and weigh'' technique. A 5 ft × 0.25 in. 15% XF-1150 on 60/80 Chromosorb W column gave overall satisfactory separation of the major products except for the insertion products (**2**, **3**, and **4**) which gave a broad, long-retention peak. However, a 5 ft × 0.25 in. 10% QF-1 on 60/80 Chromosorb W was needed to achieve good separation of **5** from **6**.

Products **5** and **6** were identified by comparison of retention times with those of and coinjection with authentic samples. Products **1**, **2**, **3**, and **4** were identified by collection from the gas chromatograph and comparison of nmr and ir spectra with published data.[4] To obtain calibration factors to correct for differences in detector sensitivity, it was assumed that products **1**, **2**, **3**, and **4** (isomers) have the same sensitivity. The relative ratios given are therefore corrected for the differences in detector sensitivity for **6** and **5** and **1**, **2**, **3**, and **4**.

Registry No.—Ethoxycarbonylnitrene, 2655-26-7; cyclohexene, 110-83-8; $(Me)_4Sn$, 594-27-4; $(Me)_4Si$, 75-76-3; ethyl azidoformate, 817-87-8.

Radiation and Ultraviolet Induced Addition of Alcohols to Ethyl Crotonate

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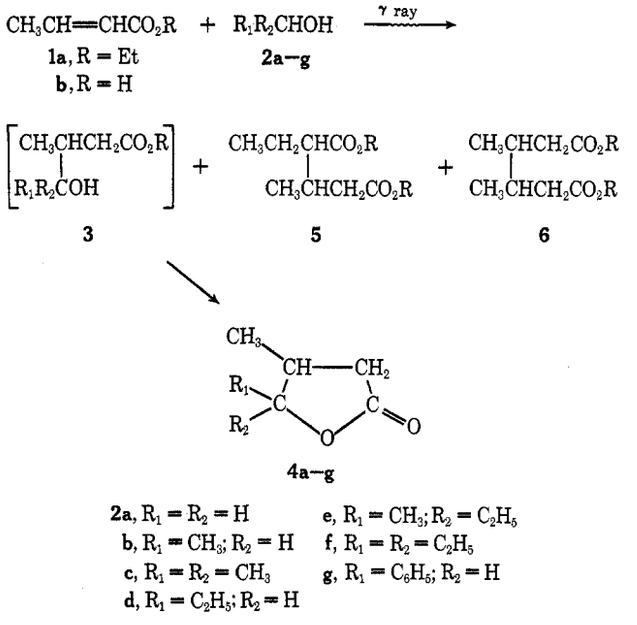
Received May 7, 1971

Radical addition reactions of alcohols to double bonds have been reported to be carried out using radical initiators,[2a-c] ultraviolet light,[2a,d-g] and radiation techniques.[3]

Although the radiation-induced addition of alcohol to ordinary olefins has been described to give both telomeric products and 1:1 adduct,[3a] the reaction with a relatively stable substrate such as halogeno olefin is known to produce mainly 1:1 adduct[3b-e] in good yield. The photochemical addition of alcohols to α,β-unsaturated acid derivatives in the presence of a sensitizer was reported to yield γ-butyrolactones by Schenck[2d] and Pfau,[2e-g] but the analogous radiation-induced reaction has not been known. Consequently, as a part of our studies on organic synthesis by means of radiation-induced reactions, γ-ray and ultraviolet-induced addition reactions to α,β-unsaturated acids and esters,[4] which seem to be considerably stable to γ radiation,[4b] were studied.

Irradiation of ethyl crotonate (**1a**) or crotonic acid (**1b**) in an excess of alcohol with ^{60}Co γ rays gave the corresponding 3-methyl-4-alkyl substituted γ-butyrolactones (**4**), small amounts of telomeric products of crotonate (**5**, **6**) and polymeric products.



2a, $R_1 = R_2 = H$ **e**, $R_1 = CH_3$; $R_2 = C_2H_5$
b, $R_1 = CH_3$; $R_2 = H$ **f**, $R_1 = R_2 = C_2H_5$
c, $R_1 = R_2 = CH_3$ **g**, $R_1 = C_6H_5$; $R_2 = H$
d, $R_1 = C_2H_5$; $R_2 = H$

The yield of lactones and conversion of ethyl crotonate in the radiation-induced addition reactions are summarized in Table I. The formation of γ-butyrolactone (**4**) seems to proceed through a radical chain mechanism initiated by an α-hydroxyalkyl radical. This is supported by the fact that the reaction was retarded by the addition of a radical scavenger.

