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Studies in Haloketones. I. Synthesis and Reactions of α-Bromo-β-chlorovinyl Aryl Ketones

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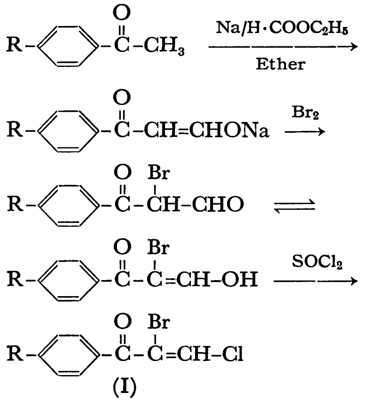
The reactivity of halogen atom in haloketones varies considerably depending upon the nature of the organic moiety and the position of the halogen atom with respect to the carbonyl group. The halogen atom of α-haloketones is activitated for S_N2 displacement reactions and is attributed with positive character. When these compounds are warmed with acidified potassium iodide solution, iodine is liberated.[1,2] Usually a vinylic halogen atom is very inert and cannot be replaced by direct substitution reactions. However, a keto group at the β-position of the vinyl moiety makes this halogen atom very susceptible to displacement reactions. For example, β-chlorovinyl aryl ketones react with ammonia[3,4] and amines[5,6] to eliminate hydrogen chloride and form corresponding amino compounds.

In the present work α-bromo-β-chlorovinyl ketones (I) have been synthesised by the following general route. These ketones are quite stable at room temperature.

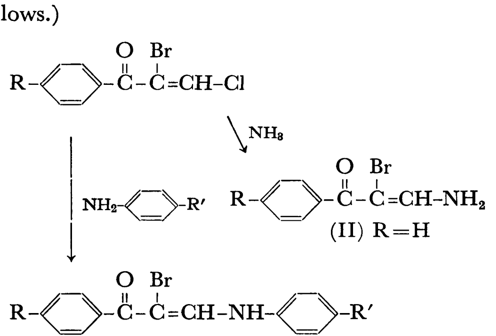


(I)

(a) R=H (b) R=CH_3 (c) R=Cl
(d) R=Br

The reactions of these compounds with ammonia and anilines have also been studied. It has been observed that it is only β-chlorine atom that undergoes substitution, whereas α-bromine atom remains intact in all the reactions.[7]

(The structures of the reaction products are as follows.)



(III)

(III) (a) R=R′=H (b) R=H, R′=Cl
(c) R=H, R′=Br (d) R=CH_3, R′=H
(e) R=CH_3, R′=Cl (f) R=CH_3, R′=Br

Experimental

Synthesis of α-Bromo-β-chlorovinly *p*-Chlorophenyl Ketone (Ic). A mixture of equimolecular quantities of α-bromo-β-hydroxy vinyl *p*-chlorophenyl ketone (10 g), thionyl chloride (4.5 g) and dry benzene (40 m*l*) was refluxed on a water bath for eight hours. Benzene was removed by distillation and the residue, when distilled under reduced pressure (140°C/1 mmHg), yielded yellow coloured oil (4 g). IR spectrum (liquid film of the compound) showed a carbonyl frequency at 1667 cm^{-1}.

Found: C, 38.8; H, 1.9; (Cl+Br), 53.3%. Calcd for $C_9H_5OCl_2Br$: C, 38.6; H, 1.8; (Cl+Br), 53.9%.

The same procedure was adopted for the synthesis of other ketones. Data for these products are given in Table 1.

Action of Ammonia on α-Bromo-β-chlorovinyl Phenyl Ketone (II). α-Bromo-β-chlorovinyl phenyl ketone (1 g) was treated with aqueous ammonia (10 m*l*) (in the presence of air) at room temperature. The reaction mixture was kept for three days for the completion of the reaction when a brown coloured solid separated. It was filtered, washed with water and crystallised

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[1] K. H. Mayer, *Ber.*, **44**, 2755 (1911); **46**, 2847 (1912).

