# Behavior of Halogenated Nitrobenzenes with β-Diketones. III

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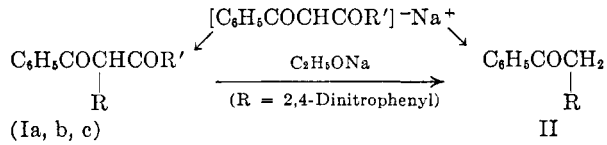
The sodio derivatives of benzoylacetone, dibenzoylmethane, and ethyl benzoylacetate when heated with 1-chloro-2,4-dinitrobenzene yield in ether the corresponding β-diketonic derivatives Ia, b, c while in alcoholic medium only the monoketonic derivative II is formed. In *tert*-butyl alcohol, however, both the β-diketonic as well as the monoketonic derivative have been isolated.




Ia. R = $CH_3$; Ib. R′ = $C_6H_5$; Ic. R′ = $OC_2H_5$

Compound II is also obtained from Ia, b, c by heating with sodium ethoxide and subsequent acidification; in alcoholic solution the cleavage of —COR′ group in compounds Ia, b, c apparently occurs during the progress of the reaction. With those halogenated dinitrobenzenes that are substituted in both *ortho* positions with respect to the reactive halogen atom, such as, 1,2-dichloro-4,6-dinitrobenzene and 1-chloro-2-bromo-4,6-dinitrobenzene, the sodio derivatives of β-diketonic compounds yield both in alcohol and ether the corresponding diketonic derivatives and no cleavage of —COR′ to form monoketonic derivatives takes place.

The dinitrophenyl derivatives of benzoylacetone and dibenzoylmethane, like those of acetylacetone,[1] react with hydrazine hydrate, phenylhydrazine, semicarbazide acetate, and hydroxylamine acetate to form pyrazole, phenylpyrazole, pyrazoleamide, and isoxazole derivatives, respectively. Thus, 2,4-dinitrophenyldibenzoylmethane(Ib) yields with hydrazine hydrate in acetic acid 3,5-diphenyl-4-(2,4-dinitrophenyl)pyrazole (III), with phenylhydrazine in acetic acid 1,3,5-triphenyl-4-(2,4-dinitrophenyl)pyrazole (IV), with semicarbazide acetate in alcohol 3,5-diphenyl-4-(2,4-dinitrophenyl)pyrazole-1-amide (V), and with hydroxylamine acetate in alcohol 3,5-diphenyl-4-(2,4-dinitrophenyl)isoxazole (VI).

2,4-Dinitrophenylbenzoylacetylmethane (Ia) can, however, yield two pyrazole derivatives according as one or the other carbonyl group reacts; but under the usual experimental conditions only one is isolated. Since in benzoylacetone the carbonyl group adjacent to the methyl group first reacts to form a hydrazone which cyclizes to a pyrazole, the compound Ia, too, is expected to behave in the same way. The dinitrophenyl derivatives of benzoylacetone and dibenzoylmethane, in which the 2,6- positions are substituted, do not behave normally. They fail to react with these reagents. This is in conformity with the behavior of ethyl (2,6-dinitrophenyl)acetoacetate with phenylhydrazine, etc.[2]

The dinitrophenyl substituted benzoylacetylmethanes, dibenzoylmethanes, and ethyl benzoylacetates when heated with concentrated sulfuric acid on a water bath are hydrolyzed to monoketones by cleavage of acetyl, benzoyl, and carbethoxy groups, respectively, giving identical products. Thus, 2,4-dinitrophenylbenzoylacetylmethane (Ia), 2,4-dinitrophenyldibenzoylmethane (Ib), and ethyl (2,4-dinitrophenyl)benzoylacetate (Ic) all yield 2,4-dinitrophenylbenzoylmethane (II). The cleavage of these groups takes place with difficulty when the β-ketonic compounds have one or more benzoyl groups or the dinitrophenyl groups are diortho substituted.