TABLE I
RADIATION-INDUCED ADDITION OF ALCOHOL TO ETHYL CROTONATE[a]

Alcohol	Conversion[b,c] of 1a, %	Yield,[b,c] % 4	5	6
Methanol	68	1	Trace	Trace
Ethanol	96	16[d]	1	0.5
2-Propanol	97	54	4	2
1-Propanol	94	9[e]	3	2
2-Butanol	95	18[f]	3	1
3-Pentanol	95	10	2	3
Benzyl alcohol	45	23[g]	0	0

[a] Irradiation time, 72 hr; dose rate, 0.9–1.0 × 10^6 r/hr; molar ratio of alcohol to ethyl crotonate, 15. [b] Based on ethyl crotonate employed. [c] By glpc analysis. [d] Trans:cis, 4:5. [e] Trans:cis, 2:3. [f] Trans and cis isomers were not separated in glpc analysis. [g] Trans:cis, 2:1.

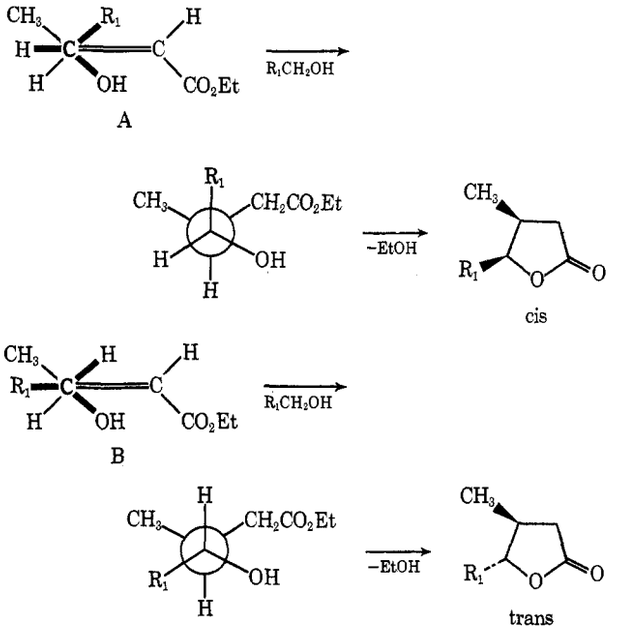
It is of interest that a considerable amount of cis lactone was obtained from the reaction of crotonate with ethanol, 1-propanol, and benzyl alcohol. 2-Butanol also produced trans- and cis lactones, but their relative ratio could not be determined by glpc analysis. The formation of two isomeric lactones may well be the result of alternate approaches of the hydroxyalkyl radical to the double bond of ethyl crotonate. For example, if the hydroxyalkyl radical attacks the carbon–carbon double bond as shown in A, and the resulting intermediate radical abstracts hydrogen from alcohol, the cis isomer would be obtained. The attack of hydroxyalkyl radical as depicted in B would give rise to the trans isomer. Although the predominance of cis isomer in ethanol and 1-propanol, and trans isomer in benzyl alcohol, has not been adequately explained, it may well be due to the relative degree of steric interaction in pathways A and B. Similar isomeric ratios

(1) Deceased.

(2) (a) W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *J. Amer. Chem. Soc.*, **76**, 450 (1954); (b) J. P. LaZerte and R. J. Koshar, *ibid.*, **77**, 910 (1955); (c) E. V. Kirkland, *Ind. Eng. Chem.*, **52**, 397 (1960); (d) G. O. Schenck, G. Koltzenburg, and H. Grossmann, *Angew. Chem.*, **69**, 177 (1957); (e) R. Dulou, M. Vilkas, and M. Pfau, *C. R. Acad. Sci.*, **249**, 429 (1959); (f) M. Pfau, R. Dulou, and M. Vilkas, *ibid.*, **251**, 2188 (1960); (g) M. Pfau, *ibid.*, **254**, 2017 (1962).

