[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Dinitrophenylhydrazones of α-Halo Ketones. II

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A number of α-bromo-2,4-dinitrophenylhydrazones (α-bromo-DNP's) were prepared. Some of the α-bromo-DNP's, such as α-bromobutyrophenone DNP (IVb) and 8-bromo-2,3-benzocycloöctene-2-one-1 (VIIIb) lost hydrogen bromide readily in hot acetic acid solution to form the corresponding α,β-unsaturated DNP's. Others, such as 2-bromo-1-indanone DNP (Vb) and 2-bromo-1-tetralone DNP (VIb) were recovered unchanged; 2-bromobenzosuberone DNP (VIIb) underwent partial and sluggish dehydrohalogenation. These differences in reactivity are ascribed to a steric inhibition of resonance associated with the size and geometry of the alicyclic ring fused on to the benzene. Acetic acid treatment of α-bromopropiophenone DNP (IIIb) gave what appears to be an α,β-unsaturated azo structure. The replacement of halogen in the α-halo-DNP's by methoxyl and by acetoxyl is described and discussed in terms of a general scheme for the reaction of α-halo-DNP's. Several DNP's were isolated as pairs of stereoisomers differing in configuration about the C═N bond.

We have recently reported[2a] that the lability of the halogen in α-halo-2,4-dinitrophenylhydrazones[3] (α-halo-DNP's) appears to be markedly dependent on the structure of the parent α-halo ketone as well as on the type of reaction involved. For example 2-bromocyclohexanone DNP (Ib) (see Chart I) underwent facile dehydrohalogenation in hot acetic acid with formation of 2-cyclohexen-1-one DNP. The behavior of simple alicyclic α-halo-DNP's was thus found to be similar to that of the steroidal α-bromo DNP's previously studied by Mattox and Kendall[2b,d] and by Djerassi.[2c] On the other hand, 2-bromo-1-tetralone DNP (VIb) (as well as 2-bromo-1-keto-1,2,3,4-tetrahydrophenanthrene DNP) was not affected by heating in acetic acid. In either type of α-halo-DNP (Ib or VIb) the halogen was replaced by methoxyl upon boiling with methanol.

As part of a more general study of the behavior of α-substituted ketones toward carbonyl reagents and in an effort to interpret the differences in reactivity noted above, we have now prepared the series of compounds illustrated in Chart I (II to XI). These compounds together with their absorption maxima in the ultraviolet are listed in Table I. Several DNP's were obtained as pairs of stereoisomers differing in configuration about the C═N bond and separable by fractional crystallization. A discussion of the stereochemistry of these compounds and of their spectra in the ultraviolet and in the infrared is presented in Part III[4] of this study. The present paper reports observations pertaining to the course of elimination and replacement reactions of α-halo-DNP's and discusses some of the factors which seem to affect the reactivity of the halogen in these compounds.

Experimental[5]

Preparation of Halo Ketones.—With the exceptions described below the halo ketones used have been previously prepared. α-Bromoacetophenone (Eastman Kodak Co.), α-bromopropiophenone,[6] α-bromobutyrophenone,[7] 2-bromo-1-indanone.[8]

2-Bromobenzosuberone.—The benzosuberone[9] (b.p. 123–125° (6 mm.), $n^{26}\text{D}$ 1.5608) was prepared according to directions kindly furnished by Prof. A. Anderson, University of Washington, Seattle, Wash. (Ph.D. Thesis of Shih Yi Wang, 1952). The ketone was brominated in ether solution by dropwise addition of one equivalent of bromine in chloroform at ice-bath temperature[10]; b.p. 139–141° (1 mm.), $n^{25}\text{D}$ 1.5940.

Anal. Calcd. for $C_{11}H_{11}OBr$: C, 55.3; H, 4.6; Br, 33.4. Found: C, 55.4; H, 4.7; Br, 33.2.

8-Bromo-2,3-benzocycloöctene-2-one-1.—2,3-Benzocycloöctene-2-one 1, b.p. 105–108° (1 mm.), $n^{26}\text{D}$ 1.5579, was prepared in 63% yield from ε-phenylcaproic acid,[11] by cyclization of the acid chloride, $n^{24}\text{D}$ 1.5136, utilizing high dilution techniques ($AlCl_3$–CS_2) according to the procedure recently described by Huisgen and Rapp.[12] The ketone was brominated as described above; yield 80%, b.p. 149–150° (1.2 mm.), $n^{26}\text{D}$ 1.5837.

Anal. Calcd. for $C_{12}H_{13}OBr$: C, 56.9; H, 5.2; Br, 31.6. Found: C, 56.9; H, 5.4; Br, 31.6.

α-Bromo-α-phenylpropionaldehyde.—From 13.4 g. of α-phenylpropionaldehyde 7 g. of the bromoaldehyde was obtained by the procedure described above; b.p. 86–87° (1 mm.), $n^{25}\text{D}$ 1.5620. Proper analytical figures for this somewhat unstable bromoaldehyde appear difficult to obtain.

