ment, 10% of IV and 45% of V were obtained, while in a second run 61% of the former and none of the latter was isolated. Although the factors involved were not investigated further, an examination of the mechanism indicates that small variations in experimental conditions might account for large fluctuations in the yields. For example, the rate of addition of the benzoyl chloride may control the formation of V and of VI, which acts essentially as a catalyst for the condensation. Acylation of the dimethylamide ion formed in the reversible condensation step also may influence the relative rates of formation of V and VII.

Experimental

Benzoylation of III.—A saturated ethereal solution of 2.33 g. (0.0133 mole) of N,N-dimethylcinnamamide, prepared by the method of Staudinger and Kon,[5] was added to a solution of phenylmagnesium bromide (from 3.55 g. (0.023 mole) of bromobenzene) and stirring continued for one-half hour. The addition of the amide was carried out slowly enough to avoid the precipitate which is characteristic of the formation of complex products and was ended when the precipitate persisted.[6]

The mixture was cooled in an ice-bath and 2.82 g. (0.02 mole) of freshly distilled benzoyl chloride in 50 ml. of ether added slowly with stirring. The mixture was hydrolyzed with 70 ml. of cold 8% hydrochloric acid and stirred for one-half hour. On filtration, 2.13 g. (45%) of N,N-dimethyl-α-benzoyl-β,β-diphenylpropionamide, m.p. 211.6–212.2° from 95% ethanol, was obtained.

Anal. Calcd. for $C_{24}H_{23}O_2N$: C, 80.64; H, 6.49. Found: C, 80.90; H, 6.51.

Evaporation of the dried ether extract of the hydrolysate after filtration yielded 0.3 g. (10%) of N,N-dimethyl-α,γ-dibenzhydrylacetoacetamide, identified by a mixed melting point with the sample obtained below.

In a second run, a 1.7-mole excess of benzoyl chloride over the amide was used and the addition carried out more rapidly. Under these conditions, no IV was isolated but a 61% yield of V was obtained, m.p. 194.8–195.4°.

Anal. Calcd. for $C_{32}H_{31}O_2N$: C, 83.23; H, 6.72; N, 3.04. Found: C, 83.36; H, 6.56; N, 3.24.

Hydrolysis of III.—Phenylmagnesium bromide from 5 g. (0.032 mole) of bromobenzene was treated with an ethereal solution of 2.45 g. (0.014 mole) of N,N-dimethylcinnamamide. Stirring was continued for one-half hour longer. The solution was hydrolyzed with 70 ml. of 8% hydrochloric acid and the ether solution separated and dried. On evaporation of the solvent, 4 g. of a yellow solid was obtained which contained 3.33 g. (93%) of N,N-dimethyl-β,β-diphenylpropionamide, m.p. 114–114.2°, recrystallized from 60–68° petroleum ether. The substance did not depress the melting point of an authentic sample prepared from β,β-diphenylpropionyl chloride and dimethylamine.

Anal. Calcd. for $C_{17}H_{19}ON$: C, 80.60; H, 7.57. Found: C, 80.83; H, 7.24.

Hydrolysis of IV.—A solution of 0.13 g. of IV, 25 ml. of 95% ethanol and 4 g. of potassium hydroxide was maintained at reflux for four hours. The solvent was removed under reduced pressure, the residue dissolved in 25 ml. of water, extracted with ether to remove neutral material and the ether extract dried over anhydrous sodium sulfate. Removal of the solvent yielded 0.033 g. of N,N-dimethyl-β,β-diphenylpropionamide, m.p. 111–112°. A mixed melting point with an authentic sample showed no depression.

The water solution of the potassium salts was made acidic with cold concentrated hydrochloric acid and extracted with ether. On removal of the solvent, a mixture of two acids was obtained which was separated by sublimation under reduced pressure on a steam-bath. The sublimate crystallized from water in long needles, m.p. 119–121°. A mixed melting point with an authentic sample of benzoic acid showed no depression. The sublimation residue was recrystallized from 60–68° petroleum ether, m.p. 155–156°. A mixed melting point with an authentic sample of β,β-diphenylpropionic acid showed no depression.

Hydrolysis of V.—This compound (0.38 g.) was refluxed for four hours with 20 ml. of 95% ethanol and 20 ml. of 10% sodium hydroxide solution. The solvent was removed under reduced pressure, and the residue taken up in water and extracted with ether. The ethereal solution was dried, the solvent removed and the residue recrystallized from 60–68° petroleum ether; m.p. 111–112°. A mixed melting point with an authentic sample of N,N-dimethyl-β,β-diphenylpropionamide showed no depression.