(3) (a) H. Hirota and M. Hatada, *Bull. Chem. Soc. Jap.*, **34**, 1644 (1961); (b) H. Muramatsu, *J. Org. Chem.*, **27**, 2325 (1962); (c) H. Muramatsu, K. Inukai, and T. Ueda, *ibid.*, **30**, 2546 (1965); (d) H. Muramatsu, S. Moriguchi, and K. Inukai, *ibid.*, **31**, 1306 (1966); (e) H. Muramatsu, K. Inukai, and T. Ueda, *Bull. Chem. Soc. Jap.*, **40**, 903 (1967).

(4) (a) M. Itoh, M. Tokuda, K. Kihara, and A. Suzuki, *Tetrahedron*, **24**, 6591 (1968); (b) M. Itoh, M. Tokuda, Y. Yokoyama, and A. Suzuki, *Bull. Chem. Soc. Jap.*, **42**, 3340 (1969).



were also reported by Fukunishi, *et al.*,[5] in a radical-initiated addition of alcohols to maleic acid esters. Precise studies on these problems are currently under investigation in our laboratory.

Photochemical addition of alcohols to *trans*-ethyl crotonate (**1a**) in the presence of benzophenone as sensitizer produced γ-butyrolactones (**4**), *cis*-ethyl crotonate (**7**), ethyl 3-butenoate (**8**), polymer, and other products. Compounds **7** and **8** are known photochemical isomerization products of *trans*-ethyl crotonate.[6] Conversions of ethyl crotonate and yields of **4**, **7**, and **8** from irradiation in a quartz tube are listed in Table II. It was previously shown by us that photochemical

TABLE II

PHOTOCHEMICAL ADDITION OF ALCOHOL TO ETHYL CROTONATE IN A QUARTZ TUBE[a]

Alcohol	Conversion[b,c] of **1a**, %	Yield,[b,c] % **4**	**7**	**8**
Methanol	59	1	18	3
Ethanol	86	4[d]	10	16
2-Propanol	90	12	14	11
1-Propanol	88	4[e]	14	13

[a] A reaction mixture of ethyl crotonate (10 mmol), alcohol (40 mmol), and benzophenone (1.2 mmol) was externally irradiated in a quartz tube for 50 hr with a 500-W high-pressure mercury vapor lamp. [b] Based on ethyl crotonate employed. [c] By glpc analysis. [d] Trans:cis, 4:5. [e] Trans:cis, 4:5.

isomerization to β,γ isomer is not observed when an alcoholic solution of ethyl crotonate is irradiated with Pyrex-filtered light (>300 mμ).[6d] Thus, in order to avoid side reactions, reaction mixtures sealed in Pyrex tubes were irradiated with a high-pressure mercury vapor lamp (Table III).

The isomeric ratio of *trans*- and *cis*-γ-butyrolactones obtained from the photochemical reaction with ethanol and 1-propanol was almost identical with that from the radiation-induced addition reaction, even though cis–trans isomerization of ethyl crotonate was observed in the photochemical addition reaction. This might be explained by the fact that, since trans olefins are more reactive to a radical than cis isomers,[7] *trans*-ethyl crotonate would be attacked predominantly by the hydroxyalkyl radical, even if photochemical cis–trans isomerization should occur.

TABLE III

PHOTOCHEMICAL ADDITION OF ALCOHOL TO ETHYL CROTONATE IN A PYREX TUBE[a]

	Conversion[b,c] of **1a**, %	Yield,[b,c] % **4**	**7**
Methanol	24	1	20
Ethanol	56	1[d]	11
2-Propanol	83	12	5
1-Propanol	75	5[e]	7
2-Butanol	98	22[f]	Trace
3-Pentanol	78	9	
Benzyl alcohol	23	6[f]	12

[a] A reaction mixture of ethyl crotonate (1.5 mmol), alcohol (60 mmol), and benzophenone (0.18 mmol) was externally irradiated in a Pyrex tube for 72 hr with a 500-W high-pressure mercury vapor lamp. [b] Based on ethyl crotonate employed. [c] By glpc analysis. [d] Trans:cis, 4:5. [e] Trans:cis, 4:5. [f] Trans:cis, not determined.