Anal. Calcd. for C_9H_6OBr: Br, 37.5. Found: Br, 36.6.

Preparation of the Halo 2,4-Dinitrophenylhydrazones. (a).—Compounds IIbA, IIIbB, IVbA and IVbB, VbA and VIIbB were prepared from the corresponding α-halo ketones as previously described.[2a] The time allowed between precipitation of the α-halo-DNP and filtration varied somewhat in different cases and ranged between three and five hours. When this procedure was applied to 8-bromo-2,3-

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(1) From the Ph.D. thesis of A. F. Kirby. Presented at the Meeting-in-Miniature of the New York Section of the American Chemical Society, Brooklyn, New York, February 20, 1953.

(2) (a) F. Ramirez and A. F. Kirby, THIS JOURNAL, **74**, 4331 (1952). For previous work see: (b) V. R. Mattox and E. C. Kendall, *ibid.*, **70**, 882 (1948); (c) C. Djerassi, *ibid.*, **71**, 1003 (1949); (d) V. R. Mattox and E. C. Kendall, *ibid.*, **72**, 2290 (1950).

(3) The α-halo-DNP's reported in ref. 2a were obtained from the corresponding α-halo ketones. J. G. Aston and J. D. Newkirk (*ibid.*, **73**, 3901 (1951)), have just described the DNP of 4-chloro-3-heptanone and 2-chloro-3-heptanone. According to V. R. Mattox and E. C. Kendall (see ref. 2d) who first utilized the action of dinitrophenylhydrazine in acetic acid on steroidal bromoketones to introduce a double bond, bromination of the 3-DNP of methyl 3.11-diketo-12α-bromocholanate in chloroform leads to a rather unstable α-bromo-DNP.

(4) F. Ramirez and A. F. Kirby, THIS JOURNAL, **76**, Feb (1954).

(5) The microanalyses were carried out by Micro-Tech Laboratories, Skokie, Ill., and Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. The ultraviolet absorption spectra were taken in chloroform solution in a Cary Recording Spectrophotometer, Model 11, on the analytical samples. Infrared spectra were determined in approximately 3% chloroform solutions in a Baird Associates, Inc., spectrophotometer (sodium chloride prism, 0.1 mm. cell). For other curves, see ref. 4. When comparison among compounds was required, ultraviolet and infrared[4] absorption data as well as mixed m.p. were employed. All m.p. are uncorrected.

(6) L. Higginbotham, A. Lapworth and C. Simpson, *J. Chem. Soc.*, **125**, 2339 (1924).

(7) C. K. Bradsher and R. Rosher, THIS JOURNAL, **61**, 1524 (1939).

(8) W. S. Johnson and W. E. Shelberg, *ibid.*, **67**, 1745 (1945).

(9) (a) J. Horton and F. E. Walker, *ibid.*, **74**, 758 (1952); (b) P. L. Plattner, *Helv. chim. acta*, **27**, 801 (1944).

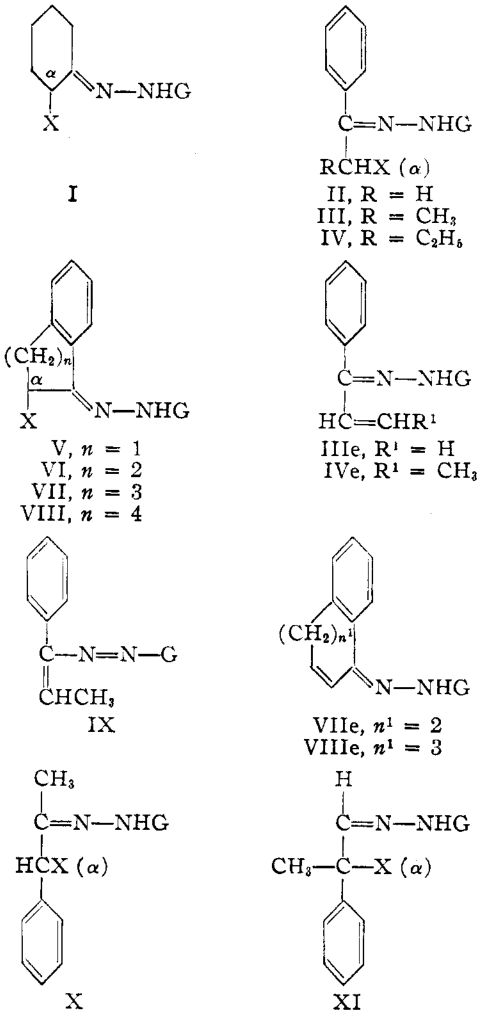
(10) *Cf.* D. S. Tarbell, H. F. Wilson and E. Ott, THIS JOURNAL, **74**, 6263 (1952).

(11) D. Papa, E. Schwenk and H. Hankin, *ibid.*, **69**, 3018 (1947).

