

of a 6 $\beta$ -ol- $\Delta^4$ -3-one under acid conditions has been described.<sup>3</sup>

**Acknowledgment.**—We are indebted to Messrs. Louis M. Brancone and Samuel S. Modes for the microanalytical data, and to Messrs. William Fulmer and George Morton and Miss Anne Callaghan for the optical rotation data and the infrared absorption spectra.

#### Experimental

**Melting Points.**—All melting points are uncorrected, and were determined with uncalibrated Anschütz thermometers.

**Optical Rotation.**—The rotations are for chloroform solution at 24–25°.

**Absorption Spectra.**—The ultraviolet absorption spectra were determined in absolute alcohol with a Beckman spectrophotometer (model DU). The infrared absorption spectra (pressed potassium bromide) were determined with a Perkin-Elmer spectrophotometer (model 21).

**Petroleum Ether.**—The fraction used had b.p. 60–70° (Skellysolve B).

All evaporations were carried out under reduced pressure.

**Pregnane-5,6 $\beta$ -diol-3,20-dione 3,20-Bis-ethylene Ketal (II).**—A solution of  $\Delta^4$ -pregnene-3,20-dione 3,20-bis-ethylene ketal (I, 3 g. (7.46 millimoles)) in benzene (80 ml.) and pyridine (2.5 ml.) was treated with osmium tetroxide (2 g. (8.0 millimoles)), and the mixture was allowed to stand at room temperature for 36 hours. The osmate ester was then decomposed by being stirred for 4 hours with sodium sulfite (12.4 g.), potassium bicarbonate (12.4 g.), water (120 ml.) and methanol (40 ml.). The precipitate was separated by filtration, and washed with hot chloroform (1 liter). The filtrate and chloroform washings were combined, and the organic layer was separated. The extract was washed with saturated saline, dried and evaporated. The residue was crystallized from acetone-petroleum ether to furnish 1.59 g. (49%) of the diol, m.p. 195–196°. Recrystallization from the same solvent pair did not change the m.p.;  $\lambda_{\max}$  none;  $\nu_{\max}^{\text{KBr}}$  3700 and 1058  $\text{cm}^{-1}$ ;  $[\alpha]_{\text{D}} +28^\circ$  ( $c$  1.07).

**Anal.** Calcd. for  $\text{C}_{25}\text{H}_{40}\text{O}_6$  (436.57): C, 68.77; H, 9.24. Found: C, 68.51; H, 9.40.

The mother liquor on concentration afforded two further fractions of solid, 0.55 g., m.p. 158–173°, and 0.48 g., m.p. 143–163°, which were combined. Attempts to purify this material by recrystallization were unsuccessful. Likewise chromatography (alumina or silica gel), and partition chromatography (Celite) failed to resolve the mixture. The latter afforded two fractions in order of increasing polarity; 0.44 g., m.p. 162.5–170°,  $\nu_{\max}^{\text{KBr}}$  3597 and 1058  $\text{cm}^{-1}$  (infrared spectrum very similar but not identical with that of the 5,6 $\beta$ -diol II); and 20 mg., m.p. 125–127°;  $\nu_{\max}^{\text{KBr}}$  3610, 1718 (strong) and 1058  $\text{cm}^{-1}$ . Recrystallization of the less polar fraction did not sharpen the m.p. The presence of ketonic material in the more polar fraction may be ascribed to inadvertent hydrolysis, or may possibly have been a trace impurity in the starting material I.

**$\Delta^4$ -Pregnene-6 $\beta$ -ol-3,20-dione (III).**—A solution of the 5,6 $\beta$ -diol II (0.35 g.) in 90% (v./v.) acetic acid (10 ml.) was heated on a steam-bath for 2 hours. Cold water was added, and the cloudy mixture was neutralized with a saturated potassium hydroxide solution. Chilling gave crystals which were collected, and washed well with water. This afforded 171 mg. (65%) of crude III, m.p. 162–168°. Recrystallization from acetone-petroleum ether raised the m.p. to 178.5–180.5°,  $\lambda_{\max}$  236–237  $\text{m}\mu$  ( $\epsilon$  13,500),  $[\alpha]_{\text{D}} +103^\circ$  ( $c$  1.095). Its infrared absorption spectrum was identical to that of an authentic sample.<sup>5</sup>

**Allopregnane-3,6,20-trione (IV).**<sup>6</sup>—A solution of the 5,6 $\beta$ -diol II (0.5 g.) in methanol (30 ml.) containing 8% (v./v.)

