

*Anal.* Calcd. for  $C_{10}H_8Br_4$ : Br, 71.4. Found: Br, 71.8.

As deposited from chloroform solution, the crystals were transparent; they become opaque on standing, although no other evidence of decomposition was noted over a period of two months.

When 3.9 g. of tetrabromide was heated at  $140^\circ$  for three hours, bromine and hydrogen bromide were evolved. Fractional sublimation of the 2.5 g. of residue at 18 mm. pressure yielded 0.41 g. of  $\alpha$ -bromonaphthalene and 1.8 g. of a solid analyzing for 52.8% bromine (corresponding to 82 mole % of dibromonaphthalenes and 18 mole % of monobromonaphthalenes). On this basis, 8.7 millimoles of naphthalene tetrabromide gave 3.2 millimoles of monobromonaphthalenes and 5.4 millimoles of dibromonaphthalenes.

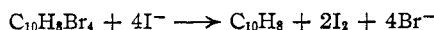
Behavior of the addition compound toward several reagents is summarized in Table V, the reactions being carried out by refluxing 0.2 g. of tetrabromide in 10 ml. of solution. The extent of reaction was determined by titration of the bromide ion in experiments 1-4, by titration of iodine<sup>25</sup> in experiments 5-6.

(25) R. T. Dillon, W. G. Young and H. J. Lucas, *THIS JOURNAL*, **52**, 1953 (1930).

TABLE IV

Expt.	Solvent	Reagent	DEHALOGENATION OF NAPHTHALENE TETRABROMIDE	
			Br removed, %	Time, hr.
1	60% EtOH	H <sub>2</sub> O	39	2.5
2	75% EtOH	4% NaOH	63	2.3
3	75% EtOH	4% NaOH	62	5.0
4	75% EtOH	AgNO <sub>3</sub>	71	2.5
5	99% MeOH	Excess KI	94	1.5
6	99% MeOH	Excess KI	96	2.0

Since not more than 50% of the halogen could be removed by simple elimination of hydrogen bromide (to give dibromonaphthalenes), it appears that the action of alkali must cause some hydrolysis or effective elimination of bromine as well. Since no acid is formed in the reaction of potassium iodide with the addition compound, the reaction of potassium iodide with the tetrabromide is represented by the equation



SCHENECTADY, N. Y.

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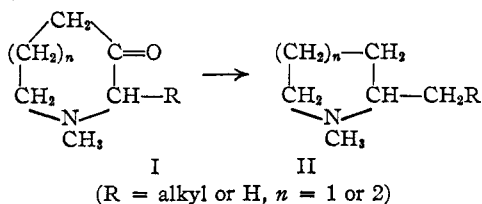
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Rearrangement of $\alpha$ -Thiaketones During Clemmensen Reduction<sup>1,2</sup>

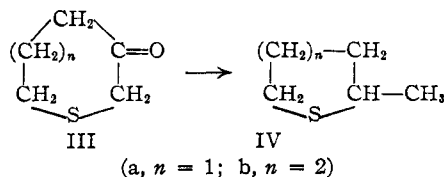
BY NELSON J. LEONARD AND JOHN FIGUERAS, JR.

It has been shown that monocyclic six- and seven-membered ring  $\alpha$ -thiaketones undergo rearrangement during Clemmensen reduction. Specifically, 3-ketothiacyclohexane is converted to 2-methylthiacyclopentane and 3-ketothiacycloheptane is converted to 2-methylthiacyclohexane upon reduction with zinc amalgam and hydrochloric acid.

Reports from this Laboratory<sup>3</sup> have indicated that monocyclic  $\alpha$ -aminoketones of the type I undergo reduction-rearrangement to II when subjected to treatment with zinc amalgam and hydrochloric acid. It was reasonable to expect that analogous monocyclic  $\alpha$ -thiaketones would undergo



similar ring contraction during Clemmensen reduction. This prediction has been confirmed by the observation that 3-ketothiacyclohexane (IIIa) and 3-ketothiacycloheptane (IIIb) are converted to 2-methylthiacyclopentane (IVa) and 2-methylthiacyclohexane (IVb), respectively, under Clemmensen reduction conditions.



