passing the gas into a saturated potassium iodide solution, acidifying, and then titrating with standard thiosulfate solution to a starch endpoint. Minor liquid reactants, such as the organic peroxides, were vaporized into a bypassed fraction of the hydrocarbon stream and were metered by controlling the temperature of the container according to previously prepared calibration curves. Hydrogen peroxide was introduced directly into the reactor throat as a liquid and was metered through a calibrated capillary and the flow rate controlled by varying the air pressure on the liquid in a closed container.

Product analysis was done for carbonyl compounds (in each layer), nitro paraffins (total nitrogen by the Kjeldahl method, distribution by gas chromatographic and mass spectrographic methods), strong acid, weak acid, and the gases carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, ethylene, and propylene (in an Orsat absorption apparatus) as previously described.[5]

Some 134 nitration experiments were completed and form the basis for the conclusions drawn in the discussion part of this paper. However, only a few pertinent data are included n Table I to illustrate the effects observed.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IDAHO STATE COLLEGE AND AVERY LABORATORY, THE UNIVERSITY OF NEBRASKA]

The Reaction of *N*-Bromosuccinimide with *p*-Bromophenyl Benzyl Ether[1]

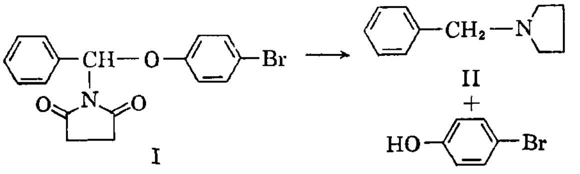
LOREN L. BRAUN[2] AND J. H. LOOKER

Received May 23, 1960

p-Bromophenyl benzyl ether, on treatment with an equimolar quantity of *N*-bromosuccinimide, yields a small amount of DL-*N*-α-(*p*-bromophenoxy)benzylsuccinimide. A structure proof of the latter compound is presented. Yields are increased by increasing the molar ratio of *N*-bromosuccinimide to *p*-bromophenyl benzyl ether, provided bromine is distilled from the reaction mixture. A mechanism for the reaction is proposed.

Although bromination with *N*-bromosuccinimide has been the subject of numerous investigations,[3] both from the standpoint of its mechanism and its synthetic utility, only a few studies[4] have reported the isolation of succinimidyl derivatives from the products of the reaction. A recent study on the synthesis of aldehydes from benzyl ethers by Markees[5] has reported the formation of DL-*N*-α-methoxy-*p*-nitrobenzylsuccinimide from *N*-bromosuccinimide and *p*-nitrobenzyl methyl ether. In the present investigation, a similar starting material, *p*-bromophenyl benzyl ether, has yielded DL-*N*-α-(*p*-bromophenoxy)benzylsuccinimide(I). This unexpected product was obtained in small yield (*ca.* 5%), along with benzaldehyde[6] and a copious evolution of hydrogen bromide, when the reaction was carried out in carbon tetrachloride, under reflux, with an equimolar ratio of *N*-bromosuccinimide to ether.

Evidence for the structure of I was provided by elementary analysis, molecular weight determination, infrared spectrum (with an imide carbonyl peak at 1700 cm.$^{-1}$), and degradative reduction studies.[7] Lithium aluminum hydride reduction resulted in the formation of *N*-benzylpyrrolidine (II, isolated as the picrate) and *p*-bromophenol (III, isolated as the *N*-α-naphthylcarbamate). Thus both the fact that a succinimidyl group has been incorporated into the molecule, and that its point of attachment is at the *alpha* carbon atom by



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(1) This investigation was supported in part by a research grant (E-1703) from the National Institute of Allergic and Infectious Diseases, Public Health Service.

(2) Department of Chemistry, Idaho State College, Pocatello, Idaho.

(3) Several reviews of the reactions of *N*-bromosuccinimide have appeared in the literature. See (a) L. Horner and E. H. Winkelmann, *Angew. Chem.*, **71**, 149 (1959); (b) C. Djerassi, *Chem. Rev.*, **43**, 271 (1948); (c) W. Ringli, *Bromierungen mit Bromsuccinimid*, Leeman, Zurich, 1948; (d) T. D. Waugh, *NBS, Its Reactions and Uses*, Boulder, Colo., Arapahoe Chemicals, Inc., 1951; (e) N. P. Buu-Hoï, *Record Chem. Prog.*, **13**, 30 (1952).

