rated ammonium chloride solution. The remaining clear liquid was filtered, the ether layer removed and dried over anhydrous magnesium sulfate. After removal of the ether, there remained an oily residue boiling at 94–98.5° (1.0 mm.), $n^{25}D$ 1.5122, yield 81 g., 63%.

Sodium. Di-(2-thienyl)-carbinol.—A sodium amalgam sand[12] containing 25 g. (1.09 g. atoms) of sodium and 10 g. (0.05 gram-atom) of mercury was covered with 200 ml. of ether to which 63 g. (0.75 mole) of thiophene was added. The mixture was cooled to 5°, and 78 g. (0.5 mole) of bromobenzene added over a 1-hour period.[13] Stirring of the cooled mixture was continued for one hour, after addition, and then refluxed for two hours, after which it was cooled, and 77.6 g. (0.4 mole) of 2-thiophenecarboxaldehyde added slowly with cooling. The mixture was hydrolyzed after one hour with a saturated solution of ammonium chloride, the reaction mixture becoming quite clear when an excess of NH_4Cl solution was added. The solution was filtered, dried over anhydrous magnesium sulfate, and the ether removed. The residue was poured into petroleum ether with vigorous agitation and a tan solid was collected and dried, m.p. 74–76°, yield 84.5 g. (76%). Further purification from an ether/petroleum ether mixture yielded long white needles, m.p. 57.5–58.3°. *Anal.* Calcd. for $C_9H_8OS_2$: S, 16.33. Found: S, 16.48.

Dehydration Products. 2-Vinylthiophene.—Forty grams of 1-(2-thienyl)-ethanol was distilled under reduced pressure (50 mm.) through a tube filled with activated alumina which was heated to 250°. The condensed water–olefin mixture was separated, the olefin taken up in 100 ml. of ether and the solution dried over anhydrous magnesium sulfate. After removal of the ether, there remained a clear colorless oil which was distilled through a 10-plate column; b.p. 50.5–51° (28 mm.), $n^{25}D$ 1.5731. *Anal.* Calcd.: H, 6.51; C, 67.68. Found: H, 6.60; C, 67.45.

Urethans.—To 2 g. of the pure 2-thienylalkanol in a small glass stoppered vial, was added an equal volume of phenyl isocyanate. The reaction mixture was placed in a desiccator under refrigeration for about 2 weeks at which time a white, soft, solid was observed. This residue was stirred for 15 minutes in 100 ml. of boiling petroleum ether (b.p. 30–60°), the mixture filtered, cooled and let stand for several days. The white crystals formed were collected on a filter. After two more crystallizations in the same manner, the dried sample was sent in for analysis.

Acknowledgment.—The authors wish to thank the Research Corporation for a Frederick Gardner Cottrell grant-in-aid supporting this project. We also wish to thank the Carbon and Carbide Chemicals Co. for generous donations of most of the aldehydes used in this investigation.

HOLLAND, MICHIGAN

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[12] Reference 5, p. 506.

[13] J. C. Schick and H. D. Hartough, THIS JOURNAL, **70**, 1645 (1948).

[CONTRIBUTION FROM THE DIVISION OF NATURAL SCIENCES, GRINNELL COLLEGE]

Studies in the Synthesis of Long-chain Compounds[1,2]

BY HANS WYNBERG AND A. LOGOTHETIS

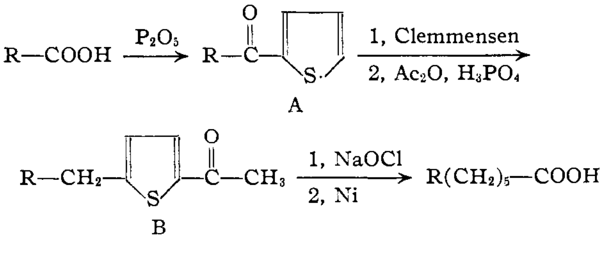
RECEIVED OCTOBER 21, 1955

A synthetic scheme is described for the preparation of long-chain mono- and dicarboxylic acids, ketones, alcohols and hydrocarbons.

