The Liquid Phase Oxidation of the Lower Olefins[1]

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The nature of the epoxides, aldehydes, and ketones obtained as major products by the autoxidation of the lower olefins indicates that reaction at the double bond is the predominant primary process occurring in the oxidation of most olefins. The formation of different products from 1-butene and 2-butene, notably, is incompatible with oxidation by a mechanism emphasizing α-hydrogen abstraction. Reactivity may be estimated from structure using empirical rules. The dependency of oxidation rate on olefin concentration, in concentrated benzene solutions, is very strong.

Although the liquid phase autoxidation of many unsaturated compounds has been studied, the simple low molecular weight olefins, whose study should be uniquely able to contribute to the understanding of olefin oxidation, have been largely neglected. This paper reports the oxidation of olefins with five carbons or less. The effect of structure on the products and reactivity were studied in benzene or without solvent using oxygen above atmospheric pressure.

The formation of epoxide as the major product from propylene and butene and of glycol from isobutylene has been reported.[2] The catalytic oxidation of butenes in acetic acid[3] and the related oxidation of butenes in the dense vapor phase[4] yielded mostly glycol esters and acids. Since this work was completed a study of the kinetics and products for the oxidation of butene-1 has been described which stresses the importance of hydroperoxide as a primary product.[5]

Experimental

Olefins were Phillips's pure grade and were charged into the reactor from a weighing bomb. Benzene was purified by fractionation.

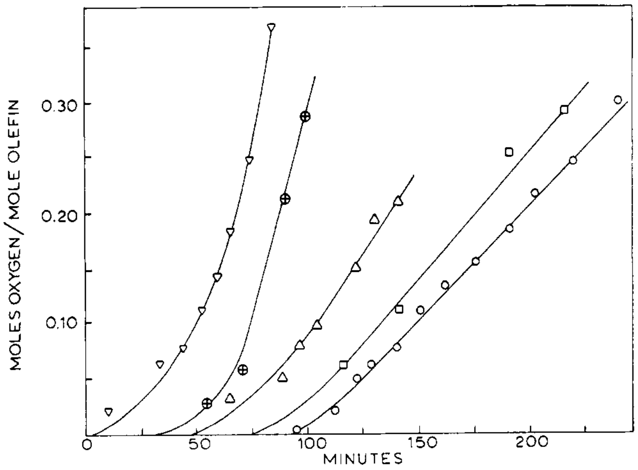

Fig. 1.—Oxygen absorption of olefins at 120°, 50 mole % in benzene: ▽, cis-2-butene; ⊕, 3-methyl-1-butene (displaced 25 min.); △, 1-butene (displaced 50 min.); □, isobutylene (displaced 75 min.); ○, propylene.

Oxidations were conducted in a 1.4-l. autoclave, 4.5 in. in diameter and 5.5 in. deep, equipped with cooling coils, a Teflon-coated liner, baffles, and a reflux condenser. A Magnedrive stirrer (Autoclave Engineers, Inc., Erie, Pa.) allowed magnetic stirring at 1000 r.p.m. The entire apparatus was well barricaded as occasional explosions occurred.

U.S.P. oxygen was fed from a 3-l. calibrated reservoir equipped with a 16-in. test gage to the reactor using a dome loaded regulator to maintain a constant set reaction pressure. An exit gas was maintained to monitor gaseous products and prevent their accumulation. The oxygen vented was measured with a wet test meter after trapping organic vapors and removing carbon dioxide. A complete material balance including gaseous reactants and products was obtained from each reaction.

The maximum rates were obtained from plots of oxygen absorbed against time. Typical absorption curves are shown in Fig. 1.

Major products were isolated by gas chromatography, by fractionation, or a combination of both. Identification utilized the infrared and mass spectra and retention times. Where the known epoxides were not available for comparison, as for the methylbutenes, the appropriate distillate or the crude oxidate was oxidized with periodic acid until the peak corresponding to the epoxide disappeared on gas chromatography and new peaks corresponding to the expected carbonyl products appeared. Hydroxy esters and diesters were prepared by reaction of carboxylic acids with the appropriate epoxide.

