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Reactive Methylene Compounds. Part X. Behaviour with some Polynitrohalogenobenzenes

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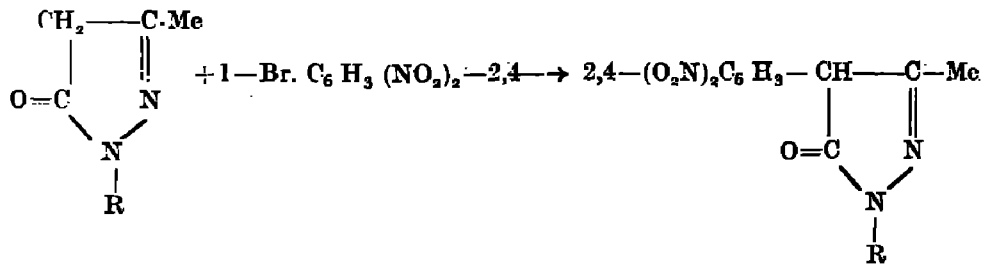
Behaviour of several polynitrohalogenobenzenes with reactive methylene compounds has been investigated and characteristics of the derivatives are described.

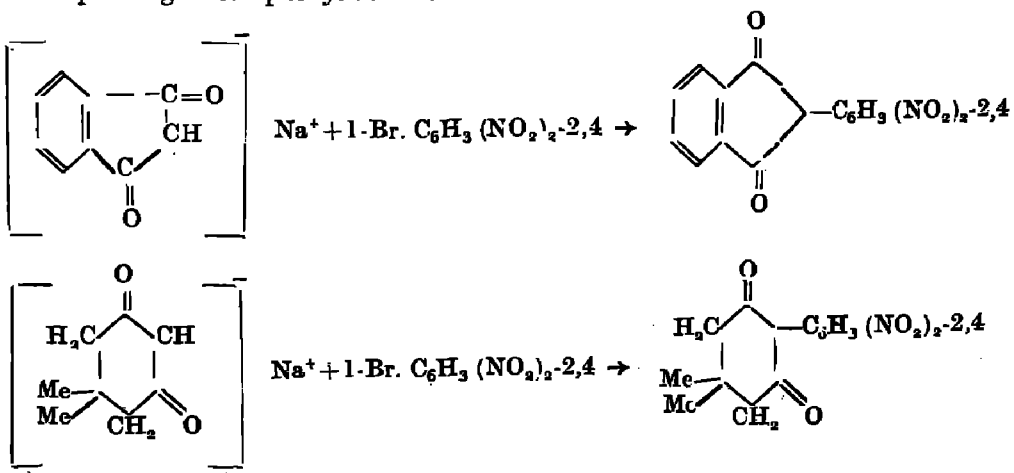
The relative reactivity of the (-CH_2-) in reactive methylene compounds usually depends on the character of the attached electronegative groups. With a view to subjecting the above postulate to experimental verification the condensation of a number of methylene compounds with polynitrohalogenobenzenes has been investigated.

In 1-phenyl-3-methyl-5-pyrazolone and 1-(4-nitrophenyl)-3-methyl-5-pyrazolone, the hydrogen atom of the methylene group at 4-position is very reactive, so much so, that they react with 1-bromo-2, 4-dinitrobenzene in ethanolic solution containing sodium acetate and yield the substituted derivative (cf. Rowe and Twitchett, *J. Chem. Soc.*, 1936, 1704). The various compounds, thus prepared, are described in Table I and II.



(R=Phenyl or substituted phenyl)

1-Bromo-2,4-dinitrobenzene did not however react with indane-1, 3-dione, methone, benzoylacetones, acetoacetic esters, or diethyl malonate under these conditions; sodium salts of these had to be prepared which reacted with 1-bromo-2,4-dinitrobenzene to afford the corresponding dinitrophenyl derivatives.



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In the case of benzoylacetic ester or dibenzoylmethane even the sodium salt did not react smoothly (cf. Borsche, *Ber.*, 1909, **42**, 601) and the potassium salts had to be prepared which yielded the required dinitrophenyl derivatives (cf. Gambhir, Ph.D. Thesis, *Agra Univ.*, 1956).

EXPERIMENTAL*

1-Phenyl-3-methyl-5-pyrazolone (Knorr, *Ber.*, 1883, **16**, 2597), 1-(4-nitrophenyl)-3-methyl-5-pyrazolone (Altschul, *Ber.*, 1892, **25**, 1853), indane-1, 3-dione (Teeters and Shriner, *J. Amer. Chem. Soc.*, 1933, **55**, 3027), methone (Vörlander, *Z. anal. Chem.*, 1929, **77**, 245) and benzoylacetones (Garg, this *Journal*, 1961, **38**, 113) were prepared by known methods.

Reactive halogen compounds were obtained either by nitration of the corresponding halogenobenzenes or by treatment of polynitrophenols with *p*-toluenesulphonyl chloride in diethylaniline.

1-*Phenyl-3-methyl-4-(2,4-dinitrophenyl)-5-pyrazolone.*—1-Bromo-2, 4-dinitrobenzene (0.01-*M*) was added to a boiling solution of 1-phenyl-3-methyl-5-pyrazolone (0.01-*M*) in ethanol (100c.c.) containing sodium acetate (8 g.). The mixture was refluxed for 4 hours and then diluted with water. The crude product after recrystallisation from a mixture of ethanol and acetic acid furnished a crystalline compound.

