51% yield by means of a Gattermann reaction similar to that previously described.

5-Bromo-2-iodo-(trifluoromethyl)-benzene.—In a manner similar to that already described, 4-bromo-2-(trifluoromethyl)-aniline was converted to 5-bromo-2-iodo-(trifluoromethyl)-benzene in 41% yield. The white material after recrystallization from aqueous ethanol melted at 77–78°.

Anal. Calcd. for $C_7H_3BrF_3I$: C, 23.93; H, 0.85. Found: C, 23.86; H, 0.91.

4-Bromo-2-(trifluoromethyl)-benzoic Acid.—The Grignard reagent, readily prepared from 35 g. (0.095 mole) of 5-bromo-2-iodo-(trifluoromethyl) benzene in the usual manner, was carbonated with carbon dioxide pellets. After acidification of the complex with dilute hydrochloric acid, the ether layer was removed and extracted with sodium hydroxide solution. After decolorization of the alkaline solution with Norite, acidification gave a white precipitate of 15.6 g. (0.058 mole, 61% yield) of 4-bromo-2-(trifluoromethyl)-benzoic acid which melted at 124–125° after recrystallization from aqueous ethanol.

Anal. Calcd. for $C_8H_4BrF_3O_2$: C, 35.69; H, 1.49. Found: C, 35.82; H, 1.49.

5,5′-Dibromo-2,2′-bis-(trifluoromethyl)-1,1′-diazoaminobenzene.—During the course of an attempted Gattermann reaction on 23.5 g. (0.098 mole) of 4-bromo-2-(trifluoromethyl)-aniline, a vigorous evolution of gas, at least partly nitrogen dioxide, was observed during the addition of the sodium nitrite. A yellow solid was formed which after filtration and drying weighed 14.5 g. It darkened somewhat on exposure to air over a two-week period. A sample recrystallized from petroleum ether (90–100°) melted at 139–140°. The material does not appear to be soluble in either cold or warm hydrobromic acid. Analytical data are in good agreement with the calculated values for 5,5′-dibromo-2,2′-bis-(trifluoromethyl)-1,1′-diazoaminobenzene.

Anal. Calcd. for $C_{14}H_7Br_2F_6N_3$: C, 34.2; H, 1.43; N, 8.56. Found: C, 34.38; H, 1.55; N, 8.70

Acknowledgment.—The authors are indebted to the Moorman Manufacturing Company, Quincy, Illinois, for the financial assistance which made this work possible.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

Rearrangements Involving 2-Thenylmagnesium Chloride

BY RUSSELL GAERTNER

2-Thenylmagnesium chloride has been prepared and its reactions with carbon dioxide, ethyl chlorocarbonate, acetyl chloride, acetic anhydride, formaldehyde and ethylene oxide have been shown to give 3-substituted-2-methylthiophenes by rearrangement. Only in the case of carbon dioxide has the normal product also been isolated.

The preparation and some properties of 2-thenylmagnesium chloride were recently outlined[1]; in this report we wish to describe that work in detail and to indicate certain extensions of these rearrangements.

The production of a stable Grignard reagent indicates that 2-thenyl chloride must be considered an isoster of benzyl chloride rather than a β-halosulfide.[2] The recent development by Rowlands, Greenlee and Boord[3] of a "cyclic reactor" designed to minimize coupling made possible the preparation of 2-thenylmagnesium chloride in yields as high as 98%, whereas usual techniques gave only 7.3%. Rearrangements involving benzylmagnesium halides have been investigated extensively.[4]

Of more pertinence to this work is the literature concerning halomethyl heterocycles. In the pyridine series, Gilman and Towle[5] have shown that α-picolinyl reagents give rise only to normal products. On the other hand, both 3-thenyl[6] and 3-furfuryl[7] halides readily form reagents, which undergo rearrangement to give 2-substituted derivatives when treated with appropriate reactants.