Ethyl (2,4-dinitrophenyl)benzoylacetate (Ic) when kept with concentrated sulfuric acid in the cold is hydrolyzed to 2,4-dinitrophenylbenzoylacetic acid (VII), a β-keto acid. The latter when heated with concentrated sulfuric acid on a water bath decomposes to give 2,4-dinitrophenylbenzoylmethane (II).

## Experimental

**2,4-Dinitrophenylbenzoylacetylmethane (Ia) and 2,4-Dinitrophenylbenzoylmethane (II). Method A.**—A suspension of the monosodio derivative of benzoylacetone (1.62 g.) in dry ether (30 ml.) and 1-chloro-2,4-dinitrobenzene (2.0 g.) was refluxed for 3 hr. The ethereal solution was acidified with acetic acid and allowed to stand overnight. A pale yellow crystalline product separated, which after washing with ether and recrystallizing from a mixture of alcohol and acetic acid, gave 1.77 g. of 2,4-dinitrophenylbenzoylacetylmethane (Ia), pale yellow needles, m.p. 110°.

*Anal.* Calcd. for $C_{16}H_{12}N_2O_6$: C, 58.54; H, 3.66; N, 8.54. Found: C, 58.36; H, 3.61; N, 8.62.

It is soluble in dilute caustic soda, is reprecipitated on acidification, and gives a violet coloration with ferric chloride solution.

**Method B.**—A suspension of the monosodio derivative of benzoylacetone (1.62 g.) in absolute alcohol (15 ml.) and 1-chloro-2,4-dinitrobenzene (2.0 g.) was refluxed for 2 hr. and filtered. The filtrate was acidified with acetic acid and allowed to stand; a semisolid mass separated which on purification with activated charcoal and recrystallization from dilute acetic acid gave 1.4 g. of 2,4-dinitrophenylbenzoylmethane (II), colorless needles, m.p. 137°.

*Anal.* Calcd. for $C_{14}H_{10}N_2O_5$: N, 9.79. Found: N, 9.64.

**Method C.**—A suspension of the monosodio derivative of benzoylacetone (1.62 g.) in *tert*-butyl alcohol (15 ml.) and 1-chloro-2,4-dinitrobenzene (2.0 g.) was refluxed for 2 hr. and filtered. The filtrate was concentrated and extracted with ether. The ether-insoluble oily layer was dissolved in excess of ethyl alcohol and allowed to stand; a dirty yellow

(1) S. S. Joshi and I. R. Gambhir, *J. Am. Chem. Soc.*, **78**, 2222 (1956).

(2) W. Borsche and D. Rantscheff, *Ann.*, **379**, 152 (1911).

solid separated which on purification with activated charcoal and recrystallization from a mixture of ethyl alcohol and acetic acid gave 1.1 g. of 2,4-dinitrophenylbenzoylacetylmethane (Ia), pale yellow needles, m.p. 110°. Its mixed melting point with A was undepressed.

The ether-soluble fraction was evaporated and extracted with alcohol containing a few drops of acetic acid; a colorless crystalline solid separated on cooling which was washed with dilute caustic soda, water, and recrystallized from dilute acetic acid to give 0.54 g. of 2,4-dinitrophenylbenzoylmethane (II), colorless, silky needles, m.p. 137°. Its mixed melting point with B was undepressed.

**Method D.**—A solution of 2,4-dinitrophenylbenzoylacetylmethane (Ia) (1.0 g.) in absolute alcohol (10 ml.) was heated with sodium ethoxide (0.3 g.) for 2 hr. The excess of alcohol was boiled off and the product acidified; a dirty white precipitate was formed which after washing with dilute caustic soda and recrystallizing from dilute acetic acid gave 0.77 g. of 2,4-dinitrophenylbenzoylmethane (II), m.p. 137°.