(12) R. Huisgen and W. Rapp, *Ber.*, **85**, 826 (1952).

CHART I

In formulas below, G = 2,4$(NO_2)_2 \cdot C_6H_3$. Set a denotes X = H; b, X = Br; c, X = OCH_3; d, X = OAc. Series A and B as used in this paper refer to geometrical isomers about the C=N double bond. In series A the NHG and the α-carbon are considered to be on the same side of the C=N double bond (*syn*); in series B, on opposite sides (*anti*).



benzocycloöctene-2-one-1 no immediate precipitate appeared. The DNP which separated on standing overnight was found to be halogen free and appeared to be the methoxy-DNP.

IVbA and IVbB were separated by fractional crystallization, first using chloroform and then ethyl acetate as solvents. One isomer of α-bromoacetophenone DNP ("orange" m.p. 220°) was recently reported.[13] This is the form (IIbA, m.p. 212–213°) which precipitated when the above procedure was applied to α-bromoacetophenone.

In those cases in which the halogen is easily eliminated, better results are obtained by carrying out the reaction at ice-bath temperature (*cf.* 2-chlorocyclohexanone DNP). With the exception of 2-bromocyclohexanone DNP (which slowly deteriorates on standing) all the α-halo-DNP's prepared in this investigation appear to be stable when pure. The constants of these compounds are listed in Table II.

(b).—Compounds IIIbB, IVbB and VIIIbB were prepared from the corresponding DNP's (IIIaA, IVaA and VIIIa) by the following procedure: A stirred solution of the DNP in a chloroform–ether mixture (1:1 for IIIa and IVa, 1:4 for VIIIa) kept at room temperature (IIIa, IVa) or at 35–40° (VIIIa) was treated dropwise with a solution containing one equivalent of bromine in chloroform. After standing for an additional 15–20 minutes the solution was poured into an ice-water mixture and the organic layer collected, washed with water and dried. Removal of the solvent gave the corresponding halo hydrazone (see Table II).

TABLE I

2,4-Dinitrophenylhydrazone of	λ_{max}, mμ[a]	ε × 10^{-4} (chl.)
Acetophenone (IIaA)	378^{o-r}	2.66
α-Bromoacetophenone (IIbA)	377^{y-o}	2.66
α-Bromoacetophenone (IIbB)	362^{y}	2.63
	258	1.30
α-Acetoxyacetophenone (IIdA)	375^{o-y}	2.62
Propiophenone (IIIaA)	378^{r}	2.67
α-Bromopropiophenone (IIIbB)	362^{y}	2.60
	258	1.25
α-Methoxypropiophenone (IIIcA)	383^{o}	2.81
α-Methoxypropiophenone (IIIcB)	362^{y}	2.47
	258	1.36
α-Phenylacetone (Xa)	362^{y}	2.28
α-Phenyl-α-methoxyacetone (XcB)	359^{y}	2.31
α-Phenylpropionaldehyde (XIa)	357^{y}	2.31
α-Phenyl-α-methoxypropionaldehyde (XIcB)	353^{y}	2.32
Phenyl vinyl ketone (IIIe)	383^{o-r}	2.78
Butyrophenone (IVaA)	380^{o-r}	2.67
α-Bromobutyrophenone (IVbA)	373^{y}	2.53
α-Bromobutyrophenone (IVbB)	362^{o-y}	2.62
	260	1.19
α-Methoxybutyrophenone (IVcA)	383^{o-y}	2.83
α-Methoxybutyrophenone (IVcB)	362^{y}	2.48
	258	1.33
Phenyl propenyl ketone (IVe)	386^{r-o}	2.87
1-Indanone (VaA)	386^{o-r}	3.02
2-Bromo-1-indanone (VbA)	387^{o}	3.02
2-Methoxy-1-indanone (VcA)	390^{o}	3.27
2-Acetoxy-1-indanone (VdA)	384^{o}	3.08
1-Tetralone[b] (VIaA)	385^{r}	2.86
2-Bromo-1-tetralone[b] (VIbA)	387^{o}	2.88
2-Methoxy-1-tetralone[b] (VIcA)	389^{y-o}	3.10
2-Acetoxy-1-tetralone (VIdA)	384^{o}	2.87
Benzosuberone (VIIaA)	372^{o-r}	2.57
Benzosuberone (VIIaB)	369^{y}	2.35
	258	1.20
2-Bromobenzosuberone (VIIbB)	364^{y}	2.65
	258	1.10
2-Methoxybenzosuberone (VIIcB)	364^{y}	2.55
	258	1.30
2-Acetoxybenzosuberone (VIIdA)	367^{o}	2.43
2-Acetoxybenzosuberone (VIIdB)	363^{y}	2.25
	258	1.15
Benzosuber-2-ene-1-one (VIIe)	380^{r}	2.73
2,3-Benzocycloöctene-2-one-1 (VIIIa)	366^{y}	2.49
8-Bromo-2,3-benzocycloöctene-2-one-1 (VIIIbB)	362^{y}	2.67
	259	1.17
8-Methoxy-2,3-benzocycloöctene-2-one 1 (VIIIcB)	360^{y}	2.43
	255	1.19
2,3-Benzocycloöctadiene-2,7-one-1 (VIIIe)	386^{r}	2.95
2-Acetoxycyclohexanone (Id)	358^{y}	2.24
1-Phenyl-1-(2′,4′-dinitrophenylazo)-propene-1 (IX)	305^{o-y}	0.67
	413	2.86

[a] r = red; y = yellow; o = orange (crushed crystals). [b] Reference 2a.