(4) C. P. Balant and M. Ehrenstein, ref. 3, report m.p. 178–179°,  $\lambda_{\max}^{\text{alc}}$  235.5  $\text{m}\mu$  ( $\epsilon$  12,390),  $[\alpha]_{\text{D}} +106.8^\circ$  (chloroform); C. Amendola, G. Rosenkranz and F. Sondheimer, ref. 3, give m.p. 179–180°,  $\lambda_{\max}^{\text{alc}}$  236  $\text{m}\mu$  ( $\epsilon$  13,600),  $[\alpha]_{\text{D}} +105^\circ$  (chloroform).

(5) We are indebted to Dr. T. F. Gallagher of the Sloan-Kettering Institute for this spectral comparison.

(6) C. P. Balant and M. Ehrenstein, ref. 3, give m.p. 232.5–233°,  $[\alpha]_{\text{D}} +61.0^\circ$  (chloroform); C. Amendola, G. Rosenkranz and F. Sondheimer, ref. 3, found m.p. 231–233°,  $[\alpha]_{\text{D}} +65^\circ$  (dioxane).

sulfuric acid (5 ml.) was refluxed for 2 hours. It was poured into ice-water, and the mixture was neutralized with solid sodium bicarbonate. The resulting crystalline product was collected by filtration. Recrystallization from acetone gave 193 mg., m.p. 237–240°. Concentration of the mother liquor furnished an additional 66 mg., m.p. 232–235°, for a total "crude" yield of 67%. Recrystallization of the first crop from acetone-petroleum ether raised the m.p. to 239.5–242°;  $\lambda_{\max}$  none;  $\nu_{\max}^{\text{KBr}}$  1710 and 1695 (shoulder)  $\text{cm}^{-1}$ ;  $[\alpha]_{\text{D}} +62^\circ$  ( $c$  1.263).

**Anal.** Calcd. for  $\text{C}_{21}\text{H}_{30}\text{O}_3$  (330.45): C, 76.32; H, 9.15. Found: C, 76.02; H, 9.24.

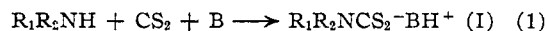
MEDICINAL CHEMICAL RESEARCH SECTION  
LEDERLE LABORATORIES, RESEARCH DIVISION  
AMERICAN CYANAMID COMPANY  
PEARL RIVER, NEW YORK

## The Reaction of Dithiocarbamates with Acrylamide

BY CHARLES M. BUSS

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In a study of Michael-type reactions, the action of substituted dithiocarbamates on acrylamide was investigated in an attempt to prepare a series of substituted carbamoyl ethyl dithiocarbamates (II, equation 2 below). The proposed sequence of reactions was



The dithiocarbamates were readily prepared according to equation 1. As the reaction of the second equation probably initially involves attack by the anion of the dithiocarbamate salt, I, on the  $\beta$ -carbon atom of acrylamide, the base, B, must be strong enough that the salts have sufficient ionic character. Pyridinium salts of the substituted dithiocarbamates, for example, react sluggishly if at all. On the other hand, when B is too strong a base, it can interact with the products, II, resulting in undesired side-reactions.

Triethylamine, which is a base of the proper strength, was chosen for this study. Being a tertiary amine, it cannot add to acrylamide, as some of the primary and secondary amines,  $\text{R}_1\text{R}_2\text{NH}$ , used in the preparation of the dithiocarbamates, were found to do under the conditions of the reaction. Triethylamine, therefore, may be used in excess so that the formation of the salts by equation 1 is essentially complete and there is no need for isolating these salts prior to the addition of acrylamide. Furthermore, triethylamine is a stronger base than most of the primary and secondary amines employed so that there is little tendency for the latter to function as the base B in the formation of the salts. With the exception of the experiments using aromatic amines as  $\text{R}_1\text{R}_2\text{NH}$ , the formation of the salts was observed to be rapid with the evolution of heat. If desired, most of the triethylammonium dithiocarbamates may be isolated (see Experimental, Triethylammonium Benzyldithiocarbamate). The dithiocarbamates from secondary amines, such as morpholinodithioformate, may be heated in water or alcohol without inducing serious decomposition, but those from primary amines are less stable.