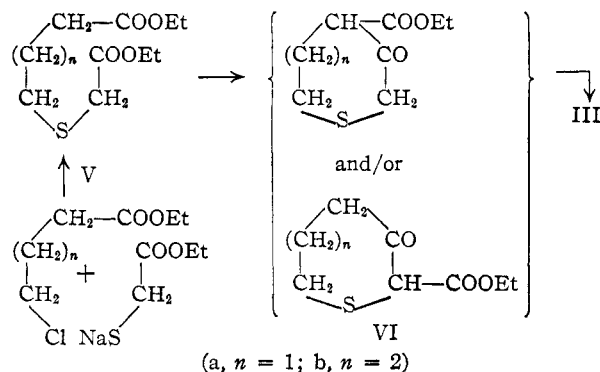
3-Ketothiacyclohexane (IIIa) was obtained by

(1) Reported at the Twelfth National Organic Symposium of the American Chemical Society, Denver, Colorado, June 14, 1951.

(2) This work was supported in part by a grant from E. I. du Pont de Nemours and Company, Inc.

(3) N. J. Leonard and W. V. Ruyle, *THIS JOURNAL*, **71**, 3094 (1949); N. J. Leonard and E. Barthel, Jr., *ibid.*, **71**, 3098 (1949); N. J. Leonard and E. Barthel, Jr., *ibid.*, **72**, 3632 (1950).

hydrolysis and subsequent decarboxylation of the  $\beta$ -ketoester (VIa) resulting from the Dieckmann ring closure of carbethoxymethyl  $\gamma$ -carbethoxypropyl sulfide (Va). The diester sulfide (Va) was available through the condensation of ethyl  $\gamma$ -



chlorobutylate with the sodio derivative of ethyl thioglycolate. While the position of the carbethoxyl group in the  $\beta$ -keto ester (VIa) is regarded as equivocal, either of the possible structures would produce 3-ketothiacyclohexane (IIIa). The structure of the  $\alpha$ -thiaketone IIIa was confirmed by analysis, infrared absorption spectrum, and the formation of ketone derivatives. The seven-membered ring  $\alpha$ -thiaketone IIIb was synthesized by the same route (Vb  $\rightarrow$  VIb  $\rightarrow$  IIIb), starting with ethyl  $\delta$ -chlorovalerate.

The identity of the cyclic sulfides resulting from the Clemmensen reductions of IIIa and IIIb was established by comparison of their infrared spectra with those of authentic samples of 2-methylthiacyclopentane (IVa) and 2-methylthiacyclohexane

