the solvent and recrystallizing the reaction product from pure acetone, the hydroxymethyl-phthalimide was again obtained.

Table II

The Solubilities of the Ethers

Solvent Required to Dissolve 0.25 g. of Ether

	Solvents				
Ether	Ethyl alc. Cc.	Methyl alc. Cc.	Benzene Cc.	Ether Cc.	Acetone Cc.
Methylmethyl	40	10	3	40	2
Methylethyl	20	2	1	2	1
Methyl *n*-propyl	10	1	1	1	1

Summary

1. It has been shown that the bromomethyl-phthalimide will react readily with certain alcohols under anhydrous conditions and can be used for their identification and separation under these conditions, but that it cannot be used in solutions where moisture is present.

2. A description of several new derivatives of methyl-phthalimide has been given.

This research was performed under the direction of Professor Treat B. Johnson.

New Haven, Connecticut

[Contribution from the Chemical Laboratory of the University of Michigan]

THE DISSOCIATION OF N-PENTAMETHYLENE (OR N-PIPERIDYL)-S-TRIARYLMETHYL-DITHIO-URETHANES WITH THE FORMATION OF TRIARYL METHYLS[1]

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It has been shown by J. v. Braun and co-workers[2] that salts of substituted dithiocarbamic acid (such as the piperidine salt of pentamethylenedithiocarbamic acid) react very readily with acid chlorides (benzoyl chloride for example) according to the following equation:

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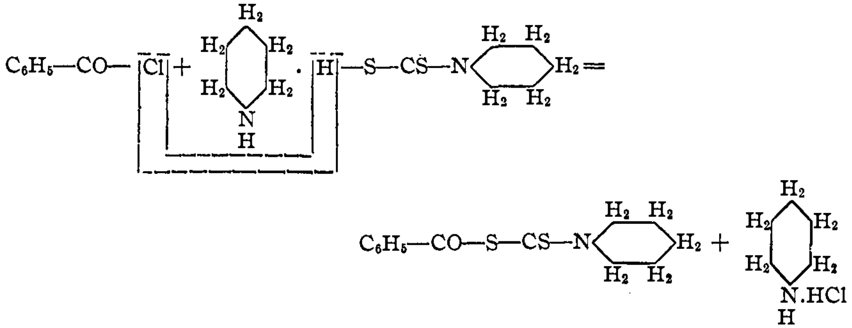
[1] The term *n*-piperidyl-S-triarylmethyl-dithio-urethane is a misnomer when applied to the compounds described in this paper; the above-mentioned term, when strictly applied, must refer to compounds containing two atoms of nitrogen in a molecule. However, since the misnaming of the piperidyl-dithio-urethanes has been continued throughout the literature ever since their discovery (1884) the customary name has been given to them in this paper. Correct names for the compounds described in this paper have been obtained by replacing the term "*n*-piperidyl-" by "*n*-pentamethylene."

[2] V. Braun, *Ber.*, **36**, 3520 (1903). V. Braun and Kaiser, *ibid.*, **55**, 1306 (1922).



I

The resulting compound, I, *n*-pentamethylene-S-benzoyl-dithiourethane, decomposes spontaneously, after a short time, into benzoylpiperidine, II, and carbondisulfide.

$$C_6H_5—CO \mid S—CS \mid NC_5H_{10} = C_6H_5—CO—NC_5H_{10} + CS_2.$$

II

Since the chlorine in the triaryl chloromethanes is comparable in reactivity to the chlorine in the acid chlorides it might be expected that the former class of compounds would also react quite readily with the salts of substituted dithiocarbamic acid; furthermore, would not subsequent decomposition of the resulting compounds lead to the formation of free triaryl methyl radicals rather than to analogues of II?

To test this hypothesis *p*-bromodiphenyl-α-naphthyl-chloromethane was dissolved in benzene and added to a benzene solution of the piperidine salt of pentamethylene-dithiocarbamic acid. Almost instantly a heavy precipitate, consisting of piperidine hydrochloride, appeared. After a short time the precipitate was removed by filtration and the slightly yellow filtrate was poured into a flask just large enough to contain it; the flask was then securely closed with a stopper, to protect the solution from air. After several hours the filtrate was deep cherry red. Upon very brief exposure to the air the color changed to pale yellow but after exclusion of the air the red color of the solution reappeared.