The amines,  $\text{R}_1\text{R}_2\text{NH}$ , used included aliphatic,

TABLE I  
 2-CARBAMOYLETHYL DITHIOCARBAMATES,  $R_1R_2NCS_2CH_2CH_2CONH_2$ , PREPARED IN CHLOROFORM

Amine, $R_1R_2NH$	Yield, %	M.p., °C.	Formula	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
Diethylamine	90 <sup>a</sup>	104–105 <sup>g</sup>	$C_8H_{16}N_2OS_2$	43.60	43.78	7.32	7.54
Di- <i>n</i> -butylamine	82 <sup>b</sup>	61–62 <sup>g</sup>	$C_{12}H_{24}N_2OS_2$	52.13	52.37	8.75	9.18
Benzylamine	76 <sup>c</sup>	158–159 <sup>h</sup>	$C_{11}H_{14}N_2OS_2$	51.94	51.75	5.55	5.62
Dibenzylamine	93 <sup>a</sup>	104–105 <sup>i</sup>	$C_{18}H_{20}N_2OS_2$	62.76	63.25	5.85	6.02
Ethylenediamine	69 <sup>d</sup>	188–189 <sup>i</sup>	$C_{10}H_{18}N_4O_2S_4$	33.88	34.02	5.12	4.82
Piperidine	76 <sup>e</sup>	114–115 <sup>g</sup>	$C_9H_{16}N_2OS_2$	46.52	46.70	6.94	7.04
Piperazine	86 <sup>e</sup>	235–236 <sup>h</sup>	$C_{12}H_{20}N_4O_2S_4$	37.87	37.88	5.30	5.52
Morpholine	64 <sup>e</sup>	145–146 <sup>g</sup>	$C_8H_{14}N_2O_2S_2$	41.00	41.14	6.02	6.28
Aniline	90 <sup>e</sup>	139–140 <sup>h</sup>	$C_{10}H_{12}N_2OS_2$	49.98	49.89	5.04	5.42
N-Methylaniline	93 <sup>f</sup>	124–125 <sup>h</sup>	$C_{11}H_{14}N_2OS_2$	51.94	52.07	5.55	5.73
N-Ethylaniline	96 <sup>f</sup>	95–96 <sup>g</sup>	$C_{12}H_{16}N_2OS_2$	53.70	54.01	6.01	6.28

<sup>a</sup> Crystallized from benzene. <sup>b</sup> Product does not crystallize from reaction medium. On dilution, an oil separates which crystallizes after repeated extraction with ligroin and chilling. Recrystallized from dilute ethanol. <sup>c</sup> Crystallized from ethanol. <sup>d</sup> Crystallized from acetic acid, nitromethane or benzonitrile as rapidly as possible. <sup>e</sup> Crystallized from large amount of ethyl acetate. <sup>f</sup> Crystallized from chloroform. <sup>g</sup> Needles. <sup>h</sup> Plates. <sup>i</sup> Microcrystalline.

aromatic and heterocyclic compounds, both primary and secondary. With salts from primary amines, no tendency to carbamoylethylate at the nitrogen was observed even when excess acrylamide was used. When diamines were employed, bis-carbamoylethyl dithiocarbamates were readily obtained.

The reactions were all carried out both in chloroform and 95% ethanol. Generally, chloroform was found to be the superior solvent. Due to the insolubility of the salts from the diamines in these solvents, those reactions were also carried out in water. The yields were not, however, greatly improved. Benzene may also be used as the solvent and excellent yields may be obtained therein. The salts are, however, less soluble in benzene and it is more difficult to attain complete reaction with acrylamide.

Addition occurred as stated by equation 2 with eleven of the twelve substituted dithiocarbamates studied. With these, reaction occurs with acrylamide in a manner analogous to that previously reported with acrylonitrile<sup>1</sup> and unsaturated ketones.<sup>2</sup>

Aqueous ammonium dithiocarbamate reacts similarly with acrylamide yielding 2-carbamoylethyl dithiocarbamate,  $NH_2CS_2CH_2CH_2CONH_2$ , if the concentrations are controlled so that crystallization of the product occurs within four hours. Some  $\beta,\beta'$ -thiodipropionamide,  $S(CH_2CH_2CONH_2)_2$ , is also obtained. This latter compound becomes the major product if the dithiocarbamate salt is allowed to decompose prior to the addition of acrylamide.  $\beta,\beta'$ -Thiodipropionamide may also be obtained by direct reaction of acrylamide with sodium sulfide<sup>3</sup> or with hydrogen sulfide as reported in the Experimental section.