2-Furfuryl chloride does not yield a reagent under usual conditions.[8] 2-Thenyl chloride was reported[9] previous to the present work to yield largely the dithienylethane and a small amount of a liquid, possibly the product of reaction with ethylene oxide, no other evidence being presented that a reagent was present. 5-Methyl-2-thenyl bromide was shown by Lecocq and Buü-Hoi[10] to rearrange readily to 3-bromo-2,5-dimethylthiophene and to give 2,5-dimethyl-3-thenoic acid upon reaction with magnesium followed by carbonation. Thus, 2-thenylmagnesium chloride is apparently the first example of a Grignard reagent prepared from an α-halomethyl heterocycle.

Several reactions of 2-thenylmagnesium chloride (I) are represented in Chart A. Only in the case of the reaction with carbon dioxide was a "normal" product isolated. 2-Thienylacetic acid (II) and the amide were identified by comparison with authentic samples. The minor product of carbonation, 2-methyl-3-thenoic acid (III), melted at 115–117°[11] and was oxidized with alkaline permanganate to the known thiophene-2,3-dicarboxylic acid which yielded the anhydride.[12] All products of rearrangements were characterized initially in this manner.

The same acid, III, was obtained exclusively when the thenyl reagent was added to excess ethyl chlorocarbonate and the crude ester saponified. It was possible to obtain satisfactory yields only when the mixture was cooled in an acetone–Dry Ice-bath, as was also the case in the reactions with

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(1) Gaertner, THIS JOURNAL, **72**, 4326 (1950).

(2) See Amstutz, *J. Org. Chem.*, **9**, 310 (1944), concerning cleavage of compounds of this class by active metals.

(3) Rowlands, Greenlee and Boord, Abstracts of Papers, American Chemical Society Meeting, Philadelphia, Penna., April 9 to 13, 1950, p. 8L. Dr. K. W. Greenlee kindly supplied a detailed description of the apparatus and technique.

(4) See, for example, (a) Austin and Johnson, THIS JOURNAL, **54**, 647 (1932); (b) Coleman and Forrester, *ibid.*, **58**, 27 (1936); (c) Johnson, *ibid.*, **55**, 3029 (1933); (d) Burtle and Shriner, *ibid.*, **69**, 2059 (1947); (e) Moser and Sause, *J. Org. Chem.*, **15**, 631 (1950).

(5) Gilman and Towle, *Rec. trav. chim.*, **69**, 428 (1950).

(6) Campaigne and LeSuer, THIS JOURNAL, **70**, 1555 (1948).

(7) Sherman and Amstutz, *ibid.*, **72**, 2195 (1950).

(8) Gilman and Hewlett, *Rec. trav. chim.*, [4] **51**, 93 (1932).

(9) Blicke and Burckhalter, THIS JOURNAL, **64**, 477 (1942).

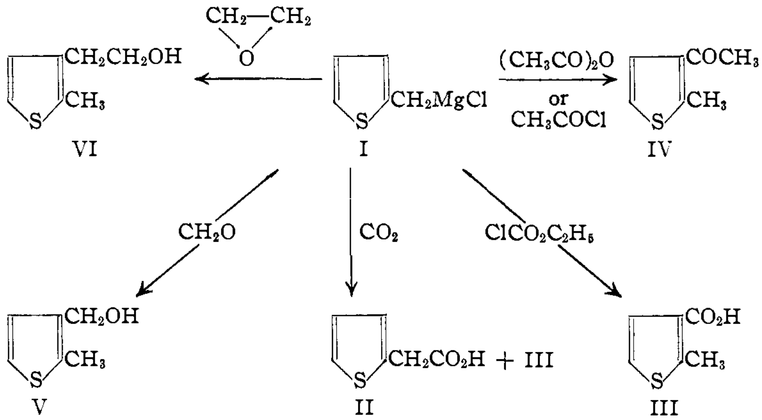
(10) Lecocq and Buũ-Hoi, *Compt. rend.*, **224**, 658 (1947).

(11) Steinkopf and Jacob, *Ann.*, **515**, 273 (1935).

