The total yield of 2-bromo-2'-carboxybiphenyl was 3.4 g. (38%). The analytical sample melted at 144.5-146°.

Anal. Calcd. for  $C_{1_3}H_9O_2Br$ : C, 56.33; H, 3.27; neut. equiv., 277. Found: C, 56.44, 56.32; H, 3.33, 3.32; neut. equiv., 277.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF MEERUT COLLEGE, INDIA]

## Behavior of Halogenated Nitrobenzenes with $\beta$ -Diketones. Part I. 1-Chloro-2,4-dinitrobenzene and Acetylacetone

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2,4-Dinitrophenyldiacetylmethane (I) and bis-(2,4-dinitrophenyl)-diacetylmethane (II) have been obtained by the interaction of 1-chloro-2,4-dinitrobenzene and acetylacetone and characterized. Their behavior with hydrazines, semicarbazide, hydroxylamine, etc., has been studied and cyclic compounds such as pyrazole, indole and isoxazole derivatives prepared. 6-Nitroanthranil has been isolated by the action of concentrated sulfuric acid on 2,4-dinitrophenylacetone and identified.

1-Chloro-2,4-dinitrobenzene easily reacts with the monosodium derivative of acetylacetone to form 2,4-dinitrophenyldiacetylmethane (I).<sup>1</sup> The sodium derivative of the latter reacts with 1chloro-2,4-dinitrobenzene to form bis-(2,4-dinitrophenyl)-diacetylmethane (II) but fails to form a methyl derivative with methyl iodide. In the disubstituted compound II, the two dinitrophenyl groups appear to be linked to the same carbon atom, as acetylacetone yields the same dinitrophenyldinitrotolyl derivative IV whether it reacts first with chlorodinitrobenzene and then with chlorodinitrotoluene or in reverse sequence.

$$\begin{array}{c} R'\\ CH_{3}COCHCOCH_{3} \longleftarrow CH_{3}COCCOCH_{3} \longleftarrow \\ R & I \\ R & I \\ R & I \\ R' & IV \\ CH_{3}COCHCOCH_{3} \\ R' & III \\ R' & III \\ R' & III \\ R' & 2,4-dinitrophenyl \\ R' & 2,4-dinitro-5-tolyl \end{array}$$

The bis-(2,4-dinitrophenyl)-diacetylmethane (II) resists hydrolysis by sulfuric acid, dilute or concentrated. This appears to be due to steric factors and is in agreement with the observation of Zaheer and Sidhu<sup>2</sup> that diethyl 2,4-dinitrophenyl-n-propylmalonate is not hydrolyzed due to the large size of the substituents. Its II ketonic groups, compared to those of the dinitrophenyl derivative, are very unreactive and do not condense with the usual reagents for the carbonyl group. The dinitrophenyldiacetylmethane (I), on the other hand, readily reacts with hydrazine hydrate, phenylhydrazine and semicarbazide hydrochloride. In alcoholic solution hydrazine hydrate gives a hydrazone as well as a pyrazole while other hydrazines give only the former; in acetic acid solution, however, only the pyrazole derivatives are obtained. With hydroxylamine hydrochloride in alcoholic or acetic acid solution the corresponding isoxazoles are formed. The structure of these isoxazoles and pyrazoles follows from the analogous derivatives of acetylacetone.<sup>3,4</sup>

Benzoyl chloride forms a derivative V with the sodium derivative of I in ether. The yield is poor by the Schotten and Baumann method and no benzoylation takes place with benzoyl chloride in pyridine solution. The benzoyl derivative is stable toward dilute or concentrated sulfuric acid and toward aniline, while with hot 2% alcoholic caustic potash it is hydrolyzed back to I and benzoic acid. This indicates that the benzoyl group is most likely linked to the oxygen atom rather than to the carbon atom of the methylene group. This view is also supported by the fact that identical products are not obtained by acetylation of chlorodinitrophenylbenzoylacetylmethane (VI) and benzoylation of chlorodinitrophenyldiacetylmethane (VII).