The formation of piperidine hydrochloride, in the reaction described above, indicated that the following reaction had taken place.

$$(C_6H_5)\ (BrC_6H_4)\ (C_{10}H_7)C—Cl + C_5H_{10}NH{\cdot}H—S—CS—NC_5H_{10} =$$
$$(C_6H_5)\ (BrC_6H_4)\ (C_{10}H_7)C—S—CS—NC_5H_{10} + C_5H_{10}NH{\cdot}HCL.$$

III

The deep color of the solution and its disappearance and reappearance upon very brief exposure to the air are phenomena identical with those observed with solutions of free radicals when they are being converted into their respective peroxides.

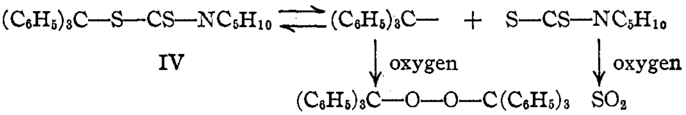
In conformity with the above mentioned behavior of solutions of free radicals it was found that our colored solution, too, actually absorbed oxygen from the air.

In order to make the study of the phenomena simpler, the reaction was carried out with triphenyl-chloromethane, the corresponding free radical of which has been so thoroughly described. Upon the addition of a solution of triphenyl-chloromethane to the piperidine salt of pentamethylene-dithio-urethane, the mixture, colorless at first, gradually became yellow. After 3 hours a deep yellow color had developed, very similar to the color of a solution of triphenylmethyl. Piperidine hydrochloride was precipitated in theoretical amount, and after its removal by filtration a colorless, crystalline material was obtained from the filtrate. This material proved to be *n*-pentamethylene-S-triphenylmethyl-dithio-urethane, $(C_6H_5)_3C\text{-}S\text{-}CS\text{-}NC_5H_{10}$.

When this compound, after isolation, was redissolved it formed a yellow solution which readily adsorbed oxygen with the formation of *triphenylmethyl peroxide* and sulfur dioxide.[3]

$$C_6H_5\text{—}O\text{—}CS\text{—}N(CH_3)_2 + O\ \text{(excess)} \longrightarrow C_2H_5\text{—}O\text{—}CO\text{—}N(CH_3)_2 + SO_2 + SO_3.$$

The formation of the peroxide, as well as of the color of the solutions, and the disappearance and reappearance of the color upon brief exposure to air, can be explained only by the following assumption: pentamethylene-S-triphenylmethyl-dithio-urethane, in solution, must dissociate to some extent into the radical triphenylmethyl; the latter then reacts with oxygen forming the peroxide and the solution becomes colorless; thereupon, more dissociation of IV takes place and, finally, all of it is converted into peroxide.[4]



$$\begin{array}{cccc} (C_6H_5)_3C\text{—}S\text{—}CS\text{—}NC_5H_{10} \rightleftharpoons & (C_6H_5)_3C\text{—} & + & S\text{—}CS\text{—}NC_5H_{10} \\ \text{IV} & \downarrow \text{oxygen} & & \downarrow \text{oxygen} \\ & (C_6H_5)_3C\text{—}O\text{—}O\text{—}C(C_6H_5)_3 & & SO_2 \end{array}$$

Such a dissociation in solution, at ordinary temperature, with the formation of triphenylmethyl and, upon exposure to air, of triphenylmethyl peroxide, is shown by hexaphenylethane, triphenyl-iodomethane,[5] azo-triphenylmethane (at 0°),[6] phenylazotriphenylmethane (at some-

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[3] It has been found that *n*-dimethyl-thio-urethane and its homologs are oxidized spontaneously upon exposure to air or oxygen with the formation of *n*-dimethyl-urethane and oxides of sulfur. O. Billeter, *Ber.*, **43,** 1853 (1910).

[4] It cannot be assumed that pentamethylene-S-triphenylmethyl-dithio-urethane decomposes, in the above instance, into carbon disulfide and triphenylmethyl-piperidine and that the free radical arises from a dissociation of the latter substance; *n*-triphenylmethyl-piperidine was synthesized and in the dissolved state, at ordinary temperature, absorbs no oxygen, and hence does not dissociate into triphenylmethyl.

[5] Gomberg, THIS JOURNAL, **24,** 621 (1902).

[6] Wieland, *Ber.*, **42,** 3023 (1909).

what higher temperature),[7] and finally by octaphenylpropane.[8] To this list must now be added the pentamethylene-S-triarylmethyl-dithio-urethanes.

The substituted pentamethylene-dithio-urethanes which have been studied so far are the diphenyl-α-naphthylmethyl, the diphenyl-mono-biphenylmethyl and the *p*-bromodiphenyl-α-naphthylmethyl. In each case the dithio-urethane formed a colored solution and reacted with oxygen, yielding the peroxide of the corresponding triarylmethyl.

