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.

DEPARTMENT OF CHEMISTRY,
MEERUT COLLEGE,
MEERUT (INDIA)

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

H. G. GARG[1]

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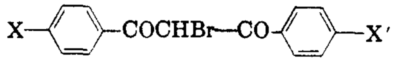
The hydrogen atom of the methylene groups in β-diketones can be directly replaced not only by metals but also by halogen atoms. Thus 1,3-diphenyl- and 1-anisyl-3-phenylpropanedione were found to yield mono bromo derivatives when treated with bromine in a suitable solvent[2a,b] The author has previously 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.

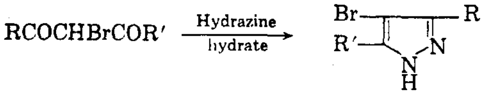
Diphenylpropane-1,3-diones required for this purpose were prepared by the known methods.[5-8] Sodium salts of these β-diketones can be obtained by the acylation of an acetophenone with an ester in presence of sodium or sodium amide.[7] The copper salt is obtained by treating the β-diketone with a saturated 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.

TABLE I

CHARACTERISTICS OF 2-BROMO-SUBSTITUTED DIPHENYLPROPANE-1,3-DIONES

			Yield, % from					Halogen, %	
No.	R	R′	Sodium salt	Copper salt	M.P.	Color	Formula	Found	Calcd.
1[a]	Phenyl	Phenyl	60	79	93	Colorless	$C_{15}H_{11}BrO_2$	26.01	26.40
2	*p*-Bromophenyl	Phenyl	70	81	114	Colorless	$C_{15}H_{10}Br_2O_2$	41.25	41.80
3	*p*-Chlorophenyl	Phenyl	68	80	118	Colorless	$C_{15}H_{10}BrClO_2$	34.84	34.22
4	Anisyl	Phenyl	54	79	128	Colorless	$C_{16}H_{13}BrO_3$	24.40	24.02
5	*p*-Tolyl	Phenyl	62	80	110	Colorless	$C_{16}H_{13}BrO_2$	25.15	25.22
6	Anisyl	Anisyl		81	97	Colorless	$C_{17}H_{15}BrO_4$	21.94	22.03

[a] Ref. (1).

TABLE II

CHARACTERISTICS OF 4-BROMOPYRAZOLES

							Halogen, %	
No.	R	R′	Yield, %	M.P.	Color	Formula	Found	Calcd.
1[b]	Phenyl	Phenyl	72	198	Colorless	$C_{15}H_{11}BrN_2$	26.31	26.75
2	Phenyl	*p*-Bromophenyl	67	223	Colorless	$C_{13}H_{10}Br_2N_2$	42.11	42.32
3	Phenyl	*p*-Chlorophenyl	68	221	Dirty white	$C_{15}H_{10}BrClN_2$	34.22	34.63
4	Phenyl	Anisyl	63	178	Colorless	$C_{16}H_{12}BrN_2O$	24.20	28.31
5	Phenyl	*p*-Methylphenyl	65	172	Dirty white	$C_{16}H_{13}BrN_2$	25.35	25.55
6	Anisyl	Anisyl	64	228	Colorless	$C_{17}H_{15}BrN_2O_2$	22.11	22.28

[a] Ref. (12).

under reflux for about an hour. On cooling shining crystals separated. These were recrystallized from alcohol.

The different pyrazole derivatives prepared are summarized in Table II.

Acknowledgment. The author's sincere thanks go to Dr. S. S. Joshi, Director, School of Chemistry and Principal, Meerut College, Meerut, for his interest and to the Ministry of Scientific Research and Cultural Affairs, Government of India, for a research scholarship.

DEPARTMENT OF CHEMISTRY
MEERUT COLLEGE
MEERUT, INDIA

Reaction of *t*-Alkylazomethines with Ketene

DAVID H. CLEMENS AND WILLIAM D. EMMONS

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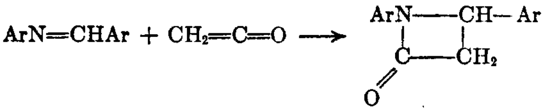
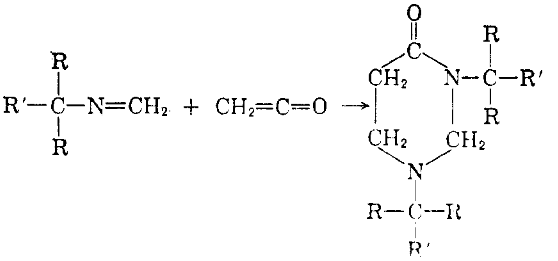
Staudinger[1] and more recently Pfleger and Jager[2] have examined the reaction of ketene with a variety of substituted benzal anilines. Invariably they found that the reaction proceeded to give *β*-lactams of the type I, this being analogous to the formation of *β*-lactones from ketene and aldehydes.



I

The present work describes the zinc chloride catalyzed reaction of *N*-*t*-butyl-and *N*-*t*-octylazomethines with ketene.

No reaction was observed between the azomethines IIa and IIb and ketene at temperatures in excess of 100°. However, when a catalytic amount of zinc chloride was used, both IIa and IIb reacted exothermally with ketene at room temperature. The viscous oily products of these reactions were not the expected *β*-lactams but rather had empirical formulas corresponding to a combination of two moles of the azomethine, IIa or IIb, with one mole of ketene.



IIa. $R = R' = -CH_3$
IIb. $R = -CH_3$
$R' = -CH_2-C(CH_3)_3$

IIIa. $R = R' = -CH_3$
IIIb. $R = -CH_3$
$R' = -CH_2-C(CH_3)_3$

The postulated structure, IIIa, was proved by the following experiments. With 2,4-dinitrophenylhydrazine reagent IIIa gave cleanly a 70% yield of formaldehyde dinitrophenylhydrazone which is in agreement with the methylene diamine structure for IIIa. Acid hydrolysis of IIIa yielded the crystalline *β*-*t*-butylamino-*N*-*t*-butylpropionamide(IV), the structure of which was established by synthesis from *t*-butylamine and *N*-*t*-butylacrylamide.

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