dropwise addition of a solution prepared from 100 ml. of water and 5.5 ml. of concentrated sulfuric acid. The aqueous layer was separated and extracted once with ether. The combined ether–benzene solution was washed once with water and freed of ether and benzene *in vacuo*. Refluxing the brown liquid residue for 2 hours with 10 g. (0.25 mole) of sodium hydroxide in 100 ml. of water gave an upper brown 2-ethylhexanol layer and a lower dark-reddish aqueous layer. Ether was added, the layers were separated, and the aqueous layer was extracted three times with ether. After boiling the aqueous solution to reduce its volume by one-half, the solution was acidified with 22 ml. of concentrated hydrochloric acid and refluxed for one hour. The cooled mixture was filtered to remove a brown, insoluble viscous liquid. The yellow aqueous filtrate was freed of water *in vacuo* and the salt residue was extracted with ten 10-ml. portions of warm ether. After drying the ether with magnesium sulfate and filtering off the magnesium sulfate, the ether was removed *in vacuo* to leave 7.90 g. of reddish-brown liquid. The color was due to free iodine as shown by adding water and sodium sulfite to a drop of the liquid.

Preliminary distillation of 4.94 g. of the crude product at 0.01 mm. gave a forerun (1.48 g.) containing iodine and a pale yellow fraction weighing 2.70 g. Redistillation of the main fraction gave a pale yellow VI of b.p. 141–144° (0.1 mm.) and $n^{25}\text{D}$ 1.4731.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.81; H, 7.01. Found: C, 55.23; H, 7.19.

The *p*-phenylphenacyl ester prepared as previously described was not obtained pure by recrystallization. The purest material prepared had m.p. 122–125.5°. The melting point of a mixture of this solid with the pure derivative of m.p. 125–126.5° was 123–125.5°. The infrared spectrum of this sample of ester was identical with those of the samples derived from II and VII. Comparison of the infrared spectra of the purest VI derived from II, VII and that synthesized by the Grignard route indicated that the samples differed only in purity.

Acknowledgments.—The author is indebted to T. L. Gresham for his interest and encouragement, to J. R. Kubik for analyses and to J. J. Shipman, J. P. Kiehl and A. Hawthorne for the determination and interpretation of infrared spectra.

BRECKSVILLE, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF TEXTILE INDUSTRIES, BRADFORD INSTITUTE OF TECHNOLOGY]

The Reactions of N-Mercaptomethylpolyhexamethyleneadipamide Disulfide

BY CHRISTOPHER EARLAND AND DAVID J. RAVEN

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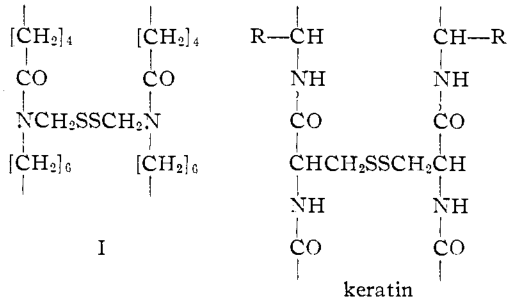
The properties and preparation of N-methylenepolyhexamethyleneadipamidesulfonic acid and N-mercaptomethylpolyhexamethyleneadipamide monosulfide from the corresponding disulfide are described. An alternative method for preparing N-alkylthiomethylpolyamides is given also.

The preparation of the disulfide of N-mercaptomethylpolyhexamethyleneadipamide[1] has been described by Cairns, *et al.*[2] Since this cross-linked polymer has a structure similar to that accepted for the keratins of animal hairs and horn, in that the $-CH_2SSCH_2-$ group forms a bridge between long-chain polyamide molecules

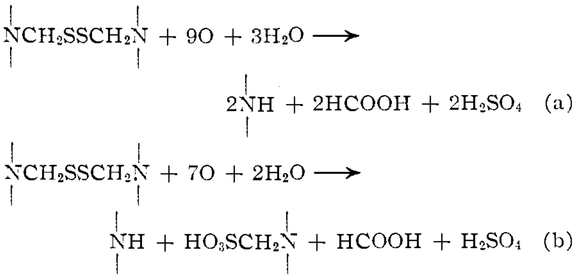


I

keratin

it was decided to investigate the reactions of N-mercaptomethyl-66 disulfide with particular emphasis on the use of reagents which react with the disulfide cross-linkage of keratin.[3]