We have also found that triphenylmethyl disulfide,[9] and presumably its analogs, dissociates in solution at ordinary temperature, with the formation of a free radical; this phenomenon has escaped the notice of Vorländer and Mittag, the discoverers of this compound. The results of this observation will be published in a later paper.

Experimental Part

***n*-Pentamethylene-S-triphenylmethyl-dithio-urethane,** $(C_6H_5)_3C\text{-}S\text{-}CS\text{-}NC_5H_{10}$.—The piperidine salt of pentamethylene-dithiocarbamic acid[10] required for the preparation of this compound is readily prepared by the addition of an absolute ether solution of 7 cc. of carbon disulfide to 24 cc. of piperidine, dissolved in a large volume of ether. The precipitated salt of the carbamic acid is filtered, washed with ether and then air-dried.

A solution of 4.2 g. of triphenyl-chloromethane in 25 cc. of benzene was added to 3.7 g. of the piperidine salt of (piperidyl pentamethylene)-dithiocarbamic acid, dissolved in 25 cc. of warm benzene; the colorless mixture was poured into a flask just large enough to contain it and tightly stoppered. The flask was protected from light and after 4 hours the deep yellow mixture was quickly filtered from the precipitated piperidine hydrochloride. The weight of this salt obtained was 1.76 g.; calculated weight, 1.81 g. The filtrate was poured at once into an evaporating dish and 150 cc. of petroleum ether (25–40°) was added. After 10 minutes the liquid was decanted from the precipitated material, the latter was well washed with petroleum ether, filtered and air-dried; 4–5 g. of slightly yellow, glistening crystals was obtained. When heated fairly rapidly the freshly prepared material softened at about 140° and melted with decomposition at 155–160°. The compound is very soluble in benzene and chloroform, less soluble in ether and acetone and fairly insoluble in alcohol and petroleum ether.

Analyses. Calc. for $C_{25}H_{25}NS_2$: C, 74.37; H, 6.24; S, 15.90. Found: C, 74.43; H, 6.42; S, 15.87.

Attempted recrystallization of the compound from glacial acetic acid resulted in the formation of triphenyl carbinol. The addition of a small amount of hydrochloric acid facilitates the conversion into the carbinol; 2.0 g. of the material was dissolved in 15 cc. of hot glacial acetic acid, and 2 cc. of hydrochloric acid was added. The solution was then boiled for 3 minutes, carbon disulfide being evolved. Water was added and the resulting precipitate was filtered, washed and dried. The product melted at 161–162°.

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[7] Wieland, Popper and H. Seefried, *Ber.*, **55**, 1822 (1922).

[8] Schlenk and Mark, *ibid.*, **55**, 2286 (1922).

[9] Vorländer and Mittag, *ibid.*, **46**, 3459 (1913).

[10] Cahours, *Ann. chim. phys.*, [3] **38**, 88 (1853).

When mixed with triphenyl carbinol, the melting point was 160–162°; yield, 1.2 g.; calc., 1.3 g. The acetic acid filtrate, after the addition of solid sodium hydroxide, smelled strongly of piperidine.

A practically quantitative yield of triphenyl carbinol was obtained by treatment of the solid material with conc. nitric acid.

$(C_6H_5)_3C—S—CS—NC_5H_{11} + H_2O\ (HNO_3) = (C_6H_5)_3C—OH + CS_2 + C_5H_{11}N.HNO_3$.

Dissolved in acetone, the substance instantly decolorized an acetone solution of potassium permanganate. Triphenyl carbinol was obtained in good yield.

Hydrogen chloride converted the dissolved material quantitatively into triphenylchloromethane and piperidine hydrochloride.

The above reactions show how readily the triphenylmethyl group is detached from the sulfur in pentamethylene-triphenylmethyl-dithio-urethane.

When the solid material was heated, carbon disulfide was evolved; 1.0 g. of the compound was heated somewhat above the melting point and a stream of dry air was passed over the molten material. The evolved gas was passed through a cold, ether solution of piperidine; 0.25 g. of the piperidine salt of pentamethylene-dithiocarbamic acid was precipitated. The calculated amount, assuming a complete decomposition of the substance into carbon disulfide, is 0.62 g. A small amount of triphenylmethane was obtained from the molten residue.

Reaction with Oxygen.—A test-tube containing 3.0 g. of the isolated dithio-urethane, dissolved in 20 cc. of benzene, was placed in an oxygen-absorption apparatus[11] and allowed to remain in contact with oxygen for 24 hours, the tube being shaken frequently. After 2 hours the solution had absorbed about 60 cc. of oxygen[12] and a precipitate then began to form. The latter increased in amount as more and more oxygen was absorbed. After 24 hours about 260 cc. of oxygen had been taken up by the solution. The apparatus was opened and a strong odor of sulfur dioxide was evident; the precipitated material was filtered, washed with benzene and then with ether; yield, 0.6 g. After recrystallization from toluene the compound melted at 185°. When mixed with peroxide, prepared from triphenyl-chloromethane and silver, the mixture melted at 185–186°.