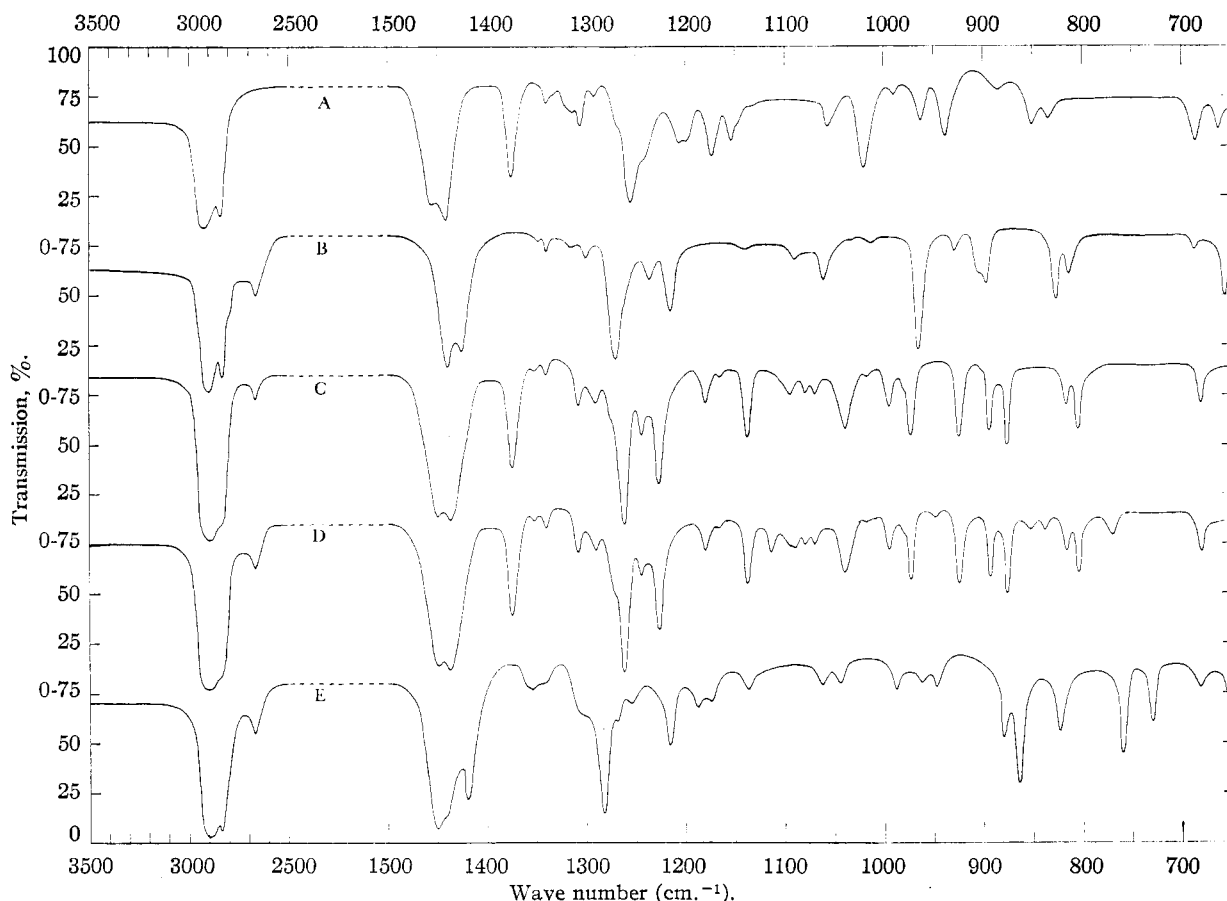
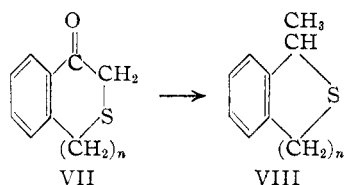


Fig. 1.—Infrared absorption spectra: A, 2-methylthiacyclopentane; B, thiacyclohexane; C, authentic 2-methylthiacyclohexane; D, 2-methylthiacyclohexane from Clemmensen reduction of 3-ketothiacycloheptane; E, thiacycloheptane.

(IVb), respectively (Fig. 1). Pure specimens of 2-methylthiacyclopentane, thiacyclohexane, 2-methylthiacyclohexane and thiacycloheptane were prepared by condensation of sodium sulfide with the appropriate dihalide.

Our finding that a six-membered monocyclic  $\alpha$ -thiaketone (IIIa) undergoes ring contraction under Clemmensen reduction conditions is consistent with the earlier observation by von Braun and Weissbach<sup>4</sup> of similar contraction (in comparable yield) of a six-membered  $\alpha$ -thiaketone ring in the bicyclic series. These workers found that 4-ketothiochroman (VII,  $n = 1$ ) underwent reduction-rearrangement to give 1-methyl-1,2-dihydroisothionaphthene (VIII,  $n = 1$ ), and they



indicated that the first step in the process was the hydrogenolysis of the  $C_{\alpha}$ -S bond. Although von Braun and Weissbach made the seven- and eight-membered ring homologs (VII,  $n = 2,3$ ) of 4-ketothiochroman, apparently they did not subject these  $\alpha$ -thiaketones to Clemmensen reduction.

(4) J. von Braun and K. Weissbach, *Ber.*, **62**, 2416 (1929).