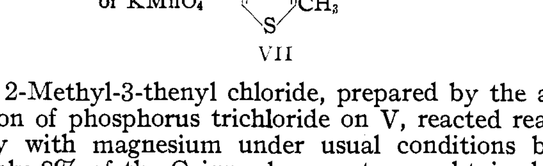
(12) Linstead, Noble and Wright, *J. Chem. Soc.*, 911 (1937).

acetyl chloride and acetic anhydride. With the latter reactants, the major product was 2-methyl-3-acetothienone (IV), identified both by degradation to III by means of sodium hypochlorite, and by synthesis from 2-methyl-3-thenoic acid, which was converted to the chloride and subjected to the action of dimethylcadmium. Comparison of the crystalline oximes from both samples completed the identification. A second higher-boiling product of the reactions with acetyl chloride and acetic anhydride, possibly 1,3-bis-(2-thienyl)-2-methylpropene, could result from initial formation of thienylacetone, followed by reaction of this ketone with another mole of reagent and dehydration. It has been observed[4a] that benzylmagnesium chloride, for example, yields tribenzylcarbinol as well as products of rearrangement when treated with ethyl chlorocarbonate or dibenzylphenylcarbinol when benzoyl chloride is the reactant.

CHART A



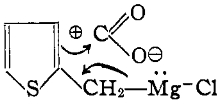
The reactions of I with gaseous formaldehyde or ethylene oxide yielded 2-methyl-3-thenyl alcohol (V) and 2-methyl-3-thenylcarbinol (VI), respectively. The former was prepared by reduction of 2-methyl-3-thenoic acid with lithium aluminum hydride; both samples yielded the same α-naphthylurethan. The ethanol, VI, and its naphthylurethan were similarly obtained from 2-methyl-3-thienylacetic acid which was prepared from IV by application of the Kindler–Willgerodt reaction. A trace of an apparently novel type of product was isolated from this reaction mixture and shown to be 2-methyl-3-thienylglyoxylic acid (VII) by degradation to V and by synthesis from IV by selective oxidation with alkaline permanganate.



2-Methyl-3-thenyl chloride, prepared by the action of phosphorus trichloride on V, reacted readily with magnesium under usual conditions but only 8% of the Grignard reagent was obtained, a solid, probably 1,2-bis-(2-methyl-3-thienyl)-ethane, being the major product.

Small but definite discrepancies between the physical properties of samples of products prepared by different methods presumably indicate that small amounts of isomers were present in the Grignard reaction mixtures; however, no difficulties were experienced in the preparation of solid derivatives with sharp melting points. Particular care was devoted to the examination of the first mother liquors for isomers without result.

Since no rearrangement to the open 5-position was observed, a mechanism involving a cyclic intermediate similar to that suggested for the benzyl case by Johnson[4c] seems indicated; it may be illustrated for the thenyl reagent as:



It is instructive to compare the tendency toward rearrangement of various arylmethyl Grignard reagents; carbonation seems to be most diagnostic of aromatic character. This is not surprising since one would expect the directive influence of this cyclic complex to be more effective the less active (less polar) the reactant. Carbon dioxide reacts so vigorously even at very low temperatures that little opportunity for selectivity is afforded. Although benzylmagnesium chloride gives no detectable *o*-toluic acid on carbonation,[4a] 3-furfurylmagnesium chloride yields principally 3-methyl-2-furoic acid and only a trace of the normal 3-furylacetic acid.[7] Since the 2-thenyl reagent gives 2-thienylacetic acid as the main product but also appreciable amounts of 2-methyl-3-thenoic acid, the decreasing order of tendency toward rearrangement stated by Sherman and Amstutz[7] may be expanded in part as follows: 3-furfuryl, 2-thenyl, benzyl. This series is in qualitative agreement with the order of resonance energies[13] of the nuclei involved: furan (23 kcal. per mole), thiophene (31), benzene (39). Thus the more stable the nucleus the less the tendency to undergo rearrangement, a conclusion which is also understandable in view of the interruption of nuclear stabilization by resonance involved in the rearrangement. It might be added that the high resonance energy (43) of pyridine is in agreement with the observed failure of α-picolinyl reagents to undergo rearrangement.[5]

Investigation of the reactions of thenyl Grignard reagents blocked in the 3-position and of other α-halomethyl heterocycles in this connection—notably those derived from benzothiophene and benzofuran—is continuing in this Laboratory.