When heated with moderately concentrated sulfuric acid or aniline or even by passing hydrochloric acid gas through warm alcoholic solution, compound I is hydrolyzed to form a product which is found to be identical with 2,4-dinitrophenylacetone (VIII) obtained from ethyl (2,4-dinitrophenyl)-acetoacetate with dilute sulfuric acid.<sup>5</sup> This compound (VIII) readily forms a phenylhydrazone which when heated with fuming hydrochloric acid in absolute alcohol is cyclized to form 2-methyl-3-(2,4-di-nitrophenyl)-indole (IX). The indole derivative fails to form the alkyl and acyl derivatives and is insoluble in hydrochloric acid, showing diminution of basic character due to presence of dinitrophenyl group in position 3.

$$\begin{array}{c} \text{RCH}_{2}\text{COCH}_{3} \longrightarrow \text{RCH}_{2}\text{CCH}_{3} \longrightarrow & \begin{array}{c} \text{NNHC}_{6}\text{H}_{3} \\ & \\ \text{WIII} \end{array} \xrightarrow{} & \begin{array}{c} \text{RCH}_{2}\text{CCH}_{3} \\ & \\ \text{H} & \text{IX} \end{array} \\ & \\ \text{R} = 2,4\text{-dinitrophenyl} \end{array}$$

When heated with concentrated sulfuric acid at about 105–110° for two hours, compound I and also VIII yield another product X, m.p. 133°. This reduces Tollens reagent and potassium permangan-

(3) T. Posner, ibid., 34, 3980 (1901).

(4) V. Knorr, *ibid.*, **20**, 1104 (1887).
(5) W. Borsche, *ibid.*, **42**, 607 (1909).

<sup>(1)</sup> F. Muttelet, Bull. soc. chim., 17, III, 808 (1897).

<sup>(2)</sup> S. H. Zaheer and G. S. Sidhu, J. Indian. Chem. Soc., 24, 134 (1947); E. Hjelt, Ber., 29, 110, 1864 (1896).

ate solution and forms with hydrazine hydrate in alcoholic solution a salt XI from which with hydrochloric acid it is obtained back. Sodium carbonate solution hydrolyzes it (X) on heating to 2-amino-4-nitrobenzoic acid (XII), while potassium dichromate and concentrated sulfuric acid oxidize it to 2,2'-dicarboxy-5,5'-dinitroazeoxybenzene (XIII).

Compound X thus behaves in the same way as anthranil<sup>6,7</sup> and may therefore be 6-nitroanthranil. A simple mechanism for its formation is



## Experimental

3-(2,4-Dinitrophenyl)-pentandione-2,4 (2,4-Dinitrophenyldiacetylmethane) (I).—The monosodium derivative of acetylacetone (2 g.) in absolute alcohol (10 ml.) and 1chloro-2,4-dinitrobenzene (4 g.) were refluxed for one hour and filtered. The filtrate on standing deposited crystals which on recrystallization from acetic acid gave 3 g. of 2,4dinitrophenyldiacetylmethane, colorless needles, m.p. 121°.

Anal. Caled. for  $C_{11}H_{11}N_2O_6;\ C,\ 49.43;\ H,\ 4.12;\ N,\ 10.48.$  Found: C, 49.50; H, 4.16; N, 10.52.

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

Bis-(2,4-dinitrophenyl)-diacetylmethane (II).—The monosodium derivative of I (1 mole) in absolute alcohol (20 ml.) and 1-chloro-2,4-dinitrobenzene (1 mole) were refluxed for four hours. The reaction mixture was allowed to stand for three days; needle-shaped crystals separated, and were washed with dilute caustic soda and recrystallized from acetic acid to give 24% of bis-(2,4-dinitrophenyl)-diacetylmethane, m.p. 176°

Anal. Calcd. for  $C_{17}H_{12}N_4O_{10}$ : C, 47.2; H, 2.77; N, 13.0. Found: C, 46.45; H, 2.59; N, 13.4.

3-Methyl-(4,6-dinitrophenyl)-diacetylmethane (III).-This compound was prepared by the procedure given for compound I using 3-methyl-4,6-dinitrochlorobenzene (4.3 Recrystallization from alcohol gave 2.8 g. of 3-methyl-(4,6-dinitrophenyl)-diacetylmethane, pale yellow needles, m.p. 98°.

Anal. Calcd. for C12H9N2O6: N, 10.1. Found: N, 10.32.

2,4-Dinitrophenyl-(3'-methyl-4',6'-dinitrophenyl)-diacetylmethane (IV). A.-The monosodium derivative of I (1 mole) in absolute alcohol (20 ml.) and 3-methyl-4,6-dinitrochlorobenzene (1 mole) were refluxed for four hours. The reaction mixture deposited needle-shaped crystals which on recrystallization from acetic acid gave 20.5% of 2,4-dinitro-phenyl-(3' - methyl-4',6'-dinitrophenyl) - diacetylmethane, m.p. 185

Anal. Calcd. for  $C_{18}H_{14}N_4O_{10}$ : C, 48.43; H, 3.14. Found: C, 48.05; H, 2.98.