[2] M. M. Bokadia and S. S. Deshpande, *J. Indian Chem. Soc.*, **27**, 548 (1957).

[3] A. Nesmeyanov, N. Kochetkov and Ya. Dombrovskii, *Izv. Akad, Nauk SSSR, Otd Khim. Nauk*, **1955**, 179.

[4] N. Kochetkov, and Ya. Dombrovskii, *Zh. Obshch, Khim*, **26**, 3081 (1956).

[5] N. Kochetkov, *et al. ibid.*, **27**, 1626 (1957).

[6] N. Kochetkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.*, **1953**, 991.

[7] H. G. Garg, Y. Singh and M. M. Bokadia, *J. Indian Chem. Soc.*, **23**, 353 (1956).

TABLE 1

Compd. No.	Formula	Boiling point	Yield %	Calcd % (Cl+Br)	Found % (Cl+Br)
Ia	C_9H_6OBrCl	145°C/1 mmHg	30	47.0	47.1
Ib	$C_{10}H_8OBrCl$	144°C/1 mmHg	33	44.5	44.7
Id	C_9H_5OBrCl	150°C/1 mmHg	30	60.3	59.8

TABLE 2

Compd. No.	Solvent	Formula	Mp °C	Yield %		C %	H %	N %	Halogen %
IIIb	Alcohol	$C_{15}H_{11}OBrClN$	165	40	Calcd	53.4	3.2	4.1	34.3
					Found	53.6	3.2	4.3	34.6
IIIc	Alcohol	$C_{15}H_{11}OBr_2N$	174	38	Calcd	47.2	2.9	3.7	41.9
					Found	47.4	3.2	3.6	41.5
IIId	Alcohol	$C_{16}H_{14}OBrN$	126	41	Calcd	60.7	4.4	4.4	25.3
					Found	60.9	4.4	4.3	25.6
IIIe	Alcohol	$C_{16}H_{13}OBrClN$	156	37	Calcd	—	—	—	32.8
					Found	—	—	—	32.4
IIIf	Alcohol	$C_{16}H_{13}OBr_2N$	162	39	Calcd	—	—	—	40.5
					Found	—	—	—	40.4

from benzene to furnish light yellow needles (0.4 g, mp 136°C). The compound was characterised as α-bromo-β-aminovinyl phenyl ketone by elemental analysis and IR spectrum. Strong absorption bands in the spectrum are 3250, 1600, 1310, 1050 and 835 cm^{-1}. The lowering of keto frequency (1600 cm^{-1}) may be due to H-bonding in the molecule.

Found: C, 47.6; H, 3.6; N, 6.1; Br, 35.3%. Calcd for C_9H_8OBrN: C, 47.8; H, 3.5; N, 6.2; Br, 35.4%.

Similar treatment of the ketone with alcoholic ammonia also yielded the same product.

Action of Aniline on α-Bromo-β-chlorovinyl Phenyl Ketones (IIIa). A mixture of α-bromo-β-chlorovinyl phenyl ketone (2 g), sodium carbonate (2 g), aniline (1.6 g) and alcohol (10 m*l*) was shaken for eight hours and then refluxed for 15 min. It was cooled to room temperature and poured into cold water (150 m*l*). A yellow coloured solid separated. It was filtered, washed with water and crystallised from alcohol to provide yellow prisms (1 g, mp 127°C). The product was characterized as α-bromo-β-anilinovinyl phenyl ketone by chemical analysis and IR spectrum.

The presence of NH group is indicated by infrared absorption at 3100 cm^{-1}. A weak absorption peak at 1610 cm^{-1} and a strong broad band at 1570 cm^{-1} indicate carbonyl frequencies. This considerable shift in NH and carbonyl frequencies can be ascribed to hydrogen bonding in the molecule.

Found: C, 59.7; H, 4.2; N, 4.3; Br, 26.6%. Calcd for $C_{15}H_{12}OBrN$: C, 59.6; H, 4.0; N, 4.0; Br, 26.5%.

Data of other products of this series prepared by the same method are given in Table 2.

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