Product yields were calculated from gas chromatographic area analysis. Peak areas produced by injecting constant volume samples of known concentrations in benzene were used to confirm epoxide values. In some cases, the benzene solvent itself was used as an internal standard. Direct titration for epoxide with hydrogen bromide in acetic acid[6] gave values usually within 10% of those obtained by peak area analysis; except for propylene oxidation products where values were 30% lower (average from four different crude products). Propylene also showed a slight phase separation, analysis of both phases being required to calculate theoretical yields.

Results and Discussion

The relative reactivities of the olefins studied fall in an order which is generally consistent with the rules proposed by Bolland[7] for correlating structure with the rate of α-hydrogen abstraction in autoxidations. From a study of a series of olefins starting with hexenes, he concluded that replacement of hydrogens at either terminal carbon in propene by alkyl groups increases the rate of abstraction. Similar replacement at the middle carbon atom is without effect. The quantitative agreement of the measured and calculated rates (see Table I) appears much poorer than that obtained by Bolland. This may be due partly to the inapplicability of over-all rates which are influenced by differences in initiation. If it is considered that initiation primarily results from hydroperoxide decomposition,

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(1) Reported in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1963.

(2) (a) J. Gardner and N. Robertson, U. S. Patent 2,780,635 (1957); (b) H. Shingn, U. S. Patent 2,985,668 (1961); (c) A. F. Millidge and W. Webster, U. S. Patent 2,741,623 (1956); (d) C. E. Schweitzer, U. S. Patent 2,644,837 (1953); (e) N. Robertson, *et al.*, U. S. Patent 2,780,654 (1957); (f) Y. Kaminya, *Kogyo Kagaku Zasshi*, **64**, 1513 (1961).

(3) W. F. Brill, unpublished work.

(4) J. C. Snyder and A. V. Grosse, Preprints of the Petroleum Division, National Meeting of the American Chemical Society, Houston, Tex., March, 1950, p. 271.

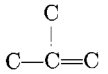
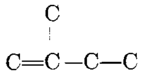
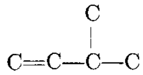
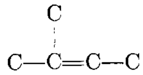
(5) A. Chauvel, G. Clement, and J. C. Balaceanu, *Bull. soc. chim. France*, 1774 (1962).

(6) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

(7) J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950).

TABLE I

EFFECT OF STRUCTURE ON RELATIVE RATE

Olefin	Calcd.[a]	Observed[b]
C—C=C	0.5	<1
 $\text{C—}\overset{\text{C}}{\text{C}}\text{=C}$	1	1
C=C—C—C	1.6	1.2
 $\text{C=}\overset{\text{C}}{\text{C}}\text{—C—C}$	2.1	2.7
C—C=C—C	3.2	4.2
 $\text{C=C—}\overset{\text{C}}{\text{C}}\text{—C}$	5.4	2.9
 $\text{C—}\overset{\text{C}}{\text{C}}\text{=C—C}$	8.7	8.2

[a] Using Bolland's rules[7] for calculating "k_3." [b] From the maximum measured rate with 50 mole % olefin in benzene using $d(O_2)/dt = k_2(\text{olefin})^2$ with concentrations expressed in moles/kg.

the anomalous position of 3-methyl-1-butene, the only olefin possessing a tertiary hydrogen, appears to be related to the fact that it alone forms hydroperoxide as a major product. It is interesting that 2,4-dimethyl-2-pentene, the only olefin containing a tertiary hydrogen which has been fitted to Bolland's scheme, is reported to have anomalously low reactivity.[8]

The dependency of the observed maximum rate for a given olefin on the olefin concentration is very strong. With increasing benzene dilution the drop in rate is, in fact, so strong that at olefin concentrations most useful for kinetic treatment no reaction or an inconveniently slow reaction occurs. On the other hand, the more reactive olefins are oxidized so rapidly in the absence of solvent that the reaction temperature can not be adequately controlled. The effect of concentration is illustrated by the second-order oxidation rates for isobutylene shown in Table II. The only reasonably adequate empirical rate constants could be obtained by assuming third-order dependency after approximating molar concentrations.