B.--This compound was prepared by the procedure given for A from the monosodium derivative of III and 1-chloro-

(6) O. Buhlmann and A. Einhorn, Ber., 34, 3788 (1901).

(7) G. Heller, J. prakt. Chem., [2] 77, 164 (1908).

2,4-dinitrobenzene. Recrystallization from acetic acid gave 22.1% of B, m.p.  $185^\circ$ . Its mixed melting point with A was undepressed.

Hydrazone of I and 3,5-Dimethyl-4-(2,4-dinitrophenyl)**pyrazole.**—A solution of I (0.5 g.) in alcohol (10 ml.) and hydrazine hydrate (3 ml.) was heated for an hour. On cooling, a yellow product separated which was treated with concentrated hydrochloric acid. The insoluble portion on recrystallization from alcohol gave 0.09 g. of hydrazone, pale yellow needles, m.p. 152°.

Anal. Calcd. for C11H12N4O5: N, 20.02. Found: N, 19.80.

The acid-soluble portion was precipitated with caustic soda and recrystallized from alcohol to give 0.25 g. of 3,5dimethyl-(2,4-dinitrophenyl)-pyrazole, yellow needles, m.p. 179°.

Anal. Caled. for C11H10N4O4: N, 21.37. Found: N, 21.05.

Acetyl derivative, m.p. 128°. Anal. Caled. for C<sub>18</sub>H<sub>12</sub>-N<sub>4</sub>O<sub>5</sub>: N, 18.42. Found: N, 18.26.

 Habitary I derivative, m. p. 145°. Anal. Calcd. for C<sub>18</sub>-H<sub>14</sub>N<sub>4</sub>O<sub>8</sub>: N, 15.30. Found: N, 15.20.
 Picrate, m.p. 199°; hydrochloride, m.p. 148°. The pyrazole derivative was also obtained by heating I with hydrazine hydrate in glacial acetic acid. It gave a silver rolt with any model of the provided silver relative to the salt with ammoniacal silver nitrate solution from which the pyrazole was recovered by treatment with concentrated hydrochloric acid and ammonium hydroxide. Phenylhydrazone of I and 3,5-Dimethyl-4-(2,4-dinitro-

phenyl)-1-phenylpyrazole.—A solution of I (0.5 g.) in alco-hol (10 ml.) and phenylhydrazine (0.2 g.) was heated for an hour and cooled. A solid separated and recrystallized from alcohol to give 0.29 g. of phenylhydrazone, red needles, m.p. 118°

Anal. Calcd. for  $C_{17}H_{16}N_4O_5$ : N, 15.93. Found: N, 16.1. On heating with glacial acetic acid for an hour it gave 0.15 g. of 3,5-dimethyl-4-(2,4-dinitrophenyl)-1-phenylpyrazole, yellow needles, m.p. 120°.

Anal. Caled. for  $C_{17}H_{14}N_4O_4$ : C, 60.35; H, 4.14; N, 16.57. Found: C, 59.83; H, 4.36; N, 16.90.

The same phenylpyrazole was also obtained by heating I with phenylhydrazine in glacial acetic acid.

p-Tolylhydrazone of I and 3,5-Dimethyl-4-(2,4-dinitro-phenyl)-1-tolylpyrazole.—This compound was prepared by the procedure given for the phenyl analog using p-tolylhy-drazine. Recrystallization from alcohol gave 0.3 g. of p-tolylhydrazone, brown needles, m.p. 126°.

Anal. Calcd. for  $C_{18}H_{18}N_4O_5$ : N, 15.14. Found: N, 15.32.

On heating with glacial acetic acid it gave 0.18 g. of 3,5dimethyl-4-(2,4-dinitrophenyl)-1-tolylpyrazole, golden yellow needles, m.p. 157°

Anal. Caled. for C18H16N4O4: N, 15.90. Found: N, 16.11.