Isomerization of Halo 2,4-Dinitrophenylhydrazones.—A solution of 900 mg. of IIbA (m.p. 212–213°, λ_{max} 377 mμ) in 90 ml. of acetic acid was concentrated over a period of 15 minutes to a final volume of 5 ml. Upon cooling in ice, 730 mg. of orange crystals precipitated and were removed by filtration (starting material). The filtrate was diluted

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[13] G. D. Johnson, THIS JOURNAL, **73**, 5888 (1951).

TABLE II

			Analyses, %							
			Calcd.				Found			
Compound	M.p., °C.	Formula	C	H	N	Br	C	H	N	Br
IIbB	127–128[a]	$C_{14}H_{11}O_4N_4Br$			14.7				14.2	
IIdA	184–185[a]	$C_{16}H_{14}O_6N_4$	53.6	3.9	15.6		53.7	4.0	15.5	
IIIbB	160–161[a]	$C_{15}H_{13}O_4N_4Br$	45.8	3.3	14.2	20.3	45.6	3.4	14.0	20.1
IIIcA	163–164[b]	$C_{16}H_{16}O_5N_4$	55.8	4.7	16.3		56.0	4.8	16.1	
IIIcB	133–134[b]	$C_{16}H_{16}O_5N_4$	55.8	4.7	16.3		55.8	4.7	16.1	
XcB	136–137[c]	$C_{16}H_{16}O_5N_4$	55.8	4.7	16.3		56.1	4.7	16.3	
XIa	136–137[b]	$C_{15}H_{14}O_4N_4$			17.8				17.6	
XIcB	149–150[b]	$C_{16}H_{16}O_5N_4$	55.8	4.7	16.3		55.7	4.8	16.4	
IIIe	195–196[b]	$C_{15}H_{12}O_4N_4$	57.7	3.9	17.9		57.9	4.1	18.0	
IVaA	192–193[d]	$C_{16}H_{16}O_4N_4$			17.1				16.8	
IVbA	140–141[a]	$C_{16}H_{15}O_4N_4Br$	47.2	3.7	13.8	19.6	47.0	3.9	13.9	20.0
IVbB	135–136[a]	$C_{16}H_{15}O_4N_4Br$	47.2	3.7	13.8	19.6	47.2	3.9	13.7	19.4
IVcA	131–133[c]	$C_{17}H_{18}O_5N_4$	57.0	5.1			57.4	5.5		
IVcB	134–136[b]	$C_{17}H_{18}O_5N_4$	57.0	5.1	15.6		57.2	5.0	15.5	
IVe	211–212[a]	$C_{16}H_{14}O_4N_4$	58.9	4.3	17.2		58.8	4.5	17.3	
VbA	205–206[e]	$C_{15}H_{11}O_4N_4Br$	46.1	2.8	14.3	20.4	46.1	2.9	14.2	20.3
VcA	248[f] dec.	$C_{16}H_{14}O_5N_4$	56.1	4.1			56.2	4.2		
VdA	231–232[a]	$C_{17}H_{19}O_6N_4$	55.1	3.8			55.4	3.8		
VIdA	186–187[a]	$C_{18}H_{16}O_6N_4$	56.2	4.2	14.6		56.1	4.3	14.5	
VIIaA[i]	211–212[f]	$C_{17}H_{16}O_4N_4$	60.0	4.7	16.4		60.1	4.7	16.1	
VIIaB	197–198[b]	$C_{17}H_{16}O_4N_4$			16.4				16.0	
VIIbB	187–188[a]	$C_{17}H_{15}O_4N_4Br$	48.7	3.6	13.4	19.1	49.4[g]	3.8	13.2	18.0
VIIcB	206–207[b]	$C_{18}H_{18}O_5N_4$	58.4	4.9	15.1		58.4	4.8	15.1	
VIIdA	212–213[a]	$C_{19}H_{18}O_6N_4$	57.3	4.5	14.1		57.2	4.7	13.5	
VIIdB[j]	213–214[a]	$C_{19}H_{18}O_6N_4$	57.3	4.5	14.1		57.1	4.3	14.1	
VIIe	218–129[a]	$C_{17}H_{14}O_4N_4$			16.6				16.4	
VIIIbB	171–172[a]	$C_{18}H_{17}O_4N_4Br$	49.9	4.0		18.4	50.3	4.3		18.1
VIIIcB	140–141[a]	$C_{19}H_{20}O_5N_4$	59.4	5.2	14.6		59.7	5.4	14.6	
VIIIe	179–180[a]	$C_{18}H_{16}O_4N_4$	61.4	4.6	15.9		61.7	4.6	15.5	
Id	167–168[h]	$C_{14}H_{16}O_6N_4$	50.0	4.8			49.7	4.6		
IX	217–218[a]	$C_{15}H_{12}O_4N_4$	57.7	3.9	17.9		57.3	3.8	17.9	

