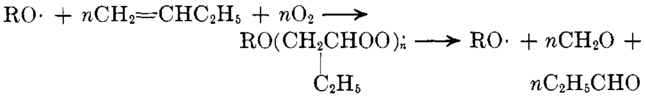
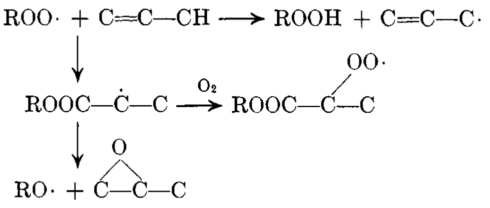
butene remains to be explained. Unless it can be demonstrated that these products result from the oxidation of epoxide, an additional sequence will be necessary to explain completely all the products obtained from olefins. Copolymerization of olefin with oxygen, followed by cleavage of the polyperoxide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



$$RO\cdot + nCH_2{=}CHC_2H_5 + nO_2 \longrightarrow RO(\underset{\displaystyle C_2H_5}{CH}{}_2CHOO)_n \longrightarrow RO\cdot + nCH_2O + nC_2H_5CHO$$

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).

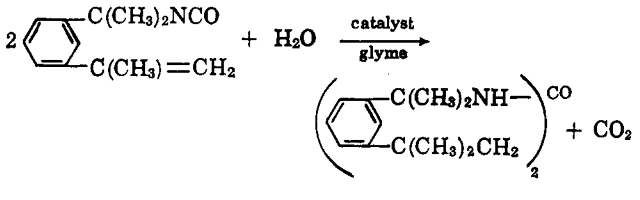
[3] F. W. Hoover and H. S. Rothrock, *ibid.*, **28**, 2082 (1963).

solvent. The reaction is strongly promoted by cationic catalysts, for example, *p*-toluenesulfonic acid, hydrogen chloride, and salts of strong acid with weak bases (*e.g.*, ammonium tosylate and octylammonium 2,2,2-trifluoroethylsulfonate). Trimerization of the isocyanic acid and polymerization of the olefin are competitive reactions, and the type of solvent used affects the extent of these reactions. Aromatic solvents have given the best yields of isocyanates. Basic solvents, such as tetrahydrofuran and diethyl ether, help to stabilize isocyanic acid against trimerization but reduce the rate of addition of HNCO to the double bond. Other polar solvents, such as acetonitrile and nitrobenzene, enhance olefin polymerization and give lower yields of isocyanate.

The addition of isocyanic acid to olefins apparently proceeds by a carbonium-ion mechanism, judged by the nature of the effective catalysts, the types of operable olefins, and the structure of isocyanates obtained.

α,α,α′,α′-Tetramethyl-*m*-xylylene diisocyanate formed polymers with diamines and with glycols. The aliphatic diamines reacted very rapidly with this isocyanate, whereas 2,4-toluenediamine and other weakly basic amines reacted relatively slowly. Reactions with glycols were slow at room temperature but were quite rapid at 80° when catalyzed with stannous octoate.

m-Isopropenyl-α,α-dimethylbenzyl isocyanate, α,α,α′,α′-tetramethyl-*m*-xylylene diisocyanate, and other tertiary isocyanates react slowly with water unless a mutual solvent and catalysts, such as tetraethylammonium cyanide and benzyltrimethylammonium hydroxide, are employed. However, under suitable conditions, a fairly rapid reaction with water can be effected to give the corresponding urea.



Experimental[4]

α,α,α′,α′-Tetramethyl-*m*-xylylene Diisocyanate and *m*-Isopropenyl-α,α-dimethylbenzyl Isocyanate.—A mixture of 320 g. of *m*-diisopropenylbenzene (obtained from Hercules Powder Company), 860 g. of isocyanic acid,[2] 3000 ml. of toluene, and 14 g. of ammonium tosylate was heated in a 1-gal. (working capacity) stainless steel autoclave equipped with a three-blade, propeller type, motor-driven stirrer for 2 hr. at 100°. The cyanuric acid (710 g.) formed was removed by filtration. Simple distillation of the filtrate gave 319 g. of a mixture of isocyanates, b.p. 92° (0.5 mm.) to 110° (1 mm.). There also was obtained 70 g. of a viscous residue. The infrared spectrum of the residue showed strong absorption at 4.4 μ (NCO).