The data in Table II also indicate that dependency on oxygen pressure does not appear until pressures as low as 200 p.s.i. are encountered. The magnitude of the effect of catalyst or initiator also is illustrated. The presence of stirred calcium oxide, a common condition in synthesizing epoxides from olefins by oxidation, has little effect on the rate.

TABLE II

OXIDATION OF ISOBUTYLENE AT 120°

Pressure,[a] p.s.i.	Catalyst[b]	Concn.,[c] moles/kg.	$k_2{}^d \times 10^{-6}$, kg. mole^{-1} sec.$^{-1}$
400 (35)		17.7	6.5
(210)		7.1	5.3
(291)		3.3	2.1
600 (485)		2.9	2.1
200 (78)		3.2	1.4
500 (399)	AIBN	3.1	6.3
600 (371)	CaO	2.9	1.2
400 (202)	CoA CaO	7.5	11.1
600 (493)	CoA	3.0	7.9
400 (196)	CoN MgO	7.8	5.0
300 (96)	CoN MgO	7.8	5.1
300 (118)	CoN MgO	6.7	5.3

[a] Gage pressure (estimated partial pressure of oxygen). [b] AIBN is azobisisobutyronitrile, 0.3 wt. %; CoA is cobaltic acetylacetonate, 0.16 wt. %; CoN is cobalt naphthenate, 0.16 wt. %; CaO and MgO, 5 wt. %. [c] In benzene. [d] From $d(O_2)/dt = k_2(\text{olefin})^2$.

Products.—As reported for the higher molecular weight olefins where the reaction products have been carefully examined,[9] oxidation of the liquid petroleum olefins produces epoxides with the oxirane ring at the position previously occupied by the double bond. Yields in some case may be better than 50% on olefin changed. Carbonyl compounds containing less carbon atoms than the original olefins also may be produced as major products, even though they are susceptible to further oxidation (Table III). It is particularly interesting that alcohol is not usually a significant product and that all the hydroxy compounds formed in more than a few per cent yield are glycols and hydroxy esters which can arise from the epoxide. Only for the single case of 3-methyl-1-butene, where a tertiary hydroperoxide may be produced, is hydroperoxide the major product.

The order of increasing yield of epoxide for the various olefins appears to be the same as the order of increasing oxidizability, presumably indicating a common structural effect on epoxide formation and oxidation rate. However, the epoxide found at the conversion of these experiments may reflect their relative reactivity to addition, rearrangement, or oxidative cleavage.

For propylene oxide, the importance of ring opening was apparent from the amounts of glycol and glycol derivatives found in the oxidation of propylene. The amount of product arising from ring opening does not appear to be entirely related to the expected reactivity of the epoxide.[10] A more reasonable correlation can be made with the tendency of the olefin to yield formic acid which is far more reactive toward epoxides than other carboxylic acids. Propylene oxide was found to be stable to oxidation under conditions equivalent to those encountered in the oxidation of propylene. When propylene oxide was added to other olefins it survived the oxidation of the mixture. Other oxides have not yet been studied in this manner but recent reports of radical reactions of epoxides[11] indicate that other structures may be expected to be resistant to further oxidation.

The detailed product analysis for propylene, given in Table III, indicates that while approximately equal quantities of formic and acetic acid formed, most of the formic acid added to the epoxide. The formation of large amounts of methanol and methyl esters distinguishes the oxidation of propylene from that of other olefins. The presence of suspended base during the oxidation not only failed to improve epoxide yields but drastically diminished glycol and glycol derivatives. The initiator concentration and the use of catalyst was found to have little effect on the products formed.

Isobutylene gives acetone, which is unusually resistant to further oxidation, in yields which may be greater than 50%. Unlike propylene, epoxide yields,

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(8) L. Bateman, *Quart. Rev.* (London), **8**, 147 (1954).

(9) E. G. E. Hawkins and D. C. Quin, *J. Appl. Chem.* (London), **6**, 1 (1956), and references therein.

(10) R. E. Parker and N. S. Issacs, *Chem. Rev.*, **59**, 737 (1959).

(11) (a) T. Wallace and R. J. Gritter, *J. Org. Chem.*, **26**, 282 (1962); (b) C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, **84**, 3326 (1962).