Although the reductive removal of sulfur from sulfur containing organic compounds has been known for over fifteen years,[3] it is only recently that this versatile reaction has been applied to synthetic problems. The conversion of a carbonyl group to a methylene group,[4] and the conversion of a thiolester to an aldehyde[5] are typical examples. More specifically related to the present work are the studies pertaining to the reductive removal of sulfur from thiophene compounds[6-8] using either Raney nickel or nickel aluminum alloy.[8]

More recently three groups of investigators[9a,b,c] have started to investigate the desulfurization of substituted thiophenes for the preparation of a number of fatty acids.

The purpose of our investigation has been to establish a synthetic route to a variety of long-chain compounds using thiophene and bithienyl as synthetic intermediates which are eventually transformed by reductive desulfurization into four and eight carbon chains, respectively. To date the type of compounds prepared include mono- and dicarboxylic saturated fatty acids, straight-chain and branched-chain hydrocarbons, straight and branched-chain secondary and tertiary alcohols and straight-chain ketones. The lengths of the chains have been varied from ten to thirty-six carbon atoms for representative examples.



The synthesis of fatty acids commences with the acylation of thiophene with a carboxylic acid,[10] the ketone A thus produced (see Table I) yielding another ketone B after reduction and reacylation. The latter (B) are converted smoothly by hypohalite oxidation, followed by Raney nickel desulfurization to the desired fatty acid. It is evident from the above scheme that the readily available even-

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[1] This work was supported in part by the Office of Ordnance Research, Contract Number DA-11-022-ORD-1579.

[2] Presented at the 128th Meeting of the American Chemical Society, September, 1955.

[3] J. Bougeault, E. Cattelain and P. Chabrier, *Bull. soc. chim. France*, **7**, 781 (1940).

[4] M. Wolfrom and J. Karabinos, THIS JOURNAL, **66**, 909 (1944).

[5] E. Mosettig, "Organic Reactions," Coll. Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 232.

[6] E. Modest and Szmuszkovicz, THIS JOURNAL, **72**, 577 (1950).

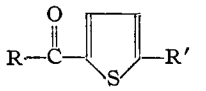
[7] F. Blicke and D. Sheets, *ibid.*, **70**, 3768 (1948).

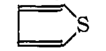
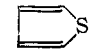
[8] D. Papa, E. Schwenk and H. Ginsberg, *J. Org. Chem.*, **14**, 723 (1949).

[9] (a) G. M. Badger, H. J. Rodda and W. H. F. Sasse, *Chemistry & Industry*, 308 (1954); (b) J. F. McGhie, H. K. Pradhan and W. A. Ross, *ibid*, 578 (1954); (c) M. M. Michel-Sy, N. P. Buu-Hoi and N. Dat. Xuong, *Compt. rend.*, **239**, 1224 (1954).

[10] H. D. Hartough and A. I. Kosak, THIS JOURNAL, **69**, 3098 (1947).

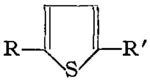
TABLE I

THIENONES 

No.	R	R'	Formula	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	Methyl	*n*-Decyl[a]	$C_{16}H_{26}OS$		63	72.12	71.86	9.84	10.02
II	Methyl	*n*-Octadedyl	$C_{24}H_{42}OS$	62	62	76.12	76.16	11.18	11.34
III	*n*-Heptyl	H[b]			67				
IV	*n*-Heptyl	*n*-Octyl	$C_{20}H_{34}OS$	32	58	74.47	74.63	10.62	10.71
V	*n*-Octyl		$C_{17}H_{20}OS_2$	75	94	66.62	66.36	7.24	7.02
VI	*n*-Nonyl	H[c]			68				
VII	*n*-Pentadecyl	H	$C_{20}H_{34}OS$	42	63	74.47	74.67	10.62	10.58
VIII	*n*-Pentadecyl	*n*-Hexadecyl	$C_{36}H_{66}OS$	71	42	79.05	79.04	12.16	12.11
IX	*n*-Heptadecyl	H[d]	$C_{22}H_{38}OS$	51	83	75.37	75.27	10.92	10.77
X	*n*-Heptadecyl		$C_{26}H_{40}OS_2$	100	35	72.17	72.26	9.32	9.01

[a] B.p. 181° (3 mm.), n^{27}_D 1.5096. [b] B.p. 183–189° (20 mm.), n^{20}_D 1.5125; E. Campaigne and J. L. Diedrich, THIS JOURNAL, **70**, 391 (1948), report b.p. 185° (23 mm.), n^{20}_D 1.5214. [c] B.p. 208–216° (20 mm.), n^{27}_D 1.5099; ref. 10 gives b.p. 179° (8 mm.), n^{20}_D 1.5083. [d] Made by A. W. Ralston and C. W. Christiansen, *Ind. Eng. Chem.*, **29**, 194 (1937), who reported m.p. 48° but no analytical data.

