The hydrolytic cleavage of polydimethylglyoxime carbonate was carried out in an identical fashion except that the isolation procedure was modified to allow for the identification of carbon dioxide. Before acidification of the reaction mixture the flask was swept with nitrogen and, upon acidification, nitrogen was bubbled through the reaction mixture and the gases conducted through two gas wash bottles filled with freshly prepared barium hydroxide solution. Barium carbonate was precipitated. After precipitation ceased to occur in the gas wash bottles, the reaction mixture was worked up as previously described to identify the α-dioximes.

Physical characterization methods. Cryoscopic molecular weights were measured in a Beckmann apparatus and ebulloscopic molecular weights were measured in a Cottrell apparatus. Infrared spectra were taken in nujol mulls or potassium bromide pellets. The infrared spectra of the polymers showed end group hydroxyl absorption (3.15–3.25 μ), low carbonyl absorption (5.6–5.7 μ), imino absorption (6.02–6.25 μ), and ether type $(-\overset{|}{\underset{/\,|}{C}}-O-N=)$ absorption (8.675–9.2 μ). This combination of bands was not present in the glyoximes or the parent fatty dibasic acids. Infrared spectra of polymers having the same structure but different average molecular weights varied slightly in the intensity of the absorbance bands characteristic of the functions present.

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WILMINGTON, DEL.

[CONTRIBUTION FROM THE PESTICIDES RESEARCH AND DEVELOPMENT DEPARTMENT, OLIN MATHIESON CHEMICAL CORP.]

The Preparation of α-Haloaldehyde 2,4-Dinitrophenylhydrazones

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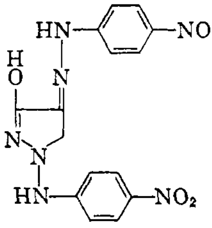
α-Halogenated aldehydes react anomalously with the usual 2,4-dinitrophenylhydrazine reagents to give halogen-free products. It has now been found that a solution of 2,4-dinitrophenylhydrazine in concentrated hydrochloric acid (6*N* to 12*N*), as solvent, will give normal hydrazones with α-haloaldehydes. Some new α-haloaldehyde 2,4-dinitrophenylhydrazones are reported.

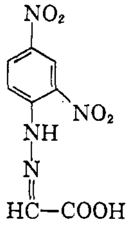
α-Halogenated aldehydes and ketones are known to react anomalously with substituted phenylhydrazines. Thus, in a study of the reaction of α-haloketones with 2,4-dinitrophenylhydrazine, Ramirez and Kirby[3] report dehydrohalogenation, replacement of the halogen by anions from the solvent (*e.g.* acetoxy from acetic acid, methoxy from methanol), and even conversion to the vicinal 2,4-dinitrophenylosazones.

Chattaway and Farinholt[4] report that dichloroacetaldehyde is converted to the glyoxal phenylosazone when treated with phenylhydrazine. We obtained the analogous osazone when treating dichloroacetaldehyde with the usual 2,4-dinitrophenylhydrazine reagents.

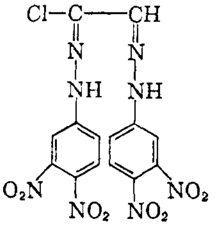
Stepanow and Kusin[5] report that chloral reacts with *p*-nitrophenylhydrazine to give a product without chlorine, for which they propose a pyrazolone structure (I). On the other hand in treating-chloral with 2,4-dinitrophenylhydrazine, Torres and Brosa[6] report obtaining only the glyoxylic acid 2,4-dinitrophenylhydrazone (II) and the chloroglyoxal bis-2,4-dinitrophenylhydrazone (III).



I



II



III

We were interested in the preparation of the 2,4-dinitrophenylhydrazones of several α-chlorinated aldehydes and ketones and particularly that of chloral. The melting point of this compound, listed as 131° in Shriner and Fuson[7] and in Vogel,[8] is probably attributable to Roduta and Quibilan[9] who claim its preparation in an acidified methanolic solution of 2,4-dinitrophenylhydrazine. We attempted the preparation of chloral 2,4-dinitrophenylhydrazone with a similar reagent, and also in anhydrous methanol, using dry hydrogen chloride as catalyst. The only product we succeeded in isolating was a chlorine-free com-

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[3] F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **74**, 4331 (1952); **75**, 6026 (1953).

[4] F. D. Chattaway and L. H. Farinholt, *J. Chem. Soc.*, 96 (1930).

