

[CONTRIBUTION OF RESEARCH AND DEVELOPMENT BRANCH, OFFICE OF SYNTHETIC LIQUID FUELS, BUREAU OF MINES]

Chemistry of the Oxo and Related Reactions. II. Hydrogenation¹

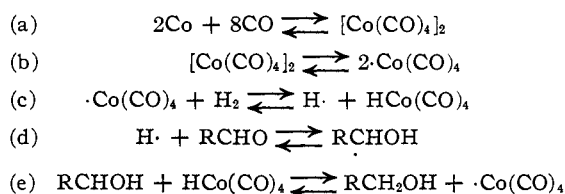
BY IRVING WENDER, ROBERT LEVINE AND MILTON ORCHIN

Of particular interest in connection with the reactivity of double bonds in the oxo reaction is the report² that α,β -unsaturated aldehydes and ketones do not undergo the hydroformylation (oxo) reaction but instead are reduced to the saturated carbonyl compound. This reaction was carried out at 200–300 atmospheres of synthesis gas (1H₂:1CO) and at 120–125°. In the present investigation it was found that, if the reaction is conducted at the same pressure but at a temperature of 180–185° instead of 120–125°, the carbonyl group as well as the double bond is reduced, and the reduction under these conditions was found to be a general reaction. Thus, heptaldehyde, butyraldehyde and 2-phenylpropionaldehyde were reduced in good yields to their corresponding alcohols. Acetone could likewise be reduced to isopropyl alcohol at 185–190°. Benzaldehyde yielded mainly dibenzyl ether, which was probably formed by the dehydration of benzyl alcohol. Crotonaldehyde, which Adkins and Krsek² had converted to butyraldehyde at 120–125°, was hydrogenated directly to butanol-1 at 180–185°.

Since carbonyl compounds are reduced in the presence of synthesis gas and a cobalt catalyst at 180–190°, it was anticipated that olefins could be converted directly to alcohols in the oxo reaction.³ It was found that hexene-1 reacted with carbon monoxide and hydrogen at 160–180° to give a 43% yield of a mixture of heptanol-1 and 2-methylhexanol-1. Octene-1 reacted similarly to give a mixture of isomeric nonyl alcohols (60%).

It is possible that the reductions which occur under oxo conditions proceed *via* a free radical mechanism. Either dicobalt octacarbonyl⁴ or cobalt hydrocarbonyl,⁵ which are formed from cobalt salts in the presence of synthesis gas, may dissociate into free radicals which function as initiators for the dissociation of hydrogen molecules into atoms. One way in which the free

radical reduction of carbonyl compounds with synthesis gas and a cobalt catalyst can be written is



Step (c) may then be repeated and the chain continued until all the aldehyde is converted to alcohol.

If the reduction is a homogeneous reaction that proceeds *via* a free radical mechanism, hydrogenation under these conditions should not be affected adversely by sulfur compounds as is the heterogeneous catalysis of hydrogenation over a solid catalyst. Indeed, it was found that 2-thiophenealdehyde, when treated with synthesis gas at 180–185°, was readily reduced in good yield to a mixture of 2-thenyl alcohol (41%) and 2-methylthiophene (26%).

Under the conditions of the oxo reaction, some types of unsaturated linkages are hydrogenated while others react by hydroformylation. The type of reaction which occurs depends, among other things, on the structure of the particular unsaturated compound. Simple olefins react by hydroformylation to give an aldehyde containing one carbon atom more than the olefin. α,β -Unsaturated aldehydes and ketones can be reduced to saturated carbonyl compounds.² Conjugated dienes undergo both types of reaction; one olefinic linkage is usually hydrogenated while hydroformylation takes place at the other. Thus, 1,3-butadiene gives *n*-valeraldehyde⁶ and 2,3-dimethylbutadiene-1,3 gives 3,4-dimethylpentanal.⁶

In the present investigation, work on the behavior of conjugated systems was extended. It was found that furan reacted with synthesis gas at 160–180° to give a 35% yield of the tetrahydrofurfuryl alcohol. Similar treatment of 2,5-dimethylfuran gave 2,5-dimethyl-3-tetrahydrofurfuryl alcohol. In these cases, as with butadiene, both hydrogenation and hydroformylation occurred. Thiophene, which has less π electron availability than furan, failed to undergo the hydroformylation reaction; instead it was slowly hydrogenated to thiolane. Phenanthrene likewise was slowly hydrogenated; 9,10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene

(1) Presented before the Division of Organic Chemistry at the 116th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1949. This paper is based on a thesis presented by Irving Wender in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Pittsburgh, February, 1950. The work was done under the joint sponsorship of the Federal Bureau of Mines and the University of Pittsburgh. Article not copyrighted.

