hydrogen chloride was passed into the resulting solution. A heavy oil separated which failed to crystallize after several hours of cooling. The supernatant ether layer was decanted and the remaining oil was dissolved in a few milliliters of acetone. Crystallization again failed to occur on cooling but, on the addition of dry ether, a few crystals were obtained. These were collected by filtration but remained unidentified; weight 20 mg., m.p. 112–115°. The filtrate was placed under reduced pressure until the solvent had been removed. To the residue was added 25 ml. of 2% sodium hydroxide solution. The mixture was extracted with 40 ml. of ether. The ether extract was washed with 25 ml. of 2% sodium hydroxide solution and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and 5 ml. of 95% ethanol was added. To the resulting solution was added 2.5 ml. of a saturated ethanol solution of picric acid. The mixture was heated for several minutes and allowed to stand overnight. The solvent was removed under reduced pressure. On the addition of a small amount of ether to the residue, crystallization occurred. The crystals were collected by filtration and recrystallized from water; yield 66 mg., m.p. 125.5–128°. A mixed melting point with picric acid was depressed; with authentic *N*-benzylpyrrolidine picrate (prepared from pyrrolidine and benzyl chloride followed by treatment with an ethanol solution of picric acid), m.p. 127–128° (lit.,[14] m.p. 128°), was not depressed.

The aqueous alkaline layer obtained upon treatment of the original reaction mixture with 10% sodium hydroxide solution (see above) was acidified with concd. hydrochloric acid. The aluminum hydroxide residue was added to this mixture and the resulting acidic solution was extracted with *ca.* 100 ml. of ether (in three portions). The combined extracts were dried over anhydrous sodium sulfate. Upon removal of the solvent an oil remained. This was dissolved in a few milliliters of benzene. α-Naphthylisocyanate (1.1 ml.) and 3 drops of pyridine were added. The mixture (protected by a soda-lime tube) was brought to boiling, then allowed to cool for *ca.* 4 hr., warmed again, and finally allowed to stand overnight. A small amount of precipitate appeared and was removed by filtration; m.p. greater than 190° (probably high-melting *N*,*N*′-di-α-naphthylurea[15]). Upon removal of the solvent from the filtrate, there remained a solid. It was washed with hot petroleum ether (b.p. 30–60°) and recrystallized from benzene; yield 35 mg., m.p. 166–166.5°; mixed m.p. with authentic *N*-α-naphthyl-*p*-bromophenylcarbamate (m.p. 168–168.5°, lit.,[15] m.p. 169°) was 165–167°.

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[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & CO., INC., EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION LABORATORY]

A New Group of Oxime Esters

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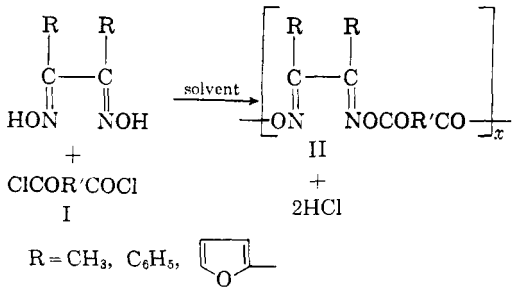
A new group of linear polymeric oxime esters has been prepared by condensation of dibasic acid chlorides with α-dioximes. The preparation, properties and characterization of these esters is described.

Recently, we have found that a new class of oxime esters can be prepared conveniently by reaction of the familiar dibasic fatty acid chlorides with α-dioximes or derivatives thereof. The products of such condensations appear to be linear polymeric oxime esters. These polymers have molecular weights in the range 1000–3000. The polymers have reasonably defined melting points and are soluble in chlorinated aliphatic hydrocarbons.



The actual preparation of the polymers can be carried out by any one of four general methods: (1) reaction of the oxime disodium salt with I, (2) reaction of the glyoxime nickel II chelate with I, (3) reaction of the glyoxime with I in a solvent containing a base to neutralize the acid formed, and (4) reaction of the glyoxime with I in pyridine. Table I shows some of the results obtained by use of these methods.