[5] A. Stepanow and A. Kusin, *Ber.*, **65B**, 1239 (1952).

[6] C. Torres and S. Brosa, *Anales soc. españ. fís. y quím.*, **32**, 509 (1934); *Chem. Abstr.*, **28**, 6104 (1934).

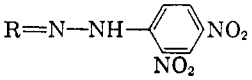
[7] R. L. Shriner and R. C. Fuson, *A Systematic Identification of Organic Compounds*, John Wiley and Sons, N. Y., 1948, p. 229.

[8] A. I. Vogel, *Practical Organic Chemistry*, Longmans, Green and Company, New York, 1948, p. 332.

[9] F. L. Roduta and G. Quibilan, *Rev. filipina med. y farm.*, **27**, 123 (1936).

TABLE I

α-HALOALDEHYDE 2,4-DINITROPHENYLHYDRAZONES

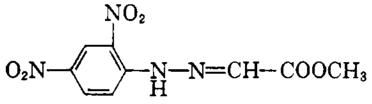


$$R{=}N{-}NH{-}C_6H_3(NO_2)_2$$

R	Yield, %	M.P.	Reported M.P.	Chlorine, % Calcd.	Chlorine, % Found
$ClCH_2CH$	98	158.5–160.5	158[a]	..	..
$BrCH_2CH$	64	157–158	155–157[b]	..	..
Cl_2CHCH	82	146	..	24.2	24.6
Cl_3CCH	84	152–158	152–153[c]	32.5	31.7
$ClCH_2CHCl{-}CH$[d]	83	118–118.5	..	23.1	22.7
$ClCH_2CCl_2{-}CH$	60	117–117.5	..	31.1	31.0
$CH_3CH_2CHClCH$	46	93–94	124 (?)[e]	12.6	12.1
Trinitrophenylhydrazone					
	64	159–160	..	11.7	11.6

[a] Meisenheimer and Schmidt, *Ann.*, **475**, 182 (1929). [b] G. T. Newbold, *J. Chem. Soc.*, 3346 (1950). [c] See Ref. (10). [d] This compound was prepared from 2,3-dichloropropionaldehyde and from 2-chloroallylidene diacetate, see Experimental. [e] A. Krallinger, *Bull. Soc. Chim. France*, 22 (1953).

pound whose analysis agrees with that calculated for methyl glyoxalate 2,4-dinitrophenylhydrazone (IV).



IV

This product can readily be explained by the methanolysis of the desired chloral 2,4-dinitrophenylhydrazone or an intermediate. In other experiments in which alcoholic solutions containing hydrochloric or sulfuric acids were used, only chlorine-free products were isolated. The desired chloral 2,4-dinitrophenylhydrazone was finally obtained when concentrated hydrochloric acid (6*N* to 12*N*) was used as solvent. Two factors dictated the use of this solvent. (1) Assuming that the desired chloral 2,4-dinitrophenylhydrazone formed initially, and then underwent reaction with the solvent (*e.g.* methanolysis), a solvent in which this initial product is almost completely insoluble was sought. Water seemed to fill this requirement. (2) The 2,4-dinitrophenylhydrazine is a weak base and is quite insoluble in water or dilute acid. By raising the acid strength to 6*N* or higher, sufficient reagent could be dissolved to carry out the desired reaction. The product obtained from this concentrated acid solvent melted at 152–158° and showed 31.7% chlorine by analysis (required—32.5%). A careful check of the literature revealed that Crane, Forrest, Stephenson, and Waters[10] had isolated the same product (m.p. 152–153, per cent Cl = 31.8%) under similar conditions while trying to identify products of another reaction.

The concentrated acid technique was extended to the preparation of other sensitive α-haloaldehydes. It was also used to prepare the 2,4-dinitrophenylhydrazones of α-haloketones, but these are, in general, more stable and can be prepared by more convenient, standard techniques. In some cases where both methods work, the strong acid procedure gives greater purity of crude product together with high yield. The preparation of chloroacetaldehyde 2,4,6-trinitrophenylhydrazone illustrates the use of this procedure on other derivatives. The compounds prepared by this strong acid technique are listed in Table I. Wherever a previous preparation has been reported, the melting point and reference are given.

