TABLE I

ALLOPHANATE FORMATION CATALYZED BY METAL CARBOXYLATES AT ROOM TEMPERATURE[a,b]

$C_6H_5NCO + C_6H_5NHCOOC_2H_5 \longrightarrow C_6H_5NHCON(C_6H_5)COOC_2H_5$

No.	Metal Carboxylate	Concentration of Metal, Mole/L. × 10^5	Time, Hr.	Yield of Allophanate, %
1	Lead naphthenate	7.7	4	96
2	Cobalt naphthenate	6.1	6	96
3	Copper naphthenate	11.2	88	69
4	Manganese naphthenate	6.0	88	69
5	Iron naphthenate	6.9	88	36
6	Cadmium naphthenate	6.0	88	10
7	Vanadium naphthenate	5.5	88	10
8	Lead 2-ethylhexanoate	5.2	5	95
9	Zinc 2-ethylhexanoate	5.2	5	95
10	Manganese 2-ethylhexanoate	7.1	88	10
11	Cobalt 2-ethylhexanoate	6.2	7	97
12	Lead linoresinate	5.4	5	96
13	Cobalt linoresinate	6.1	7	96
14	Manganese linoresinate	7.3	88	45
15	Zinc linoresinate	10.1	88	12
16	Copper linoresinate	12.2	88	50
17	Iron linoresinate	5.2	90	42

[a] The catalysts were supplied by the Harshaw Chemical Co. as mineral spirits solutions. [b] The reaction was carried out by allowing a mixture of 1.05 g. (0.0088 mole) of phenyl isocyanate, 1.48 g. (0.009 mole) of ethyl carbanilate and catalyst to stand at room temperature. The reaction mixture was then worked up in the manner described in the experimental section.

Ethyl-α,o-chlorophenyl-γ,m-methoxyphenylallophanate, yield (75%), m.p. 106°. The infrared spectrum exhibited a twin carbonyl band at 5.83 and 5.96 μ.

Anal. Calcd. for $C_{17}H_{17}N_2O_4Cl$: N, 8.1. Found: 8.1.

Ethyl-α,γ-di-p-tolylallophanate, yield (76.6%), m.p. 104–106°. The infrared spectrum exhibited a twin carbonyl band at 5.73 and 5.88 μ.

Anal. Calcd. for $C_{18}H_{20}N_2O_3$: N, 9.0 Found: 9.1.

Phenyl-α,γ-diphenylallophanate, yield (75%), m.p. 139–141°. The infrared spectrum exhibited a twin carbonyl band at 5.75 and 5.85 μ.

Anal. Calcd. for $C_{20}H_{16}N_2O_3$: N, 8.5. Found: 8.8.

Infrared absorption spectrum. Infrared absorption spectra were determined with a Perkin-Elmer Infrared Spectrophotometer Model No. 21. No solvent was used. The spectra were determined as Nujol mulls in a demountable cell using sodium chloride windows with 0.025-mm. spaces (normal thickness).

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2,2-Dinitroethylamine and Derivatives

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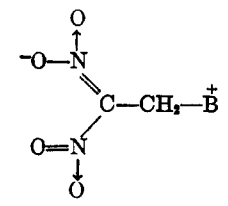
Zeldin and Shechter[1] have described the formation of 2-guanidino-1,1-dinitroethane (Ia), 1,1-dinitro-2-piperidinoethane (Ib) and trimethylammonium *N*-(2-nitroethyl-2-nitronate) (Ic) in the reaction of 1,1,1-trinitroethane with the corresponding free bases. Ultraviolet spectra, solubility behavior, and crystalline form lent strong support to the characterization of these compounds as zwitterionic salts.[2] We wish now to record the syntheses and some novel reactions of two additional members of this class of compounds, 2,2-dinitroethylamine (II) and *N*,*N*-dimethyl-2,2-dinitroethylamine (III).



Ia. B = $NH{=}C(NH_2)_2$

Ib. B = NHC_5H_{10} (piperidino)

Ic. B = $N(CH_3)_3$

II. B = NH_3

III. B = $NH(CH_3)_2$

The reaction of 1,1,1-trinitroethane with methanolic ammonia at room temperature proceeded smoothly with only a mild exotherm to yield II (85%), the by-product ammonium nitrite decomposing under the conditions of the reaction to nitrogen and water. With dimethylamine in aqueous methanol the yield of the *N*,*N*-dimethyl derivative III was 65%. The products in both instances were only slightly soluble and precipitated directly from the reaction mixture sufficiently pure for elemental analyses. Since excess base increased the

(1) L. Zeldin and H. Shechter, *J. Am. Chem. Soc.*, 79, 4708 (1957).