**Method E.**—A solution of compound Ia in moderately concd. sulfuric acid was heated on a water bath for 0.5 hr. On cooling and dilution a dirty white solid separated. Recrystallization from dilute acetic acid gave 80% of 2,4-dinitrophenylbenzoylmethane (II), m.p. 137°.

**3-Methyl-5-phenyl-4-(2,4-dinitrophenyl)pyrazole** was prepared from Ia (0.5 g.) and hydrazine hydrate (4 ml.) in glacial acetic acid (10 ml.). Recrystallization from alcohol gave lemon-yellow needles (0.32 g.) m.p. 182°.

*Anal.* Calcd. for $C_{16}H_{12}N_4O_4$: C, 59.26; H, 3.70. Found: C, 58.68; H, 3.64.

**Acetyl derivative,** m.p. 137°. *Anal.* Calcd. for $C_{18}H_{14}N_4O_5$: N, 15.30. Found: N, 15.02.

**Benzoyl derivative,** m.p. 150°. *Anal.* Calcd. for $C_{23}H_{16}N_4O_5$: N, 13.08. Found: N, 12.75.

**Hydrochloride,** m.p. 115°.

**Phenylhydrazone of Ia and 3-methyl-1,5-diphenyl-4-(2,4-dinitrophenyl)pyrazole** was prepared from Ia (0.5 g.) and phenylhydrazine (0.2 g.) in alcohol (10 ml.). Recrystallization from alcohol gave 0.34 g. of phenylhydrazone, yellow crystals, m.p. 185°.

*Anal.* Calcd. for $C_{22}H_{18}N_4O_5$: N, 13.40. Found: N, 13.15.

On heating with glacial acetic acid for 2 hr. it gave 0.21 g. of the pyrazole derivative, pale yellow needles, m.p. 194°.

*Anal.* Calcd. for $C_{22}H_{16}N_4O_4$: C, 66.00; H, 4.00. Found: C, 65.47; H, 3.93.

The same pyrazole was obtained by heating Ia with phenylhydrazine in glacial acetic acid.

***p*-Tolylhydrazone of Ia.**—Recrystallization from dilute alcohol gave light brown needles, m.p. 175°.

*Anal.* Calcd. for $C_{23}H_{20}N_4O_5$: N, 12.94. Found: N, 12.58.

**3-Methyl-5-phenyl-4-(2,4-dinitrophenyl)-1-(*p*-tolyl)-pyrazole** was formed as pale yellow needles from glacial acetic acid, m.p. 202° (yield 56%).

*Anal.* Calcd. for $C_{23}H_{18}N_4O_4$: C, 66.66; H, 4.34. Found: C, 66.37; H, 4.46.

**3-Methyl-5-phenyl-4-(2,4-dinitrophenyl)pyrazole-1-amide** was prepared from Ia (0.5 g.), semicarbazide hydrochloride (0.5 g.), and anhydrous sodium acetate (0.5 g.) in alcohol (10 ml.). Recrystallization from alcohol gave pale yellow needles (0.41 g.), m.p. 176°.

*Anal.* Calcd. for $C_{17}H_{13}N_5O_5$: N, 19.07. Found: N, 19.30.

**3-Methyl-5-phenyl-4-(2,4-dinitrophenyl)isoxazole** was prepared from Ia (0.5 g.) and hydroxylamine hydrochloride (0.5 g.) in alcohol. Recrystallization from alcohol gave lemon yellow needles (0.39 g.), m.p. 160°.

*Anal.* Calcd. for $C_{16}H_{11}N_3O_5$: N, 12.92. Found: N, 13.0.

**2,4-Dinitrophenyldibenzoylmethane (Ib).**—To a suspension of potassium *tert*-butoxide prepared from pulverized potassium (0.39 g.) and *tert*-butyl alcohol (10 ml.) in dry ether, dibenzoylmethane (3.3 g.) dissolved in ether (30 ml.) was added and the mixture warmed for a few minutes and left overnight. To the fine suspension of potassio derivative of dibenzoylmethane so obtained, 1-bromo-2,4-dinitrobenzene (2.4 g.) dissolved in ether was gradually added and the mixture warmed on a water bath for 3 hr. The ethereal suspension was acidified with acetic acid and allowed to stand overnight. A pale yellow crystalline product separated which after washing with ether, dilute alcohol and recrystallizing from acetic acid gave 2,4-dinitrophenyldibenzoylmethane, yellow cubes, m.p. 116°.