(2) Adkins and Krsek, *THIS JOURNAL*, **71**, 3051 (1949).

(3) The oxo reaction as developed in Germany was a two-stage process in which the aldehydes produced by the hydroformylation were reduced with pure hydrogen in a separate and second stage over a solid hydrogenation catalyst.

(4) Gresham and Hardy, U. S. Patent 2,473,993 (June 21, 1949).

(5) British Intelligence Objectives Subcommittee Miscellaneous Report No. 113, Netherlands Report on Additional Information on Various Catalytic Processes in Western Germany—II, Part G (1949).

(6) H. Adkins, Abstracts of the Eleventh National Organic Chemistry symposium of the American Chemical Society, University of Wisconsin (June, 1949).

TABLE I
 REACTIONS OF ORGANIC COMPOUNDS WITH SYNTHESIS GAS AND COBALT CATALYST^a AT 180-185°

Starting compound	Syn-thesis gas, H ₂ :CO	Initial pres-sure, p. s. i.	Time, hours	Products	Yield, %	Boiling point, °C.	Derivatives ^b melting point, °C.
Butyraldehyde	2:1	3100	1	Butanol-1	72	116-117	69.7-70.6 ^c
Heptaldehyde	1:1	3000	1	Heptanol-1	39	81-85 (18-19 mm.)	57.9-58.8 ^d
2-Phenylpropionaldehyde	1:4	2000	3	2-Phenylpropionaldehyde ^e 2-Phenylpropanol-1	18 38	120-145 ^f (33-34 mm.)	100-100.8 ^g
Acetone	1:1	3000	4.5	Acetone ^h Isopropyl alcohol	45 41	55-56 82-83	103.5-104.5 ^e
Benzaldehyde	1:1	3200	.75	Toluene ^h Dibenzyl ether ⁱ	5 43	109-110 133.5-134 (3 mm.)	
Crotonaldehyde	1:1	3200	.5	Butanol-1	31	116-117.5	69.5-70.6 ^c
2-Thiophenealdehyde	1:1	2300	.75	2-Thiophenaldehyde 2-Thenyl alcohol	17	88-110 (21-22 mm.) ^j	237.8-239.5 ^k 72.7-73.3 ^{d,l} 148.4-149.2 ^l
Furan	2:1	3100	4	2-Methylthiophene ^m 2-Tetrahydrofurfuryl alcohol ⁿ	26 35	55-56 (111 mm.) 76-82 (17-20 mm.)	56.6-57.8 ^d
2,5-Dimethylfuran	2:1	3000	4	2,5-Dimethyl-3-tetrahydrofurfuryl alcohol ^o	23	81-84 (17 mm.)	
Thiophene	2:1	3200	8	Thiophene Tetrahydrothiophene	86 8	83.5-84 118.5-119	130.0-131.1 ^p
Phenanthrene ^q	2:1	2700	2	Phenanthrene ^r 9,10-Dihydrophenanthrene 1,2,3,4-Tetrahydrophenanthrene	81 7 1	96.0-98.2 (m. p.)	127.8-129.2 ^s
Hexene-1	1:1	3000	3	2-Methylhexanol-1 ^t Heptanol-1	17 29	112-113.5 (100 mm.) 120.5-121 (100 mm.)	130.5-131.3 ^u 57.9-58.9 ^d
Octene-1 ^v	1:1	3000	3.5	Isomeric nonyl alcohols ^w	61	108-119 (26-27 mm.)	
Octene-1 ^x	1:1	3000	3.5	Isomeric nonyl alcohols ^y	57	108-118 (26-27 mm.)	
Octene-1 ^z	1:1	875	1.5	Isomeric nonyl aldehydes	13	62-80 (25-26 mm.)	69.7-84.6 ^{aa}