TABLE II

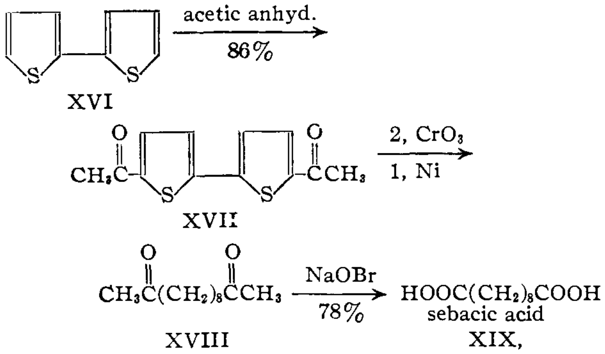
2-(*n*-ALKYL)-THIOPHENES 

No.	R	R'	Formula	B.p. °C.	B.p. Mm.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
XI	*n*-Octyl	H[a]		135	23	50				
XII	*n*-Decyl	H	$C_{14}H_{24}S$	167	17	68	74.90	74.61	10.78	10.59
XIII	Hexadecyl	H	$C_{20}H_{36}S$	147	0.2	57	77.85	77.75	11.76	11.64
XIV	Octadecyl	H[b]	$C_{22}H_{40}S$	182	0.6	65				
XV	*n*-Octyl	*n*-Octyl	$C_{20}H_{36}S$	170	0.1	62	77.85	77.85	11.76	11.82

[a] n^{20}_D 1.4866. Table I, ref. *b*, reports b.p. 107° (1 mm.), n^{20}_D 1.4824. [b] This hydrocarbon crystallized very slowly to a solid m.p. 30–32°. It was characterized through its acetyl derivative (see II, Table I).

numbered acids are in effect transformed into the odd-numbered five carbon homologs. Using commercial stearic acid as the starting acid, for instance, tricosanoic acid was prepared in an over-all yield of 24%.

The synthesis of dibasic acids is based upon the fact that bithienyl (XVI) undergoes mono- or diacylation with ease and in high yield depending upon the molar ratio of reactants. Thus, using an excess of acetic anhydride the diketone XVII[11] could be obtained in 85% yield. Attempted hypohalite oxidation of this highly insoluble diketone XVII furnished amorphous products only, but the alternative procedure, desulfurization followed by oxidation, gave the known[12] 2,11-dodecanedione (XVIII) in high yield. It is noteworthy that the combination of reagents, Raney nickel followed by chromium trioxide, furnishes ketones of good purity, thus obviating the need for the separation of ketonic and alcoholic product mixtures sometimes[8] encountered during Raney nickel desulfurizations. Final hypohalite oxidation to sebacic acid (XIX) thus provides a three-step synthesis of this important monomer.



$$CH_3\overset{O}{\overset{\|}{C}}(CH_2)_8\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[78\%]{NaOBr} HOOC(CH_2)_8COOH$$

As a complementary study to the synthesis of fatty acids, the reductive desulfurization of the synthetic intermediates was found to be an excellent method for the preparation of a variety of long-chain hydrocarbons, ketones and alcohols. A few representative conversions are

$$\text{VII (Table I)} \xrightarrow[2,\ CrO_3]{1,\ Ni} \text{5-eicosanone (90\%)}$$

$$\text{XIII (Table II)} \xrightarrow{Ni} n\text{-eicosane (74\%)}$$

$$\text{II} \xrightarrow{Ni} \text{tetracosanol-2 (78\%)}$$

$$\text{X} \xrightarrow[2,\ CrO_3]{1,\ Ni} \text{9-hexacosanone}$$

We now turn to the study of branched-chain compounds *via* the Grignard reaction on thienyl ke-

