknowledgment.—The technical assistance of Messrs. R. H. Kent and D. J. Grande is hereby gratefully acknowledged.

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(1) J. J. Bloomfield, *J. Org. Chem.*, **27**, 2742 (1962).

(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!*

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

TABLE I

VOLATILE PRODUCTS FROM THE DECOMPOSITION OF ACETOACETIC ESTER AND ITS METHYLATED DERIVATIVES

Expt no.	β-Ketonic ester[a]	Metal iodide[b]	Reacn temp, °C	Reacn time, hr	Amt of condensate, g	Amt of H_2O in the condensate[c]	Yield of products, mole/mole of β-ketonic ester				
							CO_2	Ketone[e]	EtI	EtOH	Ester[f]
1	CH_3COCH_2COOEt	$NaI \cdot 2H_2O$	150–160	2.5	55.6	1.39	0.53	0.556	0.19	0.56	Trace
2	$CH_3COCHMeCOOEt$	$NaI \cdot 2H_2O$	150–160	3	18.2	0.65	0.16	0.092	0.021	0.11	Trace
3	CH_3COCMe_2COOEt	$NaI \cdot 2H_2O$	150–160	3	19.0	1.22	0.11	0.062	0.012	Nil	Trace
4	CH_3COCH_2COOEt	$CaI_2 \cdot 4H_2O$	145–155	2	86.8	1.39	0.61[d]	0.607	0.51	0.30	0.033
5	$CH_3COCHMeCOOEt$	$CaI_2 \cdot 4H_2O$	145–155	1.5	103.8	0.98	0.70[d]	0.725	0.71	0.075	0.032
6	CH_3COCMe_2COOEt	$CaI_2 \cdot 4H_2O$	145–155	1.5	121.0	1.26	0.71[d]	0.775	0.78	Nil	0.065

[a] One-half mole of the β-ketonic ester was used in each experiment. [b] One-half gram formula weight of $NaI \cdot 2H_2O$ was used in reactions with sodium iodide; one-fourth gram formula weight of CaI_24H_2I was used in reactions with calcium iodide. [c] In moles per gram equivalent weight of the hydrated metal iodide used. [d] Including the amount of CO_2 evolved during the reaction and that produced by acidification of the residue. [e] Acetone was produced in expt 1 and 4; methyl ethyl ketone in expt 2 and 5; and methyl isopropyl ketone in expt 3 and 6. [f] Calculated as $CH_3COOC_2H_5$ in expt 4, as $CH_3CH_2COOC_2H_5$ in expt 5, and as $(CH_3)_2CHCOOC_2H_5$ in expt 6.

of the corresponding ketones were also much higher. The reaction of unsubstituted acetoacetic ester afforded acetone in a yield of 61%. With mono- and dimethylated esters, the yields of methyl ethyl ketone and methyl isopropyl ketone were 72.5 and 77.5%, respectively.

That the use of hydrated metal iodides greatly facilitated the cleavage of β-ketonic esters seems to stem from two factors. On the one hand, the hydrated metal iodides are more soluble in the β-ketonic esters under investigation, supplying a higher concentration of iodide ion to ensure a more rapid production of acetoacetate ion or α-methylated acetoacetate ion in the first phase of the reaction. In the second place, the enolate ion of acetone or its homolog readily extracts a proton from the hydrated salt at the reaction temperature (*ca.* 150°) to produce the corresponding ketone. In contrast with the use of hydroxylic solvents as proton donors, the use of hydrated salt did not decrease the concentration of the reactants to any appreciable extent, so that the reaction could proceed with its usual vigor.

The results of analyses of the key products from the reactions mentioned above are summarized in Table I. Identification of the volatile products was made by gas–liquid partition chromatography as well as by chemical means.

Discussion

The replacement of anhydrous sodium and calcium iodides with the hydrated salts in bringing about the cleavage of β-ketonic esters has several remarkable advantages. In the first place, it obviates the use of any solvent and, where calcium salt is to be used, the laborious procedure for preparing anhydrous calcium iodide. Secondly, the reaction can be carried out at lower temperatures, thus eliminating undesirable complex condensation reactions, as shown by the fact that none of the reactions gave any resinous residue. Lastly and most important of all, the use of hydrated iodides, especially that of calcium, in the cleavage of β-ketonic esters, gives high yields of the corresponding ketones. All these warrant practical applicability of the reaction in synthetical works.

To verify the capability of hydrated calcium iodide to cleave β-ketonic esters which otherwise undergo cleavage with difficulty, we have attempted the reaction with succinosuccinic ester which can be cleaved only under drastic conditions.[2] By the action of hydrated calcium iodide, it readily decomposed to give cyclohexane-1,4-dione in a yield of 60%. This, together with other reactions of derivatives of succinosuccinic ester, will be reported in subsequent papers of this series.