Our finding that a seven-membered monocyclic  $\alpha$ -thiaketone (IIIb) undergoes rearrangement indicates the probable upper limit in ring-size<sup>5</sup> for contraction to occur where the sulfur and carbonyl functions are homocyclic. The fate of a five-membered monocyclic  $\alpha$ -thiaketone (III,  $n = 0$ ) upon Clemmensen reduction is complicated by the fact that  $C_{\beta}$ -S cleavage by elimination accompanies  $C_{\alpha}$ -S cleavage by hydrogenolysis, according to the observations of Schmid and Schnetzler.<sup>6</sup>

### Experimental<sup>7</sup>

**A. Ketones.** Carbethoxymethyl  $\gamma$ -Carbethoxypropyl Sulfide (Va).—To a solution of 5.4 g. (0.23 gram atom) of sodium in 200 ml. of absolute ethanol was added 27.8 g. (0.23 mole) of redistilled ethyl thioglycolate,  $n_D^{20}$  1.4575, a trace of sodium iodide, and 34.8 g. (0.23 mole) of ethyl  $\gamma$ -chlorobutyrate. The resulting mixture was heated at the reflux temperature for two hours with stirring, after which it was cooled to 20°. The salt was removed by filtration and the ethanol was removed from the filtrate by concentration at reduced pressure. To the residue was added 70 ml. of chloroform, and the chloroform solution was washed several times with water. The chloroform was removed by distillation, and the residual liquid was fractionally distilled *in vacuo*, b.p. 85° (0.07 mm.);  $n_D^{20}$  1.4663;  $d_4^{20}$  1.086; yield 43.0 g. (89%).

(5) N. J. Leonard and R. C. Sentz, unpublished results.

(6) H. Schmid and E. Schnetzler, *Helv. Chim. Acta*, **34**, 894 (1951); see also H. Schmid and E. Grob, *ibid.*, **31**, 360 (1948).

(7) All melting points are corrected. The authors are indebted to Miss Elizabeth M. Petersen for determination of the infrared absorption spectra.

*Anal.* Calcd. for  $C_{10}H_{18}O_4S$ : C, 51.26; H, 7.74; *MRD*, 59.65. Found: C, 51.55; H, 7.72; *MRD*, 59.81.

**Dieckmann Ring Closure of Carbethoxymethyl  $\gamma$ -Carbethoxypropyl Sulfide.**—To a suspension of 1.97 g. (0.086 gram atom) of sodium in 200 ml. of dry toluene was added cautiously an excess of absolute ethanol (*ca.* 25 ml.). When the solution of sodium was complete at the boiling point of the mixture, the excess ethanol was removed as the ethanol-toluene azeotrope. When the distillation temperature had reached 105°, 20.0 g. (0.086 mole) of carbethoxymethyl  $\gamma$ -carbethoxypropyl sulfide in 75 ml. of dry toluene was added over a period of five minutes, with efficient stirring. After several minutes there was a violent ebullition of ethanol, and a white precipitate formed. The ethanol-toluene azeotrope was removed by distillation, and after 15 minutes the distillation temperature rose to 106°. The reaction mixture was cooled to 20° and poured onto a mixture of 100 g. of ice and 15 ml. of 12 *N* hydrochloric acid. The organic layer was removed and the aqueous layer was extracted with three 50-ml. portions of ether. The combined organic material was dried and the solvents were removed by distillation (*in vacuo* after removal of the ether). The residual  $\beta$ -ketoester (VIa) was fractionated, b.p. 65° (0.09 mm.);  $n_D^{20}$  1.5240;  $d_4^{20}$  1.208; yield 12.1 g. (75%).

*Anal.* Calcd. for  $C_8H_{12}O_5S$ : C, 51.05; H, 6.43; *MRD*, 46.58 (keto), 47.63 (enol). Found: C, 51.29; H, 6.66; *MRD*, 47.66.