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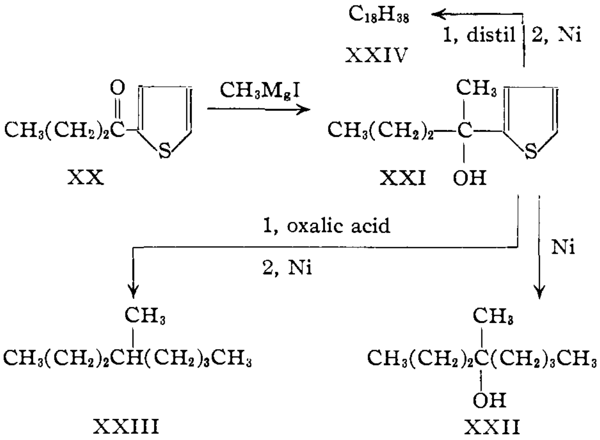
[11] W. Steinkopf and H. J. Petersdorff, *Ann.*, **543**, 119 (1939) report the preparation of this diketone in 13% yield using titanium tetrachloride as the catalyst.

[12] (a) E. G. Hawkins, U. S. Patent 2,575,014 (1951); *C. A.*, **46**, 6147 (1952); (b) M. J. Roedel, U. S. Patent 2,601,224 (1952); *C. A.*, **47**, 4363 (1953); (c) R. E. Bowman, *J. Chem. Soc.*, 322 (1950); (d) J. Cason and F. S. Prout, THIS JOURNAL, **66**, 46 (1944).

tones. As a model compound 2-(*n*-propyl) thienyl ketone (XX) was chosen in order that the various reaction products could be compared with known material. The results outlined below appear to follow the pattern expected for a styrene-type compound.



The saturated tertiary carbinol XXII is produced by direct desulfurization of the somewhat unstable alcohol XXI. Dehydration of XXI followed by reduction furnishes 4-methyloctane (XXIII). Attempted purification of the methylpropylthienylcarbinol (XXI) yielded a high-boiling oil which upon desulfurization furnished a sulfur-free hydrocarbon with properties in agreement with a highly branched $C_{18}H_{38}$ paraffin XXIV.[13]

Acknowledgment.—The authors are indebted to the Research Corporation for a Frederick Gardner Cottrell grant in support of part of this investigation. Generous samples of thiophene and fatty acids from the Texas Co. and the Armour Co. are gratefully acknowledged. We thank Mr. D. VerPloeg for valuable technical assistance.

Experimental[14]

Acylations.—Ketones I through X were prepared essentially according to the technique described by Hartough.[10] Crystallizations of the products from methanol furnished pure materials uncontaminated with the highly insoluble diketones (produced in 5–10% yields).

Reductions.—The Clemmensen reductions were carried out using a large excess of amalgamated zinc with a 1:1:1 ratio of concentrated hydrochloric acid, dioxane and glacial acetic acid as the reaction medium.

Hypohalite Oxidations. 5-(*n*-Decyl)-2-thienoic Acid.—This acid was prepared following general directions ("Organic Syntheses," Coll. Vol. II, p. 428) using however an equal volume of dioxane as a co-solvent. Two crystallizations of the crude acid (m.p. 76–77.5°, 90.5% yield) furnished the pure thienoic acid, m.p. 84–85°; neut. equiv. calcd. for $C_{15}H_{24}O_2S$, 268.4; found, 269.

5-(*n*-Octadecyl)-2-thienoic acid was prepared in 86% yield exactly as described above. Recrystallization from ether–petroleum ether yielded pure material as colorless needles, m.p. 101.8–102.7°. *Anal.* Calcd. for $C_{23}H_{40}O_2S$: C, 72.59; H, 10.59. Found: C, 72.89; H, 10.36.

Pentadecanoic Acid.—A suspension of 30–35 g. of Raney nickel prepared from 60.0 g. of nickel–aluminum alloy[15] in 100 ml. of 95% ethanol was stirred and heated under reflux with 1.50 g. of 5-(*n*-decyl)-2-thiophenecarboxylic acid, m.p. 84–85°, for 16 hours. The acid was isolated by filtration and Soxhlet extraction according to the directions of Szmuszkovicz[6] to yield 1.12 g. (81%) of pentadecanoic acid, m.p. 50–52°. One recrystallization from dilute acetone raised the m.p. to 53.0–53.4° (reported[16] m.p. 51°).