The products described in Table I are all soluble in chloroform or 1,2-dichloroethane. The polymers are not soluble in other common organic solvents. However, they are soluble in molten phenol and molten diphenylamine. The polymers were purified by successive precipitations from concentrated chloroform solutions with ether. This procedure gave good purification since the dibasic acids and α-dioximes employed are not soluble in chloroform but are soluble in ether. The polymers were relatively stable in aqueous acid solutions, but were readily hydrolyzed above *p*H 3 to the corresponding dibasic acid and α-dioxime.

The analyses in Table I indicate that the average molecule of polydimethylglyoxime succinate, polydimethylglyoxime adipate, and polyfurildioxime adipate may be terminated on both ends by carboxylic acid units rather than by one terminal oximino group and one terminal carboxyl group.

TABLE I

PREPARATION AND PROPERTIES OF SOME POLYMERIC α-DIOXIME ESTERS

Oxime	Acid Chloride	Method	Temp.	Polymer M.P. (% yield)	Average Molecular Weight
Dimethylglyoxime disodium salt (octahydrate)	Succinyl	1	Reflux	160–225° (55%)	700–780[g]
Dimethylglyoxime	Succinyl	4	10°	196–209° (75%)[a]	1074–1320[g]
Dimethylglyoxime	Succinyl	3	10°	198–209° (48%)[a]	1040[h]
Dimethylglyoxime disodium salt (octahydrate)	Adipyl	1	Reflux	Slowly decomposed up to 300° (45%)	540–555[g]
Nickel dimethylglyoxime	Adipyl	2	80–100°	166–169° (100%)[b]	1050–1200[g] 1005–1150[h]
Dimethylglyoxime	Adipyl	3	25°	145–150° (88%)[b]	800–1000[g] 990–1270[i]
Dimethylglyoxime	Sebacyl	4	80–100°	99–103° (53%)[c]	990–1020[h]
Nickel dimethylglyoxime	Sebacyl	2	80–100°	95–100° (80%)[c]	840–915[h]
Dimethylglyoxime disodium salt (octahydrate)	Sebacyl	1	25–50°	121–123° (77%)[c]	2700–3600[g,j]
Dimethylglyoxime disodium salt (octahydrate)	Sebacyl	1	Reflux	84–87° (42%)[c]	900–1000[h]
α-Benzil dioxime	Adipyl	4	80–100°	162–166° (85%)[d]	2000[h]
Nickel α-benzil dioxime	Adipyl	2	80–100°	74–79° (23%)[d]	700–900[g]
α-Furil dioxime	Adipyl	4	80–100°	61–67° (62%)[e]	1382–1420[h]
Dimethylglyoxime	Phosgene	4	25–100°	Did not melt up to 300° (42%)[f,k]	

[a] Calcd. for $C_8H_{10}N_2O_4$: C, 48.4; H, 5.05; N, 14.18; Found: C, 44.3; H, 5.53; N, 12.23. [b] Calcd. for $C_{10}H_{14}N_2O_4$: C, 53.0; H, 6.19; N, 12.39; Found: C, 51.14; H, 6.2; N, 11.49. [c] Calcd. for $C_{14}H_{22}N_2O_4$: C, 59.5; H, 7.8; N, 9.93. Found: C, 59.58; H, 7.8; N, 9.01. [d] Calcd. for $C_{20}H_{16}N_2O_4$: C, 68.5; H, 5.14; N, 8.0; Found: C, 68.29; H, 5.21; N, 7.91. [e] Calcd. for $C_{16}H_{14}N_2O_6$: C, 58.1; H, 4.24; N, 8.49; Found: C, 52.58; H, 4.46; N, 7.70. [f] Calcd. for $C_4H_6N_2O_2$: C, 42.25; H, 4.23; N, 19.71; Found: C, 42.33; H, 4.50; N, 18.94. [g] Cryoscopic in diphenylamine. [h] Ebulloscopic in 1,2-dichloroethane. [i] Cryoscopic in bromoform. [j] $MgSO_4$ added to polymerization mixture to absorb water of hydration as liberated by the reaction. [k] Insoluble in all solvents tried.

Furthermore, when contacted with nickel II ions at *p*H 5–7, these polymers did not give the characteristic red or orange coloration typical of nickel II α-dioxime chelates, as did the other polymers, until sufficient time had elapsed for hydrolysis to liberate the required oximino end groups.