^a In all cases, unless otherwise specified, the catalyst used was 1-5 mole per cent. of cobalt(II) acetate tetrahydrate. ^b In all cases, unless otherwise specified, the melting points of derivatives were compared with authentic samples by the mixed melting point technique and gave no depression. All melting points are corrected. We wish to thank Dr. R. A. Friedel for all the spectra determinations. ^c α -Naphthylurethan. ^d Phenylurethan. ^e Amount determined by hydroxylamine hydrochloride titration. Bryant and Smith, THIS JOURNAL, 57, 57 (1935). ^f Boiling range of mixture of 2-phenylpropionaldehyde and 2-phenylpropanol-1. ^g Golumbic and Cottle, *ibid.*, 61, 996 (1939). ^h n_D^{20} 1.4956; infrared absorption spectrum identical with that of authentic sample. ⁱ Melting point 4-5°. Analysis, calculated for C₁₄H₁₄O: C, 84.81; H, 7.12. Found: C, 84.82; H, 7.25; infrared absorption spectrum identical with that of authentic sample. ^j Boiling range of mixture of 2-thiophenaldehyde and 2-thenyl alcohol. ^k 2,4-Dinitrophenylhydrazones. Dunn, Waugh and Dittmer, *ibid.*, 68, 2181 (1946). ^l Dunn and Dittmer, *ibid.*, 68, 2561 (1946). ^m Infrared absorption spectrum identical with that of API spectrum of an authentic sample of 2-methylthiophene. ⁿ Treatment with CH₃MgI in *n*-butyl ether yielded 92 per cent. of the theoretical amount of methane. ^o Treatment with CH₃MgI in *n*-butyl ether yielded 102 per cent. of the theoretical amount of methane; Analysis, calculated for C₇H₁₄O₂: C, 64.57; H, 10.83. Found: C, 64.12; H, 10.82. ^p Addition product with mercuric chloride. Mzingo, Harris, Wolf, Hoffhine, Easton and Folkers, *ibid.*, 67, 2094 (1945). ^q Pure phenanthrene was prepared by Mr. J. Feldman of this Laboratory. ^r Mixture of phenanthrene and reduction products separated by chromatography using an alumina column. Analysis of fractions made by ultraviolet absorption. ^s Complex with 1,3,5-trinitrobenzene. ^t The mixture of heptyl alcohols was separated by distillation in a 2-foot Heli-grid column. ^u Hydrogen-3-nitrophenalate. Morgan, Hardy and Proctor, *Chemistry and Industry*, 51T, 7 (1932). ^v Cobalt(II) stearate used as catalyst. ^w Treatment with CH₃MgI in *n*-butyl ether yielded 94 per cent. of the theoretical amount of methane. ^x Cobalt(II) chloride hexahydrate used as catalyst. ^y Treatment with CH₃MgI in *n*-butyl ether yielded 98 per cent. of the theoretical amount of methane. ^z Cobalt(II) carbonate used as catalyst. ^{aa} 2,4-Dinitrophenylhydrazones.

were isolated from the reaction products. The hydrogenation reaction apparently becomes dominant as the degree of double-bond character of an olefinic linkage diminishes as a result of conjugation. Simple olefins react exclusively by hydroformylation; diolefins and the furans react by both hydrogenation and hydroformylation; thiophene and phenanthrene react exclusively by hydrogenation; and benzene is inert. This order of compounds is roughly their order of increasing aromaticity.

Although it has been shown that an alcohol is produced directly from an olefin in the oxo reaction at 185°, if the reaction is conducted at lower partial pressures, the aldehyde can be isolated as the major product. Thus, for example, when octene-1 was treated with synthesis gas at 875 p.s.i. initial pressure, 13% of the octene reacted to give a mixture of nonyl aldehydes (83%) and nonyl alcohols (17%). Under essentially the same conditions but at 3,000 p.s.i., a mixture of nonyl alcohols was obtained practically free of aldehydes.