(4) (a) H. L. Dryden, Jr., and Bill E. Burgert, *J. Am. Chem. Soc.*, **77**, 5633 (1955) have obtained *N*-(cyclohepta-2,4,6-trienyl)succinimide in high yield from *N*-bromosuccinimide and cycloheptatriene. (b) D. R. Howton, *J. Am. Chem. Soc.*, **69**, 2060 (1947) and (c) E. R. Buchman and D. R. Howton, *J. Am. Chem. Soc.*, **70**, 2517 (1948) have reported the formation of *N*-phenylsuccinimide when methylenecyclobutane is brominated with *N*-bromosuccinimide in benzene solution. Also (d) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946) and (e) H. Schmid and W. E. Leutenegger, *Helv. Chim. Acta*, **30**, 1965 (1947) have observed the formation of bromo- derivatives of 9-succinimidyl acridine on the reaction of *N*-bromosuccinimide with acridine.

(5) D. G. Markees, *J. Org. Chem.*, **23**, 1490 (1958).

(6) The formation of aldehydes on the treatment of benzyl ethers with *N*-bromosuccinimide was reported by M. Okawara, H. Sato, and E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **58**, 924 (1955). Their observation that phenyl ethers are brominated in the *para* position by *N*-bromosuccinimide has also been confirmed by our conversion of phenyl benzyl ether to *p*-bromophenyl benzyl ether (45% yield).

(7) Several attempts at cleavage by hydrogenation with a palladium on charcoal catalyst at various temperatures and pressures failed to yield a pure isolable product.

means of a carbon to nitrogen bond, are firmly established.

Further investigation, utilizing the recent method of Looker and Holm[8] for the removal of bromine formed during N-bromosuccinimide reactions by distillation, has given some indication of the mechanism involved in the formation of the succinimidyl derivative. By this method, equimolar ratios, or slight variations thereof, of N-bromosuccinimide to ether gave erratic yields (Table I), which were, however, usually higher than yields obtained by methods involving no bromine removal. There seemed to be no simple relationship between the yield of derivative obtained and the amount of bromine that could be recovered in the distillate.

TABLE I

YIELDS OF DL-N-α-(p-BROMOPHENOXY)BENZYLSUCCINIMIDE

Molar Ratio (NBS to Ether)	Yield of I,[a] %	Bromine Recovered,[b,c] %
1:1	20.0	76
1:1	1.9	28
1:1	7.4	24
1:1	15.1	16
0.9:1	15.0	17
1:0.9	19.1	7

[a] Based on moles of I obtained per mole of p-bromophenyl benzyl ether added. [b] As determined by titration with standard sodium bisulfite. [c] Based on moles of bromine obtained in the distillate per half mole of N-bromosuccinimide added.

When a two to one molar ratio of N-bromosuccinimide to ether was used, however, the succinimidyl derivative became the major organic product (83.3% yield) and the amount of bromine obtained by distillation became almost quantitative. Employment of intermediate molar ratios (1.25; 1.50; 1.75) of N-bromosuccinimide resulted in approximately proportionate yields of I and percentage of bromine recovered (Fig. 1).