**3-Ketothiacyclohexane (IIIa).**—A mixture of 31.0 g. (0.165 mole) of the  $\beta$ -ketoester VIa and 100 ml. of 2 *N* sulfuric acid was stirred at the reflux temperature for nine hours. The reaction mixture was cooled and extracted with three 30-ml. portions of methylene chloride. The solvent was removed from the combined extracts, and the residue was fractionated *in vacuo*, b.p. 80° (4 mm.);  $n_D^{20}$  1.5290; yield 16.3 g. (85%). The infrared absorption spectrum showed the presence of a carbonyl group (1710  $cm^{-1}$ ) and the C-S-C group (763  $cm^{-1}$ ).

*Anal.* Calcd. for  $C_6H_8OS$ : C, 51.73; H, 6.94. Found: C, 52.15; H, 6.99.

The semicarbazone was formed in aqueous ethanol and crystallized from water as small prisms, m.p. 166.5–167°.

*Anal.* Calcd. for  $C_6H_{11}N_3OS$ : C, 41.60; H, 6.40; S, 18.51. Found: C, 41.60; H, 6.21; S, 18.54.

The oxime was formed in aqueous ethanol and was purified by sublimation at 85° (0.3 mm.); small prisms, m.p. 77–77.5°.

*Anal.* Calcd. for  $C_6H_9NOS$ : C, 45.74; H, 6.91. Found: C, 45.83; H, 6.98.

**Carbethoxymethyl  $\delta$ -Carbethoxybutyl Sulfide (Vb).**—The diester sulfide Vb was prepared from ethyl  $\delta$ -chlorovalerate (b.p. 71–72° (2 mm.)),  $n_D^{20}$  1.4362) and the sodio derivative of ethyl thioglycolate following the procedure used for Va; b.p. 106° (0.2 mm.);  $n_D^{20}$  1.4659;  $d_4^{20}$  1.074; yield 78%.

*Anal.* Calcd. for  $C_{11}H_{20}O_4S$ : C, 53.20; H, 8.12; *MRD*, 64.27. Found: C, 53.50; H, 8.01; *MRD*, 64.02.

**Dieckmann Ring Closure of Carbethoxymethyl  $\delta$ -Carbethoxybutyl Sulfide.**—The  $\beta$ -ketoester Vlb was prepared from the diester sulfide Vb by the method employed for the corresponding six-membered ring compound VIa, with two modifications: the diester sulfide was added to the sodium ethoxide in toluene in a dilution of 0.1 mole in 400 ml. of dry toluene over a period of two hours, and the total reaction time was increased to 2.5 hours. The  $\beta$ -ketoester was obtained in 23% yield, b.p. 102° (0.9 mm.),  $n_D^{20}$  1.5177. It appeared to be unstable under distillation conditions and was not characterized further.

**3-Ketothiacycloheptane (IIIb).**—A mixture of 15.0 g. (0.074 mole) of the  $\beta$ -ketoester Vlb and 50 ml. of 2 *N* sulfuric acid was stirred overnight on a steam-bath. The reaction mixture was worked up in the manner described for the isolation of IIIa; b.p. 54° (0.55 mm.); m.p. 20.5–21°;  $n_D^{20}$  1.5285; yield 8.4 g. (76%). The infrared absorption spectrum confirmed the presence of the ketone function (1697  $cm^{-1}$ ).

The oxime was formed in aqueous ethanol and was purified by sublimation at 85° (0.15 mm.); small prisms, m.p. 96–97°.

*Anal.* Calcd. for  $C_6H_{11}NOS$ : C, 49.62; H, 7.64. Found: C, 49.44; H, 7.58.

The benzoyl derivative of the oxime was prepared by

shaking the oxime with benzoyl chloride and aqueous sodium hydroxide and was recrystallized from petroleum ether (b.p. 90–110°); long needles, m.p. 91–92°.

*Anal.* Calcd. for  $C_{13}H_{15}NO_2S$ : C, 62.62; H, 6.06; S, 13.16. Found: C, 63.03; H, 6.16; S, 13.06.

The semicarbazone of IIIb, formed in aqueous ethanol, crystallized from methanol as plates, m.p. 189.5–190°.