**3,5-Dimethyl-4-(2,4-dinitrophenyl)-pyrazole-2-amide.**—A solution of I (0.5 g.) in alcohol (10 ml.), semicarbazide hydrochloride (0.5 g.) and anhydrous sodium acetate (0.5 g.)was refluxed for two hours. The crude product was precipitated by adding water and recrystallized from alcohol to give 0.4 g. of 3,5-dimethyl-4-(2,4-dinitrophenyl)-pyrazole-2-amide, colorless needles, m.p. 175°

Anal. Caled. for C12H11N5O5: N, 22.95. Found: N, 23.19.

It formed a silver salt with ammoniacal silver nitrate solution which with concentrated hydrochloric acid and ammonium hydroxide gave 3,5-dimethyl-4-(2,4-dinitrophenyl)-pyrazole, m.p. 179°. 3,5-Dimethyl-4-(2,4-dinitrophenyl)-isoxazole.—This com-

pound was prepared by the procedure given for the pyra-zoleamide using a solution of I (0.5 g.) in alcohol and hydroxylamine hydrochloride (0.5 g.). Recrystallization from alcohol gave 0.4 g. of 3,5-dimethyl-4-(2,4-dinitrophen-yl)-isoxazole, colorless cubes, m.p. 98°.

Anal. Caled. for C11H9N3O5: N, 15.97. Found: N, 16.0.

**3**-(2,4-Dinitrophenyl)-4-benzoyloxy- $\Delta^3$ -penten-2-one (V). —A suspension of sodium salt of I (0.5 g.) in ether was shaken and gently warmed with benzoyl chloride (0.3 g.). A product separated which after being washed with ether, boiling alcohol and very dilute caustic soda was recrystallized from acetic acid to give 0.55 g, of 3-(2,4-dinitrophenyl)-4-benzoyloxy- $\Delta^3$ -penten-2-one, cubes, m.p. 173°.

Anal. Caled. for  $C_{18}H_{14}N_2O_7$ : C, 58.38; H, 3.78; N, 7.57. Found: C, 58.29; H, 3.74; N, 7.62.

(6-Chloro-2,4-dinitrophenyl)-benzoylacetylmethane (VI). -A suspension of the monosodium derivative of benzoylacetone (1.62 g.) in absolute alcohol (10 ml.) and 1,6-dichloro-2,4-dinitrobenzene (2.37 g.) was refluxed for two hours and steam distilled. The residue, a semi-solid mass, gave on recrystallization from acetic acid 2.35 g. of (6-chloro-2,4dinitrophenyl)-benzoylacetylmethane, pale yellow needles, m.p. 134°

Anal. Calcd. for C<sub>16</sub>H<sub>11</sub>ClN<sub>2</sub>O<sub>6</sub>: Cl, 9.77. Found: Cl, 9.69.

It was soluble in dilute caustic soda and gave violet coloration with ferric chloride solution.

Acetyl Derivative of VI.-Compound VI (0.54 g.), acetic anhydride (2 ml.) and a drop of concentrated sulfuric acid were heated on a water-bath for three hours. The product on recrystallization from alcohol gave 0.3 g. of the acetyl derivative, m.p. 200°

Anal. Caled. for C<sub>18</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>7</sub>: C, 53.46; H, 3.22; Cl, 8.78. Found: C, 53.54; H, 3.26; Cl, 8.69.

(6-Chloro-2,4-dinitrophenyl)-diacetylmethane (VII). This compound was prepared by the procedure given for compound I, using acetylacetone (1.0 g.) and 1,6-dichloro-2,4-dinitrobenzene (2.37 g.). Recrystallization from alco-hol gave 1.85 g. of (6-chloro-2,4-dinitrophenyl)-diacetylmethane, colorless needles, m.p. 108°.

Anal. Caled. for C11H9ClN2O6: Cl, 11.81. Found: Cl, 11.75.

The benzoyl derivative of VII was prepared by the procedure given for compound V. Recrystallization from acetic acid gave 65% of the benzoyl derivative of VII, m.p. 180°.

Anal. Calcd. for C<sub>18</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>7</sub>: C, 53.46; H, 3.22; Cl, 8.78. Found: C, 53.40; H, 3.20; Cl, 8.71.

3-(2,4-Dinitrophenyl)-4-acetyloxy- $\Delta^3$ -penten-2-one was prepared by the procedure given for the acetyl derivative of VI. Recrystallization from alcohol gave 53% of  $3-(2,4-dinitrophenyl)-4-acetyloxy-<math>\Delta^3$ -penten-2-one, colorless plates, m.p. 167°

Anal. Calcd. for  $C_{13}H_{12}N_2O_7$ : C, 50.65; H, 3.87. Found: C, 50.97; H, 3.92.