TABLE III

OXIDATION PRODUCTS[a]

Olefin[b]	Propylene	Isobutylene	1-Butene	*cis*-2-Butene[c]	2-Methyl-1-butene	2-Methyl-2-butene
Catalyst[d]	DDM	CaO			MgO CoN	MgO CoN
Conversion, %	36.0	32.2	18.4	18.6	52.5	55.4
Epoxide	8.2	18.4	19.4	48.2[e]	32.6	49.2
Glycol	3.9	7.1				
Monoformate	10.7	1.2	3.9			
Diformate	5.2	6.6	1.7			
Monoacetate	2.3	0.8				
Methanol	26.8					
Methyl esters	8.0					
Acetaldehyde				34.5		
Acetone		41.7			6.0	34.8
Propionaldehyde			15.9			
Methyl ethyl ketone			10.1		30.9	
Crotonaldehyde			7.6	10.4		
Acrolein				6.9		
Biacetyl				4.6		
Formic acid	5.1					
Acetic acid	21.6	5.9	9.9	6.9		
Acrylic acid	3.7		3.6			
Propionic acid	0.2		12.5			
Butyric acid			1.5	2.5		

[a] Theoretical yield of products based on olefin reacted. [b] 3-Methyl-1-butene gave 44% hydroperoxide, 9% epoxide, 9% acetone, and 2.5% isobutyraldehyde at 30% conversion. [c] *trans*-2-Butene gave the same products as *cis*-2-butene. Yields were 30% *trans* epoxide, 9% *cis* epoxide, and 30% acetaldehyde at 33% conversion. No propionaldehyde was detected. [d] At 120°; 50 mole % olefin in benzene; DDM is 60% methyl ethyl ketone peroxide, 0.7 wt. %; CoN is cobalt naphthenate (6% cobalt), 0.2 wt. %; CoA is cobalt acetylacetonate, 0.2 wt. %; MgO is light magnesium oxide, 5.5 wt. %; CaO, 5.5 wt. %. [e] 19.5% *cis* epoxide and 28.7% *trans* epoxide.

and even glycol and glycol ester yields, are improved by oxidation of isobutylene in the presence of added base. Both the large amount of ester formed and extrapolation of yields back to zero conversion indicate that epoxide is actually formed as a primary product in yields above 30%. However at practical conversions, careful control of reaction conditions is necessary to obtain up to 20% epoxide.

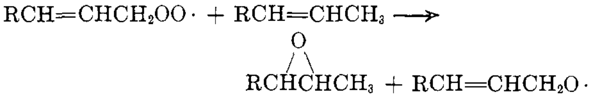
A comparison of the products from 1-butene and *cis*- or *trans*-2-butene is particularly interesting since if the course of oxidation is determined by abstraction of α-hydrogen, the oxidation of both the α- and β-olefin would proceed through similar butenyl radicals.

$$\mathrm{CH_3\dot{C}HCH{=}CH_2 \leftrightarrow CH_3CH{=}CH{-}\dot{C}H_2}$$

All products except those formed by direct attack on the double bond would therefore be the same from each olefin. As shown in Table III, the products found in significant quantities from each olefin are very different, crotonaldehyde and acetic acid being the only common products. The major products from 1-butene, other than epoxide, are propionaldehyde and propionic acid and methyl ethyl ketone while the major product from *cis*- or *trans*-2-butene is acetaldehyde. While oxidation of epoxide may partially account for these results, it does not seem likely that aldehydes be produced from epoxide by a radical oxidation. It is even more difficult to project a scheme for the formation of propionaldehyde from 1-butene by oxidation initiated at the α-hydrogen. Assuming reaction at the α-position without isomerization, the expected products, other than acetaldehyde, would be unsaturated. Similarly, the 2-butene would yield propionaldehyde or unsaturated products.

The product distributions from 2-methyl-1-butene and 2-methyl-2-butene are analogous to those from the corresponding unsubstituted butenes. The formation of methyl ethyl ketone from the α-olefin and acetone from the β-olefin as major products is incompatible with α-hydrogen abstraction with formation of the common 2-methyl butenyl radical. The radical $\mathrm{(CH_3)_2C{=}CH{-}\dot{C}H \leftrightarrow (CH_3)_2\dot{C}{-}CH{=}CH_2}$ also can be formed from 2-methyl-2-butene. Statistically it can not account for more than one-third of the products formed by abstraction but it is a likely precursor for acetone.