**B. Sulfides. 1,4-Dibromopentane.**—A modification of the procedure of Lipp<sup>8</sup> was employed. To a stirred solution of 10.0 g. (0.115 mole) of tetrahydroxyvan<sup>9</sup> in 60 ml. of 40% hydrobromic acid, heated on the steam-bath under a reflux condenser, was added cautiously 40 g. of concentrated sulfuric acid. Heating and stirring were continued for 3.5 hours. The reaction mixture was cooled, the organic layer was removed, and the aqueous layer was extracted with a small portion of chloroform. The combined organic layers were dried, the chloroform was distilled, and the residue was carefully fractionated, b.p. 88–89° (15 mm.);  $n_D^{20}$  1.5075; yield 21.2 g. (80%).

**2-Methylthiacyclopentane (IVa).**<sup>10,11,12</sup>—This compound was prepared from 1,4-dibromopentane and sodium sulfide in aqueous ethanol; b.p. 132° (750 mm.);  $n_D^{20}$  1.4920;  $d_4^{20}$  0.960.<sup>12a</sup> The pure material exhibited the infrared absorption spectrum recorded in Fig. 1, curve A.

**Thiacyclohexane.**<sup>13,14</sup>—A slight modification of Clarke's synthesis<sup>13</sup> was employed, using sodium sulfide and 1,5-dichloropentane in aqueous ethanol; b.p. 141° (750 mm.); m.p. 15.5–16°;  $n_D^{20}$  1.5057; infrared absorption spectrum, Fig. 1, curve B.

**2-Methylthiacyclohexane (IVb).**<sup>15</sup>—A low yield of IVb was obtained by permitting equimolar portions of 1,5-dichlorohexane<sup>16</sup> and sodium sulfide to react in aqueous ethanol over a period of seven hours at the reflux temperature. The reaction mixture was steam distilled, and the distillate was extracted with ether. The combined ether extracts were dried and the ether and ethanol were removed by distillation. The residue was fractionated through a Craig still.<sup>17</sup> The first two fractions, *ca.* 0.4 g. (from a 0.1 mole run), which had the highest refractive index ( $n_D^{20}$  1.4875), were combined and distilled twice from sodium at an air-bath temperature of 155°; b.p. 151° (750 mm.);  $n_D^{20}$  1.4898; infrared absorption spectrum, Fig. 1, curve C.

*Anal.* Calcd. for  $C_6H_{12}S$ : C, 61.98; H, 10.41. Found: C, 61.99; H, 10.62.

The methiodide was formed in absolute ethanol and precipitated with ether, m.p. 160–161° (sublimes).

**Thiacycloheptane.**<sup>18</sup>—1,6-Dibromohexane and sodium sulfide reacted in aqueous ethanol to give thiacycloheptane in 7% yield. The product was distilled twice from sodium at an air-bath temperature of 170–175°; b.p. 174° (750 mm.);  $n_D^{20}$  1.5125; infrared absorption spectrum, Fig. 1, curve E.

*Anal.* Calcd. for  $C_6H_{12}S$ : C, 61.98; H, 10.41. Found: C, 62.26; H, 10.42.

The methiodide was formed in ethanol and precipitated with ether, m.p. 141.5–142°.

**C. Clemmensen Reductions. Clemmensen Reduction of 3-Ketothiacyclohexane (IIIa).**—To 50 g. of amalgamated

(8) A. Lipp, *Ber.*, **22**, 2569 (1889).

(9) Kindly supplied by the Electrochemicals Division, E. I. du Pont de Nemours and Company, Inc., Niagara Falls, New York.

(10) J. von Braun, *Ber.*, **43**, 3220 (1910).

(11) E. Grishkevich-Trokhimovskii, *J. Russ. Phys. Chem. Soc.*, **48**, 901 (1916).

(12) Yu. K. Yur'ev, *J. Gen. Chem. (U. S. S. R.)*, **8**, 1934 (1938).

(12a) Since submission of this article, E. V. Whitehead, R. A. Dean and F. A. Fidler (*THIS JOURNAL*, **73**, 3632 (1951)) have reported the synthesis of compounds IVa, IVb, and thiacyclohexane, with physical properties in satisfactory agreement with ours.