The mixture of isocyanates was redistilled through an 18-in. Nester spinning-band column[5] (about 15 plates) having an inside diameter of 10 mm. There was obtained 103 g. of monoisocyanate, b.p. 83–85° (0.9 mm.), 23 g. of a mixture of 73% monoisocyanate and 23% diisocyanate, b.p. 85–100° (0.9 mm.), and 167 g. of diisocyanate, b.p. 100–106° (mainly 106°) at 0.9 mm. The yields of the mono- and diisocyanates (based on *m*-diisopropenylbenzene) were 30 and 35%, respectively.

Anal. Calcd. for $C_{13}H_{15}NO$ (monoisocyanate): C, 77.57; H, 7.51; N, 6.96. Found: C, 77.20; H, 6.97; N, 7.22.

The infrared spectrum showed absorption at 3.25 μ (=CH–); 3.35 and 3.4 (saturated CH); 4.44 (-NCO); 6.15 (C=C); 6.25, 6.34, and 6.73 (aromatic C=C); 7.21, 7.32, and 7.33 [$(CH_3)_2C$]; and 12.52 (*meta* disubstitution).

The proton n.m.r. spectrum showed absorption at 1.57 p.p.m. ($C(CH_3)_2$), 2.08 ($CH_3C=C$), 5.05 (C=CH split, probably *cis* to CH_3), 5.37 (C=CH, probably *trans* to the CH_3 group), 7.23 (aromatic), and 7.56 (aromatic) in the ratio of 6:3:1:1:3:1, respectively.

Anal. Calcd. for $C_{14}H_{16}N_2O_2$ (diisocyanate): C, 68.83; H, 6.60; N, 11.46. Found: C, 69.14; H, 6.66; N, 11.55.

The infrared absorption spectrum showed absorption at 3.27 μ (=CH); 3.35, 3.4, and 3.46 (saturated CH); strong 4.45 (-NCO); 6.23, 6.3, and 6.72 (aromatic C=C); 7.21 and 7.32 [$>C(CH_3)_2$]; and 12.57 (*meta* disubstitution).

The proton n.m.r. spectrum showed hydrogens at 1.66 p.p.m., 7.42, and 7.75 in the ratio of 12:3:1, respectively.

The purity of these products was determined by gas chromatographic analysis with a 1-m. column packed with 10% squalene on 40–60-mesh Chromosorb W (helium flow of 100 ml./min.).

The reaction of α,α,α′,α′-tetramethyl-*m*-xylylene diisocyanate (0.42 g.) with hexamethylenediamine (0.20 g.) in dimethylformamide gave a polyurea. This reaction proceeded rapidly as evidenced by the rapid increase in solution viscosity and a large exotherm. The polymer, isolated by precipitation with acetone, melted at 200–227° and gave an infrared spectrum characteristic of a urea structure.

A low molecular weight polyurethane having isocyanate end groups was obtained by heating a mixture of 48.0 g. of polytetramethylene oxide glycol (mol. wt., 963), 19.5 g. of α,α,α′,α′-tetramethyl-*m*-xylylene diisocyanate, and 0.05 g. of stannous octoate at 80° for 1.5 hr. Chain extension of this polymer was effected by treatment with hexamethylenediamine or 2,4-toluenediamine and by exposing thin films to moisture in the presence of tetraethylammonium cyanide catalyst. The products obtained with hexamethylenediamine and with water were rubbery, and the product obtained with 2,4-toluenediamine was relatively hard and tough.