Experimental Section

Gas–liquid chromatographic analyses were carried out with a Yanagimoto Model GCG-550 and a Hitachi KGL-2A utilizing a capillary column. For preparative glpc a Wilkens Autoprep 700 was used. Infrared spectra were obtained with a Hitachi EPI-G22 and nuclear magnetic resonance spectra were measured with a Nihon Denshi 3H-60 (tetramethylsilane as the internal standard). Mass spectra were obtained with a Hitachi RMU-6E. Quantitative glpc analyses were carried out using an internal standard. All melting points and boiling points were uncorrected.

All reagents were distilled or recrystallized before use. 3-pentanol was prepared from ethylmagnesium bromide and propionaldehyde and dried over calcium oxide. Benzyl alcohol was purified by distillation. Ethyl crotonate was prepared by esterification of crotonic acid.

General Procedure for Radiation-Induced Addition.—A mixture of crotonic acid or ethyl crotonate and excess alcohol was repeatedly evacuated to *ca.* 1 mm in Dry Ice–trichloroethylene. The sample, sealed in a Pyrex tube, was irradiated with γ rays in a ^{60}Co cavity source at room temperature. The dose rate was approximately 0.9–1.0 × 10^6 r/hr. The irradiated sample was opened and analyzed by glpc. For quantitative analysis of the lactones, FFAP 15% column coated on Diasolid L was used at 160–230°, with 4-*tert*-butyltoluene and diethyl phthalate as the internal standard, and for ethyl crotonate, a capillary column of SE-30 (45 m) at 100° was used with cumene as the internal standard.

Neither evacuation of the tube to 10^{-5} mm nor filling it with nitrogen gave large differences when compared with the above procedure.

General Procedure for Photochemical Addition.—A reaction mixture in a quartz or Pyrex tube was cooled in water and externally irradiated with a 500-W high-pressure mercury vapor lamp. Nitrogen gas was allowed to pass through the mixture during the irradiation. The irradiated sample was analyzed by glpc as mentioned above. Glpc analysis of ethyl crotonate isomers was carried out with a capillary column (squarane, 45 m).

Analysis of Products.—The products were separated by preparative glpc (SE-30 or FFAP) and identified from the spectral data (ir, nmr, and mass spectrum).

***cis*-3,4-Dimethyl-γ-butyrolactone** (*cis*-**4b**) had bp 95–97° (12 mm); n^{25}D 1.4302 [lit.[8] bp 80–80.5° (5 mm), n^{20}D 1.4287];

(5) K. Fukunishi, M. Suzuka, and F. Mashio, Reprint of the 23th Annual Meeting of the Chemical Society of Japan, Vol. III, 1970, p 1667.

(6) (a) M. J. Jorgenson, *Chem. Commun.*, 137 (1965); (b) P. J. Kropp, and H. J. Krauss, *J. Org. Chem.*, **32**, 3222 (1967); (c) R. R. Rando and W. von E. Doering, *ibid.*, **33**, 1671 (1968); (d) M. Itoh, M. Tokuda, K. Seguchi, K. Taniguchi, and A. Suzuki, *Kogyo Kagaku Zasshi*, **72**, 219 (1969).

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(8) J. F. Laporte and R. Rambaud, *C. R. Acad. Sci., Ser. C.*, **262**, 1095 (1966).

ir (CCl_4) 1790 cm^{-1}. *Anal.* Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 62.85; H, 8.75.

trans-**3,4-Dimethyl-γ-butyrolactone** (*trans*-**4b**) had bp 101–103° (12 mm); $n^{25}D$ 1.4350 [lit.[8] bp 86–86.5° (5 mm), $n^{22}D$ 1.4333]; ir (CCl_4) 1785 cm^{-1}. *Anal.* Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 62.93; H, 8.72.

3,4,4-Trimethyl-γ-butyrolactone (**4c**) had bp 97° (15 mm); $n^{20}D$ 1.4373 [lit. bp 216–217° (744 mm),[9] 219° (760 mm),[2f] $n^{17}D$ 1.4402]; ir (CCl_4) 1780 cm^{-1}. *Anal.* Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.32; H, 9.48.

cis-**3-Methyl-4-ethyl-γ-butyrolactone** (*cis*-**4d**) had bp 102–105° (11.5 mm); $n^{25}D$ 1.4375; ir (CCl_4) 1780 cm^{-1}; nmr (CCl_4) τ 8.96 (t, 3), 8.86 (d, 3), 6.13 (m, 1), 7.3–8.6 (m, 3); mass spectrum M^+ 128. *Anal.* Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.31; H, 9.58.