It has been found that N-mercaptomethyl-66 disulfide (I) undergoes oxidation in two ways. Either the sulfur may be eliminated as sulfuric acid, or it may be converted to combined sulfonic acid groups to give N-methylene-66-sulfonic acid (II), according to the equations



$$\text{NCH}_2\text{SSCH}_2\text{N} + 9\text{O} + 3\text{H}_2\text{O} \longrightarrow 2\text{NH} + 2\text{HCOOH} + 2\text{H}_2\text{SO}_4 \quad \text{(a)}$$

$$\text{NCH}_2\text{SSCH}_2\text{N} + 7\text{O} + 2\text{H}_2\text{O} \longrightarrow \text{NH} + \underset{\text{II}}{\text{HO}_3\text{SCH}_2\text{N}} + \text{HCOOH} + \text{H}_2\text{SO}_4 \quad \text{(b)}$$

The only reagents which effect reaction (b) are aqueous solutions of peracetic acid[4] or alkaline potassium permanganate. Permanganate in acid solution, solutions of bromine, chlorine dioxide, sodium hypochlorite and hypochlorous acid bring about exclusively reaction a. Hydrogen peroxide in acid or alkaline solution fails to oxidize I, although I strongly catalyzes the decomposition of peroxide in alkaline solution, an effect which does not occur with polymer-66 itself in similar physical form. Solutions of permanganate, however, cause considerable weight loss and main-chain degradation of polymer-66 as shown by its number average molecular weight,[5] and only peracetic acid oxidizes

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[1] Polyhexamethyleneadipamide will be referred to as 66.

[2] T. L. Cairns, H. W. Gray, A. K. Schneider and R. S. Schreiber, THIS JOURNAL, **71**, 655 (1949).

[3] For a review of these reactions see P. Alexander and R. F. Hudson, "Wool. Its Chemistry and Physics," Chapman & Hall, London, 1954, pp. 244–283.

[4] Although performic acid may be used, it is not as convenient as peracetic acid since it is less stable and it swells or dissolves polyamides when they are not cross-linked.

[5] Determined from the specific viscosity in 88% formic acid. See M. L. Huggins, THIS JOURNAL, **64**, 2716 (1942); G. B. Taylor, *ibid.*, **69**, 635 (1947); and H. C. Haas, S. G. Cohen, A. C. Oglesby and E. R. Karlin, *J. Polymer Sci.*, **15**, 427 (1955). Thus under conditions which brought about reaction b, peracetic acid reduced $\overline{M}n$ from 13,250 for untreated polymer -66 to 12,350, whereas alkaline permanganate gave $\overline{M}n$ 4600.

I to II without degradation. Prolonging the time of treatment with peracetic acid fails to split off more than 50% of the sulfur as sulfuric acid, showing that reaction b is not the precursor of (a). No satisfactory explanation for the difference in reactivity of the sulfur atoms can be advanced.

Reaction of I with aqueous solutions of potassium cyanide leads to the elimination of half of the sulfur as thiocyanate. The sulfur in the product is in non-disulfide form, and the evidence points to the amide chains being cross-linked by a thioether group

$$\mathrm{NCH_2SSCH_2N + KCN \longrightarrow \underset{III}{NCH_2SCH_2N} + KCNS}$$

A similar reaction has been established for keratin, since lanthionine, $[\mathrm{NH_2{\cdot}CH(COOH)CH_2.}]_2\mathrm{S}$, has been isolated from wool keratin after reaction with potassium cyanide solution,[6] from which it must be concluded that the disulfide cross-link is replaced by a thioether bond.

Reduction of I with thioglycolic acid in methyl alcohol, followed by the addition of an alkyl halide, forms an alternative method to that described by Cairns,[7] *et al.*, for the preparation of N-alkylthiomethyl derivatives of 66.

$$\mathrm{NCH_2SSCH_2N + 2KSCH_2COOK \longrightarrow 2NCH_2SK + (SCH_2COOK)_2}$$

IV

$$\mathrm{NCH_2SK + C_6H_5CH_2Cl \longrightarrow NCH_2SCH_2C_6H_5 + KCl}$$

V

Oxidation of V with peracetic acid yields the sulfone

$$\mathrm{NCH_2SO_2CH_2C_6H_5}$$

VI

In general, the reactions undergone by the disulfide cross-link of the polyamide derivatives described are very similar to those which have been reported for keratin. This is particularly true for oxidation, reduction and reaction with cyanide solutions. Since, however, the disulfide cross-link in the polyamide derivatives is incorporated in the main-chain *via* a N–C bond, whereas in keratin it is a C–C bond, under vigorous reaction conditions, as for example of hydrolysis or oxidation, the whole cross-link disrupts with the elimination of sulfur in the free state or as sulfuric acid. This very rarely occurs with keratin, chlorine dioxide being one of the few reagents which splits off the sulfur as sulfuric acid.[8]