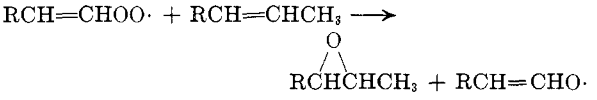
Mechanism.—It has been shown that epoxides arise during the oxidation of 2,4,4-trimethyl-1-pentene and cyclohexene by free-radical attack on the double bond and not by secondary oxidation involving hydroperoxide.[12] The products from 2,4,4-trimethyl-1-pentene were explained by a mechanism in which two molecules of epoxide and one of ketone are formed by the sequence shown.



$$\mathrm{RCH{=}CHCH_2OO\cdot + RCH{=}CHCH_3 \longrightarrow R\overset{O}{\overbrace{CHCH}}CH_3 + RCH{=}CHCH_2O\cdot} \quad (1)$$

$$\mathrm{RCH{=}CHCH_2O\cdot \longrightarrow RCH{=}CH\cdot + CH_2O} \quad (2)$$

$$\mathrm{RCH_2CH\cdot + O_2 \longrightarrow RCH{=}CHOO\cdot} \quad (3)$$



$$\mathrm{RCH{=}CHOO\cdot + RCH{=}CHCH_3 \longrightarrow R\overset{O}{\overbrace{CHCH}}CH_3 + RCH{=}CHO\cdot} \quad (4)$$

The results reported in the present paper indicate that double bond oxidation is the more important process for all olefins which do not possess an extremely reactive hydrogen. However, the proposed mechanism does not explain the major carbonyl products observed with the butenes. Since it requires that products other than epoxide arise through a common allylic radical, the high yield of propionaldehyde from 1-butene and methyl ethyl ketone from 2-methyl-1-

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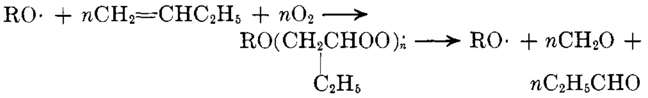
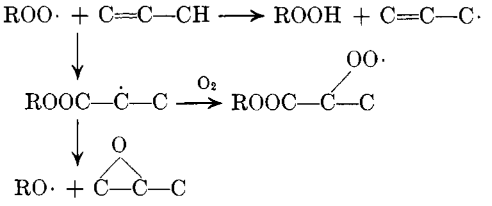
(12) W. F. Brill, *J. Am. Chem. Soc.*, **85**, 141 (1963).

butene remains to be explained. Unless it can be demonstrated that these products result from the oxidation of epoxide, an additional sequence will be necessary to explain completely all the products obtained from olefins. Copolymerization of olefin with oxygen, followed by cleavage of the polyperoxide formed to two molecules of aldehyde as suggested by Mayo to explain the oxidation of styrene to benzaldehyde and formaldehyde[13] may be appropriate.



$$RO\cdot + nCH_2{=}CHC_2H_5 + nO_2 \longrightarrow RO(\underset{C_2H_5}{CH_2CH}OO)_n \longrightarrow RO\cdot + nCH_2O + nC_2H_5CHO$$

The relationship between the reaction sequences leading eventually to the production of allylic hydroperoxide, the epoxide corresponding to the olefin oxidized, and aldehydes by fission at the double bond is illustrated.



If it is accepted that three reaction pathways, all of which are probably available for most olefins, are required to explain oxidation products, the effect of structure on reactivity becomes difficult to interpret in terms of α-hydrogen–carbon bond strengths as has been done.[7] However, as alkyl substitution α to a double bond may be expected to favor the electrophilic addition of oxygen radicals,[14] as well as α-hydrogen abstraction, the observed effect of structure on reactivity is still appropriate.

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. John O'Neill, Jr. The encouragement of Dr. L. Marshall Welch and Dr. Louis J. Croce is especially appreciated.

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[13] F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2465 (1958).

[14] R. J. Cvetanovic, *Can. J. Chem.*, **38**, 1678 (1960).