(2) For simplicity of nomenclature, however, these compounds are named as if they were in the nonionic form except where this becomes too cumbersome as with Ic.

$$\bar{C}(NO_2)_2CH_2\overset{+}{N}H_3 \xrightarrow{KOH} \underset{IV}{K^+\bar{C}(NO_2)_2CH_2NHCH_2C(NO_2)_2\bar{K}^+} + \underset{V}{K^+\bar{C}(NO_2)_2CH_2C(NO_2)_2\bar{K}^+}$$

$$\downarrow \qquad\qquad \downarrow$$

$$BrC(NO_2)_2CH_2NHCH_2C(NO_2)_2Br \qquad BrC(NO_2)_2CH_2C(NO_2)_2Br$$

solubility, probably due to the equilibrium

$$NHR_2 + \bar{C}(NO_2)_2CH_2\overset{+}{N}HR_2 \rightleftharpoons \overset{+}{N}H_2R_2 + \bar{C}(NO_2)_2CH_2NR_2$$

the best yield of III was achieved using a 2:1 molar ratio of dimethylamine to trinitroethane.

The reaction of III with concentrated aqueous potassium hydroxide involved a simple neutralization and potassium *N,N* - dimethyl - 2,2 - dinitroethylamine was readily isolated in excellent yield. With II, however, potassium hydroxide caused somewhat more profound transformations. The major product was dipotassium bis(2,2-dinitroethyl)amine (IV), but under certain conditions smaller amounts of dipotassium 1,1,3,3-tetranitropropane (V) could also be isolated. These salts were identified by elemental analyses and by conversion to the known bis(2-bromo-2,2-dinitroethyl)amine[3] and 1,3-dibromo-1,1,3,3-tetranitropropane.[4]

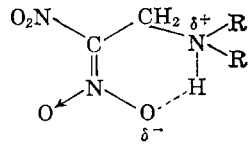
More facile methods for the preparation of IV and V are known. The former has been described by Klager[3] as a Mannich reaction product of potassium 2,2-dinitroethanol with ammonia; the latter may be prepared by treating equimolar potassium 2,2-dinitroethanol and potassium dinitromethane[5a] or, more simply, by heating a concentrated aqueous solution of potassium 2,2-dinitroethanol.[5b] Compound V has also been found to be a reaction product of 1,1,1,3-tetranitropropane with potassium hydroperoxide,[6] potassium acetate,[7] potassium methylate,[7] and ammonia followed by potassium chloride.[4]

Bromination of a suspension of II in absolute ether gave the expected ether-insoluble adduct, 2-bromo-2,2-dinitroethylammonium bromide (VI) in excellent yield. When the reaction was repeated in ether containing 0.4% water, however, the yield of VI was substantially lower and the product was contaminated with ammonium bromide. Work-up of the mother liquor led to a second product, bis(2-bromo-2,2-dinitroethyl)amine, identical with the dibromo derivative obtained from IV. Evidently VI, the salt of a very weak base, had donated a proton to water. The resultant free base then reacted with another molecule of VI yielding the disubstituted amine and ammonium bromide.

$$II \xrightarrow{Br_2} \underset{VI}{BrC(NO_2)_2CH_2NH_3^+Br^-} \xrightarrow{H_2O} BrC(NO_2)_2CH_2NH_2 + H_3O^+Br^-$$

$$VI + BrC(NO_2)_2CH_2NH_2 \longrightarrow BrC(NO_2)_2CH_2NHCH_2C(NO_2)_2Br + NH_4^+Br^-$$

Attempts to react II with formaldehyde, formaldehyde and ammonium acetate or methyl acrylate were unsuccessful under conditions which are more or less standard for formylation,[8] Mannich reactions[9] and Michael additions[10] of 1,1-dinitroalkane salts. This may have been due to decreased nucleophilic character of the anionic moiety as a result of intramolecular hydrogen bonding which would allow for mutual charge dispersal between the ammonium and the nitronitronate portions of the molecule.