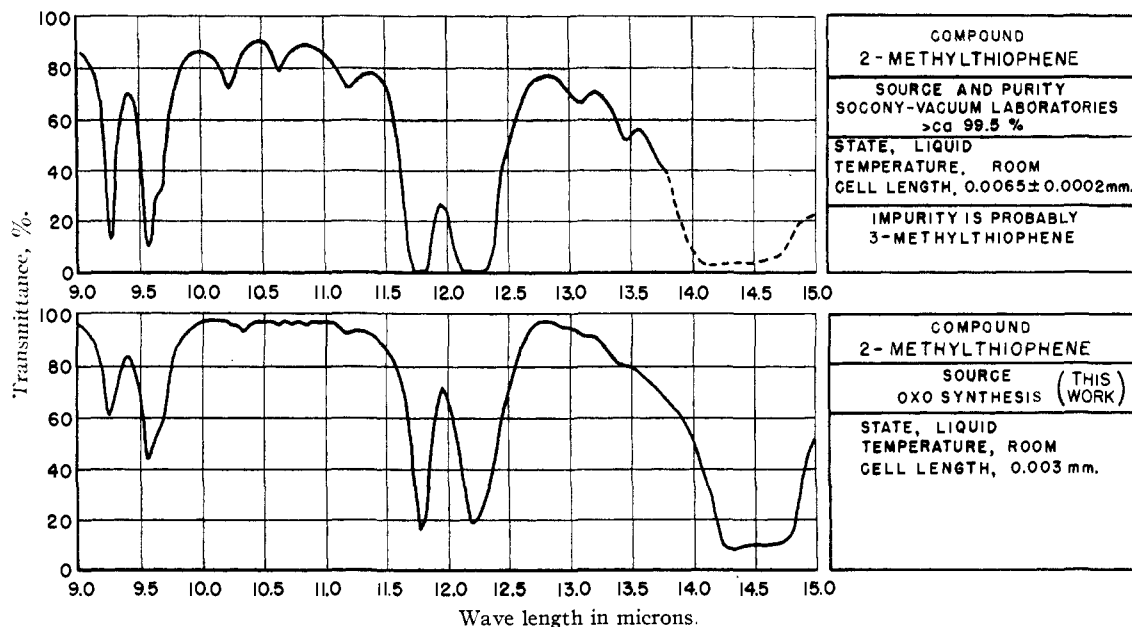


Fig. 1.

Experimental

Apparatus.—The reaction apparatus was the standard American Instrument Co. 500-ml. stainless-steel autoclave. The compressor was an Aminco motor-driven hydraulic type rated at 8000 p. s. i. The autoclave had a maximum free space, when empty, of 468 ml.; when a glass liner was used (for small amounts of material), the free space was 306 ml. Air at 25 p. s. i., applied externally, was used to cool the autoclave at the end of a reaction.

The synthesis gas used was manufactured⁷ and compressed at the Bureau of Mines.

Reduction Experiments.—The results of the experiments are shown in Table I. Modifications of standard procedures were used in each case. Most of the reactions were run only once and the yield reported for a product is not to be considered as the maximum that may be secured. The experiment with 2-thiophenealdehyde⁸ will be described in detail since it illustrates most of the techniques employed.

Reduction of 2-Thiophenealdehyde.—A solution of 42 g. (0.37 mole) of 2-thiophenealdehyde (b. p. 88–90° at 20 mm.) in 35 ml. of *n*-hexane and 3.5 g. (0.014 mole) of cobalt(II) acetate tetrahydrate were placed in the autoclave. Synthesis gas (1H₂:1CO) was added until the pressure reached 2300 p. s. i. This corresponded to approximately 2.5 moles of gas. The autoclave was heated with rocking, to 180° within 65 minutes. The maximum pressure obtained was 3,100 p. s. i. at 170°. The temperature of the autoclave was held at 180–185° for forty minutes, during which time the pressure dropped to 2,520 p. s. i. This pressure drop corresponds to approximately 0.8 mole of gas, or 2.1 moles of gas per mole of aldehyde. The reaction vessel was cooled to 39°; the pressure at this temperature was 1,590 p. s. i. The gases were then vented to the atmosphere.

The autoclave was then filled with hydrogen at 1,300 p. s. i. and heated at 125° for forty minutes to decompose any residual dicobalt octacarbonyl. There was no pressure drop during this reaction. The autoclave was cooled and vented, and the products were washed from the autoclave with benzene. After filtration, the solution was