When the sequence of reactions was carried out using  $\alpha$ -phenylethylamine as  $R_1R_2NH$ , the product which was obtained was  $\beta,\beta'$ -dithiodipropionamide,  $(-SCH_2CH_2CONH_2)_2$ . This compound might be obtained<sup>4</sup> by air oxidation of  $\beta$ -mercaptopropionamide. Apparently triethylammonium  $\alpha$ -phenylethyl dithiocarbamate decomposes in chloroform

and this decomposition occurs by a different route or at a different rate than the unsubstituted dithiocarbamate.

Preliminary reports without details of the reactions of acrylamide with mercaptans and amines were made previously.<sup>3</sup> In the course of this work, it was desired to determine the conditions for such reactions. The preparation of addition products with diethylamine, morpholine, benzyl mercaptan, hydrogen sulfide and thiolacetic acid are herein reported. The addition of hydrogen sulfide and benzyl mercaptan was accomplished by the incorporation of small amounts of sodium sulfide and potassium hydroxide, respectively, in the reaction mixtures. In the experiments using thiolacetic acid and the amines, added bases were not required.

#### Experimental

**General Method of Preparation of Triethylammonium Dithiocarbamates.**—To 6.5 ml. of triethylamine (0.047 mole) in 30 ml. of the solvent (chloroform or 95% ethanol) was added 4.5 ml. of carbon disulfide (0.075 mole) and then dropwise 0.040 mole of the primary or secondary amine (0.020 mole in the experiments using diamines). The amines employed are listed in Table I. Reaction with the aliphatic and heterocyclic amines was observed to be vigorous. The diamines used yielded sparingly soluble salts and 30 ml. of ethanol was added to the chloroform experiments in these examples. In the experiments using aromatic amines, the reaction mixture was allowed to stand 24 hours before addition of acrylamide; in other cases, acrylamide was added after 30 minutes.

**Triethylammonium benzyldithiocarbamate** is sparingly soluble in benzene. When 6.5 ml. of triethylamine, 4.5 ml. of carbon disulfide and 4.28 g. of benzylamine in 50 ml. of benzene were caused to react according to the procedure outlined above, there was obtained after filtration 9.86 g. of triethylammonium benzyldithiocarbamate (87%).

*Anal.* Calcd. for  $C_{14}H_{24}N_2S_2$ : C, 59.11; H, 8.50. Found: C, 58.81; H, 8.82.

On standing in air, the salt decomposed to an orange, gummy material.

**Morpholinium Morpholinodithioformate.**—To 4.0 ml. of carbon disulfide in 25 ml. of ethanol was added 8.0 g. of morpholine. The temperature rose immediately. After 30 minutes the solution was diluted with three volumes of water and concentrated by distillation to approximately 30 ml. On being cooled, 7.3 g. of morpholinium morpholinodithioformate (64%) separated. The salt which was obtained as prisms sublimes with decomposition without melting. It was recrystallized from water.

*Anal.* Calcd. for  $C_9H_{18}N_2O_2S_2$ : C, 43.17; H, 7.25. Found: C, 43.33; H, 7.38.

(1) M. W. Harman, U. S. Patent 2,413,917 (1947).

(2) J. E. Jansen and R. A. Mathes, *THIS JOURNAL*, **77**, 2866 (1955).

(3) American Cyanamid's New Product Bulletin No. 28, 30 Rockefeller Plaza, New York 20, N. Y., 1952.

**General Procedure for the Reaction of Dithiocarbamates with Acrylamide.**—In the examples where a precipitate of the dithiocarbamate salt was present, the mixture was stirred vigorously. A 3.0-g. quantity of acrylamide<sup>4</sup> (0.042 mole) was added and the mixture was stirred or allowed to stand for 24 hours. Any precipitate which had separated was collected, washed with water and dried. Second crops were obtained after dilution of the filtrate with 50 ml. of ligroin (60–90°) in the chloroform experiments and 100 ml. of water in the ethanol runs. The products were then crystallized from appropriate solvents as stated in the table. The percentage yields were calculated on the crude products, but in no case was the melting range of the crude sample more than 12–15° lower than the melting point of the analytical sample prepared from it.