It is of interest in this connection that while Ia–c, II, and III are all soluble in dilute acid or dilute alkali, only Ic is more than very slightly soluble in neutral media. The latter is the sole member of the series for which intramolecular hydrogen bonding is impossible and it may be that the decreased solubility of the other four is a consequence of this factor lessening the free energy of solvation.

Ultraviolet absorption spectra of compounds prepared in the present investigation are listed in Table I. Previously described precautions[11] taken in making these measurements showed that IV and V in dilute solutions were rapidly decomposed by actinic radiation. The close correspondence of λ_{max}

(3) K. Klager, *J. Org. Chem.*, **23**, 1519 (1958).

(4) S. S. Novikov, A. A. Feinsil'berg, A. Shevelev, I. S. Korsakova, and K. K. Babievskii, *Doklady Akad. Nauk S. S. S. R.*, **124**, 589 (1959).

(5) (a) Private communication, Dr. Harold Shechter, Ohio State University. (b) Private communication, Dr. Karl Klager, Aerojet-General Corporation, whose priority in the synthesis of V we herewith acknowledge.

(6) J. C. Dacons, J. C. Hoffsommer, and M. J. Kamlet, unpublished data.

(7) S. S. Novikov, A. A. Feinsil'berg, A. Shevelev, I. S. Korsakova, and K. K. Babievskii, *Doklady Akad. Nauk S. S. S. R.*, **132**, 846 (1960).

(8) (a) H. Feuer, G. B. Bachman, and J. P. Kispersky, *J. Am. Chem. Soc.*, **73**, 1360 (1951). (b) M. H. Gold, E. E. Hamel, and K. Klager, *J. Org. Chem.*, **22**, 1665 (1957).

(9) (a) M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **79**, 2953 (1957). (b) H. Feuer, G. B. Bachman, and W. May, *J. Am. Chem. Soc.*, **76**, 5124 (1954).

(10) (a) K. Klager, *J. Org. Chem.*, **16**, 161 (1951). (b) L. Herzog, M. H. Gold, and K. Klager, *J. Am. Chem. Soc.*, **73**, 749 (1951). (c) H. Shechter and L. Zeldin, *J. Am. Chem. Soc.*, **73**, 1277 (1951).

(11) M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).

and log ϵ of III and potassium *N,N*-dimethyl-2,2-dinitroethylamine in water indicates that the latter salt is a strong base. Protonation of the amine function takes place in neutral media and the predominant absorbing species is the zwitterion. It is of interest that λ_{max} (neutral) $-\lambda_{max}$ (alkaline) for this salt corresponds exactly with that reported for Ib.[1]

TABLE I

Compound	Solvent	λ_{max} (log ϵ)[a]
2,2-Dinitroethylamine, II	H_2O	362 (4.19)
N,N-Dimethyl-2,2-dinitroethylamine, III	H_2O	357 (4.25)
Potassium *N,N*-dimethyl-2,2-dinitroethylamine	H_2O	357 (4.23)
	Dil. KOH	369.5 (4.20)
2-Guanidino-1,1-dinitroethane, Ia	H_2O	364 (4.21)[b]
2-Piperidino-1,1-dinitroethane, Ib	H_2O	357 (4.05)[b]
	Dil. alk.	369 (4.14)[b]
Trimethylammonium *N*-(2-nitroethyl-2-nitronate), Ic	Dil. alk.	352 (4.17)[b]
Dipotassium bis(2,2-dinitroethyl)amine, IV	Dil. KOH	367 (4.46)[c]
Dipotassium 1,1,3,3-tetranitropropane, V	Dil. KOH	367 (4.41)[c]

[a] Spectra determined over 300–420 mμ range on a Cary, Model 14 recording spectrophotometer, solutions 3–5 $\times$ 10^{-5} molar, final dilutions carried out in protective low actinic glassware.[11] [b] Ref. 1. [c] Fade on exposure to light.

