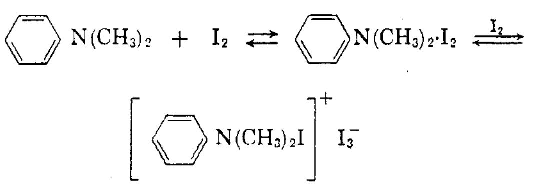
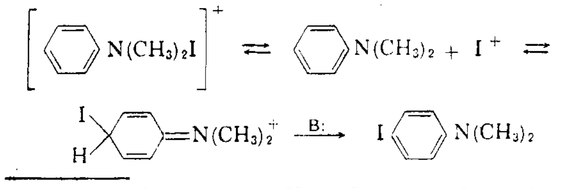
It is seen that the spectrum of the precipitate in isopropyl alcohol indicates the presence of triiodide as well as dimethylaniline. It is not likely, however, that the precipitate consists merely of dimethylaniline hydroiodide, the result of ring substitution. Nagakura[5] observed the formation of a similar ionic precipitate in the interaction of triethylamine and iodine in heptane where substitution seems improbable. Glusker and Miller[6] characterized the water-soluble precipitate formed when iodine is dissolved in $\gamma$-picoline by X-ray radial distribution methods. They concluded that no covalent bonds existed and that the structure was $Pc_2I^+I^-$. On the other hand, these authors also observed a precipitate which was water insoluble but soluble in organic solvents when water was added to a fresh solution of iodine in $\gamma$- picoline. This precipitate apparently had the structure of the charge transfer complex, $Pc\cdot I_2$. The precipitate observed by the present authors which was insoluble in cyclohexane but soluble in isopropyl alcohol may very well be an ionic species analogous to the structure assigned the water-soluble precipitate of Glusker and Miller. Moreover, when the precipitate observed in the present study was shaken with cyclohexane, molecular iodine was liberated. The spectrum of the extract when corrected for the absorbance of iodine had a maximum at 255–256 m$\mu$ and was apparently that of the dimethylaniline·iodine charge transfer complex. When the iodine was removed from the solution by means of sodium hydrosulfite, the spectrum was identical with that of pure dimethylaniline in cyclohexane. There was apparently no ring substitution at this point. This behavior does not seem likely if the precipitate observed during the course of the reaction were merely dimethylaniline hydroiodide. However, these observations might reasonably correspond to the following type of process for the formation of the precipitate:



Ring substitution might then involve the ionic intermediate in a direct reaction with uncombined dimethylaniline or in a process such as the following:



## EXPERIMENTAL

*Reagents.* *N*,*N*-Dimethylaniline, reagent grade, was obtained from Fisher Scientific Co., dried over potassium hydroxide pellets for 1 week, then distilled at reduced pressure under Argon.

Cyclohexane, Shell Oil Co., was purified by passage through a column of Davison activated silica gel, then distilled through a meter-long fractionating column packed with glass helices. The resulting solvent showed an absorbance of less than 0.1 when compared to water in the reference beam at 235 m$\mu$ and measured in 10-mm. silica cells.

Iodine, analytical reagent, resublimed, was used directly as obtained from Mallinckrodt.

*p*-Iodo-*N*,*N*-dimethylaniline was prepared by a synthesis similar to the one reported by Brewster[7] for the preparation of *p*-iodoaniline. A mixture of 24.2 g. (0.2 mole) of dimethylaniline, of 25 g. (0.3 mole) of sodium bicarbonate and 167 ml. of water were cooled to 12–15°. With mechanical stirring, 42.4 g. (0.167 mole) of powdered iodine was added in 20 min. The mixture was stirred for an additional 20 min. allowing the mixture to warm to room temperature. One hundred milliliters of water was added to the mixture, the solid was filtered and washed with 500 ml. of water. The crude material was dried at 45°, at 300 mm. The dried crude product was crystallized from petroleum ether (b.p. 55–75°) then recrystallized two more times. The melting point of the crystals was 80.2°.

*Anal.* Calcd. for $C_8H_{10}IN$: C, 38.9; H, 4.08; I, 51.4%. Found: C, 39.4; H, 4.32; I, 51.9.

*Identification of p-iodo-N,N-dimethylaniline from the iodination study.* The reaction mixture was treated with charcoal to remove the iodine and the solution was then concentrated until crystallization began. The ultraviolet and infrared spectra were compared with the spectra of the compound obtained from the aqueous synthesis and found to be identical.