(13) H. T. Clarke, *J. Chem. Soc.*, **101**, 1788 (1912).

(14) Yu. K. Yur'ev, E. Ya. Pervova and V. A. Sazonova, *J. Gen. Chem. (U. S. S. R.)*, **9**, 590 (1939).

(15) E. Grishkevich-Trokhimovskii, *J. Russ. Phys. Chem. Soc.*, **48**, 928 (1916).

(16) Prepared by the method of J. von Braun and W. Sobacki (*Ber.*, **44**, 1039 (1911)) from phosphorus pentachloride and *N*-benzoyl- $\alpha$ -picoline. The latter was obtained in 85% over-all yield by direct benzylation of the product resulting from the high-pressure hydrogenation of  $\alpha$ -picoline over Raney nickel.

(17) L. C. Craig, *Ind. Eng. Chem., Anal. Ed.*, **9**, 441 (1937).

(18) E. Grishkevich-Trokhimovskii, *J. Russ. Phys. Chem. Soc.*, **48**, 944 (1916).

zinc and 40 ml. of water were added 5.0 g. (0.043 mole) of 3-ketothiacyclohexane and 30 ml. of concentrated hydrochloric acid. The mixture was heated to boiling, and 100 ml. of concentrated hydrochloric acid was added over the course of one hour while water and steam-volatile oil were collected by distillation. The distillate was extracted with three 25-ml. portions of ether. The combined extracts were dried and the ether was removed, leaving 1.5 g. of crude product. Fractionation through a Craig still<sup>17</sup> gave 0.9 g. (21%) of a colorless liquid, with physical properties identical with those of authentic 2-methylthiacyclohexane (IVa); b.p. 132° (750 mm.);  $n_D^{20}$  1.4920;  $d_4^{20}$  0.962. The infrared absorption spectrum of the Clemmensen product was superposable on that of the authentic sulfide (Fig. 1, curve A). Of special significance is the strong absorption due to the CH<sub>3</sub>-group (1375 cm.<sup>-1</sup>) which was created by the reduction-rearrangement and the absence of absorption bands characteristic of thiacyclohexane (curve B).

**Clemmensen Reduction of 3-Ketothiacycloheptane (IIIb).**—The reduction was carried out in the manner described for IIIa, using 5.5 g. (0.042 mole) of 3-ketothiacycloheptane, with the exception that the ketone was allowed to react with the amalgamated zinc and hydrochloric acid (80 ml. of concentrated acid, 20 ml. of water) at the reflux tempera-

ture for one-half hour before distillation was begun. The product from the reaction was fractionally distilled, b.p. 85–87° (94 mm.);  $n_D^{20}$  1.4940; wt. 1.9 g. (34% yield). The higher-boiling residue was distilled twice from sodium in an air-bath at 160–165°;  $n_D^{20}$  1.5046. The infrared absorption spectrum of this portion of the product showed a strong CH<sub>3</sub> band at 1372 cm.<sup>-1</sup> and a C=C band at 1647 cm.<sup>-1</sup>, but the constitution of this unsaturated by-product was not otherwise established. The 1.9-g. distillate fraction mentioned above was distilled twice from sodium at an air-bath temperature of 170–175°; b.p. 153° (750 mm.);  $n_D^{20}$  1.4923. The infrared spectrum of this portion of the product is practically identical (Fig. 1, curve D) with that of an authentic sample of 2-methylthiacyclohexane (curve C), although the Clemmensen product exhibited extraneous weak absorption bands at 950, 850 and 775 cm.<sup>-1</sup>. Nevertheless, these spectra show that the major constituent of the Clemmensen product is 2-methylthiacyclohexane. The product which would result if the Clemmensen reduction of IIIb were to occur *without* rearrangement, namely, thiacycloheptane, has an infrared absorption spectrum (curve E) which is markedly different from curves C and D.