2,4-Dinitrophenvlacetone (VIII).-A solution of I in moderately concentrated sulfuric acid was heated on a waterbath for half an hour. On dilution and cooling a colorless precipitate was obtained which on recrystallization from acetic acid gave 85% of 2,4-dinitrophenylacetone, m.p. 75°. Anal. Caled. for C9H8N2O5: N, 12.5. Found: N,

12.59. Phenylhydrazone, red needles, m.p. 124°; 2,4-dinitro-phenylhydrazone, golden yellow, m.p. 199°. 2-Methyl-3-(2,4-dinitrophenyl)-indole (IX).—To the

phenylhydrazone of VIII (1.0 g.) in boiling absolute alcohol

(20 ml.) was added fuming hydrochloric acid (10 ml.) in small amounts and heated on a water-bath for four hours. On cooling, a product separated which on recrystallization from alcohol gave 45% of 2-methyl-3-(2,4-dinitrophenyl)-indole, red plates, m.p. 202°.

Anal. Caled. for C15H11N3O4: N, 14.14. Found: N, 14.00.

6-Nitroanthranil (X).—Compound VIII (2.3 g.) and concentrated sulfurie acid (20 ml.) were heated at  $105-110^{\circ}$  for three hours. The contents were cooled and poured on ice. A dirty white precipitate was obtained which on purification with activated charcoal and recrystallization from alcohol gave 50% of 6-nitroanthranil, colorless needles, m.p.  $133^{\circ}$ .

Anal. Caled. for C7H4N2O3: C, 51.22; H, 2.44; N, 17.07; mol. wt., 164. Found: C, 50.74; H, 2.50; N, 16.5; mol wt. (Rast), 162.

Hydrazine Salt of X (XI).-A solution of X (0.5 g.) in alcohol (10 ml.) and hydrazine hydrate (3 ml.) was heated on a water-bath for ten minutes. On cooling a yellow product separated which on recrystallization from alcohol gave 0.42 g. of the hydrazine salt of compound X, yellow needles, m.p. 175°.

Anal. Caled. for  $C_7H_8N_4O_8$ : C, 42.86; H, 4.07; N, 28.57. Found: C, 42.62; H, 4.11; N, 28.20.

2-Amino-4-nitrobenzoic Acid (XII).-Compound X (3.2 g.), sodium carbonate (10 g.) and water (30 ml.) were re-fluxed for half an hour and filtered. The filtrate on acidification gave a yellow precipitate which on purification with activated charcoal and recrystallization from acetic acid gave 60% of 2-amino-4-nitrobenzoic acid, orange plates, m.p. 264°.

Anal. Caled. for  $C_7H_8N_2O_4$ : C, 46.15; H, 3.29; N, 15.38; mol. wt., 182. Found: C, 46.24; H, 3.32; N, 15.46; mol. wt. (silver salt method), 184.

Methyl ester, m.p. 155°; ethyl ester, m.p. 94°; N-acetyl, m.p. 217°. Its mixed melting point with an authentic sample of the acid was undepressed.

2,2'-Dicarboxy-5,5'-dinitroazeoxybenzene (XIII).---To a solution of X (0.5 g.) in concentrated sulfuric acid (30 ml.) was added a saturated solution of potassium dichromate (20 ml.) and warmed. The dirty yellow precipitate formed was treated with dilute caustic soda and filtered. From the filtrate on acidification a pale yellow product separated which on recrystallization from acetic acid gave 0.39 g. of 2,2'-dicarboxy-5,5'-dinitroazeoxybenzene, lemon yellow cubes, m.p. 285°.

Anal. Caled. for  $C_{14}H_8N_4O_9$ : C, 44.68; H, 2.13; N, 14.89; mol. wt., 376. Found: C, 44.57; H, 2.14; N, 14.75; mol. wt. (Rast), 368.

Methyl ester, m.p. 182°. Anal. Calcd. for  $C_{16}H_{12}N_4O_9$ : C, 47.52; H, 2.97. Found: C, 47.32; H, 2.91. Ethyl ester, m.p. 152°. Anal. Calcd. for  $C_{18}H_{16}N_4O_9$ : C, 50.0; H, 3.70. Found: C, 49.71; H, 3.63.

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