α,α,α′,α′-Tetramethyl-*p*-xylylene Diisocyanate (VI) and *p*-Isopropenyl-α,α-dimethylbenzyl Isocyanate (V).—A mixture of 350 g. (2.2 moles) of *p*-diisopropenylbenzene (Hercules Powder Company), 860 g. (20 moles) of isocyanic acid, 4 g. of ammonium tosylate, 7 g. of hydroquinone, and 3000 ml. of toluene was treated under the conditions previously described for *m*-diisopropylbenzene. On simple distillation, there was obtained 136 g. of crude diisocyanate, b.p. 90–110° (1 mm.), and 190 g. of nondistillable residue which gave strong infrared absorption at 4.4 μ (NCO). Redistillation through a Nester still gave 38 g. (9% based on olefin) of V, b.p. 83° (0.55 mm.), and 86 g. (16%) of VI, b.p. 110° (0.55 mm.) and m.p. 78°. Analyses were made on center cuts.

Anal. of V. Calcd. for $C_{13}H_{15}NO$: C, 77.57; H, 7.51; N, 6.96. Found: C, 77.77; H, 7.57; N, 7.33.

Anal. of VI. Calcd. for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.46. Found: C, 69.19; H, 6.76; N, 11.43.

The infrared absorption spectrum of the diisocyanate showed absorption at 3.27 μ (=CH), 3.35 and 3.40 (saturated CH), 4.43 (-NCO), 6.15 and 6.63 (aromatic -C=C-), 7.22 and 7.32 (*gem*-dimethyl), and 12.06 (*para* disubstitution).

The proton n.m.r. spectrum of the diisocyanate in deuteriochloroform showed hydrogens at 1.67 p.p.m. and 7.43 in the ratio of 3:1.

When this reaction was carried out in the absence of a catalyst, 21% of the olefin was converted to monoisocyanate, virtually none to diisocyanate, and 15% to polymer. The remainder of the olefin was recovered.

α,α-Dimethylbenzyl Isocyanate.—A mixture of 2237 g. (19 moles) of α-methylstyrene, 1200 g. (28 moles) of isocyanic acid, 14 g. of ammonium tosylate, 7 g. of hydroquinone, and 3 l. of toluene was heated in an autoclave for 3 hr. at 100°. Distillation gave 1250 g. (41% based on olefin) of α,α-dimethylbenzyl isocyanate, b.p. 44° (0.75 mm.), $n^{25}\text{D}$ 1.5050; lit.[6] b.p. 50–52° (0.16 mm.), $n^{25}\text{D}$ 1.5038.

Anal. Calcd. for $C_{10}H_{11}ON$: N, 8.69. Found: N, 8.86.

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(4) All melting and boiling points are uncorrected. N.m.r. data were obtained on a Varian A60 spectrometer. N.m.r. data reported as parts per million (lower field) from tetramethylsilane (internal). Unless otherwise stated, no solvent was used.

(5) U. S. Patent 2,712,520 (1955).

(6) A. Lambert, J. D. Rose, and B. C. L. Weedon, *J. Chem. Soc.*, 42 (1949).

The infrared spectrum showed absorption at 3.25 μ and 3.28 (=CH), 3.35 and 3.40 (saturated CH), 4.44 (-NCO), 6.21 (aromatic -C=C-), 7.19 and 7.30 (>C$(CH_3)_2$), and 13.13 and 14.35 (monosubstituted aromatic bands).

The proton n.m.r. spectrum showed hydrogens at 1.51 p.p.m. and 7.37 (multiple splitting) in the ratio of 6:5. Reaction of this isocyanate with aniline gave the urea, m.p. 195–197°, lit.[6] m.p. 193–194°.

After standing 2 weeks in excess ethanol at room temperature, α,α-dimethylbenzyl isocyanate was converted (89%) to ethyl N-α,α-dimethylbenzyl carbamate, b.p. 88° (0.45 mm.), $n^{25}D$ 1.5100.

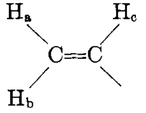
Anal. Calcd. for $C_{11}H_{17}NO_2$: C, 69.52; H, 8.27; N, 6.76. Found: C, 69.71; H, 8.34; N, 6.99.

The infrared spectrum was in agreement with the urethane structure.