The amide, prepared according to the directions in McElvain,[17] melted at 103.6–104.0° after one recrystallization from dilute ethanol (reported[16] m.p. 102.5°).

Tricosanoic Acid.—Desulfurization was carried out as described for pentadecanoic acid to yield the acid, m.p. 79.8–80.2° (reported[18] m.p. 79.1°). The methyl ester, prepared by refluxing 20 mg. of acid for two hours with 10 ml. of absolute methanol and 4 drops of sulfuric acid, melted at 50.0–52.4° (reported 53.5–54°)[18] after one recrystallization from methanol.

2-Tetracosanol.—Desulfurization of 1.00 g. of 5-(*n*-octadecyl)-2-acetylthiophene (II) in the manner described above yielded 0.76 g. (83%) of colorless powder, m.p. 71.5–72.5°. Two recrystallizations from acetone raised the m.p. to 73.3–73.8°. *Anal.* Calcd. for $C_{24}H_{50}O$: C, 81.28; H, 14.21. Found: C, 81.32; H, 14.01.

2,2′-Dithienyl (XVI).—A mixture of 42.0 g. (0.20 mole) of 2-iodothiopene,[19] b.p. 81–84 (22 mm.), 16.0 g. (0.25 gram-atom) of copper–bronze,[20] and 100 ml. of dimethylformamide[21] was refluxed for 22 hours. The reaction mixture was then diluted with 500 ml. of water and steam distilled. The distillate (1500 ml.) was cooled in an ice-bath for one hour before the solid was removed by filtration to give 11.13 g. (67%) of heavy lustrous plates of bithienyl melting at 31–33° (reported[22] m.p. 33°).[23]

5,5′-Diacetyl-2,2′-bithienyl (XVII).—Five drops of 85% phosphoric acid were added to a refluxing solution of 2.10 g. of bithienyl in 25 ml. of acetic anhydride and the boiling continued for one hour. The hot solution was poured on 200 g. of ice and stirred until the acetic anhydride had hydrolyzed. The green crystals, 2.63 g. (83%), m.p. 221–225°, were removed by filtration and recrystallized once from 75 ml. of dioxane to give 2.18 g. of the diacetyl compound, m.p. 233.5–234°, as pale yellow flakes (reported[11] m.p. 231–232°).

2,11-Dodecanedione (XVIII).—To a solution of 0.90 g. of recrystallized 5,5′-diacetyl-2,2′-bithienyl in 100 ml. of dioxane was added a suspension of Raney nickel in 150 ml. of dioxane, and the mixture was stirred and refluxed for seven hours. The Raney nickel was removed by suction filtration and washed carefully with six 50-ml. portions of hot ethanol. The solvents were removed under reduced pressure and the semi-crystalline dry residue was dissolved in 30 ml. of glacial acetic acid. Two grams of chromium trioxide was added over a period of 30 minutes with stirring and the mixture was agitated for a total of one hour, the temperature remaining at about 30°. The green solution was diluted with 200 ml. of water and extracted with five 50-ml. portions of ether. The ether extracts were washed free of acetic acid and dried. Removal of the solvent and recrystallization of the solid residue from a 1:1 mixture of ether and petroleum-ether (b.p. 34–40°) gave 0.65 g. (91%) of colorless flaky diketone melting at 69–70.5° (reported[12] m.p. 68°).

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[13] Although such a paraffin could arise from a head-to-tail dimer of the dehydrated carbinol XXI the experimental data are insufficient to exclude alternate structures.

[14] All melting points are corrected; boiling points are uncorrected.

[15] R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, This Journal, **65**, 1013 (1943).

[16] H. R. LeSuer, *J. Chem. Soc.*, **87**, 1888 (1905).

[17] S. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., Revised Edition, p. 141.

[18] F. Francis and S. H. Piper, This Journal, **61**, 577 (1939).

[19] W. Minnis, *Org. Syntheses*, **12**, 44 (1932).

[20] The grade "Natural Copper #44-F" supplied by the U. S. Bronze Powder Works, Closter, N. J., was found to be the most satisfactory and was used without further purification or activation.

[21] N. Kornblum and D. L. Kendall, This Journal, **74**, 5782 (1952).