[a] Solvent, ethyl acetate. [b] Solvent, ethyl acetate–methanol. [c] Solvent, methanol. [d] Solvent, chloroform. [e] Solvent, chloroform–ethyl acetate. [f] Solvent, chloroform–methanol. [g] Best analytical figures obtained in three samples. No satisfactory solvent could be found for this compound. [h] Solvent, ethanol. [i] *Cf.* ref. 12 in which the m.p. is given as 205.5–206.5° and λ_{max} as 375 mμ (ε 26900). [j] Mixed m.p. with VIIdA, 195–200°.

with 40 ml. of chloroform and the solution was washed with water. The chloroform solution was concentrated to a volume of 2 ml. followed by addition of 2-ml. portions of ethyl acetate and water and 6 ml. of methanol. The yellow precipitate so obtained (135 mg.) melted at 119–122° and absorbed at 262 mμ (IIbB). IIbB was easily converted into IIbA in hot methanol containing a drop of hydrochloric acid. (The use of methanol is possible here since the bromine of IIb is not replaced in methanol solution). IVbA was converted into IVbB in boiling chloroform (2.5 hours reflux) containing a drop of hydrochloric acid. Pure IIbB melted at 127–128°, the melt resolidified and remelted at 212°. A mixture of IVbA and IVbB melted at 133–135°. Thus, interconversion on heating appears to take place among the isomeric bromo-DNP's.

2,4-Dinitrophenylhydrazones.—The following previously described DNP's were prepared from the corresponding ketones by the action of the Brady reagent[14] (a solution of 2,4-dinitrophenylhydrazinium sulfate in aqueous methanol containing excess sulfuric acid). DNP of: acetophenone, m.p. 247–249° (ethyl acetate), reported[15a] m.p. 249°; phenylacetone, m.p. 154–155° (chloroform–ethanol), reported[15b] m.p. 155.5–156.5°; propiophenone, m.p. 193–194° (ethyl acetate), reported[16] m.p. 187–189°; indanone, m.p. 263° (chloroform–methanol), reported[17] m.p. 265°, 258°; 2,3-benzo-cycloöctene-2-one-1, m.p. 179–180° (ethyl acetate), reported[12] m.p. 176–177.5°, λ_{max} 367 mμ; ε 2.52 × 10^4. Data for new compounds are reported in Table II.

Elimination Reactions. (a).—The behavior of the halo-DNP's in acetic acid was observed as described previously.[2] In this way it was established that IIIbB, IVbA, IVbB and VIIIbB eliminated hydrogen bromide smoothly to give IX, IVe and VIIIe, respectively, while VIIbB underwent considerable decomposition which permitted the isolation of only very small amounts of VIIe. IIbA and VbA were recovered unchanged under similar conditions. The constants of the unsaturated hydrazones are included in Table II.

(b).—When solutions of the halo hydrazones IIIbB and IVbB in methanol containing fused potassium acetate (*ca.* 0.2%) were kept at their respective boiling points for 15 minutes the corresponding α,β-unsaturated hydrazones (IIIe and IVe) resulted. IIIe and IIIaA exhibited no mixed m.p. depression although ultraviolet and infrared[4] absorption data clearly showed their non-identity in solution. IVe and IVaA showed mixed m.p. depression.

IX was recovered unchanged from a methanolic solution containing potassium acetate treated as in (b) above; IX was not converted into IIIe on heating in acetic acid, alone or containing some iodine. Attempts to interconvert IX and IIIe by prolonged irradiation with ultraviolet light were unsuccessful; the solutions lost their color but no isomerization could be detected. IIIe could not be converted into IX upon heating in acetic acid alone, or containing hydrogen bromide or iodine.

Methanolysis of the Halo Hydrazones.—A solution of the halo hydrazone in methanol was heated for periods of time[18] indicated below and the halogen-free mixture which precipitated upon partial removal of the solvent was either recrystallized or separated by fractional crystallization using

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(14) O. L. Brady, *J. Chem. Soc.*, 757 (1931).

(15) (a) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945); (b) W. D. McPhee and E. Klingsberg, THIS JOURNAL, **66**, 1132 (1944).

(16) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 2607 (1932).

(17) (a) R. Seka and W. Kellermann, *Ber.*, **75B**, 1730 (1942); (b) C. F. H. Allen, THIS JOURNAL, **52**, 2955 (1930).