URBANA, ILLINOIS

RECEIVED JULY 30, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF FORDHAM UNIVERSITY]

## The Friedel-Crafts Alkylation of 2,5-Dimethylthiophene

BY NICHOLAS MESSINA<sup>1</sup> AND ELLIS V. BROWN

The Friedel-Crafts alkylation of 2,5-dimethylthiophene has been accomplished using various alkyl halides with aluminum chloride as the catalyst. In contradistinction to thiophene itself, it was found that this substituted thiophene alkylated readily with only a minor amount of polymerization when an active halide like *t*-butyl chloride was used. With less active halides, such as *n*-butyl chloride, some replacement of alkyl groups in 2,5-dimethylthiophene occurred and polymerization increased. Structures for most of the alkylated thiophenes prepared have been proved by synthesis.

The alkylation of thiophene was first reported by Schleicher in 1886, who used isopropyl chloride and aluminum chloride.<sup>2</sup> However, he obtained only traces of an alkylthiophene. This reaction was not investigated further until 1946 when Kutz and Corson reported the alkylation of thiophene employing olefins in the presence of an alumina-silica type catalyst.<sup>3</sup> Later Appleby, Sartor and Lee achieved the alkylation with phosphoric acid catalyst and olefins at elevated temperatures and pressure.<sup>4</sup> They reported that alkylation not only took place in the expected alpha position but considerable alkylation also occurred in the beta position. In recent years many other reports on the alkylation of thiophene have appeared in the literature,<sup>5</sup> however, in all cases these involved olefins as the alkylating agents.

In view of the fact that thiophene has not been alkylated by alkyl halides in the presence of the metallic halide catalysts, it was considered of interest to investigate the reaction with substituted thiophene using these conditions.

It was found that the Friedel-Crafts alkylation of 2,5-dimethylthiophene would take place when alkyl halides in the presence of aluminum chloride were employed. Thus replacement of both  $\alpha$ -hydrogens with methyl groups activated thiophene

to such an extent that alkylation took place before polymerization. Table I shows the results of the alkylation of 2,5-dimethylthiophene with *t*-butyl chloride, isopropyl chloride, *n*-butyl chloride and ethyl bromide in the presence of aluminum chloride. The yield of the expected  $\beta$ -alkylthiophene decreased with decreasing reactivity of the alkyl halide. This becomes quite evident when comparing the yields obtained with *t*-butyl chloride (90–93%) and *n*-butyl chloride (38–43%). In fact, when the more reactive *t*-butyl chloride was the alkylating agent, the only product isolated was the expected 2,5-dimethyl-3-*t*-butylthiophene. If the less reactive alkyl halides were employed, some replacement of one of the  $\alpha$ -methyl groups by the corresponding alkyl group of the alkyl halide occurred. Even when the alkyl halide was slightly less reactive as, for example, isopropyl chloride, the yield of the expected  $\beta$ -alkylthiophene decreased and replacement of one of the  $\alpha$ -methyl groups occurred.

The 2,5-dimethyl-3-ethylthiophene, obtained from the alkylation with ethyl bromide, was characterized by preparing it from the known 2,5-dimethyl-3-acetothienone by a Clemmenson reduction.<sup>6</sup> Both hydrocarbons were acetylated to give 2,5-dimethyl-3-ethyl-4-acetothienone. Since the ketone seemed to be hindered and did not react readily with the usual carbonyl reagents and since it was resistant to oxidation, solid derivatives were prepared by putting both samples through Willgerodt reactions according to the method of Blanch-

(1) A portion of a thesis by Nicholas Messina submitted to Fordham University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) E. Schleicher, *Ber.*, **19**, 872 (1886).

(3) W. Kutz and B. Corson, *This Journal*, **68**, 1477 (1946).

(4) W. Appleby, A. Sartor and H. Lee, *ibid.*, **70**, 1552 (1948).

(5) H. Pines, B. Kvetinakis and J. Vesely, *ibid.*, **72**, 1568 (1950); V. Weinmayr, *ibid.*, **72**, 918 (1950); P. Caesar, *ibid.*, **70**, 3623 (1948).

(6) Buu-Hoi and Nguyen-Hoan, *Rec. trav. chim.*, **67**, 309 (1948).