Measurements were made with a Beckman DU spectrophotometer using calibrated silica cells with optical path lengths of 10, 50 or 100 mm. The calibration of the instrument and cells was performed as described by Napoli, Senkowski, and Motchane.[8]

*Acknowledgment.* Funds for this study were made available by the Rutgers University Research Council.

One of the authors, B. Z. Senkowski, wishes to express his sincere thanks to Mr. E. G. E. Shafer, Dr. E. G. Wollish, and Dr. A. E. Motchane for the use of some facilities at Hoffmann-La Roche.

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# Reactive Methylene Compounds. I. Synthesis of Some Pyrazoles

H. G. GARG AND S. S. JOSHI

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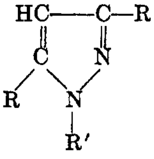
In the course of an investigation on reactive methylene compounds, the authors have had occasion to prepare pyrazole derivatives which have not previously been reported. These compounds are of

TABLE I

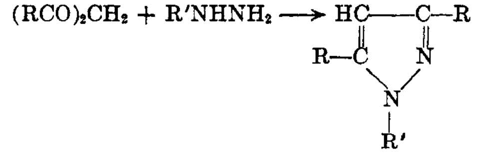
CHARACTERISTICS OF SUBSTITUTED PYRAZOLES



| S.No. | R′ | R | Yield, % | M.P. | Color | Formula | Analyses, % Found | Analyses, % Calcd. |
|---|---|---|---|---|---|---|---|---|
| 1 | 2,4-Dinitrophenyl | Methyl | 75 | 114 | Lemon yellow | $C_{11}H_{10}N_4O_4$ | N, 21.12 | 21.37 |
| 2 | 2,6-Dinitrophenyl | Methyl | 71 | 128 | Dirty white | $C_{11}H_{10}N_4O_4$ | N, 21.31 | 21.37 |
| 3 | 2-Nitro-4-chlorophenyl | Methyl | 74 | 129 | Colorless | $C_{11}H_{10}ClN_3O_2$ | Cl, 14.01 | 14.11 |
| 4 | 2-Nitro-5-chlorophenyl | Methyl | 73 | 106 | Dirty white | $C_{11}H_{10}ClN_3O_2$ | Cl, 14.11 | 14.11 |
| 5 | 4-Nitro-2-chlorophenyl | Methyl | 74 | 110 | Lemon yellow | $C_{11}H_{10}ClN_3O_2$ | Cl, 13.98 | 14.11 |
| 6 | 4-Nitro-2-bromophenyl | Methyl | 75 | 124 | Colorless | $C_{11}H_{10}BrN_3O_2$ | Br, 26.84 | 27.02 |
| 7 | 2,4-Dinitro-5-chlorophenyl | Methyl | 74 | 124 | Colorless | $C_{12}H_{12}N_4O_4$ | N, 19.96 | 20.28 |
| 8 | 2,4-Dinitro-5-chlorophenyl | Methyl | 72 | 162 | Pale yellow | $C_{11}H_9ClN_4O_4$ | Cl, 11.63 | 11.97 |
| 9 | 2-Nitro-4,5-dichlorophenyl | Methyl | 69 | 110 | Colorless | $C_{11}H_9Cl_2N_3O_2$ | Cl, 24.34 | 24.82 |
| 10 | 2,4-Dinitrophenyl | Phenyl | 76 | 149 | Golden yellow | $C_{21}H_{14}N_4O_4$ | N, 14.18 | 14.50 |
| 11 | 2,6-Dinitrophenyl | Phenyl | 73 | 164 | Yellow | $C_{21}H_{14}N_4O_4$ | N, 14.21 | 14.50 |
| 12 | 2-Nitro-4-chlorophenyl | Phenyl | 75 | 102 | Yellow | $C_{21}H_{14}ClN_3O_2$ | Cl, 9.45 | 9.45 |
| 13 | 2-Nitro-5-chlorophenyl | Phenyl | 74 | 150 | Light Orange | $C_{21}H_{14}ClN_3O_2$ | Cl, 9.28 | 9.45 |
| 14 | 4-Nitro-2-chlorophenyl | Phenyl | 75 | 154 | Lemon yellow | $C_{21}H_{14}ClN_3O_2$ | Cl, 9.38 | 9.45 |
| 15 | 4-Nitro-2-bromophenyl | Phenyl | 74 | 167 | Light yellow | $C_{21}H_{14}BrN_3O_2$ | Br, 18.98 | 19.04 |
| 16 | 2,4-Dinitro-5-methylphenyl | Phenyl | 77 | 201 | Pale yellow | $C_{22}H_{16}N_4O_4$ | N, 13.81 | 14.00 |
| 17 | 2,4-Dinitro-5-chlorophenyl | Phenyl | 78 | 195 | Yellow | $C_{21}H_{13}ClN_4O_4$ | Cl, 8.18 | 8.44 |
| 18 | 2-Nitro-4,5-dichlorophenyl | Phenyl | 71 | 143 | Light yellow | $C_{21}H_{13}Cl_2N_3O_2$ | Cl, 17.01 | 17.31 |
| 19 | 2,4-Dinitrophenyl | Anisyl | 78 | 164 | Chocolate | $C_{23}H_{18}N_4O_6$ | N, 12.41 | 12.55 |
| 20 | 2,6-Dinitrophenyl | Anisyl | 74 | 198 | Yellow | $C_{23}H_{18}N_4O_6$ | N, 12.31 | 12.55 |
| 21 | 2-Nitro-4-chlorophenyl | Anisyl | 77 | 136 | Canary yellow | $C_{23}H_{18}ClN_3O_4$ | Cl, 8.15 | 8.15 |
| 22 | 2-Nitro-5-chlorophenyl | Anisyl | 76 | 149 | Pale yellow | $C_{23}H_{18}ClN_3O_4$ | Cl, 8.02 | 8.15 |
| 23 | 4-Nitro-2-chlorophenyl | Anisyl | 77 | 168 | Golden yellow | $C_{23}H_{18}ClN_3O_4$ | Cl, 8.08 | 8.15 |
| 24 | 4-Nitro-2-bromophenyl | Anisyl | 76 | 165 | Bright yellow | $C_{23}H_{18}BrN_3O_4$ | Br, 16.46 | 16.66 |
| 25 | 2,4-Dinitro-5-methylphenyl | Anisyl | 79 | 188 | Yellow | $C_{24}H_{20}N_4O_6$ | N, 12.01 | 12.17 |
| 26 | 2,4-Dinitro-5-chlorophenyl | Anisyl | 80 | 168 | Yellow | $C_{23}H_{17}ClN_4O_6$ | Cl, 7.22 | 7.38 |
| 27 | 2-Nitro-4,5-dichlorophenyl | Anisyl | 72 | 149 | Pale yellow | $C_{23}H_{17}Cl_2N_3O_4$ | Cl, 14.84 | 15.10 |