*Anal.* Calcd. for $C_{21}H_{14}N_2O_6$: C, 64.61; H, 3.59; N, 7.18. Found: C, 64.49; H, 3.55; N, 7.10.

The mother liquor and the ether washings were collected and shaken with 5% dilute caustic soda solution (500 ml.). The combined aqueous extracts were acidified with dilute hydrochloric acid; a pale yellow, milky solution was formed which after standing for some time deposited a yellowish semisolid mass. This on purification with activated charcoal in acetic acid gave more of the above product. (Total yield 52%.)

**3,5-Diphenyl-4-(2,4-dinitrophenyl)pyrazole (III)** was prepared from Ib (0.5 g.) and hydrazine hydrate (4 ml.) in glacial acetic acid. Recrystallization from alcohol gave lemon yellow needles (0.29 g.), m.p. 142°.

*Anal.* Calcd. for $C_{21}H_{14}N_4O_4$: C, 65.28; H, 3.62. Found: C, 64.83; H, 3.59.

**1,3,5-Triphenyl-4-(2,4-dinitrophenyl)pyrazole (IV)** was prepared from Ib (0.5 g.) and phenylhydrazine (0.3 g.) in glacial acetic acid. Recrystallization from alcohol gave lemon yellow needles (0.25 g.), m.p. 136°.

*Anal.* Calcd. for $C_{27}H_{18}N_4O_4$: C, 70.13; H, 3.89. Found: C, 69.68; H, 3.82.

**3,5-Diphenyl-4-(2,4-dinitrophenyl)-1-(*p*-tolyl)pyrazole.**—Recrystallization from alcohol gave yellow needles, m.p. 144° (yield 32%).

*Anal.* Calcd. for $C_{28}H_{20}N_4O_4$: C, 70.58; H, 4.20. Found: C, 70.01; H, 4.12.

**3,5-Diphenyl-4-(2,4-dinitrophenyl)pyrazole-1-amide (V)** was prepared from Ib (0.5 g.) and semicarbazide hydrochloride (0.5 g.) in alcohol. Recrystallization from alcohol gave pale yellow needles (0.36 g.), m.p. 154°.

*Anal.* Calcd. for $C_{22}H_{15}N_5O_5$: N, 16.31. Found: N, 16.28.

**3,5-Diphenyl-4-(2,4-dinitrophenyl)isoxazole (VI)** was prepared from Ib (0.5 g.) and hydroxylamine hydrochloride (0.5 g.) in alcohol. Recrystallization from alcohol gave colorless needles (0.36 g.), m.p. 139°.

*Anal.* Calcd. for $C_{21}H_{13}N_3O_5$: N, 10.85. Found: N, 10.78.

**Ethyl (2,4-dinitrophenyl)benzoylacetate (Ic).**—To a suspension of pulverized sodium (0.23 g.) in dry ether (30 ml.) was added ethyl benzoylacetate (2.8 g.) dissolved in ether (20 ml.) and the mixture warmed for 1 hr. and left overnight. To the fine suspension of the sodio derivative of ethyl benzoylacetate so obtained, an ethereal solution of 1-bromo-2,4-dinitrobenzene (2.4 g.) was added and the contents refluxed for 3 hr. The product was acidified with acetic acid and allowed to stand overnight. Orange-yellow crystals separated which after washing with ether and recrystallizing from a mixture of alcohol and acetic acid (3:1) gave ethyl (2,4-dinitrophenyl)benzoylacetate, lemon-yellow needles, m.p. 94°.