Chemistry of Isocyanic Acid. III. Reaction of Isocyanic Acid with Olefins

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The synthesis of isocyanates has been effected by the addition of isocyanic acid to *m*- and *p*-diisopropenylbenzenes, isoprene, styrene, α-methylstyrene, and other olefins. Several of the isocyanates obtained are new.

Organic isocyanates have been prepared by such routes as phosgenation of amines, decomposition of acid azides, dehydration of hydroxamic acids, reaction of inorganic cyanates with esters of inorganic acids, and thermal decomposition of ureas.[1]

In previous papers in this series, the preparation of isocyanates by the reaction of isocyanic acid with carbonyl compounds[2] and with α,β-unsaturated ethers[3] was described. We now report the synthesis of isocyanates by the addition of isocyanic acid to certain olefins as illustrated.

$$C_6H_5C(CH_3){=}CH_2 + HNCO \xrightarrow{H^+} C_6H_5C(CH_3)_2NCO$$

In Table I are listed some of the olefins studied and the isocyanates obtained.

In addition to the products described in Table I, isocyanates were obtained in low yields from divinylbenzene, dicyclopentadiene, vinylacetylene, 1-methyl-3-methylene-1-phenylcyclobutane, 1-methylcyclohexene, 2,3-dimethyl-1,3-butadiene, and *p*-methoxy-α-methylstyrene. In general, the most reactive olefins were those having terminal double bonds with at least one electron-releasing group, such as methyl or phenyl, on the 2-carbon. Isopropenylbenzenes were considerably more reactive than the other olefins studied.

TABLE I

ISOCYANATES FROM OLEFINS AND ISOCYANIC ACID

Olefin	Isocyanate	Yield,[a] %
$C_6H_5C(CH_3){=}CH_2$	$C_6H_5C(CH_3)_2NCO$	41
$C_6H_5CH{=}CH_2$	D,L-$C_6H_5CH(CH_3)NCO$	5
$C_6H_4(C(CH_3){=}CH_2)_2$ (*m*)	$CH_2{=}C(CH_3)C_6H_4C(CH_3)_2NCO$ (*m*)	30
	and	
	$OCNC(CH_3)_2C_6H_4C(CH_3)_2NCO$ (*m*)	35
$C_6H_4(C(CH_3){=}CH_2)_2$ (*p*)	$CH_2{=}C(CH_3)C_6H_4C(CH_3)_2NCO$ (*p*)	9
	and	
	$OCNC(CH_3)_2C_6H_4C(CH_3)_2NCO$ (*p*)	16
$CH_2{=}CHC(CH_3){=}CH_2$	$CH_2{=}CHC(CH_3)_2NCO$	3
$(CH_3)_2C{=}CH_2$	$(CH_3)_3CNCO$	10

[a] Based on the amount of olefin charged.

The reaction of isocyanic acid with isoprene gave α,α-dimethylallyl isocyanate (II) in low yield. An alternative route to II was found in the reaction of silver cyanate with γ,γ-dimethylallyl chloride (I). This reaction also gave the isomer (III) in about an equal amount. Interestingly, treatment of α,α-dimethylallyl chloride (IV) with silver cyanate gave mainly III with only a small amount of II.

$$\underset{\text{I}}{(CH_3)_2C{=}CHCH_2Cl} \xrightarrow{AgOCN} \underset{\text{II}}{CH_2{=}CHC(CH_3)_2NCO} + \underset{\text{III}}{(CH_3)_2C{=}CHCH_2NCO}$$

$$\underset{\text{IV}}{CH_2{=}CHC(CH_3)_2Cl} \xrightarrow{AgOCN} \text{III (main product)} + \text{II}$$

The addition of isocyanic acid to olefins has been effected under autogenous pressure at 100–110° in a

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[1] R. Arnold, J. Nelson, and J. Verblanc, *Chem. Rev.*, **57**, 47 (1957).

[2] F. W. Hoover, H. B. Stevenson, and H. S. Rothrock, *J. Org. Chem.*, **28**, 1825 (1963).

[3] F. W. Hoover and H. S. Rothrock, *ibid.*, **28**, 2082 (1963).