The aqueous solution was acidified precipitating a white solid which was recrystallized from alcohol–water solution; m.p. 154.5–156°. A mixed melting point with an authentic sample of β,β-diphenylpropionic acid showed no depression.

IV.—One gram (0.0029 mole) of ethyl α-benzhydrylbenzoylacetate prepared by the method of Kohler and Tishler[4] was mixed with 0.2 g. (0.003 mole) of dry dimethylamine hydrochloride and placed in a small test-tube. The mixture was melted and kept at 190–205° while a brisk stream of dimethylamine was passed in. After one-half hour the melt solidified and the product was cooled and recrystallized from an alcohol–water solution; m.p. 209–211°, yield 0.4 g. (39%). A mixed melting point with IV obtained above showed no depression.

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(5) H. Staudinger and N. Kon, *Ann.*, **384**, 119 (1911).

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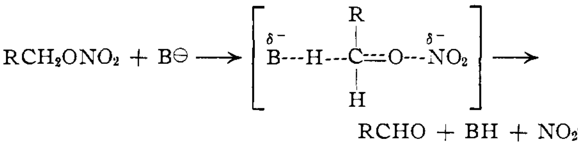
The Synthesis of Diketones from Nitratoketones[1]

By William D. Emmons and Jeremiah P. Freeman

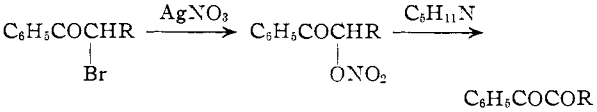
Received March 21, 1955

Previously it had been shown that trichloroethyl nitrate is degraded to chloral in almost quantitative yields when treated with secondary amines.[2] This reaction is an example of the α-elimination reaction[3] of nitrate esters which involves abstraction of an α-hydrogen atom by the base and elimination of nitrite ion, the process probably being concerted.



$$RCH_2ONO_2 + B^{\ominus} \longrightarrow \left[\overset{\delta-}{B}\text{---}H\text{---}\underset{H}{\overset{R}{C}}\text{==}O\text{---}\overset{\delta-}{N}O_2 \right] \longrightarrow RCHO + BH + NO_2^{\ominus}$$

The rapid rate at which this reaction proceeded and the high yields obtained from it suggested that it might be a useful synthetic route to negatively substituted ketones and aldehydes. Indeed it has been found that aryl α-diketones may be prepared conveniently by reaction of the corresponding α-nitratoketones with piperidine.



$$C_6H_5CO\underset{Br}{CH}R \xrightarrow{AgNO_3} C_6H_5CO\underset{ONO_2}{CH}R \xrightarrow{C_5H_{11}N} C_6H_5COCOR$$

The nitratoketones were synthesized readily from the α-bromo compounds by means of silver nitrate in acetonitrile.[4] The over-all yields both of nitratoketones and diketones are summarized in Table I.

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-234.

[2] W. D. Emmons, K. S. McCallum and J. P. Freeman, *J. Org. Chem.*, **19**, 1472 (1954).

[3] J. W. Baker and D. M. Easty, *J. Chem. Soc.*, 1207 (1952).

[4] A. F. Ferris, K. W. McLean, I. G. Marks and W. D. Emmons, This Journal, **75**, 4078 (1953).

TABLE I

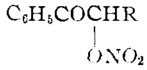
CONVERSION OF KETONES TO α-DIKETONES

Ketone	Yield,[a] % of nitratoketone	Yield,[a] % of diketone
Acetophenone	68	35
Propiophenone	80	71
Butyrophenone	93	79
n-Valerophenone	82	67
Isovalerophenone	84	65

[a] Based on α-bromoketone.

TABLE II

PROPERTIES OF α-NITRATOKETONES,



$C_6H_5COCHR(ONO_2)$

R	B.p., °C.	B.p., Mm.	$n^{25}D$	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
H[a]	M.p. 4–5°								
CH_3	101–103	0.4	M.p. 27–29°	55.38	55.59	4.65	4.54	7.18	7.21
C_2H_5	105–106	.2	1.5260	57.41	57.39	5.30	4.80	6.70	6.60
n-C_3H_7	108–110	.4	1.5206	59.18	59.36	5.87	5.04	6.28	6.09
i-C_3H_7	105–106	.25	1.5214	59.18	59.82	5.87	5.39	6.28	6.14

[a] This compound evolved nitrogen oxides on standing and could not be distilled or recrystallized.

There is one previous report of the conversion of α-bromoketones to α-diketones by means of silver nitrate but this reaction certainly involved a different course. When *m*-nitrophenacyl bromide was treated with aqueous silver nitrate, *m*-nitrophenylglyoxal was obtained.[5] It was postulated that hydrolysis to the keto alcohol followed by oxidation of the alcohol with silver oxide had occurred.