α,α-Dimethylallyl Isocyanate.—A mixture of 2000 ml. of xylene (toluene free), 1020 g. (15 moles) of isoprene, 840 g. (19.5 moles) of isocyanic acid, 14 g. of ammonium tosylate, and 5 g. of hydroquinone was heated with stirring in an autoclave for 3 hr. at 100°. The product was filtered, and the filtrate distilled through a column packed with glass helices. On redistillation through a 24-in. Podbielniak column, there was obtained 35 g. of α,α-dimethylallyl isocyanate, b.p. 104.5°, $n^{25}D$ 1.4100. The infrared spectrum showed bands at 2.7 μ (common to tertiary NCO), 4.43 (NCO), 6.1 (CH_2=CH–), 7.26 and 7.35 (*gem*-dimethyl), and 10.1 and 10.8 (CH_2=CH–), consistent with the proposed structure.

Anal. Calcd. for C_6H_9NO: C, 64.80; H, 8.10; N, 12.60. Found: C, 64.84; H, 8.22; N, 12.62.

The proton n.m.r. resonance spectrum showed peaks at 1.31 p.p.m. (methyl hydrogens) and several peaks from 4.8 to 6.1 (vinyl hydrogens). The ratio of methyl to vinyl hydrogens was 2:1 The chemical shifts and coupling constants of the vinyl hydrogens



were approximately H_a, 4.92 p.p.m.; H_b, 5.16; and H_c, 5.81; $J_{H_bH_c}$ = 17 c.p.s.; $J_{H_aH_c}$ = 9.8; and $J_{H_aH_c}$ = 1.4.

Reaction with 2-ethylhexylamine gave N-2-ethylhexyl-N′-α,α-dimethylallylurea, $CH_2=CHC(CH_3)_2NHCONHCH_2CH(C_2H_5)C_4H_9$, an oil.

Anal. Calcd. N, 11.65. Found: N, 11.11.

The infrared spectrum was consistent with the urea structure.

Alternatively, α,α-dimethylallyl isocyanate was obtained from the reaction of silver cyanate with $(CH_3)_2C=CHCH_2Cl$, prepared from isoprene and hydrogen chloride.[7] The tertiary chloride, $CH_2=CHC(CH_3)_2Cl$, gave predominantly $(CH_3)_2C=CHCH_2NCO$ and only minor amounts of the tertiary isocyanate. Thus, γ,γ-dimethylallyl chloride (13.5 g., 0.14 mole) was added dropwise over a period of 20 min. to a stirred mixture of 100 ml. of ether and 30 g. (0.2 mole) of silver cyanate during which time the temperature rose from 23° to 31°. The mixture was then heated under reflux for 10 min. After removal of the solid by filtration, distillation yielded 5 g. (32%) of $CH_2=CH(CH_3)_2NCO$, b.p. 104–105° (infrared spectrum same as that of an authentic sample), and 6 g. (39%) of $(CH_3)_2C=CHCH_2NCO$, b.p. 139–140°, $n^{25}D$ 1.4393.

Anal. Calcd. for C_6H_9NO (b.p. 139–140°): N, 12.60. Found: N, 12.72.

The infrared spectrum of the higher boiling isocyanate showed bands at 3.4 μ (CH), 4.43 (NCO), 6.02 (-C=C-), and 11.5 ($CR_1R_2=CHR_3$), consistent with the proposed structure.

t-Butyl Isocyanate.—A mixture of 200 ml. of toluene, 43 g. (1.0 mole) of isocyanic acid, 28 g. (0.5 mole) of isobutylene, and 0.5 g. of p-toluenesulfonic acid was heated in a stainless steel bomb for 8 hr. at 100–110°. Distillation of the product through a Vigreux column and then through a precision still gave about 5 g. (10% on isobutylene) of t-butyl isocyanate, b.p. 85–86° lit.[8] 85°; about 18 g. of isobutylene was recovered. The proton resonance spectrum of the isocyanate showed only methyl hydrogens. The infrared spectrum was consistent with this structure.

