

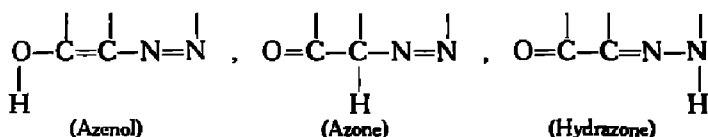
REACTIVE METHYLENE COMPOUNDS. PART IV. CONDENSATIONS WITH BENZENEDIAZONIUM SALTS

BY H. G. GARG AND S. S. JOSHI

Benzenediazonium salts have been condensed with different types of reactive methylene compounds in an attempt to assign correct configurations to the stable forms.

Several compounds containing reactive methylene group have been found to couple readily with aromatic diazonium compounds. Thus, diethyl malonate (Meyer, *Ber.*, 1891, 24, 1241; Fries *et al.*, *Annalen*, 1934, 511, 241; Leonard *et al.*, *J. Org. Chem.*, 1947, 12, 47), ethyl acetoacetate (Meyer, *Ber.*, 1877, 10, 2075; Chattaway *et al.*, *Proc. Roy. Soc.*, 1932, A 137, 489; 1932, A 135, 282; *J. Chem. Soc.*, 1933, 475; 1933, 1143; 1934, 1985), acetylacetone (Beyer and Claisen, *Ber.*, 1888, 21, 1697; Chattaway and Ashworth, *J. Chem. Soc.*, 1934, 930), and benzoylacetone (Beyer and Claisen, *loc. cit.*; Dimroth and Hartman, *Ber.*, 1907, 40, 4460; 1908, 41, 4012), yielded the corresponding derivatives with benzenediazonium salts.

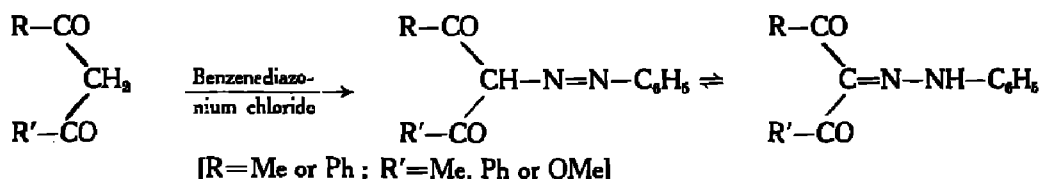
The possible structural configurations of these derivatives are three in number, namely,



In spite of the considerable amount of attention devoted to these compounds, it cannot be claimed that the constitutions of the stable forms have been satisfactorily determined.

A systematic study of the condensations of benzenediazonium salts with different classes of reactive methylene compounds has now been undertaken in an effort to assign a structural configuration to the stable forms of these compounds.

The behaviour of a number of substituted benzenediazonium salts with methyl acetoacetate, acetylacetone, benzoylacetone, and dibenzoylmethane has been investigated.



The so-called benzeneazo derivatives are coloured compounds, varying from yellow to orange-red in colour, soluble in ethanol, acetic acid, etc. The solubility of the derivatives in these solvents decreases with the increasing molecular weight. These compounds give characteristic red coloration with concentrated sulphuric acid.

*EXPERIMENTAL

Methyl acetoacetate and acetylacetone were commercially available. Benzoylacetone was obtained by the condensation of acetophenone with ethyl acetate in presence of sodium ethoxide. Dibenzoylmethane was prepared by Bodfors' method (*Ber.*, 1918, 51, 214).

* All melting points are uncorrected.