**2-Carbamoyl ethyl Dithiocarbamate.**—To a solution of 1.50 g. of ammonium dithiocarbamate<sup>5</sup> in 5 ml. of water was added 1.00 g. of acrylamide. The solution was filtered and allowed to stand for two hours. The resulting mixture was filtered of 0.73 g. of 2-carbamoyl ethyl dithiocarbamate (m.p. 119–120°) and an additional 0.82 g. crystallized from the filtrate (m.p. 115–118°); yield 1.55 g.; 70%. The product was recrystallized from ethanol and the analytical sample melted at 125–126°.

*Anal.* Calcd. for  $C_4H_8N_2OS_2$ : C, 29.25; H, 4.91. Found: C, 29.51; H, 5.23.

From the second filtrate there crystallized within 24 hours 0.24 g. of  $\beta, \beta'$ -thiodipropionamide, m.p. 165–170°. By recrystallization from water or ethanol, the melting point of the product obtained as colorless, lustrous plates was raised to 176–177°. The melting point of this compound has been reported as 177–178.5°.<sup>6</sup>

*Anal.* Calcd. for  $C_5H_{12}N_2O_2S$ : C, 40.89; H, 6.87. Found: C, 40.68; H, 6.82.

Hydrolysis of  $\beta, \beta'$ -thiodipropionamide through the use of concentrated hydrochloric acid followed by crystallization from hot water afforded  $\beta, \beta'$ -thiodipropionic acid, lustrous plates, m.p. 127–128°. The melting point of this acid has been reported as 128°.<sup>7</sup>

Attempts to prepare ammonium dithiocarbamate through the use of aqueous ammonia were apparently unsuccessful in agreement with the more recent literature,<sup>8</sup> as the only product isolated after acrylamide was added was  $\beta, \beta'$ -thiodipropionamide.

**$\beta, \beta'$ -Dithiodipropionamide.**—When 6.5 ml. of triethylamine, 4.5 ml. of carbon disulfide and a 4.9 ml. of  $\alpha$ -phenylethylamine were mixed in chloroform according to the general procedure described above, a significant temperature rise was observed. After 30 minutes, 2.84 g. of acrylamide was added and the mixture was allowed to react by the general procedure. There was obtained 4.0 g. of a light yellow product, m.p. 125–135°. By recrystallization from 95% ethanol, there was isolated 2.2 g. of  $\beta, \beta'$ -dithiodipropionamide, m.p. 167–168° (54%), microcrystalline.

*Anal.* Calcd. for  $C_5H_{12}N_2O_2S_2$ : C, 34.59; H, 5.81; S, 30.78. Found: C, 34.68; H, 5.97; S, 30.92.<sup>9</sup>

Hydrolysis of  $\beta, \beta'$ -dithiodipropionamide with dilute hydrochloric acid afforded  $\beta, \beta'$ -dithiodipropionic acid as plates, m.p. 154–155°. The melting point of this compound previously has been reported as 154–155°.<sup>9</sup>

**$\beta$ -(Diethylamino)-propionamide.**—Diethylamine reacts with acrylamide very slowly at room temperatures. Therefore, a solution of 2.84 g. of acrylamide in 7.0 ml. of diethylamine was refluxed for two hours and then allowed to stand overnight. The mixture was filtered of a small amount of polyacrylamide and the filtrate was vacuum distilled.  $\beta$ -(Diethylamino)-propionamide distilled at 154–157° at 8 mm. (4.6 g., 79%). The amide is hygroscopic and cannot be dried *in vacuo* over sulfuric acid.

*Anal.* Calcd. for  $C_7H_{16}N_2O$ : C, 58.29; H, 11.18. Found: C, 56.36, 56.17, 56.48; H, 11.25, 11.12, 11.48.

For identification, a derivative of the amide was prepared with methyl iodide. The derivative was crystallized from a mixture of ethyl acetate and ethanol and melted at 93–94°.

(4) Generously supplied by the American Cyanamid Company.

(5) R. A. Mathes, "Inorganic Syntheses," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 48.

(6) G. M. Bennett and L. V. D. Scoria, *J. Chem. Soc.*, 196 (1927).