The results of the present work provide additional evidence in support of the general mechanism of reaction suggested in our previous paper. In consideration of the suppression of most of the condensation processes by the substitution of anhydrous iodides by hydrated ones, it may be inferred that the major part of ethyl alcohol was produced by hydrolysis of ethyl iodide. In effect, in most of the experiments, the yield of ethyl iodide alone or plus that of ethyl alcohol was slightly higher than that of the ketone. This would confirm our view of considering ethyl iodide as the product formed in the first phase of the reaction. In the reactions using hydrated sodium iodide, the amount of carbon dioxide in mole/mole of ester collected during the reaction was close to that of the ketone. In the reactions using hydrated calcium iodide, however, the amount of carbon dioxide similarly collected was much less than that of the ketone, but on acidification of the residue an additional amount of carbon dioxide was formed, with the result that the total yield of carbon dioxide was close to that of the ketone. Undoubtedly a part of the carbon dioxide formed during the course of decarboxylation of the acetoacetate ion or the methylated acetoacetate ion was fixed by the hydroxide ion which resulted from the abstraction of a proton from water by the enolate ion of acetone or its homolog to give the bicarbonate ion.

An attempt has been made to bring about the cleavage of acetoacetic ester by the action of hydrated aluminum iodide. The results indicated that the reaction proceeded with a vigor intermediate between the reaction using hydrated sodium iodide and that using hydrated calcium iodide, affording acetone in a yield of 60%. A more extensive investigation on the cleavage of β-ketonic esters brought about by the action of hydrated iodides of aluminum and other metals, as well as a comparative study of the effect of varying the amounts of water associated with a given metal iodide, is being carried on.

Experimental Section

The apparatus used in carrying out the following reactions was similar to that described in the previous paper for the re-

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(2) A. Baeyer, *Ann.*, **278**, 91 (1894); J. R. Vincent, *et al.*, *J. Org. Chem.*, **3**, 603 (1939).

actions using anhydrous sodium iodide in the absence of any solvent. Carbon dioxide evolved during the reaction was absorbed in two Friedrichs absorption bottles connected in series and previously weighed. All the condensates, except that resulting from the reaction with unsubstituted acetoacetic ester, consisted of two layers. They were made homogeneous by addition of appropriate amounts of dioxane. Samples were taken from the homogeneous condensate, or condensates made homogeneous by addition of dioxane, for the analysis of water content by Karl Fischer's aquametric method. A weighed portion of the condensate from the reaction with the unsubstituted ester was fractionated; the fraction boiling below 90° was collected and weighed. Similar portions were taken from the homogenized condensates from the reaction with the methylated esters were also fractionated, and the fractions boiling below 110° were collected and weighed. Samples were taken from these distillates for the analyses of ethyl iodide, ketones, ethyl alcohol, and esters. The analyses of ethyl iodide and ketones were carried out in the same way as in the previous work. Ethyl alcohol was estimated exclusively by acetylation with a weighed amount of acetic anhydride, followed by hydrolysis of the excess of the anhydride and alkalimetry. For the analysis of esters, weighed samples of the distillates were saponified with an excess of alcoholic sodium hydroxide. The resulting alkaline solutions were evaporated to dryness, and the residues were dissolved in water, neutralized, acidified with dilute sulfuric acid in amounts slightly more than sufficient to liberate the organic acids, and steam distilled. Each of the distillates was absorbed in an excess of standard alkali and titrated back with standard acid. The identification of the products in the condensates was performed by gas-liquid partition chromatography as well as by chemical means, as described in the previous paper.

Action of Hydrated Sodium Iodide on Ethyl Acetoacetate.—Ethyl acetoacetate (65 g, 0.5 mole) and 93 g (0.5 gfw) of pulverized hydrated sodium iodide were placed in the reaction flask and heated. Complete dissolution of the salt soon occurred. When the temperature reached 150°, a vigorous reaction took place. The reaction temperature was maintained at 155° most of the time. Toward the end of the reaction, the temperature was raised to 160°. The reaction ended in 2.5 hr. Homogeneous condensate, weighing 55.6 g, was collected. The amount of carbon dioxide evolved was 11.6 g (0.53 mole/mole of ester). The yield of acetone amounted to 12.8 g (0.56 mole/mole of ester). The residue consisted of a brownish yellow crystalline paste which on acidification gave small amounts of unidentified brownish oil with evolution of a little carbon dioxide.

Action of Hydrated Sodium Iodide on Ethyl Methylacetoacetate.—The reaction was conducted in a manner similar to that for expt. 1 except that 72 g (0.5 mole) of methylacetoacetic ester was used instead of the unsubstituted ester. Reaction began when the temperature reached 140°. It became vigorous at 150°, but thereafter it slowed down, and at the end of 3 hr it subsided almost completely. The condensate, weighing only 18.2 g, was made homogeneous by adding 10 g of dioxane. The yield of methyl ethyl ketone amounted to 3.3 g (0.092 mole/mole of ester). The amount of carbon dioxide evolved during the reaction was 3.4 g (0.16 mole/mole of ester). Acidification of the residue did not give much more carbon dioxide. About 0.3 mole of the unreacted ester was recovered.