*Anal.* Calcd. for $C_{17}H_{14}N_2O_7$: C, 56.98; H, 3.91; N, 7.82. Found: C, 56.72; H, 3.86; N, 7.78.

The mother liquor and the ethereal washings were repeatedly treated with 5% dilute caustic soda solution (200 ml.). The alkaline extract on acidification with dilute hydrochloric acid gave a semisolid mass which on purification as before gave more of compound Ic. (Total yield 60%.)

**2,4-Dinitrophenylbenzoylacetic Acid (VII).**—A solution of compound Ic (2.0 g.) in cold concd. sulfuric acid (30 ml.) was allowed to stand for 8 hr. The contents were poured

on ice; a dirty yellow product separated which was dissolved in 5% sodium bicarbonate solution and filtered. The filtrate on acidification with ice-cold hydrochloric acid gave a yellow precipitate. This was dissolved in excess of water and then just acidified with concd. sulfuric acid. On allowing it to stand 0.99 g. of 2,4-dinitrophenylbenzoylacetic acid, yellow needles, m.p. 106°, was obtained.

*Anal.* Calcd. for $C_{15}H_{10}N_2O_7$: C, 54.54; H, 3.03. Found: C, 54.19; H, 2.98.

**Ethyl (2-Chloro-4,6-dinitrophenyl)benzoylacetate.**—To a suspension of sodio derivative of ethyl benzoylacetate (2.8 g.) in ether was added 1,2-dichloro-4,6-dinitrobenzene (2.37 g.). By adopting a procedure as for compound Ic, a dirty yellow solid was obtained which on recrystallization from acetic acid gave ethyl (2-chloro-4,6-dinitrophenyl)benzoylacetate, lemon-yellow needles, m.p. 128°.

*Anal.* Calcd. for $C_{17}H_{13}N_2O_7Cl$: Cl, 9.04. Found: Cl, 8.87.

**2-(Chloro-4,6-dinitrophenyl)dibenzoylmethane.**—To a suspension of potassio derivative of dibenzoylmethane in ether prepared from 3.3 g. of the latter was added 1,2-dichloro-4,6-dinitrobenzene (2.37 g.). By adopting a procedure as for compound Ib, a pale yellow solid was obtained which on recrystallization from acetic acid gave 2-chloro-4,6-dinitrophenyldibenzoylmethane, pale yellow needles, m.p. 179°. (Total yield 53.1%.)

*Anal.* Calcd. for $C_{21}H_{13}N_2O_6Cl$: Cl, 8.36. Found: Cl, 8.15.

**2-Chloro-4,6-dinitrophenylbenzoylmethane. Method A.**—A solution of 2-chloro-4,6-dinitrophenylbenzoylacetylmethane in concd. sulfuric acid was heated on a water bath for 1 hr. On cooling and dilution, a dirty white precipitate was obtained which on purification with activated charcoal and recrystallization from dilute acetic acid gave 81% of 2-chloro-4,6-dinitrophenylbenzoylmethane, colorless needles, m.p. 104°.

*Anal.* Calcd. for $C_{14}H_9N_2O_5Cl$: Cl, 11.07. Found: Cl, 10.89.

**Method B.** It was prepared by using 2-chloro-4,6-dinitrophenyldibenzoylmethane and concd. sulfuric acid as in method A above (yield 85%).

**Method C.**—It was prepared by using ethyl (2-chloro-4,6-dinitrophenyl)benzoylacetate and concd. sulfuric acid as in method A above (yield 76%). The mixed melting points of compounds prepared by methods A, B, C remained undepressed.