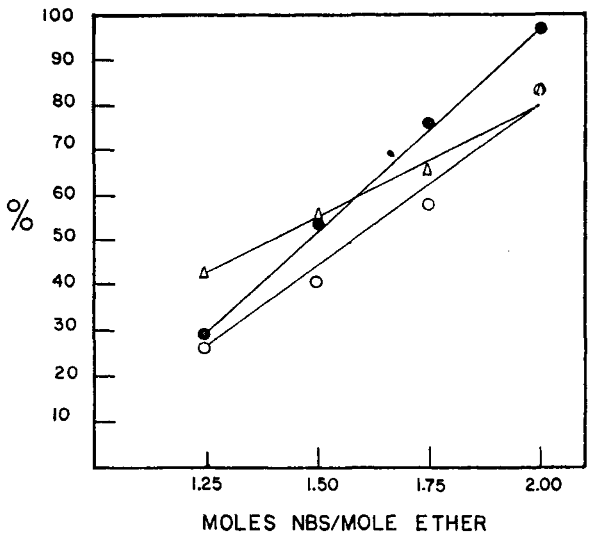


Fig. 1. Variation of yield of I with molar ratio of N-bromosuccinimide to p-bromophenyl benzyl ether and with bromine obtained in the distillate. ●—percentage yield of bromine recovered in distillate based on moles of bromine obtained per half-mole of N-bromosuccinimide added; ○—percentage yield of I based on moles of I obtained per mole of ether added; △—percentage yield of I based on moles of I obtained per half-mole of N-bromosuccinimide added

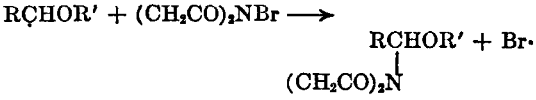
On the basis of these data, the following mechanism is suggested;

Initiation

$$(CH_2CO)_2NBr \longrightarrow (CH_2CO)_2N\cdot + Br\cdot \quad (1)$$

Propagation

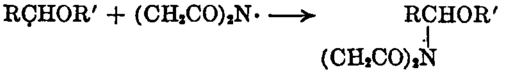
$$(CH_2CO)_2N\cdot + RCH_2OR' \longrightarrow R\dot{C}HOR' + (CH_2CO)_2NH \quad (2a)$$



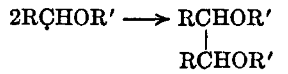
$$R\dot{C}HOR' + (CH_2CO)_2NBr \longrightarrow \underset{(CH_2CO)_2N}{\underset{|}{RCHOR'}} + Br\cdot \quad (2b)$$

$$Br\cdot + (CH_2CO)_2NBr \longrightarrow Br_2 + (CH_2CO)_2N\cdot \quad (2c)$$

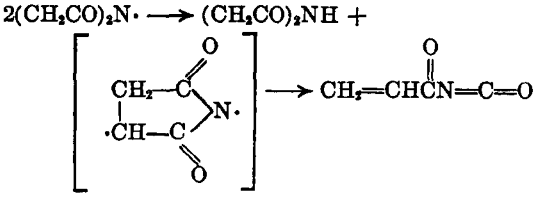
Termination



$$R\dot{C}HOR' + (CH_2CO)_2N\cdot \longrightarrow \underset{(CH_2CO)_2N}{\underset{|}{RCHOR'}} \quad (3a)$$

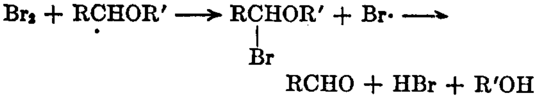


$$2R\dot{C}HOR' \longrightarrow \underset{RCHOR'}{\underset{|}{RCHOR'}} \quad (3b)$$



(3c)

Side Reactions



$$Br_2 + R\dot{C}HOR' \longrightarrow \underset{Br}{\underset{|}{RCHOR'}} + Br\cdot \longrightarrow RCHO + HBr + R'OH \quad (4a)$$

$$HBr + (CH_2CO)_2NBr \longrightarrow Br_2 + (CH_2CO)_2NH \quad (4b)$$

R = phenyl; R' = p-bromophenyl

Initial succinimidyl radical formation is generally attributed to photochemical homolysis[9] (1). This may be followed by hydrogen abstraction (2a) by the succinimidyl radical[10] leaving the ether free radical to attack another molecule of N-bromosuccinimide (2b). Thus two molecules of N-bromosuccinimide are required for each molecule of

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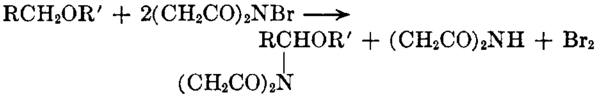
[8] J. H. Looker and M. J. Holm, *J. Org. Chem.*, **24**, 567 (1959).