special interest because many drugs and dyes contain the pyrazole nucleus.

1,3-Dicarbonyl compounds react with hydrazines[1] giving pyrazole derivatives. This paper includes the condensations of acetylacetone, dibenzoylmethane, and dianisoylmethane with nitrophenylhydrazines. For this purpose, 2,4-dinitro-, 2,6-dinitro-, 2-chloro-4-nitro-, 2-nitro-4-chloro-, 2-nitro-5-chloro-, 2-bromo-4-nitro-, 2,4-dinitro-5-methyl-, 2,4-dinitro-5-chloro- and 2-nitro-4,5-dichlorophenylhydrazine have been used and corresponding pyrazoles were isolated.



(R = $CH_3$, $C_6H_5$ or 4—$CH_3O.C_6H_4$; R′ = substituted phenyl)

These pyrazoles are crystalline compounds from nearly colorless to yellow, insoluble in water, and soluble in common organic solvents.

## EXPERIMENTAL[2]

*Preparation of β-diketones.* The compounds were made by previously described procedures.[3,4]

*Preparation of phenylhydrazines.* The phenylhydrazines, such as, 2,4-dinitro-,[5] 2,6-dinitro-,[5] 2-nitro-4-chloro-,[6] 2-nitro-5-chloro-,[7] 4-nitro-2-chloro-,[8] 4-nitro-2-bromo-,[8] 2,4-dinitro-5-methyl-,[9] 2,4-dinitro-5-chloro-,[10] and 2-nitro-4,5-dichloro-,[11] required for the present work were prepared by known methods.

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(3) Commercially available.