## An Improved Synthesis of Dicarbonates[1]: Di-*t*-butyl Dicarbonate

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Since 1939 a number of alkyl and mixed alkyl aryl dicarbonates (pyrocarbonates) have been prepared and characterized. These diesters were first synthesized in a solvent by the reaction of alkyl chloroformates with potassium hydroxide in the presence of the alkaloid, emetine,[2,3] and more recently by the anhydrous reaction of metal alkyl carbonates with alkyl chloroformates.[4-6]

A convenient, one-step synthesis of dicarbonates by the direct reaction of phosgene with the sodium or potassium salt of the desired carbonic acid ester was developed and is illustrated as follows:

$$\mathrm{ROCO}\left\{\begin{matrix}\mathrm{Na}\\ \mathrm{K}\end{matrix}\right. + \mathrm{COCl_2} \longrightarrow \mathrm{ROCOCOR} + \mathrm{CO_2}\uparrow + \left\{\begin{matrix}\mathrm{Na}\\ \mathrm{K}\end{matrix}\right\}\mathrm{Cl}$$

This process eliminates the necessity of preparing and isolating the intermediate chloroformates, some of which are too unstable to isolate and store readily. Generally, over-all yields of the dicarbonates prepared thus far have been improved over those described in the literature, with little or no formation of by-product dialkyl carbonate as a contaminant.[2]

It is of interest, also, to report the preparation and isolation in low yield (5%) of di-*t*-butyl dicarbonate by this direct phosgenation technique. An unsuccessful attempt to synthesize and isolate this ester by a different method has been reported[6] previously. Although the yield of di-*t*-butyl dicarbonate was low, it was felt that improvement could be made by a shorter work-up time and a more carefully controlled reaction temperature. This ester was found to decompose slowly at room temperature and rapidly above 100°. The stability of di-*t*-butyl dicarbonate may be compared to that of *t*-butyl chloroformate, found to be thermally unstable above 10°. In contrast, di-*t*-butyl carbonate was reported to be a very stable solid which sublimes readily.[7]

### Experimental

**Diisopropyl Dicarbonate.**—The following synthesis of diisopropyl dicarbonate is typical. Initially a solution of sodium isopropoxide was prepared by treating 55 g. (2.4 moles) of sodium with 1085 g. (18.0 moles) of isopropyl alcohol at reflux. Carbonation of this solution for 4 hr. at 87–88° and subsequently for 2 hr. at room temperature gave a thick paste-like gel. Following filtration, vacuum drying gave 242 g. of sodium isopropyl carbonate with above 90% purity as determined by acid-base titration and measurement of carbon dioxide liberated by acid hydrolysis. Subsequently, a solution of 25.8 g. (0.26 mole) of phosgene in 200 ml. of cooled dry toluene was added dropwise to a stirred slurry of 63 g. (0.5 mole) of sodium isopropyl carbonate at 0–5° over a 4-hr. period.[8] Evidence of reaction

(1) The term "dicarbonate" is apparently preferred to "pyrocarbonate" when referring to these diesters, according to the Committee on Publications of the IUPAC [*J. Am. Chem. Soc.*, **82**, 5541 (1960)].

(2) T. Boehm and D. Mehta, *Ber.*, **71B**, 1797–1802 (1938).

(3) L. N. Parfentev and A. A. Shamshurin, *Sbornik Rabot Khim.*, **15**, 67–74 (1939); *Chem. Abstr.*, **35**, 4351 (1941).

(4) E. F. Degering, G. L. Jenkins, and B. E. Sanders, *J. Am. Pharm. Assoc.*, **39**, 624–627 (1950).

(5) V. I. Kovalenko, *J. Gen. Chem. U.S.S.R. Eng. Trans.*, **22**, 1587–1590 (1952); *J. Gen. Chem. U.S.S.R. Eng. Trans.*, **24**, 1039–1040 (1954); *Chem. Abstr.*, **48**, 4442a (1954); *Chem. Abstr.*, **50**, 6296g (1956).

(6) L. A. Carpino, *J. Am. Chem. Soc.*, **82**, 2725–2727 (1960).

(7) A. R. Choppin and J. W. Rodgers, *J. Am. Chem. Soc.*, **70**, 2967 (1948).

(8) An acetone–Dry Ice condenser was used to contain the phosgene within the reaction mixture.