Efforts to extend this method to the synthesis of cyclic diketones failed in the attempted preparation of the nitratoketone. 2-Chloro- and 2-bromocyclohexanone and 2-chlorocyclopentanone reacted very sluggishly with silver nitrate and poorly characterized products were obtained. 3-Bromocamphor was completely inert to silver nitrate in acetonitrile. Attempts also were made to synthesize pyruvic esters by the action of bases on α-nitratoesters. While the nitratoesters could be prepared quite easily and appeared to react readily with a variety of bases (as evidenced by the production of nitrite ion), none of the desired α-ketoesters could be isolated. Usually only gummy materials which were resistant to distillation were obtained. Apparently the alkaline conditions employed in their synthesis caused these sensitive compounds to undergo complex self-condensations.

Experimental[6]

α-Bromoketones.—Phenacyl bromide, α-bromopropiophenone and α-bromobutyrophenone were purchased from Sapon Laboratories and used without further purification.

α-Bromovalerophenone.—This bromoketone was prepared by the addition of 35.0 g. (0.21 mole) of bromine to 32.4 g. (0.2 mole) of *n*-valerophenone dissolved in 100 ml. of glacial acetic acid. The product was isolated in the conventional manner. It was obtained as a colorless liquid, b.p. 94–96° (0.25 mm.), yield 43.3 g. (90%).

Anal. Calcd. for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43. Found: C, 54.28; H, 5.51.

α-Bromoisovalerophenone.—This bromoketone was prepared in 87% yield by the method described above. It was obtained as a solid, m.p. 35–39° (lit. m.p. 46°[7]), and was not purified further.

α-Nitratoketones.—These compounds were all prepared by the action of silver nitrate on the corresponding α-bromoketone in acetonitrile solvent according to the procedure recently described.[4] Their physical constants and analyses are summarized in Table II.

Phenyl Ethyl Diketone.—A solution of 10.4 g. (0.05 mole) of α-nitratobutyrophenone in 50 ml. of ether was cooled to 0–10° and 4.3 g. (0.05 mole) of piperidine was added from a dropping funnel with stirring at such a rate that the temperature did not rise above 20°. During the addition a solid separated from solution. After the addition was complete the mixture was stirred at room temperature for 30 minutes and then poured into water. The layers were separated and the water layer was extracted with ether. The combined organic extracts were washed with 10% hydrochloric acid and water and dried over magnesium sulfate. Upon evaporation of the ether and distillation of the residue there was obtained 7.0 g. (86%) of phenyl ethyl diketone, b.p. 74–76° (0.5 mm.), $n^{19}D$ 1.5239. It formed a dioxime, m.p. 201–203° (lit. m.p. 205°[8]).

Phenyl Methyl Diketone.—Following the general method 15.2 g. (0.078 mole) of α-nitratopropiophenone was converted to 9.3 g. (88%) of the diketone, b.p. 55–56° (0.3 mm.). It formed a dioxime, m.p. 237–240° (lit. m.p. 239–240°[8]).

Phenyl Propyl Diketone.—Following the general procedure from 8.9 g. (0.04 mole) of α-nitratovalerophenone there was obtained 6.3 g. (81%) of the diketone, b.p. 82–84° (3 mm.), $n^{18.5}D$ 1.5215 (lit. $n^{18.5}D$ 1.5215[9]).

Phenyl Isopropyl Diketone.—Similarly, 12.3 g. (0.055 mole) of α-nitratoisovalerophenone was converted to 7.8 g. (77%) of phenyl isopropyl diketone, b.p. 58–60° (0.1 mm.), $n^{20}D$ 1.5158.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.04. Found: C, 74.94; H, 6.20.

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(5) W. L. Evans and E. J. Witzeman, THIS JOURNAL, **33**, 1772 (1911).

(6) We are indebted to Miss Annie Smelley for the micro-combustion data.

(7) F. Kunckell and K. Stahel, *Ber.*, **37**, 1088 (1904).

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The Oxidation of Sodium Diphenylcyanomethide with Nitrate Esters[1]

BY WILLIAM D. EMMONS AND JEREMIAH P. FREEMAN

RECEIVED MARCH 21, 1955

The reaction of active methylene compounds with acetone cyanohydrin nitrate to produce the corresponding nitro compounds recently has been described.[2] In connection with this work the reaction between acetone cyanohydrin nitrate and sodium diphenylcyanomethide (I) was investigated. Since this reaction took a completely different course from that described for the other active methylene compounds, it is being reported separately.

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(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) W. D. Emmons and J. P. Freeman, THIS JOURNAL, **77**, 4387 (1955).