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*Preparation of pyrazole derivatives.* Substituted phenylhydrazine (0.01 mole) was dissolved in concd. sulfuric acid (3 ml.) and alcohol (30 ml.). It was then added to the β-diketone (0.01 mole) dissolved in alcohol-acetic acid mixture and heated on a water-bath for several hours. On cooling and diluting shining crystals separated which were recrystallized from alcohol or glacial acetic acid.

The substituted pyrazoles which were prepared are summarized in Table I.

*Acknowledgment.* One of the authors (H. G. G.) is grateful to the Government of India for the award of a scholarship.

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## Reactive Methylene Compounds. II. Preparation of Some 2-Bromo-substituted Diphenylpropane-1,3-diones

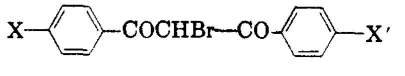
H. G. GARG[1]

*Received May 20, 1960*

The hydrogen atom of the methylene groups in β-diketones can be directly replaced not only by metals but also by halogen atoms. Thus 1,3-diphenyl- and 1-anisyl-3-phenylpropanedione were found to yield mono bromo derivatives when treated with bromine in a suitable solvent[2a,b] The author has previously described a new method, furnishing better and purer products, for the preparation of bromooxymethyleneacetophenones[3,4] through their copper salts.

In the present study on reactive methylene compounds, synthesis of 2-bromo derivatives of substituted diphenylpropane-1,3-diones, such as 1,3-diphenyl-, 1-(*p*-bromophenyl)-3-phenyl-, 1-(*p*-chlorophenyl)-3-phenyl-, 1-anisyl-3-phenyl-, 1,3-dianisyl-, and 1-(*p*-tolyl)-3-phenyl-2-bromopropanedione has been successfully carried out and their properties studied.

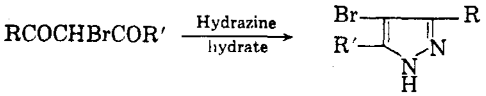
Diphenylpropane-1,3-diones required for this purpose were prepared by the known methods.[5-8] Sodium salts of these β-diketones can be obtained by the acylation of an acetophenone with an ester in presence of sodium or sodium amide.[7] The copper salt is obtained by treating the β-diketone with a saturated solution of copper acetate. Sodium or copper salts of these substituted diphenylpropane-1,3-diones suspended in carbon tetrachloride, on treatment with bromine dissolved in the same solvent yield the corresponding bromo derivatives.



X = H or —OCH$_3$
X′ = Cl, Br, H, —CH$_3$, or —OCH$_3$

The bromo compounds are all colorless, crystalline compounds soluble in alcohol, chloroform, and benzene. They however do not react with copper acetate solution nor give a color change with alcoholic ferric chloride solution. They liberate iodine when treated with alcoholic potassium iodide solution[9-11] regenerating the original diketone.

They react with hydrazine hydrate in acetic acid and form 4-bromopyrazole derivatives.[12]



(R or R′ = phenyl or substituted phenyl).

### EXPERIMENTAL[13]

*Preparation of the sodium salts of substituted diphenylpropane-1,3-diones.* A mixture of substituted ethyl benzoate (1 mole), acetophenone (1 mole), ether and granulated sodium (1 g.-atom) was kept at 0° for several days. The sodium salt was filtered and washed well with dried ether.

*Preparation of the copper salts of β-diketones.* The sodioderivative collected above was treated with ice cold dilute acetic acid and the diketone taken up in ether. On prolonged shaking of the extract with aqueous cupric acetate, voluminous precipitate of the copper derivative was obtained and crystallized from chloroform.

*Preparation of 2-bromo-substituted diphenylpropane-1,3-dione.* The sodium or copper salt of the β-diketone was suspended in carbon tetrachloride and bromine (molar quantities) dissolved in the same solvent was gradually added to the suspension kept at ice temperature. The metallic bromide was filtered off and from the filtrate most of the solvent was removed on a water bath. The filtrate gave a pale yellow product. This was purified by recrystallizing it from alcohol.

The different bromo derivatives prepared are summarized in Table I.

*Preparation of 4-bromopyrazole derivatives.* A mixture of equimolecular quantities of 2-bromodiphenylpropane-1,3-dione and hydrazine hydrate in glacial acetic acid was heated

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[1] Present address: National Chemical Laboratory, Poona 8, India.

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[13] Melting points are uncorrected.