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Experimental Part[14]

2-Thenylmagnesium Chloride.—The preparation of the

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[13] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 136.

[14] Melting points are corrected; boiling points are not.

Grignard reagent from 2-thenyl chloride[15] was carried out in the "cyclic reactor" of Rowlands, Greenlee and Boord.[3] It was convenient and effective to perform the amalgamation by dry-packing the column with uniform alternate small additions of magnesium turnings (about 24 g.) and powdered anhydrous mercuric bromide (6 g.), and then adding ether all at once. All operations were carried out in an atmosphere of purified nitrogen. Starting was ensured by placing a small crystal of iodine in the take-off head to be dissolved by the first drops of halide solution.

In most runs 25–30 g. of halide was converted to the reagent in 80–90% yield, indicated by titration of aliquots; the best yield was 98%. The rate of addition of halide was regulated to allow definite boiling in the column. In one run hydrolysis led to 2-methylthiophene (b.p. 111–113°) in 86% yield (this and all subsequent yields are based on the reagent present).

To furnish a comparison with the results employing the "cyclic reactor," an attempt was made to prepare the reagent by conventional means[9]; the yield, determined by titration, was only 7.3%.

Carbonation of 2-Thenylmagnesium Chloride.—A solution (227 ml., 0.620 *N*) containing 0.141 mole of the reagent was added slowly with stirring to about 100 g. of Dry Ice covered with ether. The mixture was allowed to warm to room temperature, acidified with dilute hydrochloric acid, and extracted repeatedly with ether. Recrystallization of the product from petroleum ether (b.p. 60–70°) yielded a crude mixture of acids; m.p. 47–51°; further recrystallization from this solvent furnished pure seed crystals but was inefficient. A better method of fractionation consisted in dissolving about 5 g. of the mixture in 100 ml. of hot water by addition of 10 ml. of glacial acetic acid. During cooling (seeding) in the ice-box overnight, nearly all of the 2-methyl-3-thenoic acid separated as light yellow stubby needles; m.p. 115–117°.[11] Extraction of the mother liquors with ether and recrystallization of the recovered acids from hexane gave the nearly pure thienylacetic acid. In this manner, there was isolated a total of 3.13 g. (15.6% of the theoretical based on reagent) of 2-methyl-3-thenoic acid (m.p. at least 113–115.5°) and 5.82 g. (29.1%) of 2-thienylacetic acid; m.p. 61–62.5°[16] (no depression with authentic[16a] material) except a last crop of 1.04 g. melting at 55–59°. No more than a trace of any other compound could have been present.

2-Thienylacetamide from either source melted at 147–148°[16b,c,d] and a mixture showed no depression.

To a solution of 2.00 g. of 2-methyl-3-thenoic acid and 2.85 g. of sodium hydroxide in 25 ml. of water was added in portions with shaking and cooling at intervals during 30 minutes 4.6 g. of potassium permanganate. The mixture was stirred for 45 minutes and then heated at 100° for two hours. Addition of a few crystals of sodium bisulfite, filtration, acidification of the filtrate, and exhaustive extraction with ether gave a total of 0.72 g. (30%) (triturated with cold benzene) of thiophene-2,3-dicarboxylic acid; m.p. 272–274°[12] (dec., aluminum block).

The acid was heated under reflux for 30 minutes with 15 ml. of acetic anhydride, aspirated, and the residue sublimed at 100° (1 mm.) to give thiophene-2,3-dicarboanhydride,[12] m.p. 140–141°. A similar procedure was used in the identification of each rearrangement product; in every case the acid was converted to its anhydride.