Experimental

Sulfur Analyses.—Total sulfur was determined by oxidation to sulfate with sodium peroxide on the macro scale.

To determine disulfide sulfur, 0.5 g. of material was hydrolyzed with 5 ml. of 5 *N* hydrochloric acid in a sealed tube for 4 hours at 125°. This treatment converted 60% of the disulfide to elemental sulfur

$$\mathrm{NCH_2SSCH_2N + 2H_2O \longrightarrow 2NCH_2OH^{9} + H_2S + S}$$

The excess sulfur over theory is probably due to oxidation of hydrogen sulfide. The sulfur was filtered from the hydrolysate and determined after oxidation to sulfate.

Sulfur present as sulfonic acid groups was determined by shaking 1.0 g. of powdered material with 10 successive quantities of 10 ml. of *M* potassium chloride solution, whereby the proton exchanged with potassium ions

$$\mathrm{NCH_2SO_3H + KCl \longrightarrow NCH_2SO_3K + HCl}$$

The bulked washings were titrated against standard alkali solution using methyl red as indicator. Prior to ion-exchange, the material was allowed to stand in 25 ml. of 0.10 *N* sulfuric acid solution for one hour, and then washed with distilled water until the *p*H of the washings remained constant at 5.

Determination of Amino Groups.[10]—Since the presence of amino groups reduced the quantity of hydrochloric acid liberated by ion-exchange by an equivalent amount, it was necessary to determine these groups in the polymers. It was then possible to account for 99–101% of the total sulfur present in I after oxidation, as disulfide and sulfonic acid sulfur.

Molten 2,4-dinitrofluorobenzene (0.2 ml.), dissolved in 5 ml. of ethyl alcohol, was added to 0.5 g. of the polymer-66 derivative and 2.5 ml. of water containing 0.25 g. of sodium bicarbonate. The mixture was allowed to stand 24 hours at room temperature with occasional shaking. The product was filtered and washed successively with methyl alcohol, water, acetone and vacuum dried; 0.25 g. of the DNP derivative was hydrolyzed with 2.5 ml. of hydrochloric acid as described above. The solution was made alkaline with 15% sodium hydroxide solution and the hexamethylenediamine and its mono-DNP derivative extracted three times with ether. The yellow ether extract was washed with 5 ml. of 2 *N* sodium hydroxide solution followed by 5 ml. of water, filtered and then evaporated on the water-bath. The residue was dissolved in 25 ml. of 0.10 *N* hydrochloric acid and filtered. The color intensities were compared on a Hilger Spekker photoelectric absorptiometer, using a 0.5-cm. cell and a No. 1 blue filter, with the DNP derivative of polymer-66 itself,[11] containing a known number of amino-end groups, diluted to different concentrations with 0.10 *N* hydrochloric acid.

N-Methylene-66-sulfonic Acid.—N-Mercaptomethyl-66-disulfide (I) was prepared by the method of Cairns, *et al.* (% S 4.30, % $\mathrm{CH_3O}$ (Zeisel) 2.2)[12]; 3.00 g. of I was allowed to react with 75 ml. of 2% aqueous peracetic acid for 48 hours at 20° with occasional shaking. The oxygen uptake was 3.7 atoms per atom of sulfur.[13] The product was filtered,

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[6] M. J. Horn, D. B. Jones and S. J. Ringel, *J. Biol. Chem.*, **138**, 141 (1941).

[7] T. L. Cairns, H. D. Foster, A. W. Larchar, A. K. Schneider and R. S. Schreiber, THIS JOURNAL, **71**, 651 (1949).

[8] D. B. Das and J. B. Speakman, *J. Soc. Dyers and Cols.*, **66**, 583 (1950).

[9] Finally hydrolyzes to the diamine, dicarboxylic acid and formaldehyde.

[10] F. Sanger, *Biochem. J.*, **39**, 507 (1945).