TABLE I

S. No.	Substituted benzenezo derivative	Methyl acetoacetate.			Acetylacetone.			Formula.	Found.	Calc.				
		Yield.	M.P.	Colour.	Formula.	M.P.	Colour.				Yield.	M.P.	Colour.	
1.	Benzenezo	79%	64°	Canary-yellow	C ₁₁ H ₁₂ O ₂ N ₄	N: 12.61%	12.72%
2.	4-Methoxy-	77	98°	Golden yellow	C ₁₂ H ₁₄ O ₄ N ₃	N: 11.10	11.20	82%	99°	Light brown	C ₁₂ H ₁₄ O ₂ N ₃	N: 11.68%	11.96%	14.88
3.	4-Chloro-	83	125°	Yellow	C ₁₁ H ₁₁ O ₃ N ₂ Cl	Cl: 13.69	13.94	90	128°	Pale yellow	C ₁₁ H ₁₁ O ₂ N ₂ Cl	Cl: 14.64	14.88	14.88
4.	3-Chloro-	82	76°	Pale yellow	C ₁₁ H ₁₁ O ₃ N ₂ Cl	Cl: 13.78	13.94	92	88°	Light yellow	C ₁₁ H ₁₁ O ₄ N ₂ Cl	Cl: 14.59	14.88	14.88
5.	2-Chloro-	82	140°	Golden yellow	C ₁₁ H ₁₁ O ₃ N ₂ Cl	Cl: 13.94	13.94	91	122°	Pale yellow	C ₁₁ H ₁₁ O ₂ N ₂ Cl	Cl: 14.68	14.88	14.88
6.	4-Nitro-	90	185°	Pale yellow	C ₁₁ H ₁₁ O ₂ N ₃	N: 15.61	15.84
7.	3-Nitro-	90	119°	Golden yellow	C ₁₁ H ₁₁ O ₃ N ₃	N: 15.70	15.84
8.	4-Methyl-	77	82°	Light yellow	C ₁₂ H ₁₄ O ₂ N ₃	N: 11.76	11.96	83	98°	Do	C ₁₂ H ₁₄ O ₂ N ₃	N: 12.69	12.84	12.84
9.	3-Methyl-	77	74°	Orange-brown	C ₁₂ H ₁₄ O ₂ N ₃	N: 11.81	11.96	82	79°	Do	C ₁₂ H ₁₄ O ₂ N ₃	N: 12.58	12.84	12.84
10.	2-Chloro-4-nitro-	89	169°	Light yellow	C ₁₁ H ₁₀ O ₂ N ₂ Cl	Cl: 11.62	11.85	94	165°	Yellow	C ₁₁ H ₁₀ O ₂ N ₂ Cl	Cl: 12.31	12.52	12.52
11.	4-Chloro-2-nitro-	90	171°	Canary-yellow	C ₁₁ H ₁₀ O ₂ N ₂ Cl	Cl: 11.70	11.85	93	164°	Do	C ₁₁ H ₁₀ O ₂ N ₂ Cl	Cl: 12.34	12.52	12.52

TABLE II

S. No.	Yield.	M.P.	Benzoylacetone.			Dibenzoylmethane.			Mol. formula.	Found.	Calc.	
			Colour.	Mol. formula.	Found.	Calc.	Yield.	M.P.				Colour.
1.	
2.	84%	82°	Pale yellow	C ₁₇ H ₁₆ O ₂ N ₃	N: 9.23%	9.45%	87%	145°	Orange	C ₁₇ H ₁₆ O ₂ N ₃	N: 7.71%	7.82%
3.	92	113°	Canary-yellow	C ₁₆ H ₁₄ O ₄ N ₂ Cl	Cl: 11.72	11.81	90	137°	Yellow	C ₁₆ H ₁₄ O ₄ N ₂ Cl	Cl: 9.61	9.79
4.	91	146°	Pale yellow	C ₁₆ H ₁₄ O ₂ N ₂ Cl	Cl: 11.48	11.81	90	194°	Yellow	C ₁₆ H ₁₄ O ₂ N ₂ Cl	Cl: 9.38	9.79
5.	92	108°	Light yellow	C ₁₆ H ₁₄ O ₂ N ₂ Cl	Cl: 11.51	11.81	90	122°	Yellow	C ₁₆ H ₁₄ O ₂ N ₂ Cl	Cl: 9.41	9.79
6.	95	174°	Yellow	C ₁₇ H ₁₆ O ₄ N ₃	N: 10.93	11.26
7.	93	108°	Light yellow	C ₁₆ H ₁₄ O ₄ N ₃	N: 13.25	13.50	92	192°	Yellow	C ₁₆ H ₁₄ O ₄ N ₃	N: 10.98	11.26
8.	85	104°	Light yellow	C ₁₇ H ₁₆ O ₄ N ₃	N: 9.82	10.00	84	176°	Dirty yellow	C ₁₇ H ₁₆ O ₂ N ₃	N: 8.43	8.18
9.	84	89°	Orange-yellow	C ₁₇ H ₁₆ O ₂ N ₃	N: 9.79	10.00	83	150°	Yellow	C ₁₆ H ₁₄ O ₂ N ₃	N: 8.18	8.18
10.	93	170°	Light yellow	C ₁₆ H ₁₄ O ₄ N ₂ Cl	Cl: 10.01	10.27	91	183°	Yellow	C ₁₆ H ₁₄ O ₄ N ₂ Cl	Cl: 8.41	8.71
11.	92	180°	Pale yellow	C ₁₆ H ₁₂ O ₄ N ₂ Cl	Cl: 10.21	10.27	91	158°	Golden yellow	C ₁₆ H ₁₂ O ₄ N ₂ Cl	Cl: 8.46	8.71

*The number of benzenezo derivatives corresponds to those listed in Table I.

Methyl Benzeneazoacetoacetate.—Aniline (0.1 *M*) was diazotised in the usual manner. The filtered diazonium solution was run into a well-cooled stirred mixture of sodium acetate (100 g.) and methyl acetoacetate (0.15 *M*) in ethanol (25 c.c.) and water (25 c.c.). It was recrystallised from ethanol. Different derivatives are recorded in Table I.

By adopting a similar procedure as above, several benzeneazoacetylacetones, described in Table I, were prepared. Benzeneazobenzoylacetones and benzeneazodibenzoylmethanes were also similarly prepared (Table II).

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SCHOOL OF CHEMISTRY,
MEERUT COLLEGE, MEERUT.

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