Reaction of the Thenyl Reagent with Ethyl Chlorocarbonate.—A solution (205 ml., 0.85 *N*, 0.179 mole) of the reagent was added during a period of 30 minutes to a well-stirred solution of 95.3 ml. (1 mole) of redistilled ethyl chlorocarbonate in 200 ml. of absolute ether, previously cooled in a Dry Ice–acetone-bath and contained in a system protected by a positive pressure of nitrogen. The bath was removed and the mixture was allowed to warm to about 0°; water was added. To this stirred mixture, under spontaneous reflux, was added cautiously in small portions 100 g. of sodium hydroxide pellets. The resulting alkaline mixture was acidified carefully to allow escape of the carbon dioxide, and the aqueous layer extracted repeatedly with ether. The residual oil was saponified with alcoholic alkali. There remained 3.05 g. of unsaponifiable oil, extracted by ether, which crystallized and proved to be mainly dithienylethane, m.p. 63–65°.

Usual methods gave a total of 17.85 g. (72% yield) of 2-methyl-3-thenoic acid, m.p. 115–117°. It was isolated in four crops from ether and then petroleum ether, the third of which melted at 112–115.5° (0.62 g.) and the fourth, 109–111° (0.35 g.). Thus no other product could have been produced in more than traces. Less than a gram of gummy resin remained from the recrystallization of the last crop.

An indication that this reaction may proceed in much better yield than in the above experiment was found when the crude ester from the reaction of 0.190 mole of reagent with ethyl chlorocarbonate gave a total of 23.14 g. (95%) of 2-methyl-3-thenyl alcohol (b.p. 77–79° at 0.4 mm.; n^{20}_D 1.5497) when reduced directly with 5.7 g. of lithium aluminum hydride.

Reaction of 2-Thenylmagnesium Chloride with Formaldehyde.—The gas formed from 50 g. of dry paraformaldehyde[17] was carried by dry purified nitrogen into 173 ml. of a stirred solution at room temperature containing 0.242 mole of the thenyl reagent. A white gummy precipitate separated rapidly; the Gilman test was negative after one hour. The mixture was cooled in an ice-bath and ice and saturated ammonium chloride solution were added. The product (15.1 g., 49%) boiled at 62–65° (0.4 mm.).

2-Methyl-3-thenyl alcohol is a water-white liquid with the following properties: d^{20}_4 1.1840; n^{20}_D 1.5667; *MR* (calcd.) 35.12,[18] (obsd.) 35.36. The α-naphthylurethan formed clumped white needles from petroleum ether (b.p. 60–70°); m.p. 119–120°.

Anal. Calcd. for $C_{17}H_{15}NO_2S$: C, 68.66; H, 5.09. Found[19]: C, 68.92; H, 5.10.

The carbinol (4.0 g.) was oxidized to 1.83 g. (34%) of thiophene-2,3-dicarboxylic acid.

Reduction of 2-Methyl-3-thenoic Acid.—Addition of an ethereal solution of 6.0 g. of the acid to a stirred suspension of 3.6 g. of lithium aluminum hydride in 100 ml. of ether, followed by usual procedures, and distillation of the residual oil gave a total of 4.60 g. (85%) of a colorless liquid boiling principally at 78–79° (0.9 mm.); d^{20}_4 1.1741; n^{20}_D 1.5501; *MR* (calcd.) 35.12, (obsd.) 35.13.

Anal. Calcd. for C_6H_8OS: C, 56.22; H, 6.29. Found: C, 55.94; H, 6.29.

The α-naphthylurethan melted at 117–119° and no depression was noted after mixture with a sample prepared from the alcohol described previously.