By adopting a similar procedure other substituted pyrazolones from 1-phenyl-3-methyl-5-pyrazolones and 1-(4-nitrophenyl)-3-methyl-1-5-pyrazolones were prepared; their characteristics are given in Table I and II respectively.

TABLE I

No.	4-Substituted-1-phenyl-3-methyl-5-pyrazolone	Yield	M.P.	Colour	Formula	Found	Calc.
1.	4-(2,4-Dinitrophenyl)-	82%	216°	Orange	$C_{16}H_{12}O_5N_4$	N : 16.24	16.47
2.	4-(5-Chloro-4, 6-dinitrophenyl)-	70	236°	Yellow	$C_{16}H_{11}ClO_5N_4$	Cl : 9.32	9.48
3.	4-(3-Methyl-4, 6-dinitrophenyl)-	48	215°	,,	$C_{17}H_{14}O_5N_4$	N : 15.67	15.81
4.	4-(2-chloro-4, 6-dinitrophenyl)-	58	218°	Orange	$C_{16}H_{11}O_5ClN_4$	Cl : 9.28	9.47
5.	4-(2-Bromo-4, 6-dinitrophenyl)-	58	216°	,,	$C_{16}H_{11}O_5BrN_4$	Br : 18.89	19.09
6.	4-(2,6-Dinitro-4-bromophenyl)-	49	220°	Yellow	$C_{16}H_{11}O_5BrN_4$	Br : 18.92	19.09
7.	4-(3,5-Dibromo-2, 4-dinitrophenyl)-	49	202°	,,	$C_{16}H_{10}O_5Br_2N_4$	Br : 32.34	32.12
8.	4-(2,4,6-Trinitro-3-methylphenyl)	46	252°	Dark brown	$C_{17}H_{13}O_7N_5$	N : 17.41	17.54
9.	4-(2,4,6-Trinitrophenyl)-	51	220°	Brown	$C_{16}H_{11}O_7N_5$	N : 18.01	18.18

TABLE II

No	4-Substituted-1-(4-nitrophenyl)-3-methyl-5-pyrazolone.	Yield	M.P.	Colour	Formula	Found	Calc.
1.	4-(2,4-Dinitrophenyl)-	80%	285°	Chocolate	$C_{16}H_{11}N_5O_7$	N : 18.02	18.18
2.	4-(3-Chloro-4, 6-dinitrophenyl)-	74	261°	Yellow	$C_{16}H_{10}ClN_5O_7$	Cl : 8.38	8.46
3.	4-(3-Methyl-4, 6-dinitrophenyl)-	40	259°	,,	$C_{17}H_{13}N_5O_7$	N : 17.41	17.54
4.	4-(2-Chloro-4, 6-dinitrophenyl)-	60	221°	Brown	$C_{16}H_{10}ClN_5O_7$	Cl : 8.31	8.46
5.	4-(2-Bromo-4, 6-dinitrophenyl)-	61	226°	,,	$C_{16}H_{10}BrN_5O_7$	Br: 17.14	17.24
6.	4-(2,6-Dinitro-4-bromophenyl)-	52	248°	Blackish brown	$C_{16}H_{10}BrN_5O_7$	Br: 17.14	17.24
7.	4-(3-Methyl-2,4,6-trinitrophenyl)-	42	Above 300°	Dark brown	$C_{17}H_{12}N_6O_9$	N : 18.78	18.91
8.	4-(2,4,6-Trinitrophenyl)-	53	Above. 300°	,,	$C_{16}H_{10}N_6O_9$	N : 19.48	19.53
9.	4-(3,5-Dibromo-2,4-dinitrophenyl)-	49	226°	Brown	$C_{16}H_9Br_2N_5O_7$	Br: 29.21	29.46

*Melting points are uncorrected.

2-(2,4-Dinitrophenyl)-indane-1,3-dione.—A suspension of the monosodium derivative of indane-1,3-dione (0.05-*M*) in ethanol (15c.c.) and 1-bromo-2, 4-dinitrobenzene (0.05 *M*) were refluxed for 5 hours and filtered. The filtrate was acidified with acetic acid and allowed to stand. A gummy product separating after treatment with activated charcoal gave a crystalline product from acetic acid.

By adopting a similar procedure derivatives from methone and benzoylacetones were prepared. Characteristics are summarized in Table III.

TABLE III

No.	2,4-Dinitrophenyl-derivative of	Yield	M.P.	Colour.	Formula.	Found.	Calc.
1.	Indane-1,3-dione	58%	242°	Yellow	$C_{15}H_8O_6N_2$	N : 8.68	8.97
2.	Methone	60	254°	Light yellow	$C_{14}H_{14}O_6N_2$	N : 9.07	9.15
3.	4-Chlorobenzoylacetone	46	138°	Colourless	$C_{16}H_{11}O_6ClN_2$	Cl : 9.61	9.79
4.	4-Bromobenzoylacetone	45	168°	Colourless	$C_{16}H_{11}O_6BrN_2$	Br: 19.51	19.65
5.	4-Methylbenzoylacetone	34	112°	Pale yellow	$C_{17}H_{14}O_6N_2$	N : 7.98	8.18
6.	4-Methoxybenzoylacetone	31	118°	Pale yellow	$C_{17}H_{14}O_7N_2$	N : 8.01	7.82
7.	3,4-Dichlorobenzoylacetone	40	138°	Pale yellow	$C_{16}H_{10}O_6Cl_2N_2$	Cl: 17.61	17.88
8.	2-Chloro-5-methyl benzoylacetone	39	122°	Colourless	$C_{17}H_{13}O_6ClN_2$	Cl: 9.21	9.42

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