[11] The polymer 66 used in this work contained 44 and 78 equivalents of terminal amino and carboxyl groups per 10^6 g., respectively, and was the gift of British Nylon Spinners. Prior to use, the polymer, which was in yarn form, was extracted with ether and washed in distilled water.

[12] Neither our analyses nor those of Cairns, *et al.*,[2] are in accordance with the reaction $\mathrm{NCH_2OCH_3 \rightarrow NCH_2S\text{–}}$, as considerably more sulfur is introduced than corresponds to the loss of methoxy groups from the starting material. After examining in some detail and rejecting the possibilities that this was due to the occlusion of elementary sulfur or a polysulfide cross-link had been formed, it was found that methylol groups are converted to methoxymethyl under the conditions used in the preparation of the disulfide. The apparent discrepancy in the analyses corresponds to the methylol content of the N-methoxymethyl-66 used.

[13] Determined by iodometric titration on the peracetic acid solution, blank experiments being performed to correct for the decomposition of the peracetic acid and the oxidation of methoxymethyl groups present in the polymer. A sample of disulfide containing 10.03%S took up 3.4 atoms O per atom of S. Equation b required O:S = 3.5:1.

washed neutral with water, then acetone and vacuum dried; yield 3.19 g. The sulfur eliminated as sulfuric acid in the peracetic acid solution corresponded to 2.36% on the weight of I,[14] and the product II contained 1.95% S (total sulfur accounted for 100.2%). The product gave 1.75% S by ion-exchange and 0.087% NH_2, equivalent to 0.174% S. Total sulfonic acid sulfur was thus 1.92% (98.5% of that present). The product dissolved completely in 90% formic acid at 18° in 3 hours, whereas compound I remained insoluble after 10 weeks. It had a considerably increased affinity for the basic dye methylene blue and a marked decrease in affinity for the acid dye Orange II.

The ammonium salt was prepared by adding a few drops of *N* ammonia solution to 1.0 g. of a preparation of N-methylene-66-sulfonic acid (*Anal.* Found: S, 1.99; N, 10.6) and vacuum drying the product.

Anal. Calcd. for ammonium salt: N, 11.5. Found: N, 11.7.

N-Mercaptomethyl-66 Monosulfide (III).—Eight grams of N-mercaptomethyl-66 disulfide (I) (%S 4.30) was allowed to react with 400 ml. of 0.10 *M* potassium cyanide solution at 65° for 6 hours with occasional shaking. The monosulfide was filtered, washed with water, acetone and vacuum dried; yield 7.79 g. *Anal.* Found: S, 2.32. This corresponds to 54.0% of the original sulfur. The solution and washings contained thiocyanate equivalent to 46.5% of the original sulfur.[15] After reaction with cyanide solution for 20 hours, 46.5% of the sulfur was in the product and 53.7% was in solution.

The product III was completely devoid of disulfide sulfur and thiocyanate groups. The latter could not be detected chemically, and the infrared absorption spectrum showed no maximum at 2,000 $cm.^{-1}$ [16] characteristic of the thiocyanate group. The product had the characteristics of a cross-linked polymer in that it remained insoluble in *m*-cresol after 10 weeks. Although N-mercaptomethyl-66 disulfide shows the same insolubility, it dissolves in 24 hours when the disulfide cross-links have been ruptured by reaction with peracetic acid for 24 hours. After reaction of the monosulfide III with peracetic acid, it required 18 days for solution in *m*-cresol.

N-Benzylthiomethyl-66 (V).—N-Mercaptomethyl-66 disulfide (I) was treated with 0.1 *M* hydrochloric acid for 2 hours at 65° and then for 2 hours at 100°.[17] Two grams of I (S 4.16%) was warmed with a solution of 9.2 g. of thioglycolic acid and 11.2 g. of potassium hydroxide in 100 ml. of 80% methanol. After cooling to room temperature, 16.5 g. of benzyl chloride was added with cooling and the mixture was allowed to stand overnight; 200 ml. of water was then added when the original small precipitate dissolved and a fine white granular precipitate was obtained. The N-benzylthiomethyl-66 was filtered, washed with water, dilute ammonia and ether and vacuum dried; yield 2.04 g. *Anal.* Found: S, 3.82; disulfide S, 0.09. Calcd. for $-S-S \rightarrow 2-SCH_2.C_6H_5$: S, 3.72. Compound V showed infrared absorption maxima at 699 and 768 $cm.^{-1}$ (monosubstituted benzene derivative) and was readily soluble in formic acid and warm 80% methanol.