Reaction of the Thenyl Reagent with Acetyl Chloride.—To a mixture of 79 g. (1 mole) of reagent acetyl chloride and about 300 ml. of absolute ether in a system protected by a positive pressure of nitrogen and cooled by a Dry Ice–acetone-bath was added 197 ml. of a solution containing 0.246 mole or 181 ml. containing 0.267 mole of reagent dropwise during one hour. The bath was removed and the mixture allowed to warm to ice temperatures, when water and ice were added to hydrolyze the excess acetyl chloride. 2-Methyl-3-acetothienone (10.62 or 12.68 g., 31 or 34% yield) boiled at 58–61° (2.1 mm.) and successive cuts in this range had closely similar constants: d^{20}_4 1.1427; n^{20}_D 1.5485; *MR* (calcd.) 38.22; (obsd.) 38.99. A smaller fraction (7.68 or 7.72 g.; 28 or 26%) was collected from 104–110° (2.1 mm.); it was very faintly yellow and became darker in color on standing. The sample submitted for analysis was taken from the 106–108° cut; d^{20}_4 1.6660; n^{20}_D 1.5999; *MR* (calcd.) 64.52, (obsd.) 64.64.

Anal. Calcd. for $C_{12}H_{12}S_2$: C, 65.41; H, 5.49; S, 29.10. Found: C, 63.64; H, 5.70; S, 29.21, 29.05.

2-Methyl-3-acetothienone formed an oxime only after heating with strongly alkaline aqueous hydroxylamine; it separated from hexane in compact prisms, m.p. 68.5–69.5°, which sublimed rapidly at 56° (1 mm.).

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(15) Blicke and Leonard, THIS JOURNAL, **68**, 1934 (1946); Wiberg and McShane, *Org. Syntheses*, **29**, 31 (1949).

(16) (a) Blicke and Zienty, THIS JOURNAL, **63**, 2945 (1941), reported a melting point of 75–76°. However, (b) Ford, Prescott and Colingsworth, *ibid.*, **72**, 2109 (1950), reported a value of 62–63°; (c) Crowe and Nord, *J. Org. Chem.*, **15**, 81 (1950), one of 63–64°; and (d) Cagniant, *Bull. soc. chim. France*, 847 (1949), one of 66°. The amide melts at 147–148°.[b,c,d]

(17) Gilman and Catlin, "Organic Syntheses," 2nd edition, Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 188.

(18) The molecular refractions for thiophene derivatives were calculated on the basis of the value of 24.365 for the parent compound determined by Fawcett and Rasmussen, THIS JOURNAL, **67**, 1705 (1945).

(19) Microanalyses were by Mr. Charles W. Beazley, Micro-Tech Laboratories, Skokie, Illinois.

Anal. Calcd. for C_7H_9NOS: C, 54.17; H, 5.84. Found: C, 54.45; H, 6.05.

Oxidation of 2.50 g. of the ketone with alkaline permanganate in the usual manner yielded 0.75 g. (31%) of thiophene-2,3-dicarboxylic acid. When oxidized with sodium hypochlorite solution,[20] 2.00 g. of ketone gave 1.07 g. (53%) of 2-methyl-3-thenoic acid (m.p. 114–116°).

Reaction of 2-Methyl-3-thenoyl Chloride with Dimethylcadmium.—The acid (6.00 g.) was converted by the action of purified thionyl chloride to its chloride (6.24 g., 92%); b.p. 98–100° (16 mm.). It was dissolved in 20 ml. of dry benzene and added dropwise rapidly with stirring to a solution of dimethylcadmium prepared[21] from 11.4 g. of methyl iodide, 1.95 g. of magnesium turnings and 8.25 g. of anhydrous cadmium chloride. The mixture was heated under reflux 75 minutes and decomposed with ice and dilute sulfuric acid. A total of 2.65 g. (49% yield) of colorless material was obtained; b.p. 64–67° (2.0 mm.); d^{20}_4 1.1165; $n^{20}_{\rm D}$ 1.5467; *MR* (calcd.) 38.22, (obsd.) 39.78. The analytical sample was taken from the 65–66° cut.

Anal. Calcd. for C_7H_8OS: C, 59.97; H, 5.75. Found: C, 60.33; H, 6.00.