(18) When the α-halo ketone is of the cyclohexanone-type best results are obtained on short (3–5 minutes) methanolyses (*cf.* ref. 2a).

the solvents indicated. From IIIbB after 90 minutes: *ca.* 50% of IIIcA (prisms from ethyl acetate–methanol) and *ca.* 13% of IIIcB (plates from ethyl acetate–methanol).[19] IIIcA was recovered unchanged from a solution in methanol containing few drops of concentrated hydrochloric acid (3 hours at the boiling point); under similar conditions IIIcB was converted into IIIcA. From IVbB after 25 minutes: mostly IVcA (plates from methanol) and some IVcB (needles from ethyl acetate–methanol) was obtained. IVcB was converted into IVcA in hot methanol solution containing a few drops of hydrochloric acid (3 hours at the boiling point).

From VbA, VIIbA and VIIIb only one isomeric methoxy hydrazone could be obtained. IIbA was recovered unchanged under similar conditions.

Acetolysis of the Halo Hydrazones. (**a**).—2-Chlorocyclohexanone DNP[2a] (250 mg.) was dissolved in acetic acid containing fused sodium acetate (*ca.* 1%) and the solution kept at 60° for 25 minutes. The only product isolated after the usual work-up was the acetoxy DNP (Id) (130 mg.).

(**b**).—A solution of VIIb in acetic acid containing sodium acetate was refluxed for 15 minutes and the two resulting acetoxy DNP's (VIIdA and VIIdB) were separated using ethyl acetate as the solvent. A similar procedure gave VdA from VbA and VIdA from VIbA.

(**c**).—VIdA was obtained also when a solution of VIbA in acetic anhydride–acetic acid (5:1) was refluxed for 20 minutes or when a solution of VIbA in acetic acid containing fused zinc chloride was refluxed for 30 minutes. Zinc chloride in dioxane solution seemed to have no action on VIb. From IIbA, acetic acid and zinc chloride, IIdA was obtained after 40 minutes reflux. The constants of these compounds are included in Table II. Attempts to prepare acetoxy DNP's from IIIb and IVb led to dehydrohalogenation.

α-Phenyl-α-methoxypropionaldehyde DNP (XIcB).—This was prepared directly from the bromoaldehyde in methanolic solution containing 2,4-dinitrophenylhydrazine hydrochloride (see Table II). XIcB was clearly different from either IIIcA or IIIcB of the same empirical formula.

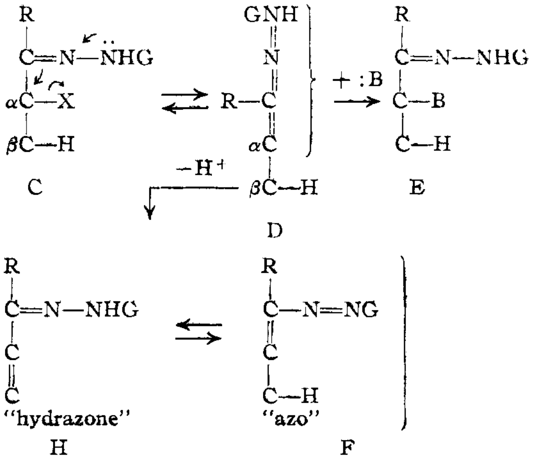
α-Phenyl-α-methoxyacetone DNP (XcB).—α-Phenyl-α-methoxyacetone (semicarbazone, m.p. 157–158°, reported[20] m.p. 157–158°) was prepared from α-bromopropiophenone by the procedure described by v. Auwers.[20] The DNP was prepared using the Brady reagent (see Table II). XcB was different from either IIIcA or IIIcB of the same empirical formula.

Phenyl Vinyl Ketone.—Prepared as previously described.[21] The 1,3-diphenyl-2-pyrazoline obtained from phenyl vinyl ketone by the action of phenylhydrazine in acetic acid solution melted at 154–155°, $\lambda_{\max}^{\text{Chl.}}$ 361 mμ, ϵ 1.86 × 10^4; reported[21,22] m.p. 154–155°. The action of 2,4-dinitrophenylhydrazine in acetic acid solution on phenyl vinyl ketone gave mixtures not investigated further. When an ice-cold solution of phenyl vinyl ketone in methanol was treated with the Brady reagent a precipitate was rapidly formed. This precipitate was immediately filtered off and from it, after several recrystallizations from ethyl acetate, small amounts of a substance found to be identical with IIIe could be isolated.

Color Reactions with Methanolic Potassium Hydroxide.—Most of the substances isolated were tested with 2% methanolic potassium hydroxide. A purple-red color was observed in all cases with the exception of IX whose solution showed no color change.