[9] H. J. Dauben and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 4863 (1959).

[10] That succinimidyl radicals, rather than bromine radicals, are responsible for the abstraction of allylic hydrogen, was first proposed by (a) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944). See also (b) H. J. Dauben and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 5404 (1959).

succinimidyl derivative formed. The bromine free radical may then attack N-bromosuccinimide (2c) to continue chain propagation. Each mole of succinimidyl derivative formed would result in the formation of a mole of bromine. The overall reaction may be written as follows:



$$\mathrm{RCH_2OR'} + 2(\mathrm{CH_2CO})_2\mathrm{NBr} \longrightarrow \underset{(\mathrm{CH_2CO})_2\mathrm{N}}{\mathrm{RCHOR'}} + (\mathrm{CH_2CO})_2\mathrm{NH} + \mathrm{Br_2}$$

A side reaction, leading to the formation of benzaldehyde or other products,[11] is represented by (4a). The sequence (2c), (2a), (4a) may become predominant if the bromine concentration becomes high. Another reaction which is detrimental to succinimidyl derivative formation is represented by (4b), in which more bromine is produced, promoting (4a), and, at the same time, removing N-bromosuccinimide from the possibility of attack by ether free radicals. Hence, bromine removal favors formation of the succinimidyl derivative at the expense of the aldehyde. The rapidity with which bromine is removed, during the period in which the competing reactions take place, may become a critical factor in the determination of the sequence followed (and hence, the product formed) and may account for the variation in yield observed at, or near, the one:one mole ratio. Deviations from an exactly straight line relationship between yield and increasing N-bromosuccinimide to ether ratio are also explained.

Chain termination may occur by the reaction of ether radicals with succinimidyl radicals (3a), a reaction between ether radicals (3b) or a reaction between succinimidyl radicals[9] (3c).

Recently, the possibility was presented that cycloheptatrienylium bromide may be an intermediate in the formation of N-(cyclohepta-2,4,6-trienyl)succinimide from N-bromosuccinimide and cycloheptatriene.[4a] It was suggested that this bromide intermediate then would react with N-bromosuccinimide or succinimide. Our mechanism is an alternative to this explanation. It is interesting that the formation of N-(cyclohepta-2,4,6-trienyl)succinimide could be explained by our mechanism, since the rapid reaction of bromine with cycloheptatriene would be equivalent to bromine removal by distillation.

EXPERIMENTAL

DL-*N-α-(p-Bromophenoxy)benzylsuccinimide.* To 13.1 g. (0.05 mole) of *p*-bromophenyl benzyl ether dissolved in 30 ml. of carbon tetrachloride was added 8.9 g. (0.05 mole) of N-bromosuccinimide. On heating and stirring under reflux, the mixture gradually became reddish-brown. After 45 min. the mixture was irradiated with a G.E. Black Light H100-BL4 lamp[12] (through the Pyrex reaction flask). There resulted an evolution of hydrogen bromide gas and a discoloration of the reaction mixture. After 75 min. of irradiation (with heating and stirring) the reaction mixture was cooled and extracted with 150 ml. of *ca.* 0.2N sodium hydroxide solution (in three portions), washed with water, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and crystallization of the resulting oil began slowly. A few milliliters of ether were added and the mixture was placed under reduced pressure. As the mixture cooled and became more concentrated, crystallization occurred. The crystalline product was collected by filtration and recrystallized from 95% ethanol; yield 0.85 g. (4.7%) m.p. 142–144.5°. An analytical sample prepared from a similar run melted at 144–145°. The product showed no rotation of plane polarized light in chloroform solution.

Anal. Calcd. for $\mathrm{C_{17}H_{14}BrNO_3}$ (360): C, 56.58; H, 3.92; Br, 22.19; N, 3.89. Found: C, 56.70; H, 3.83; Br, 22.38; N, 3.61. Mol. wt.: 383, 401.