[22] W. Steinkopf, R. Leitsmann and K. H. Hoffmann, *Ann.*, **546**, 180 (1941); J. W. Sease and L. Zechmeister, This Journal, **69**, 270 (1947); C. D. Hurd and K. L. Kreuz, *ibid.*, **72**, 5543 (1950).

[23] Although we have successfully repeated this preparation many times we have encountered a few erratic results (low yields) for which neither the activity of the copper–bronze, the temperature or time of the reaction nor the purity of the starting material or solvent *appeared* to be responsible. See for instance P. E. Fanta, *Chem. Revs.*, **38**, 139 (1946). We believe that reduction (by the hydrogen on the copper) may in part be responsible as we have isolated thiophene and 2-methylthiophene from poor runs using 2-iodothiophene and 5-methyl-2-iodothiophene.

Sebacic Acid (XIX).—Following the procedure of Johnson,[24] 198 mg. (1 mmole) was oxidized in the presence of 1.5 ml. of bromine, 4.2 g. of sodium hydroxide, 20 ml. of water and 15 ml. of dioxane during a period of one hour to give 170 mg. (84%) of crude dibasic acid, m.p. 124–128°. One recrystallization from 3 ml. of water sufficed to give pure sebacic acid as shiny plates, m.p. 133–134° (reported m.p. 134°).

***n*-Eicosane.**—2-(*n*-Hexadecyl)-thiophene (1.15 g.) was desulfurized by heating under reflux with 15 g. of Raney nickel and 100 ml. of dioxane for 16 hours. The catalyst was removed by filtration and the filtrate concentrated to yield 0.70 g. of fine white powder, m.p. 36.5–37.0°, $n^{42.0}\mathrm{D}$ 1.4354 (reported m.p. 38°, $n^{42.9}\mathrm{D}$ 1.434).

5-Eicosanol.—Desulfurization of 6.75 g. of 2-(*n*-pentadecyl)-thienone with 90 g. of Raney nickel furnished 5.74 g. (90%) of the alcohol, m.p. 51–52° after one crystallization from acetone. *Anal.* Calcd. for $C_{20}H_{42}O$: C, 80.46; H, 14.18. Found: C, 80.63; H, 13.94.

5-Eicosanone.—The alcohol obtained above (1.37 g.) was oxidized at 25–35° with 2.04 g. of chromium trioxide in 20 ml. of glacial acetic acid to yield 1.25 g. (91.2%) of white powder, m.p. 51–52° (m.m.p. with 5-eicosanol 46–48°), reported[25] m.p. 53–54° (uncor.).

4-Methyloctane.—Redistilled 2-butanoylthiophene[10] (20.0 g.), b.p. 141–142° (41 mm.), $n^{18}\mathrm{D}$ 1.5426, in 100 ml. of anhydrous ether was added over a period of 1 hr. to the Grignard reagent prepared from 3.50 g. of magnesium, 25.0 g. of methyl iodide and 100 ml. of ether. Stirring and gentle refluxing was continued for 1 hour. The reaction mixture was decomposed with ice-cold dilute hydrochloric acid, the organic phase carefully washed free of acid, dried and concentrated to a yellow sirup. This oil (16.6 g., 73%) was divided into three parts:

Part I, 6.00 g., was distilled at reduced pressure; no material distilled in the expected range (140–175°). However a straw-colored oil came over between 215–265°. Upon redistillation the boiling point was 220–245° (28 mm.), $n^{20}\mathrm{D}$ 1.5663–1.5666. Three grams of this oil was heated under reflux for 6 hr. with 40 g. of Raney nickel in 175 ml. of 95% alcohol. Isolation in the usual manner furnished 2.05 g. (82%, based on dimer) of colorless oil, $n^{25}\mathrm{D}$ 1.4551. Two redistillations at atmospheric pressure yielded constant boiling material, b.p. 263–266° (740 mm.), $n^{23}\mathrm{D}$ 1.4496–1.4500. *Anal.* Calcd. for $C_{18}H_{38}$: C, 84.95; H, 15.05; mol. wt., 254. Found: C, 85.16; H, 14.89; mol. wt., 230 (Rast).