EXPERIMENTAL[12,13]

2,2-Dinitroethylamine. (II). Anhydrous ammonia was bubbled into a well stirred solution of 66.0 g. (0.40 mole) of 1,1,1-trinitroethane in 500 ml. of methanol with moderate cooling to hold the temperature between 35 and 40°. After 3 hr. the nicely crystalline yellow product was allowed to settle, the supernatant liquor decanted, the product stirred with an additional 100 ml. of methanol and filtered. This first crop, after washing with further methanol and with ether and air drying (33.9 g., 63%), melted sharply with frothing at 122.4°. By applying a vacuum to the mother liquor to remove dissolved ammonia (which increases the solubility of II in methanol) an additional 11.9 g. (85% total) m.p. 117° dec. was recovered.

Anal. Calcd. for $C_2H_5N_3O_4$: C, 17.79; H, 3.70; N, 31.10. Found: C, 17.73, 17.53; H, 3.60, 3.60; N, 30.94, 31.04.

Compound II is soluble in mineral acids, only slightly soluble in acetone, alcohols, or water and insoluble in nonpolar solvents. Melting point is a poor index of purity, samples melting sharply with frothing between 108 and 132° depending on crystal size and rate of heating. A sample decomposed spontaneously but not violently after three months standing at room temperature.

Bromination of II. (*a*) *In anhydrous ether.* Dropwise addition of bromine to a stirred suspension of 2.0 g. II in 200 ml. absolute ether[14a] gave 3.8 g. (87%) of insoluble *2-bromo-2,2-dinitroethylammonium bromide* (VI), m.p. 128° dec. Purification was effected by dissolving 1.0 g. in 5 ml. of methanol, filtering to remove a small amount of unchanged II, and adding the solution to 50 ml. of ether. The analytical sample of VI precipitated as a white powder, m.p. 129–129.5° dec.

Anal. Calcd. for $C_2H_5N_3O_4Br_2$: C, 8.16; H, 1.71; N, 14.30; Br, 54.2. Found: C, 8.25, 8.38; H, 2.00, 2.10; N, 14.11, 14.24; Br, 54.7, 55.2.

(*b*) *In wet ether.* Eleven grams of II in 300 ml. of ether,[14b] treated as above, yielded only 10.5 g. (44%) of insoluble VI. Evaporation of the mother liquor left a gummy solid which was taken up in ether-pentane, filtered to remove a little insoluble material, and concentrated to furnish three crops, totalling 5.77 g. (34.5%) of the crude ether soluble product, m.p. 60 to 69°. Recrystallization of 4.5 g. from ether-hexane gave 3.75 g. of *bis(2-bromo-2,2-dinitroethyl)amine* as elongated cream-colored platelets, m.p. 67–69°. A further recrystallization from hexane raised the melting point to 69–70°. Klager[3] has recorded a melting point of 70°.

Anal. Calcd. for $C_4H_5Br_2N_5O_8$: C, 11.66; H, 1.22; N, 17.04; Br, 38.9. Found: C, 11.77, 12.00; H, 1.26, 1.42; N, 17.19. 16.93; Br, 39.4, 39.4.

Dipotassium bis(2,2-dinitroethyl)amine (IV). Five grams (0.037 mole) of II, suspended in 25 ml. of water containing equimolar potassium hydroxide, was allowed to stand 3 days at room temperature. The mixture was then cooled to 5° and the product filtered off, washed with methanol followed by ether, and air dried to yield 4.65 g. (73%) of bright yellow elongated platelets, m.p. 140° dec. The material was readily recrystallized from water, but difficulty was encountered in obtaining satisfactory analyses due to its tendency to explode in the combustion tube. The best analysis corresponded to the monohydrate of IV.

Anal. Calcd. for $K_2C_4H_5N_5O_8 \cdot H_2O$: C, 13.81; H, 2.01; N, 20.1. Found: C, 13.61; H, 1.98; N, 20.1.

The structure of the dipotassium salt was confirmed by bromination of a suspension of the material in ether to form *bis-(2-bromo-2,2-dinitroethyl)amine*, which melted at 69–70° and showed no depression on admixture with the soluble product obtained by brominating II in wet ether.

Dipotassium 1,1,3,3-tetranitropropane (V). Individual pellets of 85% potassium hydroxide (10.0 g.) were added at 0.5-min. intervals to a well-stirred suspension of 5.0 g. II in 200 ml. water. The mixture became clear when about 2.3 g. (equimolar) had been added and a yellow precipitate began to form when about 5 g. had been added. This insoluble product, filtered off, washed with methanol then with ether and air dried, weighed 280 mg. It began to discolor at 120°, turned gunmetal grey at 220° and black at 240°, but did not melt sharply. Purification was effected by dissolving the crude product in excess hot water and adding methanol to precipitate V as tiny yellow equant crystals.