N-Benzylthiomethyl-66 Sulfone (VI).—N-Benzylthiomethyl-66 (S 3.82%, 1.0 gram) was allowed to react with 25 ml. of 2% aqueous peracetic acid solution for 24 hours at 18°, with occasional shaking. The oxygen take-up was 2.01 atoms per atom of sulfur. The sulfone VI was filtered off, washed with water and vacuum dried. Compound VI showed infrared absorption maxima at 1,119 and 1,323 $cm.^{-1}$ ($<SO_2$), in addition to those at 698 and 769 $cm.^{-1}$.

Anal. Calcd. for $-SCH_2C_6H_5 \rightarrow -SO_2.CH_2C_6H_5$: S, 3.58. Found: S, 3.64.

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[14] After 24, 48, 96 and 192 hours reaction with peracetic acid, 53.7, 54.8, 54.4 and 53.3%, respectively, of sulfur was removed from the disulfide as sulfuric acid, showing that equation b represents a terminal reaction.

[15] W. W. Scott and N. H. Furman, "Standard Methods of Chemical Analysis," Lancaster Press, Inc., Lancaster, Pa., 1952, p. 277.

[16] Determined on a Grubb–Parsons double-beam spectrometer, using the potassium bromide disk technique. See M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).

[17] This was to remove methoxymethyl groups, which show an infrared absorption peak at 1080 $cm.^{-1}$, and may be confused with one of the sulfone peaks. The removal of these groups is not essential for the preparation.

BRADFORD, ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Diacyl Peroxides. III.[1] The Reaction of Phthaloyl Peroxide with Olefins

BY FREDERICK D. GREENE AND WILLIAM W. REES

RECEIVED DECEMBER 18, 1957

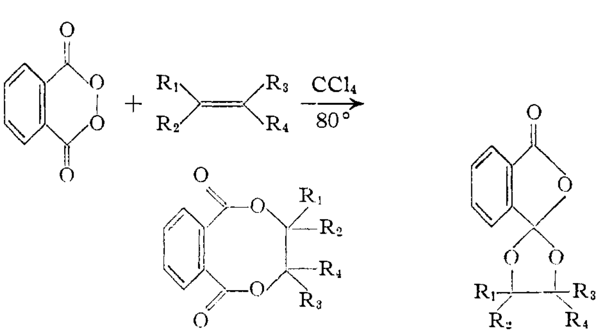
Oxidation of olefins by phthaloyl peroxide has been shown to be general and to obey second-order kinetics. With olefins lacking allylic hydrogen, mixtures of cyclic phthalate (I) and lactonic *ortho*-ester (II) are obtained. Involvement of the allylic position is observed with olefins such as cyclohexene in which 2-cyclohexenyl hydrogen phthalate is a major product (45% yield) of the reaction. A kinetic study has revealed a marked similarity of phthaloyl peroxide to peracetic acid, dibromocarbene and bromine in relative reactivity toward aliphatic olefins, and a reaction constant, rho, of −1.65 for reaction of phthaloyl peroxide with substituted *trans*-stilbenes. Preference is indicated for a mechanism involving bimolecular reaction of neutral peroxide and olefin rather than attack on olefin by diradical derived from oxygen–oxygen fission.

Comparison of the cyclic diacyl peroxide, monomeric phthaloyl peroxide, with acyclic analogs has revealed marked differences in behavior.[1-3] Of particular interest is the behavior toward olefins. Phthaloyl peroxide has been shown to undergo a stereospecific addition reaction with *cis*- and *trans*-stilbene.[1]

In the present paper, the reaction of phthaloyl peroxide with a series of olefins is considered in detail.

Results

Kinetics.—Phthaloyl peroxide reacts with olefins in carbon tetrachloride in a process that is first



	I	II
$R_1 = R_3 = C_6H_5$ $R_2 = R_4 = H$	40%	60%
$R_1 = R_4 = C_6H_5$ $R_2 = R_3 = H$	25%	75%

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[1] Part II, F. D. Greene, THIS JOURNAL, **78**, 2250 (1956).

[2] K. E. Russell, *ibid.*, **77**, 4814 (1955).

[3] F. D. Greene, *ibid.*, **78**, 2246 (1956).