Action of Hydrated Sodium Iodide on Ethyl Dimethylacetoacetate.—The reaction was performed in the same manner as in expt 1, except that 79 g (0.5 mole) of dimethylacetoacetic ester was used in place of the unsubstituted ester. The temperature was held at 150–160°. The reaction first took place at a moderate rate, then slowed down. It subsided almost completely at the end of 3 hr. The condensate, which was collected in a receiver cooled in ice and salt, consisted of crystals of ice and organic liquid, and weighed 19 g. It was warmed to room temperature, and made homogeneous by addition of 25 g of dioxane. The yield of methyl isopropyl ketone amounted to 4.5 g (0.11 mole/mole of ester). No ethyl alcohol was present in the condensate. The amount of caron dioxide evolved was 2.5 g (0.11 mole/mole of ester). From the residue was recovered 36 g (about 0.25 mole) of the unreacted ester.

Action of Hydrated Calcium Iodide on Ethyl Acetoacetate.—Ethyl acetoacetate (65 g, 0.5 mole) and 92 g (0.25 gfw) of hydrated calcium iodide were introduced in the reaction flask and heated. Complete dissolution of the salt rapidly occurred. Vigorous reaction took place when the temperature reached 140°. Subsequently the temperature was maintained at 145–155°. At the end of 2 hr the reaction was complete, and crystalline paste was left in the reaction flask. The amount of carbon dioxide evolved during the reaction was 9.7 g. Acidification of the residue produced 3.8 g more, making a total of 13.5 g (61.4 moles/mole of ester). The condensate collected, weighing 86.8 g, consisted of two layers. It was made homogneous by adding 37.2 g of dioxane. The yield of acetone amounted to 35.1 g (0.607 mole/mole of ester). Serious foaming might occur at the latter phase of the reaction. This can be suppressed by addition of a little anisole.

Action of Hydrated Calcium Iodide on Ethyl Methylacetoacetate.—Ethyl methylacetoacetate (72 g, 0.5 mole) and 92 g (0.25 gfw) of hydrated calcium iodide were placed in the reaction flask and heated. Dissolution of the salt soon occurred. A vigorous reaction began when the temperature reached 140°. The temperature was maintained at 145–155°. At the end of 1.5 hr the reaction was complete. The condensate, consisting of two layers, weighed 108 g. It was made homogeneous by adding 88 g of dioxane. The yield of methyl ethyl ketone was 26.1 g (0.725 mole/mole of ester). The amount of carbon dioxide evolved during the reaction was 8.3 g. Acidification of the residue gave 7.0 g more, making a total of 15.3 g (0.70 mole/mole of ester).

Action of Hydrated Calcium Iodide on Ethyl Dimethylacetoacetate.—Ethyl dimethylacetoacetate (79 g, 0.5 mole) and 92 g (0.25 gfw) of hydrated calcium iodide were introduced into the reaction flask and were heated. At 140°, a vigorous reaction began to take place. The temperature was maintained at 145–155°. The reaction was complete at the end of 1.5 hr. The condensate, when cooled in ice and salt, consisted of a mixture of large crystals of ice and organic liquid and weighed 121 g. The freshly collected condensate, when stored in a well-stoppered flask and warmed to room temperature, built up a pressure inside the flask, showing the presence of ethylene. To make the condensate homogeneous, 137 g of dioxane was added. The yield of methy isopropyl ketone attained 33.3 g (0.775 mole/mole of ester). Butyl alcohol was absent in the condensate. The amount of carbon dioxide evolved during the reaction was 6.7 g; acidification of residue gave 8.7 g more, making a total of 15.4 g (0.71 mole/mole of ester.

Registry No.—CH_3COCH_2COOEt, 141-97-9; $CH_3COCHMeCOOEt$, 609-14-3; CH_3COCMe_2COOEt, 597-04-6; $NaI \cdot 2H_2O$, 13517-06-1; $CaI_2 \cdot 4H_2O$, 13640-62-5.

The Reaction of Benzyne with Benzene[1]

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The thermal decomposition of benzenediazonium-2-carboxylate (**1**) in benzene was reported[2] to produce a mixture of hydrocarbons from which three 1:1 adducts of benzyne and benzene were characterized, namely, biphenyl (**2**), benzocyclooctatetraene (**3**), and benzobicyclo[2.2.2]octatriene (**4**). Further examination of this hydrocarbon mixture has revealed a 2:1 adduct as well. Elemental analysis and molecular weight determination indicated the molecular formula $C_{18}H_{14}$ for the new hydrocarbon, mp 154°. The ultraviolet spectrum above 220 mμ contained only the bands expected for benzenoid chromophores. The compound readily absorbed 1 molar equiv of hydrogen (Pd–C) to form a dihydro derivative.

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(1) Financial support by the Petroleum Research Fund (2363-C) of the American Chemical Society is gratefully acknowledged.

(2) R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963).