distilled and yielded 9.3 g. (26%) of 2-methylthiophene, b. p. 55–56° at 111 mm. The infrared spectrum of this fraction was identical with that of an authentic sample of 2-methylthiophene (Fig. 1). Distillation of the residue under nitrogen at reduced pressure, yielded 24.5 g. of a liquid boiling at 88–110° at 21–22 mm. Treatment of a part of this higher-boiling fraction with phenyl isocyanate resulted in the formation of the phenylurethan of 2-thenyl alcohol, m. p. 72.7–73.3° (Table I); the α -naphthylurethan of 2-thenyl alcohol made from another portion of this fraction melted at 148.4–149.2° (Table I). The presence of unchanged 2-thiophenealdehyde was demonstrated by treating a third portion of the fraction with 2,4-dinitrophenylhydrazine, whereupon the 2,4-dinitrophenylhydrazone of this aldehyde, melting point 237.8–239.5° (Table I), was obtained. Calculations made from the amount of methane liberated when a portion of this higher-boiling fraction dissolved in pyridine was treated with methylmagnesium iodide in *n*-butyl ether⁹ showed that the fraction was composed of approximately 17.4 g. of 2-thenyl alcohol and 7 g. of 2-thiophenealdehyde. This corresponds to a yield of 41% of 2-thenyl alcohol and 17% of recovered 2-thiophenealdehyde.

Decomposition of Dicobalt Octacarbonyl.—In working up the products of the reaction, it is usually desirable to destroy the dicobalt octacarbonyl dissolved in the product. This can be done by any of three methods, and the choice depends upon convenience and the nature of the products. The preferred procedure consists of treatment with hydrogen. After the reaction with synthesis gas is complete and the autoclave purged, it is filled with hydrogen at 1,000–1,300 p. s. i. and the mixture heated at 110–135° for forty-five minutes. The cobalt in dicobalt octacarbonyl is transformed to cobalt metal by this procedure. In experiments where easily reducible compounds were present, or where it was desired to prove that hydrogenation could be achieved under oxo conditions, this method for destroying the carbonyl was not used. If the product did not contain readily oxidizable substances, the mixture containing dicobalt octacarbonyl was heated in air on a steam bath whereby copious evolution of carbon monoxide occurred, accompanied by the deposition of a cobalt mirror. The third procedure for destroying dicobalt octacarbonyl consisted of shaking the reaction products with a dilute sulfuric acid solution until gas evolution ceased.

(7) E. L. Clark, R. H. Kallenberger, R. Y. Browne and J. R. Phillips, *Chem. Eng. Prog.*, **45**, 651 (1949).

(8) We are indebted to H. D. Hartough of the Socony-Vacuum Oil Co., Inc., for a sample of this aldehyde.

(9) M. Orchin and I. Wender, *Anal. Chem.*, **21**, 875 (1949).

Summary

Aldehydes and ketones can be reduced to alcohols by hydrogen and carbon monoxide (synthesis gas) in the presence of a cobalt catalyst, and the reaction can be applied to the reduction of compounds containing sulfur. A free radical mechanism is proposed for the hydrogenation.

When olefins are treated with 150–300 atmospheres of synthesis gas and a cobalt catalyst at 180–185°, alcohols containing one carbon atom more than the olefin are the principal products. Double bonds in some compounds, when treated under these conditions, are hydrogenated rather than hydroformylated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Fluorinated Ethers

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A fluorinated cluster, such as a CF₃ group, has a pronounced inductive effect on an adjacent function; it increases the acidity of an acid² or alcohol,³ reduces the basicity of an amine,⁴ reverses the polarity of a double bond,⁵ and protects a CH bond from free radical attack.⁶ The present paper considers the influence of fluorinated groups on an ether function,⁷ when these groups are on one or on both sides of the oxygen bridge, in alpha or beta position.

In synthesizing new fluorinated ethers, good results were obtained by addition of alcohols to perfluoroethylene, a procedure which is here extended to fluorinated alcohols. Williamson type of reactions also succeeded well. The treatment of a fluorinated alcohol with diazomethane gave the expected methyl ether, but an attempt to use trifluorodiazomethane failed. Attempted acid dehydrations of trifluoroethanol and trifluoropropanol also failed and this was attributed to the loss of basic character of their oxygen, which hampered the formation of positive ions such as CF₃CH₂-OH₂⁺, followed or not by loss of a molecule of water to form CF₃CH₂⁺; supporting this interpretation is the fact that trifluoroethanol gives only traces of the expected fluoroalkyl sulfate after long heating at 140° with sulfuric acid.³

Fluorinated groups lower the basic properties of the oxygen bridge. A group in alpha position is more effective than one further removed, and the presence of fluorinated groups on both sides of the bridge greatly enhances this effect: solubility in concentrated acids, and formation of complexes with Lewis acids such as ferric chloride is depressed by fluorine substitution on one side of the ether function and completely prevented by substitution on both sides. The loss of basic character is also shown in measurements of the heat of

mixing with chloroform.⁸ The formation of peroxides is, likewise, hampered or prevented.