EXPERIMENTAL

Preparation of polyoxime esters. 1. The disodium salt of the oxime was suspended in ether (1 mole) and an equimolar quantity of the diacid chloride was added dropwise with vigorous agitation. The reaction mixture got warm and refluxed vigorously. When the addition was complete, the mixture was allowed to stir 2 hr., acidified with 10% hydrochloric acid and filtered. The filter cake was washed thoroughly with ether and then with hot water. The crude material was dried in a vacuum oven. The dry product was then boiled with an excess of chloroform and filtered. The filtrate was concentrated and the product precipitated by the addition of an excess of ether. The resin was again dried in a vacuum drying oven. This process was repeated until the melting point was constant.

2. The nickel complex of the dioxime was suspended in pyridine (0.5 mole/l.) and stirred vigorously. The thick suspension was heated until the mixture became mobile. An equimolar quantity (based on dimethylglyoxime) of the diacid chloride was added dropwise at a fast rate. The mixture refluxed very violently and turned from a red to a gray color. The mixture was allowed to stir until it cooled to room temperature. The mixture was then diluted with a large excess of water and acidified (*p*H 0–1). The acid solution was allowed to stand until the polymer was white. The liquid was then removed by filtration or, if the product were an oil, by decantation. The crude product was then dissolved in chloroform, the chloroform solution extracted with 10% hydrochloric acid, washed with water, and dried. The dry solution was concentrated and the polymer precipitated by the addition of ether. The product was dried in the vacuum drying oven. The purification steps were repeated until the melting point was constant.

3. The dioxime was dissolved in a solvent (ether, tetrahydrofuran, dioxane) and sufficient pyridine added to react with two molar equivalents of hydrogen chloride. The dibasic acid chloride was added dropwise as in procedures 1 and 2 and the same isolation procedure followed as in 2.

4. The procedure followed in 3 was employed except that pyridine was used as a solvent. The isolation procedure for 2 was used.

Hydrolytic cleavage of polyoxime esters. The hydrolytic degradation of the polymers was carried out in the following manner. Portions (2–4 g.) of the polymers were dissolved in 50 ml. portions of 10% aqueous sodium hydroxide. These mixtures were refluxed 1–3 hr. and then cooled. The cold mixtures were acidified and the crude solid α-dioxime precipitate removed by filtration. The solid filter cakes obtained in this manner were thoroughly triturated with dilute sodium bicarbonate solution, filtered, and washed with water. All filtrates were combined and acidified. Fifty milliliters of 10% nickelous chloride hexahydrate solution was added to the combined filtrates and the *p*H was then raised to 7. The red precipitate in each case was removed by filtration and dried at 50° and 50 mm. pressure. After acidification and saturation with salt, each filtrate from the nickel treatment was extracted with six 100-ml. portions of ether. The ether was then removed from the dry extracts by distillation to leave residual organic materials which showed the characteristic solubilities of organic acids. The dry, colored metal chelates and recrystallized α-dioxime precipitates were each identified by comparison of infrared spectra. The organic acids were purified by recrystallization from appropriate solvents and identified by comparison of infrared spectra and by mixed melting points.

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

The Preparation of α-Haloaldehyde 2,4-Dinitrophenylhydrazones

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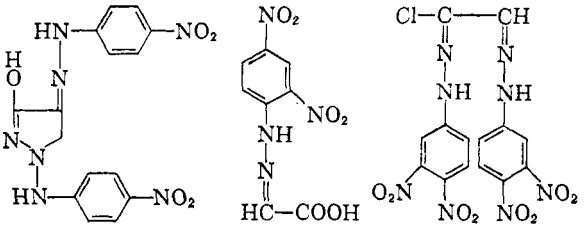
α-Halogenated aldehydes react anomalously with the usual 2,4-dinitrophenylhydrazine reagents to give halogen-free products. It has now been found that a solution of 2,4-dinitrophenylhydrazine in concentrated hydrochloric acid (6*N* to 12*N*), as solvent, will give normal hydrazones with α-haloaldehydes.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