EXPERIMENTAL

Chloroacetaldehyde 2,4-dinitrophenylhydrazone. Chloroacetaldehyde (39.2 g. of a 40% aqueous solution) (0.20 mole) was added with stirring to a solution of 19.8 g. (0.10 mole) of 2,4-dinitrophenylhydrazine in 1500 ml. of 3*N* hydrochloric acid maintained at 40°. After cooling to room temperature, the precipitated product was filtered, washed with water to remove all acid, and dried, yielding 25.4 g. (98% yield) of chloroacetaldehyde 2,4-dinitrophenylhydrazone as an orange-yellow powder, m.p. 158.5–160.5°, (previously reported, m.p. 158°, Table I, ref. *a*).

Bromoacetaldehyde 2,4-dinitrophenylhydrazone. A solution of 5.00 g. of 2,4-dinitrophenylhydrazine (0.0255 mole) in 600 ml. of 12*N* hydrochloric acid was slowly added at room temperature to a rapidly stirred mixture of 5.05 g. of bromoacetaldehyde diethylacetal (0.0255 mole) in 100 ml. of the same solvent. The yellow solid which separated was vacuum filtered and washed with petroleum ether (b.p. 65–110°). The crude product (6.1 g.; 64.2% yield; m.p. 152.5–154.0°) was washed with methanol, leaving orange-yellow crystals of bromoacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 155.8–157.0°. Recrystallization from anhydrous ether

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[10] C. W. Crane, J. Forrest, O. Stephenson, and W. A. Waters, *J. Chem. Soc.*, 829 (1946).

raised the melting point to 157.0–158.0°, (previously reported m.p. 155–157°, Table I, ref. *b*.).

Dichloroacetaldehyde 2,4-dinitrophenylhydrazone. Freshly distilled dichloroacetaldehyde (33.9 g., 0.30 mole) was slowly added with stirring to a solution of 50.0 g. (0.25 mole) of 2,4-dinitrophenylhydrazine in 2600 ml. of 12*N* hydrochloric acid at 30°. The precipitated product was filtered and washed repeatedly with water until the filtrate was free of chloride ion. The crude product (60.1 g., 82%) melted at 143.5–144.5° and was contaminated by a trace of higher melting orange material (probably the bis-2,4-dinitrophenylhydrazone of glyoxal). Recrystallization from carbon tetrachloride gave yellow-orange needles of dichloroacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 146°.

Anal. Calcd. for $C_8H_6Cl_2N_4O_4$: Cl, 24.20. Found: Cl, 24.59.

Chloral 2,4-dinitrophenylhydrazone. A solution of 50.0 g. (0.252 mole) of 2,4-dinitrophenylhydrazine in 3 l. of 12*N* hydrochloric acid at 45° was slowly added to a stirred solution of 81.72 g. (0.494 mole) of chloral hydrate in 100 ml. of the same solvent. During the 1-hr. addition period, the maximum reaction temperature was 38°. After stirring for an additional hour, the mixture was chilled. The yellow solid product was filtered, washed with distilled water until the filtrate was free of chloride ion, and dried, yielding 69.1 g. (83.7% yield) of yellow crystalline chloral 2,4-dinitrophenylhydrazone, m.p. 152–158°. (A m.p. of 152–153° has previously been reported.)

Anal. Calcd. for $C_8H_5Cl_3N_4O_4$: Cl, 32.5. Found: Cl, 31.7.

2,3-Dichloropropionaldehyde 2,4-dinitrophenylhydrazone. From 2-chloroallylidene diacetate. A solution of 5.0 g. (0.025 mole) of 2,4-dinitrophenylhydrazine in 600 ml. of 12*N* hydrochloric acid was slowly added to a solution of 9.6 g. (0.050 mole) of 2-chloroallylidene diacetate in 10 ml. of the same solvent at 25°. As soon as the addition was completed, the precipitated product was filtered and washed with water until the filtrate was free of chloride ion. Orange-yellow solid (4.2 g.) was obtained, m.p. 111° dec. On standing, a second crop of 0.7 g. of similar material, m.p. 117.8 dec., was obtained. Both crops gave positive Beilstein tests for halogen. A sample of the second crop was recrystallized from petroleum ether (b.p. 30–60°) to give orange-yellow needles, m.p. 118.0–118.5°. The chlorine analysis of the product corresponded to the theoretical for 2,3-dichloroacetaldehyde 2,4-dinitrophenylhydrazone. When mixed with the product prepared directly from 2,3-dichloropropionaldehyde (see below) the melting point was undepressed. It is concluded that hydrogen chloride was added to the allylic unsaturation during the reaction.

Anal. Calcd. for $C_9H_8Cl_2N_4O_4$: Cl, 23.09. Found Cl, 22.71.