Anal. Calcd. for $K_2C_3H_2N_4O_8$: C, 11.96; H, 0.66; N, 18.60. Found: C, 11.36, 11.76; H, 0.89, 0.86; N, 18.13, 18.38.

Addition of methanol to the original mother liquor caused precipitation of 2.7 g. (36%) of impure IV, m.p. 140° dec. By taking the latter up in 30 ml. of water and recovering the insoluble residue, an additional 70 mg. of the higher melting V was obtained. Melting behavior, however, was a poor criterion for distinction between the two products of this reaction because their decomposition points were strongly influenced by impurities, particle size and rate of heating. In addition, their ultraviolet spectra were remarkably similar (Table I) and their dibromo derivatives melted within 1° of one another. Our initial attempts to distinguish between IV and V were confused by these coincidental similarities together with the problems encountered in obtaining satisfactory elemental analyses for IV. The only real difference between the two arose by virtue of their differing solubilities; IV was moderately soluble in water, V much less so.

(12) Melting points are uncorrected. Microanalyses by Prof. Mary Aldridge, Dept. of Chemistry, American University, Washington, D. C.

(13) The compounds herein described are explosive in nature and appropriate precautions should be taken. II, IV, and V are particularly sensitive to friction or heat. The salts should be stored in the refrigerator under solvent.

(14) (a) Mallinkrodt Analytical Reagent, H_2O = 0.01%. (b) Merck Reagent A. C. S., H_2O = 0.4%.

These difficulties were resolved with the synthesis of IV and V by independent methods. Thus, our sample of V was identical in appearance, melting behavior, and ultraviolet spectrum with a sample prepared by reacting 1,1,1,3-tetranitropropane with ammonia and treating the product with potassium chloride as described by Novikov and co-workers.[4] *1,3-Dibromo-1,1,3,3-tetranitropropane*, prepared by brominating suspensions of both samples in ether, melted at 67–69° (lit.[4] m.p. 69–69.5°), and showed no depression on admixture but did show melting point depression with the soluble dibromide, m.p. 70°, prepared by the bromination of II in wet ether.

Anal. Calcd. for $C_3H_2Br_2N_4O_8$: Br, 41.9. Found: Br, 41.5.

N,N-Dimethyl-2,2-dinitroethylamine (III). A solution of 20.0 ml. (0.114 mole) of 25% aqueous dimethylamine and 9.29 g. (0.057 mole) of 1,1,1-trinitroethane was refluxed 5 min. then allowed to stand overnight at room temperature. After filtering and washing with methanol followed by ether, the pale yellow columnar equant crystals which separated weighed 5.13 g. and had m.p. (dec.) 99.2–99.8°.

Anal. Calcd. for $C_4H_9N_3O_4$: C, 29.42; H, 5.51; N, 25.78. Found: C, 29.17; H, 5.42; N, 25.46.

After 3 days further standing in the freezer an additional 0.43 g. of III (total yield 66%), m.p. 94–94.6° dec. precipitated. The compound was soluble in dilute acid or dilute alkali, but even less soluble in water than II.

Two grams of III dissolved readily in a solution of 2.0 g. 85% potassium hydroxide in 5.0 ml. water at 70°. On cooling the solution 2.02 g. (82%) of *potassium N,N-dimethyl-2,2-dinitroethylamine* precipitated as small columnar yellow crystals, m.p. 161–163° dec.

Anal. Calcd. for $KC_4H_8N_3O_4$: C, 23.89; H, 3.98; N, 20.90. Found: C, 24.14, 24.32; H, 3.98, 4.11; N, 20.48, 20.49.

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5-Ethoxy-8-aminoquinoxaline[1]

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Received January 6, 1961

A number of carbocyclic substituted quinoxalines having fungistatic and medicinal properties have been reported in the literature. We deemed it of interest to undertake the preparation of 5-ethoxy-8-aminoquinoxaline and some of its derivatives.