Results and Discussion

The action of carbonyl reagents such as 2,4-dinitrophenylhydrazine (DNPH) on α-halo ketones appears to involve the formation of an intermediate, *viz.*, an α-halo-DNP. In the present study the α-halo-DNP's were isolated and their behavior examined under several experimental conditions. The following scheme, which does not necessarily imply classification into a fixed mechanistic category[23] and which is essentially based on an earlier suggestion of Mattox and Kendall[2d] seems capable of accommodating the results described here and in Part I. As with other replacement and elimination reactions, the scheme is to be considered in connection with the "solvent" in which the behavior of the α-halo-DNP's is examined.[23]



That the halogen in those α-halo-DNP's whose geometry does not interfere with the coplanarity requirements implicit in formula D exhibit a remarkable lability in solvents such as acetic acid appears amply demonstrated. Thus, α-halo-DNP's of such varied structure as 2-bromocyclohexanone DNP (Ib), α-bromopropiophenone DNP (IIIb), α-bromobutyrophenone DNP (IVb) and 8-bromo-2,3-benzocycloöctene-2-one-1 (VIIIb) lost hydrogen halide smoothly in hot acetic acid. On the other hand 2-bromo-1-indanone DNP (Vb) and 2-bromo-1-tetralone DNP (VIb), which possess electronic features (aromatic ring conjugated to the hydrazone group) common to IIIb, IVb and VIIIb were recovered unchanged on heating in acetic acid. Examination of Fisher–Hirshfelder–Taylor atom models of these structures suggests that the difference in reactivity between the α-halo-DNP's in acetic acid might be partly due to steric effects (affecting the resonance stabilization depicted in D) associated with the size and geometry of the alicyclic ring fused onto the benzene ring.[24]

The competition between elimination and replacement suggested in the above scheme is substantiated by the isolation of 2-acetoxycyclohexanone DNP (Ib) when sodium acetate was added to the acetic acid solution of 2-chlorocyclohexanone DNP at 60°; at higher temperatures or in the absence of sodium acetate elimination is the predominant reaction. Addition of (a) sodium acetate, (b) acetic anhydride or (c) zinc chloride to an acetic acid solution of 2-bromo-1-tetralone DNP (VIb) resulted in replacement of the halogen and formation of 2-acetoxy-1-tetralone DNP (VId) (*cf.* conversion of 2-bromo-1-indanone DNP (Vb) into 2-acetoxy-1-indanone DNP (Vd)). In dioxane as

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[19] These figures are rough ones based on isolated material of sharp m.p. and do not intend to represent relative proportion of isomers in equilibrium in solution.

[20] K. v. Auwers, H. Ludewig and A. Muller, *Ann.*, **526**, 143 (1936).

[21] W. G. Young and J. D. Roberts, This Journal, **68**, 649 (1946).

[22] K. v. Auwers, *Ber.*, **65**, 831 (1932).

[23] C. G. Swain and W. P. Langsdorf, Jr., This Journal, **73**, 2813 (1951).

[24] For a discussion of the geometry of tetrahydronaphthalene and its bearing on the infrared spectra of *cis-* and *trans-*1,2-diols, see L. P. Kuhn, *ibid.*, **74**, 2492 (1952).

a solvent zinc chloride appeared to exert no effect on 2-bromo-1-tetralone DNP (VIb).[25]

With one exception (α-bromoacetophenone DNP (IIb)) the halogen in all the α-halo-DNP's studied[26] could be replaced by a methoxyl group upon short boiling in methanol.[27] From the above considerations it appears that the push–pull effect[23] presumably involved in methanolysis is capable of effecting the replacement in all the secondary halo-DNP's studied. A more effective push or pull (acetate ion or zinc chloride, respectively) seems, however, necessary for replacement of halogen by acetoxyl group in acetic acid solution. In acetic acid alone, elimination, not replacement, was observed and this only in those relatively more reactive α-halo-DNP's already mentioned.

The scheme shown above suggests that in acetic acid the rapid removal of a proton from D might first yield the unsaturated azo compound[28] F which would then—presumably under the influence of hydrogen halide and subject to thermodynamic considerations—tautomerize to the unsaturated hydrazone H. Ultraviolet and infrared absorption spectra substantiate the α,β-unsaturated hydrazone structure of the products isolated from acetic acid in all cases but one. The exception referred to was found in the reaction of α-bromopropiophenone DNP (IIIb) in hot acetic acid. The resulting substance IX of empirical formula $C_{15}H_{12}O_4N_4$, showed an abnormal spectrum in the ultraviolet with maxima at 305 and 413 mμ unlike any of the substituted or unsubstituted DNP's isolated in this study. Although no directly comparable model was at hand the recorded observations on the ultraviolet absorption spectra of azo compounds[29] point to an α,β-unsaturated azo structure for IX.[30,31] The infrared spectra of the dinitrophenylhydrazones studied exhibited bands at 3.0, 6.18 and 6.25 μ; the spectrum of IX, however, showed no N–H stretching band at 3.0 μ and a marked weakening of the 6.25 μ band relative to the 6.18 μ band, which seems consistent with the azo structure shown.[32]

Acknowledgment.—We thank the Eli Lilly Co., Indianapolis, Ind., for financial assistance in this work.