From 2,3-dichloropropionaldehyde. Diethyl ether (80 ml.) was added to 88.8 g. of a 50% solution of 2,3-dichloropropionaldehyde (0.35 moles) in benzene (Union Carbide Corp.). This solution was cooled to 0° and a solution of 35.0 g. (0.176 mole) of 2,4-dinitrophenylhydrazine in 3850 ml. of 12*N* hydrochloric acid was slowly added, with stirring, over a period of 65 min. After stirring for an additional hour, the yellow product was vacuum-filtered and washed with distilled water until the filtrate was free of chloride ion. A yield of 44.7 g. (82.8%) of 2,3-dichloropropionaldehyde, 2,4-dinitrophenylhydrazone was obtained; m.p. 113–115° dec. An undepressed mixed melting point with the product of the 2-chloroallylidene diacetate reaction (see above) is evidence for the identity of the product.

2,2,3-Trichloropropionaldehyde 2,4-dinitrophenylhydrazone. A solution of 4.51 g. (0.028 mole) of 2,2,4-trichloropropionaldehyde in 10 ml. of diethyl ether was slowly added with stirring to a solution of 4.95 g. (0.025 mole) of 2,4-dinitrophenylhydrazine in 500 ml. of 12*N* hydrochloric acid. The yellow crystalline product was vacuum-filtered and washed with ligroin. A yield of 5.1 g. (60.0%) of 2,2,3-trichloropropionaldehyde 2,4-dinitrophenylhydrazone was obtained, m.p. 113.0–115.5°. Recrystallization from petroleum ether (b.p. 65–110°) gave yellow crystals, m.p. 117.0–117.5°.

Anal. Calcd. for $C_9H_7N_4O_4$: Cl, 31.14. Found: Cl, 30.98.

2-Chlorobutyraldehyde 2,4-dinitrophenylhydrazone. 2-Chlorobutyraldehyde (3.0 g., 0.028 mole) in 20 ml. of diethyl ether was added slowly with stirring to a solution of 5.0 g. (0.024 mole) of 2,4-dinitrophenylhydrazine in 600 ml. of 12*N* hydrochloric acid. The precipitated product was vacuum-filtered and washed with ligroin yielding 3.3 g. (45.9%) of yellow crystals, m.p. 84.5–86.0. Two recrystallizations from petroleum ether (b.p. 30–60°) gave 2-chlorobutyraldehyde 2,4-dinitrophenylhydrazone, m.p. 93.0–94.0 (previously reported m.p. 124°, Table I, ref. *e*).

Anal. Calcd. for $C_{10}H_{11}ClN_4O_4$: Cl, 12.57. Found: Cl, 12.07.

Chloroacetaldehyde 2,4,6-trinitrophenylhydrazone. 2,4,6-Trinitrophenylhydrazine (3.0 g., 0.013 mole) was dissolved in 7.5 ml. of warm 12*N* hydrochloric acid. Chloroacetaldehyde (4.9 g., 0.025 mole, of a 40% aqueous solution) was slowly added at about 40°. The yellow precipitate, which formed after the mixture had been chilled, was separated by vacuum-filtration and washed with methanol. A yield of 2.1 g. (64%) of chloroacetaldehyde 2,4,6-trinitrophenylhydrazone was obtained as yellow crystals, m.p. 159–160°. Recrystallization from glacial acetic acid did not increase the melting point.

Anal. Calcd. for $C_8H_6ClN_5O_6$: Cl, 11.68; N, 23.07. Found: Cl, 11.55; N, 23.00.

Reaction of chloral with 2,4-dinitrophenylhydrazine in methanol. 2,4-Dinitrophenylhydrazine (2.0 g., 0.01 mole) was slurried in 100 ml. of dry methanol and gaseous hydrogen chloride was passed through the mixture until solution occurred. After cooling in an ice bath, 1.1 g. (0.0075 mole) of freshly distilled chloral dissolved in 5 ml. of methanol was added. After 2 days at room temperature, the product was filtered and dried. It appeared to be a mixture of orange crystals and yellow crystals. Chromatography on an Attaclay/Celite column, using benzene as elutant gave a pure yellow product, m.p. 200.5–201°, which had an analysis corresponding to the methyl glyoxalate 2,4-dinitrophenylhydrazine (IV).

Anal. Calcd. for $C_9H_8N_4O_6$: C, 40.31; H, 3.01; N, 20.90. Found: C, 40.31; H, 3.65; N, 20.94.

By extracting the original precipitate with methanol, the same product was obtained without resorting to chromatography.

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