The oxime was identical with that obtained through the thenyl reagent.

Reaction of the Thenyl Reagent with Acetic Anhydride.—To a mixture of 102 g. (1 mole) of reagent acetic anhydride in 250 ml. of absolute ether cooled in a Dry Ice–acetone-bath with the usual precautions was added with stirring during one hour 146 ml. of a solution containing 0.190 mole of 2-thenylmagnesium chloride. The bath was then removed and when the mixture had warmed to ice temperature saturated ammonium chloride solution was added, followed by dilute hydrochloric acid, and then the whole was stirred vigorously for ten hours. The oil isolated by usual methods was distilled, fractionation giving both 2-methyl-2-acetothienone (6.52 g., 25%; $n^{20}_{\rm D}$ 1.5468; b.p. 43–50° at 0.3 mm.) and the higher-boiling compound presumed to be 1,3-bis-(2-thienyl)-2-propene (9.08 g., 31%; b.p. 100–107° at 0.3–0.7 mm.; $n^{20}_{\rm D}$ 1.6083).

Willgerodt–Kindler Reaction with 2-Methyl-3-acetothienone.—The ketone (6.00 g., product of the reaction with acetyl chloride) was heated under reflux for 15 hours with 4.6 g. of sulfur and 17.2 g. of morpholine. The excess morpholine was removed at the aspirator and 300 ml. of 10% potassium hydroxide solution was added. The mixture was heated under reflux for 11 hours. After being extracted with ether, the aqueous layer was acidified and extracted repeatedly. Removal of the solvents and distillation of the tarry residue *in vacuo* in a sausage flask gave 10.70 g. (b.p. 109–111° at 0.6–0.7 mm.) of light-colored material which solidified, m.p. 55–62°. Recrystallization from hexane gave large crystals. By manual separation and recrystallization of both types, 2-methyl-3-thienylacetic acid (8.2 g.; 52%), plates, m.p. 66.5–68,5°, and a minor product (0.35 g.), light tan prisms, m.p. 83.5–85.5°, were obtained. After repeated crystallization from hexane the former melted at 68.3–69.3°.

Anal. Calcd. for $C_7H_8O_2S$: C, 53.83; H, 5.16. Found: C, 53.84; H, 5.27.

From a smaller run, the solid thiomorpholide was obtained in low yield. It crystallized from ethanol in hard colorless prisms; m.p. 107.8–108.4°.

Anal. Calcd. for $C_{11}H_{15}NOS_2$: C, 54.74; H, 6.26. Found: C, 54.83; H, 6.47.

The minor product was recrystallized from hexane and sublimed twice at 80° (0.3 mm.). 2-Methyl-3-thienylglyoxylic acid, m.p. 88.3–89.1°, formed very light yellow crystals.

Anal. Calcd. for $C_7H_6O_3S$: C, 49.40; H, 3.55; S, 18.84. Found: C, 49.43; H, 3.88; S, 18.84.

Oxidation with sodium hypochlorite[20] gave, after two sublimations, impure colorless material melting at 106–111°. A mixture melting point with authentic 2-methyl-3-thenoic acid (m.p. 115–117°) was 109–114°. The melting point was profoundly depressed by added 2-thenoic acid.

The procedure of Ruffi[22] for the oxidation by alkaline permanganate of methyl thienyl ketones to thienylglyoxylic acids was applied to 2-methyl-3-acetothienone. From 1.00 g. of the pure ketone (prepared from pure 2-methyl-3-thenoic acid) was obtained, after sublimation, 0.31 g. of 2-methyl-3-thienylglyoxylic acid, m.p. 85–87.5°. A mixture with material isolated in the Willgerodt procedure showed no depression.