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[25] V. R. Mattox and E. C. Kendall (*J. Biol. Chem.*, **185**, 601 (1950)), have reported the isolation of appreciable amounts of the 4-acetoxyhydrazone on treatment of methyl 3,11-diketo-4,12-α-dibromocholanate with 2,4-dinitrophenylhydrazine in acetic acid containing large excess of sodium acetate or pyridine.

[26] As reported elsewhere (F. Ramirez and R. J. Bellet, THIS JOURNAL, **76**, Jan. (1954): 2-bromocyclobutanone DNP can be recovered unchanged from hot acetic acid or methanolic solutions.

[27] The methanolyses of *anti*-α-bromopropiophenone DNP (IIIbB) and of *anti*-α-bromobutyrophenone DNP (IVbB), which represent the more stable form of the respective isomeric pairs, gave mixtures of stereoisomeric α-methoxy DNP's. On the basis of interconversions among isomers it appears that members of the A-series (*syn*) are more stable than members of the B-series (*anti*) among α-methoxy DNP's. The same is true for *syn*- and *anti*-α-bromoacetophenone DNP's. These observations are consistent with the geometry of the molecules as revealed by atom models.

[28] Working in the 3-keto-4-bromosteroid series with *p*-nitrophenylhydrazine, W. F. McGuckin and E. C. Kendall (*ibid.*, **74**, 5811 (1952)), have recently mentioned the isolation of a "highly colored. . . α,β-unsaturated azo structure" for which details are promised.

[29] W. R. Brode, J. H. Gould and G. M. Wyman, *ibid.*, **75**, 1856 (1953).

[30] An α,β-unsaturated azo structure ($C_2H_5O_2C—CH=C(CH_3)—N=N—C_6H_4 \cdot NO_2$-*p*) has been assigned (J. van Alphen, *Rec. trav. chim.*, **64**, 305 (1945) to the product isolated from the action of *p*-nitrophenylhydrazine on ethyl α-chloroacetoacetate.

[31] A pyrazoline structure for IX was excluded since phenyl vinyl ketone DNP (IIIe) prepared in two ways (see experimental) was found to be stable in acetic acid solution. Pyrazolines have been postulated, without proof, in several instances involving dinitrophenylhydrazine and α,β-unsaturated ketones (G. Morgan and C. F. Griffith, *J. Chem. Soc.*, 841 (1937); C. F. H. Allen and J. H. Richmond, *J. Org. Chem.*, **2**, 222 (1937)).

[32] *Cf.* R. J. W. LeFevre, M. F. O'Dwyer and R. L. Werner, *Chemistry and Industry*, 378 (1953).

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Derivatives of Sulfenic Acids. XIII. The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with Styrene[1]

BY WILSON L. ORR AND NORMAN KHARASCH

RECEIVED JUNE 8, 1953

The structure of the adduct of 2,4-dinitrobenzenesulfenyl chloride to styrene is shown by alternate synthesis to be 2-chloro-2-phenylethyl 2′,4′-dinitrophenyl sulfide. This is in accord with the anticipated structure, assuming ionic addition of the sulfenyl chloride, $(NO_2)_2C_6H_3S\delta^+Cl\delta^-$. Formation of the adduct in dry acetic acid follows the rate expression $-dArSCl/dt = k[ArSCl][styrene]$; Ar = 2,4-dinitrophenyl. The reaction is homogeneous, is not sensitive to ordinary illumination, and shows a positive salt effect with lithium chloride and sodium perchlorate. Values of k (min.$^{-1}$) at 25, 35 and 45°, respectively, were 0.0442, 0.0889 and 0.174, corresponding to $E_a = 12.9 \pm 0.3$ kcal./mole. The rate of disappearance of ArSCl was followed by an iodimetric method, within the accuracy of which (*ca.* 1%), the addition of ArSCl to styrene is quantitative. The rate of addition in acetic acid is very much greater than in carbon tetrachloride. The kinetic data are consistent with the postulation that the addition of ArSCl to olefins involves initial formation of a cyclic sulfonium ion, followed by addition of Cl^- to yield the β-chloro sulfide. The formation of the cyclic ion is considered to be the most likely rate-determining step.

Introduction

In other papers of this series[2] the reaction of sulfenyl halides with olefins and alkynes has been described, with particular emphasis on the use of 2,4-dinitrobenzenesulfenyl chloride (I) for the characterization of these substances. Since this reaction is of general interest, investigations concern-

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[2] (a) N. Kharasch, H. L. Wehrmeister and H. Tigerman, THIS JOURNAL, **69**, 1612 (1947); (b) N. Kharasch and C. M. Buess, *ibid.*, **71**, 2724 (1949); (c) N. Kharasch, C. M. Buess and S. I. Strashun, *ibid.*, **74**, 3422 (1952); (d) N. Kharasch and S. J. Assony, *ibid.*, **75**, 1081 (1953).