In this publication we wish to report the synthesis of 5-ethoxy-8-acetylaminoquinoxaline (IV), 5-ethoxy-8-aminoquinoxaline (V), 5-ethoxy-8-*p*-tolylsulfonamidoquinoxaline (VII), 5-ethoxy-8-*N*-acetylsulfanilamidoquinoxaline (VIII), and 5-ethoxy-8-sulfanilamidoquinoxaline (IX). Also, we wish to report an improved procedure for the preparation of 1-ethoxy-2,3-dinitro-4-acetamidobenzene.[5]

The synthesis of 5-ethoxy-8-aminoquinoxaline was achieved according to the following sequence: *p*-phenacetin (I) was converted to 1-ethoxy-2,3-dinitro-4-acetamidobenzene (II), catalytic reduction of (II) with hydrogen in the presence of 5% palladium-on-charcoal catalyst yielded the intermediate 1-ethoxy-2,3-diamino-4-acetamidobenzene (III), which was not isolated but immediately condensed with sodium glyoxal bisulfite to form 5-ethoxy-8-acetylaminoquinoxaline (IV), and acid hydrolysis of (IV) yielded 5-ethoxy-8-aminoquinoxaline (V).

The reaction of an alcoholic solution of the free amine (V) with an excess of approximately 14% hydrochloric acid yielded 5-ethoxy-8-aminoquinoxaline hydrochloride (VI). The addition of *p*-toluenesulfonyl chloride to pyridine solution of 5-ethoxy-8-aminoquinoxaline (V) yielded 5-ethoxy-8-*p*-tolylsulfonamidoquinoxaline (VII). Similarly, the reaction of *p*-acetamidobenzenesulfonyl chloride with the free amine (V), according to the method of Wolfe *et al.*,[6] afforded 5-ethoxy-8-*N*-acetylsulfanilamidoquinoxaline (VIII). The acetyl derivative (VIII) was hydrolyzed to 5-ethoxy-8-sulfanilamidoquinoxaline (IX) with alcoholic hydrochloric acid.

IV has been found to produce 36% inhibition of *Aspergillus niger* in 250 parts per million concentration. Both (IV) and (V) show some ability to inhibit the growth of *Rhizopus nigricans, Mucar sp.*, and *Penicillium sp.* Further work on the fungistatic properties of these compounds is in progress and will be published elsewhere.

EXPERIMENTAL

The corrected melting points were determined by the use of a microscopic, hot stage melting point block equipped with a calibrated thermometer. The microscope was equipped with a polarized lens which facilitated determination of the precise melting point range. The sample on the hot stage was heated at a uniform rate of 2° per min. The melting point range was taken as the temperature between which the first crystal disappeared and the entire field became dark when observed under polarized light.

1-Ethoxy-2,3-dinitro-4-acetamidobenzene. Twenty-five grams (0.14 mole) of *p*-phenacetin (Charles Pfizer, reagent grade) was placed in a 300-ml. Pyrex mortar which had been positioned in an evaporating dish containing a Dry Ice–acetone mixture. When the dry *p*-phenacetin had cooled to about 15–25° 125 ml. (2.97 moles) of Baker's fuming nitric acid (sp. gr. 1.50) was added dropwise over a period of 1 hr. The reaction mixture was stirred by means of a pestle throughout the entire addition time. Continuous cooling was necessary to maintain the temperature between 15–25°.

The cold reaction mixture was poured into 1.5 l. of cold water, and the yellowish orange product which separated was removed by filtration employing a Buchner funnel. The crude product which weighed 31.9 g. was crystallized a single time from 1.25 l. of an ethanol:acetone mixture (3:1). A second crystallization from the ethanol:acetone mixture (3:1) containing 5 g. of Nuchar afforded a pale, greenish

(1) From a thesis submitted by James E. Hutchins as partial fulfillment of the requirements for the degree of Master of Arts, East Tennessee State College, 1959.

(2) Northeast Louisiana State College, Monroe, La.

(3) University of South Florida, Tampa, Fla.

(4) Eastman Chemical Products, Inc., Kingsport, Tenn.

(5) P. E. Verkade and P. H. Witjens, *Rec. trav. chim.*, **62**, 201 (1943).

(6) E. J. Wolfe, R. H. Beutel, and J. R. Stevens, *J. Am. Chem. Soc.*, **70**, 2574 (1948).