Reduction of 2-Methyl-3-thienylacetic Acid.—The acid (6.57 g.) was subjected to reduction with lithium aluminum hydride (3.57 g.) in the usual way. The water-white 2-methyl-3-thenylcarbinol boiled at 86.5–87.5° at 2.0 mm.; a total of 5.29 g. (89%) was obtained, successive cuts having closely similar properties: d^{20}_4 1.1293; $n^{20}_{\rm D}$ 1.5468; *MR* (calcd.) 39.74, (obsd.) 39.92.

Anal. Calcd. for $C_7H_{10}OS$: C, 59.12; H, 7.09. Found: C, 59.26; H, 7.02.

The α-naphthylurethan crystallized from benzene–petroleum ether in hard clustered white crystals, m.p. 119.2–119.8°.

Anal. Calcd. for $C_{18}H_{17}NO_2S$: C, 69.42; H, 5.50. Found: C, 69.46; H, 5.45.

Reaction of the Thenyl Reagent with Ethylene Oxide.—A solution (148 ml.) containing 0.241 mole of the reagent was stirred in an ice–salt-bath under a positive nitrogen pressure while a mixture of 26.4 g. (0.6 mole) of ethylene oxide in about 30 ml. of ether was added during one hour. Vigorous reaction occurred at first with each drop and a white precipitate separated. The bath was removed and stirring continued until escape of gas subsided, then ether and excess oxide were removed by distillation until the vapor temperature rose to 34°. Dilute hydrochloric acid was added and stirring continued until dissolution of the precipitate was complete. 2-Methyl-3-thenylcarbinol (13.49 g., 39%) was obtained as a water-white liquid; the analytical sample was taken from the 84–86° (2.0 mm.) cut: d^{20}_4 1.1367; $n^{20}_{\rm D}$ 1.5468; *MR* (calcd.) 39.74, (obsd.) 39.66.

Anal. Calcd. for $C_7H_{10}OS$: C, 59.12; H, 7.09. Found: C, 59.00; H, 7.08.

The α-naphthylurethan was identical with that described above for the alcohol obtained by reduction of the acetic acid. Oxidation of 3.00 g. of the alcohol with alkaline permanganate gave 0.50 g. (14%) of thiophene-2,3-dicarboxylic acid.

2-Methyl-3-thenyl Chloride.—The alcohol (5.00 g.) obtained from 2-methyl-3-thenoic acid was dissolved in 30 ml. of hexane and cooled in an ice–salt-bath. With vigorous stirring, a solution of 2.7 g. of phosphorus trichloride in 20 ml. of solvent was added dropwise. The mixture was allowed to warm to room temperature and decanted from some tarry material onto ice. A total of 3.46 g. (60%) of the chloride was obtained. A larger run (17.25 g.) in which pyridine (2 ml.) was added gave only a 38% yield of chloride and considerable higher-boiling material (b.p. 67–106° at 3.6 mm.), presumably the ether. A portion of the 58–59° cut (3.8 mm.) was submitted for analysis; d^{20}_4 1.5560; $n^{20}_{\rm D}$ 1.2115; *MR* (calcd.) 38.46, (obsd.) 38.91.

Anal. Calcd. for C_6H_7ClS: C, 49.14; H, 4.81. Found: C, 48.96; H, 4.86.

The chloride (9.21 g.) reacted readily with magnesium in ether under usual conditions, but titration of an aliquot of the solution indicated a yield of reagent of only 7.9%. Reaction of this solution with ethyl chlorocarbonate in the manner described for the thenyl reagent gave no acidic product. However, the neutral oil obtained from this reaction mixture crystallized almost completely in the ice-box; recrystallization of the solid from hexane was attended by great loss but a small amount of a pure compound, probably 1,2-bis-(2-methyl-3-thienyl)-ethane, was finally obtained as colorless plates with a bibenzyl odor; m.p. 65.5–66.5°.

Anal. Calcd. for $C_{12}H_{14}S_2$: C, 64.82; H, 6.34. Found: C, 64.94; H, 6.42.

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[20] Newman and Holmes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 428.

[21] The procedure was similar to that described by Cason and Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 325.

[22] Ruffi, *Ber.*, **20**, 1740 (1887).