(7) J. M. Lovén, *Ber.*, **29**, 1137 (1896).

(8) Sulfur analysis by the Geller Laboratories, Hackensack, N. J.

(9) R. Andreasch, *Monatsh.*, **6**, 836 (1885).

*Anal.* Calcd. for  $C_8H_{19}IN_2O$ : C, 33.57; H, 6.69. Found: C, 33.85; H, 6.94.

**$\beta$ -Morpholinopropionamide.**—When 4.0 g. of morpholine was added to a solution of 2.84 g. of acrylamide in 95% ethanol at room temperature, the temperature rose. The solvent was evaporated in a stream of air and the residue was crystallized from benzene; yield 4.7 g. (75%). The melting point of the purified  $\beta$ -morpholinopropionamide was 98–99°.

*Anal.* Calcd. for  $C_7H_{13}N_2O_2$ : C, 53.14; H, 8.92. Found: C, 53.37; H, 9.12.

**$\beta, \beta'$ -Thiodipropionamide from Hydrogen Sulfide.**—A solution of 0.71 g. of acrylamide and 0.05 g. of sodium sulfide nonahydrate in ethanol was treated with excess hydrogen sulfide. The flask containing the reaction solution was stoppered and the mixture was allowed to stand overnight. The alcohol was evaporated in an air stream and the residue was crystallized from a mixture of benzene and ethanol; yield 0.61 g. (69%). The melting point of the product was 176–177° and this melting point was not lowered when a sample was mixed with the product from triethylammonium dithiocarbamate and acrylamide.

*Anal.* Calcd. for  $C_5H_{12}N_2O_2S$ : C, 40.89; H, 6.87. Found: C, 41.16; H, 7.13.

**$\beta$ -(Benzylthio)-propionamide.**—To a solution of 0.1 g. of potassium hydroxide and 2.5 g. of benzyl mercaptan in 95% ethanol was added 1.42 g. of acrylamide. The temperature of the solution rose to 35° and the solution was then warmed externally to 55°. After being allowed to cool, the solution was neutralized with acetic acid and concentrated in an air stream. There was obtained 3.22 g. of  $\beta$ -(benzylthio)-propionamide as plates, m.p. 110–111°, after recrystallization from benzene; yield 83%.

*Anal.* Calcd. for  $C_{10}H_{13}NOS$ : C, 61.50; H, 6.70. Found: C, 61.62; H, 6.77.

**2-Carbamoyl ethyl Thiolacetate.**—To 1.42 g. of acrylamide in warm benzene (50°) was added 2.0 g. of thioacetic acid. The resulting solution was allowed to cool and stand overnight. From the mixture was separated by filtration 2.36 g. of 2-carbamoyl ethyl thiolacetate as lustrous plates, m.p. 76–77° (80%). By recrystallization from benzene, the melting point was raised to 82–83°.

*Anal.* Calcd. for  $C_6H_9NO_2S$ : C, 40.80; H, 6.16. Found: C, 40.64; H, 6.45.

DEPARTMENT OF CHEMISTRY  
THE UNIVERSITY OF GEORGIA  
ATHENS, GEORGIA

## The Reaction of Labeled Methanol with Carbon Monoxide and Hydrogen<sup>1</sup>

By G. RICHARD BURNS

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Wender, Orchin and co-workers,<sup>2,3</sup> in their studies of the oxo reaction, have reported a variation in which an alcohol rather than an unsaturated compound is heated under pressure with hydrogen and carbon monoxide in the presence of cobalt carbonyl. Methyl alcohol gives, among other products, 40 mole per cent. of ethyl alcohol and 5 of *n*-propyl alcohol. Ziesecke<sup>4</sup> has also carried out this reaction with similar results and has postulated that the *n*-propyl alcohol was formed by the reaction of carbon monoxide with ethylene, resulting from the dehydration of the ethyl alcohol, rather

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission. Presented before the Division of Organic Chemistry at the September 1953 Meeting of the American Chemical Society.

(2) I. Wender, R. Levine and M. Orchin, *THIS JOURNAL*, **71**, 4160 (1949).

(3) I. Wender, R. A. Friedel and M. Orchin, *Science*, **113**, 206 (1951).

(4) K. H. Ziesecke, *Brennstoff Chem.*, **32**, 385 (1952).