α-Phenylethyl Isocyanate.—A mixture of 300 ml. of toluene, 54 g. (0.52 mole) of styrene, 84 g. (1.9 moles) of isocyanic acid, 1 g. of ammonium tosylate, and 1 g. of hydroquinone was heated 3 hr. at 100°. Distillation through a Vigreux column gave 2.4 g. (5.6%) of D,L-α-phenylethyl isocyanate, b.p. 38° (0.4 mm.); for L-α-phenylethyl isocyanate, lit.[9] b.p. 82–83° (12–14 mm.).

Anal. Calcd. for C_9H_9NO: N, 19.52. Found: N, 19.15.

Reaction with ammonia gave D,L-$C_6H_5CH(CH_3)NHCONH_2$, m.p. 140° (m.p. of L-α-phenylethylurea 121–122°, melting point of D,L-mixture not reported).

Anal. Calcd. for $C_9H_{12}N_2O$: N, 17.06. Found: N, 16.73.

p-Methoxy-α,α-dimethylbenzyl Isocyanate.—A solution of 12.5 g. (0.085 mole) of p-methoxy-α-methylstyrene and 5 ml. of toluene was added dropwise over a period of 32 min. to a stirred mixture of 19.2 g. (0.45 mole) of isocyanic acid, 30 ml. of toluene, and 0.1 g. of p-toluenesulfonic acid. The temperature rose to 34° and was held at this temperature for an additional 50 min. Distillation through a Vigreux column gave 3 g. of a mixture [b.p. 75–92° (0.5 mm.)], containing p-$CH_3OC_6H_4C(CH_3)_2NCO$ (89%) on the basis of infrared and nitrogen analyses.

Anal. Calcd.: N, 7.3. Found: N, 6.5.

Reaction with aniline gave the urea, p-$CH_3OC_6H_4C(CH_3)_2NHCONHC_6H_5$, m.p. 169–171°.

Anal. Calcd. for $C_{17}H_{20}O_2N_2$: C, 71.82; H, 7.09; N, 9.85. Found: C, 72.29; H, 7.08; N, 9.92.

The infrared spectrum showed absorption at 3.0 μ, 3.4, 6.05, 6.25, 6.7, 12.1, 13.3, and 14.45.

Reaction Variables.—With the reaction of isocyanic acid with α-methylstyrene as a prototype, the effect of various catalysts and solvents has been explored. Catalysts in decreasing order of effectiveness are p-toluenesulfonic acid, ammonium p-toluenesulfonate, iodine, hydrogen chloride, ammonium perfluoroisobutyrate, silver perfluoroisobutyrate, and octylammonium-2,2,2-trifluoroethylsulfonate.

Several types of solvents were employed, and the best yields of isocyanates were obtained with aromatic hydrocarbons, such as toluene or benzene. With tetrahydrofuran, the rate of isocyanic acid trimerization was only 6% compared to 30% with toluene under otherwise comparable conditions. With acetonitrile, the amount of high-boiling residue was several times that obtained with toluene and the yield of distillable isocyanates was only about one-half.

Reaction of Tertiary Isocyanates with Water.—The following example illustrates the procedure for preparing ureas from tertiary isocyanates. A mixture of 25 g. of α,α-dimethylbenzyl isocyanate, 50 ml. of water, 0.02 g. of tetraethylammonium cyanide, and 250 ml. of 1,2-dimethoxyethane was prepared at 25°. The temperature rose to about 35° on standing and within 15 min. a precipitate began to form. After the mixture had stood overnight, water was added, and the solid (21.5 g., 94%), m.p. 225–227°, lit.[6] m.p. 226–227°, was removed by filtration.

Similarly, m-isopropenyl-α,α-dimethylbenzyl isocyanate was converted to $(m\text{-}C_3H_5C_6H_4C(CH_3)_2NH)_2CO$, m.p. 171–173°, in 100% yield.

Anal. Calcd. for $C_{25}H_{22}N_2O$: N, 7.46. Found: N, 7.56.

This compound in chloroform readily added chlorine to give partial saturation (81%) of the double bonds.

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[7] A. J. Ultée, *J. Chem. Soc.*, 530 (1948).

[8] W. Siefken, *Ann.*, **562**, 75 (1949).

[9] T. L. Cairns, *J. Am. Chem. Soc.*, **63**, 871 (1941).