In a second experiment, 3.0 g. of the dithio-urethane, dissolved in 30 cc. of benzene, was placed in a Drechsel bottle and a fairly rapid stream of dry air was passed through the solution. The air escaping from the bottle was passed through dilute, aqueous potassium hydroxide. After 1.5 hours a precipitate began to appear in the benzene solution. After 8 hours the precipitate (0.3 g.) was filtered; after it had been washed with ether the material melted at 185–186°. A mixture with triphenylmethyl peroxide melted at 186°.

The peroxide, obtained as described above, dissolved in conc. sulfuric acid forming a deep yellow solution. Upon the addition of water and recrystallization of the precipitated material, the latter melted at 162°. A mixture with triphenyl carbinol melted at 161–162°.

The alkaline solution was found to contain considerable potassium sulfite, thus proving positively that sulfur dioxide had been evolved during the reaction.

***n*-(Piperidyl pentamethylene)-S-diphenyl-α-naphthylmethyl-dithio-urethane,** $(C_6H_5)_2(C_{10}H_7)C—S—CS—NC_5H_{11}$.—A solution of 3.3 g. of diphenyl-α-naphthylchloromethane in 15 cc. of warm benzene was added to 2.5 g. of the piperidine salt of pentamethylene-dithiocarbamic acid, dissolved in 10 cc. of the same solvent. Piperidine

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[11] Gomberg and Schoepfle, THIS JOURNAL, **39**, 1661 (1917).

[12] The high vapor pressure of the sulfur dioxide evolved during the reaction made quantitative determinations of the amount of oxygen absorbed impossible according to the method used.

hydrochloride was precipitated immediately. After 4 hours the brown-red mixture was quickly filtered from the piperidine hydrochloride (calc. 1.2 g.; found, 1.2 g.) 15 cc. of benzene was added to the filtrate, the latter was poured into a Drechsel bottle and a stream of air was passed through the solution of the dithio-urethane. After 10 minutes a precipitate began to appear and after 1/2 hour a considerable amount of peroxide had been formed. After 3 hours the precipitate was filtered; 3.0 g. or 80% of the calculated amount of peroxide was obtained. The compound was washed with benzene and then with hot carbon disulfide; m. p., 171°. When it was mixed with peroxide, prepared from diphenyl-α-naphthylmethyl-chloromethane and silver. the mixture melted at 171–172°.

***n*-Pentamethylene-S-diphenyl-mono-biphenylmethyl-dithio-urethane,** $(C_6H_5)_2$-$(C_6H_5$-$C_6H_4)C$—S—CS—NC_5H_{10}.—A solution of 3.35 g. of the triarylmethylchloride in 10 cc. of warm benzene was added to 2.46 g. of the piperidine salt of the carbamic acid dissolved in 10 cc. of the same solvent. After 4 hours the orange-red mixture was filtered. 1.1 g. of piperidine hydrochloride was obtained; the calculated amount was 1.2 g. After air had been passed into the filtrate for 6 hours, no precipitate having then appeared, the solution was poured into an evaporating dish. After the solvent had evaporated the gummy residue was treated with ether. The resulting crystalline compound was washed with benzene and then recrystallized from benzene with the addition of ether. The material obtained in this manner melted at 175–176°. Peroxide, prepared from the triarylmethyl chloride and silver, also melted at 176°. The mixed melting point was 175–176°. The melting point given in the literature[13] for the peroxide of diphenyl-mono-biphenyl is 180°.

In a manner entirely analogous to those given above, the peroxide of *p*-bromodiphenyl-α-naphthylmethyl was obtained from the corresponding dithio-urethane.

Summary

1. *n*-Pentamethylene (or *n*-piperidyl)-S-triphenylmethyl-dithio-urethane and several of its homologs have been prepared from the piperidine salt of pentamethylene-dithiocarbamic acid and the corresponding triaryl chloromethane.

2. The dithio-urethanes in solution, at ordinary temperature, undergo *dissociation with the formation of free triaryl methyl radicals;* the radicals were isolated in the form of their insoluble peroxides.

I wish to take this opportunity to thank Professor M. Gomberg for the interest and valuable advice which he has given me during the course of this investigation.

ANN ARBOR, MICHIGAN

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[13] Schlenk, Weickel and Herzenstein, *Ann.*, **372**, 19 (1910).