Part II, 4.00 g., was desulfurized immediately using 20.0 g. of Raney nickel yielding a colorless oil, b.p. 178–180° (740 mm.), $n^{25}\mathrm{D}$ 1.4317; reported constants for 4-methyloctanol-4 are[26,27] b.p. 178° (760 mm.), $n^{25}\mathrm{D}$ 1.4301.

Part III, 4.00 g., was heated to 100° for 30 minutes with oxalic acid, then freed of oxalic acid and water by washing and drying. The oil thus remaining was relatively unstable ($n^{25}\mathrm{D}$ 1.5035) and immediately desulfurized with 20 g. of Raney nickel to furnish a sulfur-free hydrocarbon, b.p. 138–142° (739 mm.), $n^{20}\mathrm{D}$ 1.4050–1.4092; reported[28] for 4-methyloctane, b.p. 142° (771 mm.), $n^{20}\mathrm{D}$ 1.4063.

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[24] W. S. Johnson, C. D. Gutsche and D. Offenhauer, THIS JOURNAL, **68**, 1648 (1946).

[25] F. C. Whitmore, L. H. Sutherland and J. N. Cosby, *ibid.*, **64**, 1360 (1940).

[26] O. R. Quayle and K. O. Smart, *ibid.*, **66**, 935 (1944).

[27] L. Clarke, *ibid.*, **34**, 680 (1912).

[28] *J. Research Natl. Bur. Standards*, **52**, 59 (1954), Res. Paper No. 2773.

GRINNELL, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

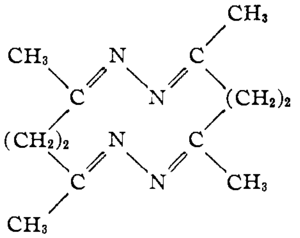
Azo Compounds.[1] Investigation of the Structure of the Products from the Reaction of Acetonylacetone and Hydrazine

BY C. G. OVERBERGER, NORMAN R. BYRD[2] AND ROBERT B. MESROBIAN

RECEIVED FEBRUARY 23, 1955

The reaction of hydrazine hydrate and acetonylacetone in the absence of solvent and added catalyst has been shown to yield as a major product a basic six-membered ring structure II which is an associated dimer, rather than structure I previously suggested for this product. (Reaction of hydrazine hydrate and acetonylacetone in acetic acid gave principally III and IV.) II has been converted to III and IV in the presence of a palladium catalyst. Catalytic hydrogenation of the high-boiling compound in acid media with a mixture of platinum oxide and 10% palladium-on-charcoal as catalysts or in neutral medium with Raney nickel gave IV. Reaction of II with hydrogen cyanide gave VI and further confirms the proposed structure of VI obtained previously by a modified procedure.

The synthesis of compound I, a 12-membered ring, has been reported by a number of investigators.[3,4,5a] Since this compound appeared to be convertible to a cyclic azo compound, a potential biradical source by hydrogenation and oxidation, we attempted to prepare I as starting material. Attempted conversion of the alleged 12-membered ring to the cyclic azo compound revealed, however, that the major product from the reaction of hydrazine hydrate and acetonylacetone without solvent was an associated dimethyldihydropyridazine. Gray[3] described the preparation of compound I by reaction of hydrazine hydrate and acetonylacetone and reported an analysis and a molecular weight but gave no melting point. Blaise[4] reported a dimeric solid compound from the same reaction and a melting point but did not characterize the product further. Blaise also reported that the reaction of acetonylacetone and hydrazine in dilute hydrochloric acid solution gave the alleged dimer I. In



I

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[1] This is the eighteenth in a series of papers concerned with the preparation and decomposition of azo compounds. For the seventeenth paper in this series, see C. G. Overberger, H. Biletch, P. Huang and H. M. Blatter, *J. Org. Chem.*, **20**, 1717 (1955).

[2] This paper comprises a portion of a thesis presented by Norman R. Byrd in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[3] T. Gray, *J. Chem. Soc.*, **79**, 682 (1901).

[4] E. E. Blaise, *Compt. rend.*, **170**, 1324 (1920).

[5] (a) B. G. Zimmerman and H. L. Lochte, THIS JOURNAL, **60**, 2456 (1938); (b) A. Smith and H. N. McCoy, *Ber.*, **35**, 2169 (1902).