Fluorinated groups in alpha position are sensitive to hydrolysis^{9,10} except when they are protected by a polyfluorinated group such as CF₃ or CHF₂ in beta positions; other halogenated groups in beta position, such as CCl₃, CHBr₂, CHCl₂ or CHFBr, do not have that protecting effect. Polyfluorinated groups in beta or gamma positions are stable against hydrolysis or hydrogen fluoride removal.

The ether bridge of a beta fluorinated compound such as CF₃CH₂OCH₂CF₃ is very easily hydrolyzed. Since this ether is formed from an acidic alcohol, it is somewhat in the nature of an anhydride, and the situation recalls the fact that diaryl ethers are more easily cleaved than dialkyl ethers. The ether bridge of alpha fluorinated ethers could not be tested on account of the sensitivity of the alpha fluorinated group to hydrolysis. The ether bridge of perhalogenated ethers was found completely immune to hydrolysis with concentrated hydrogen iodide or oxidation with fuming nitric acid at high temperature.

The boiling points of several fluorinated ethers

TABLE I
BOILING POINTS, °C.

CH ₃ OCH ₃	-23.6	C ₂ H ₅ OC ₂ H ₅	34.5
C ₂ F ₅ H ₃ O	(30.1) ^a	C ₂ F ₅ OC ₂ F ₅	5.0 ^b
CF ₃ OCF ₃	-59 ¹¹	CH ₃ CF ₂ OC ₂ H ₅	35.0
		CH ₃ CF ₂ OCH ₂ CF ₃	37.8
CH ₃ OC ₂ H ₅	10.8	CF ₃ CH ₂ OC ₂ H ₅	49.8
CF ₃ HOCC ₂ H ₅	23.7	CF ₃ HCF ₂ OCH ₂ CF ₃	56.7
CH ₃ OCH ₂ CF ₃	31.2	CF ₃ HCF ₂ OC ₂ H ₅	57.5
CH ₃ OCF ₂ CF ₃ H	39.5	CF ₃ HCH ₂ OC ₂ H ₅	66.5
CH ₃ OCH ₂ CF ₂ H	47.0 ^c	CF ₃ HCH ₂ OCH ₂ CF ₃	70.5
CH ₃ OC ₂ H ₇	39.0	C ₂ H ₅ OC ₃ H ₇	63.6
CH ₃ OCH ₂ CH ₂ CF ₃	54.8	C ₂ H ₅ OCH ₂ CH ₂ CF ₃	72.2
C ₄ H ₉ OC ₃ H ₉	142.0	CF ₃ HCF ₂ OCH ₂ CH ₂ CF ₃	88.2
C ₄ F ₉ OC ₃ F ₉	100.4 ¹¹	CF ₃ HCH ₂ OC ₃ H ₇	89.0

^a Booth and Burchfield, *THIS JOURNAL*, **57**, 2070 (1935), do not give a developed formula; we believe this could not be CF₃OCH₃, but only CF₃HOCH₂F. ^b Data from Minnesota Mining and Manufacturing Co., St. Paul, Minnesota. ^c Swarts, *Bull. Acad. Roy. Belg.*, [3] **37**, 357 (1899).

(8) Lacher, McKinley and Park, *ibid.*, **70**, 2598 (1948).

(9) Hanford and Rigby, U. S. Patent 2,409,274 (1946).

(10) Young and Tarrant, *THIS JOURNAL*, **71**, 2432 (1949), and paper in preparation.

(1) Socony-Vacuum Fellow, 1948–1949.

(2) Swarts, *Bull. Sci. Roy. Acad. Belg.*, **8**, 343 (1922).

(3) Swarts, *Bull. Soc. Chim. Belg.*, **43**, 471–481 (1934).

(4) Gilman and Jones, *THIS JOURNAL*, **65**, 1458 (1943).

(5) Henne and Kay, *ibid.*, **72**, 3369 (1950).

(6) Henne, Hinkamp and Zimmerschied, *ibid.*, **67**, 1906 (1945);

J. V. Schmitz, Ohio State Ph.D. dissertation, 1949; H. Schechter and F. Conrad, *ibid.*, **72**, 3371 (1950).

(7) J. D. Park, *ibid.*, **70**, 1550 (1948), gives a good bibliography.