The mother (ether) liquor of the crystalline product was placed under reduced pressure until the solvent had been removed. A hot solution of 4 g. of 2,4-dinitrophenylhydrazine, 5 ml. of concd. hydrochloric acid, and 30 ml. of ethanol was added. The resulting thick, orange mixture was heated for a few minutes and allowed to stand overnight. The orange solid was collected by filtration and recrystallized from acetone; yield 1.9 g., m.p. 232–235° (uncorrected, lit.[13] m.p. of the 2,4-dinitrophenylhydrazone of benzaldehyde, 237°).

Other preparations of DL-N-α-(*p*-bromophenoxy)benzylsuccinimide were similar but included the distillation of carbon tetrachloride, carrying with it bromine, from a three necked flask, fitted with a dropping funnel to replace the solvent removed with fresh solvent (essentially the procedure of Looker and Holm[8]). The bromine in the distillate was titrated with standard sodium bisulfite solution. The increased yields, obtained on the higher molar ratios of N-bromosuccinimide to ether, by this method, often resulted in the crystallization of the product from the reaction mixture on cooling. In these cases, the product was collected by filtration and the filtrate was treated as the reaction mixture (above) to provide additional yield.

Reductive cleavage of DL-*N-α-(p-bromophenoxy)benzylsuccinimide.* Into a three necked flask, fitted with mechanical stirrer, dropping funnel, and Soxhlet extractor, protected with a soda-lime tube, was placed *ca.* 250 ml. of anhydrous ether (dried over lithium aluminum hydride) and 1.1 g. of lithium aluminum hydride. Into the thimble of the Soxhlet extractor was placed 0.85 g. (0.0024 mole) of DL-N-α-(*p*-bromophenoxy)benzylsuccinimide. Upon heating and stirring the mixture, ether condensed in the thimble, dissolved a part of the slightly soluble solid, and carried it to the reaction flask on each drainage, with a resulting hydrogen evolution. This procedure was terminated after 9 hr. Water (10 ml.) was added dropwise from the dropping funnel followed by *ca.* 60 ml. of 10% sodium hydroxide solution. More ether and water were added (to increase the volume of both layers) and the mixture was filtered through a fluted filter paper to remove insoluble aluminum hydroxide. The ether layer was separated from the aqueous alkaline layer (which was saved for further treatment as described below), washed with water, and dried over anhydrous sodium sulfate. On removal of the solvent, there remained a small amount of oil. Anhydrous ether (20 ml.) was added and dry

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(11) M. F. Shostakovsky and A. V. Bogdanova, *Zhur. Obschei Khim.*, **21**, 388 and 429 (1951) through *Chem. Abstr.*, **45**, 7514dg (1951) have reported the formation of aldehydes and aldehyde-phenol resins on the decomposition of α-halo ethers. Such decomposition was hastened by the presence of moisture. Okawara, *et al.*,[6] have obtained similar products from benzyl ether reactions with N-bromosuccinimide.

(12) Similar runs were made with a 150 watt clear glass lamp or benzoyl peroxide as a catalyst.

(13) S. M. McElvain, *The Characterization of Organic Compounds*, The MacMillan Company, New York, 1945, p. 200.

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°.

POCATELLO, IDAHO

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[14] J. Schlinck, *Ber.*, **32**, 952 (1899).

[15] H. E. French and A. F. Wirtel, *J. Am. Chem. Soc.*, **48**, 1736 (1926).

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

A New Group of Oxime Esters

L. GUY DONARUMA

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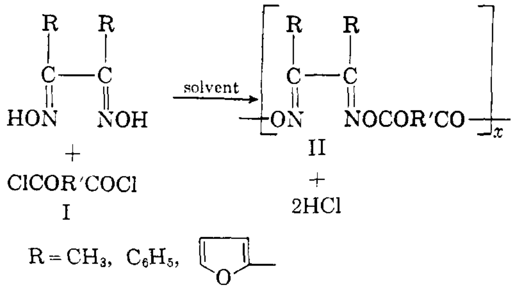
A new group of linear polymeric oxime esters has been prepared by condensation of dibasic acid chlorides with α-dioximes. The preparation, properties and characterization of these esters is described.

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.



R' = CO, $-(CH_2)_2-$, $-(CH_2)_4-$, $-(CH_2)_8-$

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.