trans-**3-Methyl-4-ethyl-γ-butyrolactone** (*trans*-**4d**) had bp 102–105° (11.5 mm); $n^{25}D$ 1.4403; ir (CCl_4) 1775 cm^{-1}; nmr (CCl_4) τ 8.97 (t, 3), 9.00 (d, 3), 5.8 (m, 1), 7.3–8.7 (m, 3). *Anal.* Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.35; H, 9.52.

trans- **and** *cis*-**3,4-Dimethyl-4-ethyl-γ-butyrolactone** (**4e**) had bp 110–112° (15 mm); $n^{25}D$ 1.4435; ir (CCl_4) 1760–1780 cm^{-1} (broad); nmr (CCl_4) τ 8.65 [s, 3, $-OC(CH_3)$ of cis isomer], 8.78 [s, 3, $-OC(CH_3)$ of trans isomer], 8.99 (t, 3), 8.91 (d, 3), 7.66 (m, 2), 8.45 (q, 2), 7.3–8.1 (m, 1). *Anal.* Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.40; H, 9.99.

3-Methyl-4,4-diethyl-γ-butyrolactone (**4f**) had bp 80–84° (2 mm); $n^{20}D$ 1.4512; ir (CCl_4) 1770 cm^{-1}; mass spectrum M^+ 156. *Anal.* Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.92; H, 10.41.

trans- **and** *cis*-**3-Methyl-4-phenyl-γ-butyrolactone** (**4g**) had bp 128–130° (2.5 mm); $n^{25}D$ 1.5290; ir (CCl_4) 1788 cm^{-1}; nmr (CCl_4) τ 9.35 [d, 3, J = 7 Hz, $-CH(CH_3)$ of cis isomer], 8.85 [d, 3, J = 6 Hz, $-CH(CH_3)$ of trans isomer], 7.58 (m, 2), 7.1–8.2 (m, 1), 5.17 [d, 1, J = 8 Hz, $-CH(C_6H_5)O$ of trans isomer], 6.51 [d, 1, J = 6 Hz, $-CH(C_6H_5)O$ of cis isomer], 2.8 (s, 5); mass spectrum M^+ 176. *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.12; H, 6.86.

3-Methyl-γ-butyrolactone (**4a**).—The infrared spectrum of the condensed crude product revealed $\nu_{C=O}$ of γ-butyrolactone at 1780 cm^{-1}, although it could not be isolated because the quantity was so small [lit.[10] 1780 cm^{-1} ($\nu_{C=O}$ of **4a**)].

Diethyl 2-ethyl-3-methyl glutarate (**5**) had bp 105–107° (2 mm); $n^{25}D$ 1.4302; ir (CCl_4) 1735 cm^{-1}; nmr (CCl_4) τ 8.75 (t, 6), 9.07 (t, 3), 9.07 (d, 3), 5.93 (q, 4), 7.9 (m, 6); mass spectrum M^+ 230. *Anal.* Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.83; H, 9.53.

Diethyl 3,4-dimethyladipate (**6**) had bp 103–105° (2 mm), $n^{25}D$ 1.4353 [lit.[11] bp 103° (1.5 mm), $n^{25}D$ 1.4324]. *Anal.* Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.88; H, 9.47.

Registry No.—**1a**, 10544-63-5; *cis*-**4b**, 10150-95-5; *trans*-**4b**, 10150-96-6; **4c**, 2981-96-6; *cis*-**4d**, 34405-50-0; *trans*-**4d**, 34405-51-1; *cis*-**4e**, 34405-52-2; *trans*-**4e**, 34405-53-3; **4f**, 34405-54-4; *cis*-**4g**, 26620-41-7; *trans*-**4g**, 26704-17-6; **5**, 34405-57-7; **6**, 10348-54-6; **7**, 6776-19-8; **8**, 1617-18-1.

(9) J. W. Huffman and J. W. Bethea, *J. Org. Chem.*, **30**, 2956 (1965).
(10) *French Patent* 1,319,239 (1963); *Chem. Abstr.*, **59**, 8600*d* (1963).
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Reductive Synthesis of α,α-Dimethylphenethylamine

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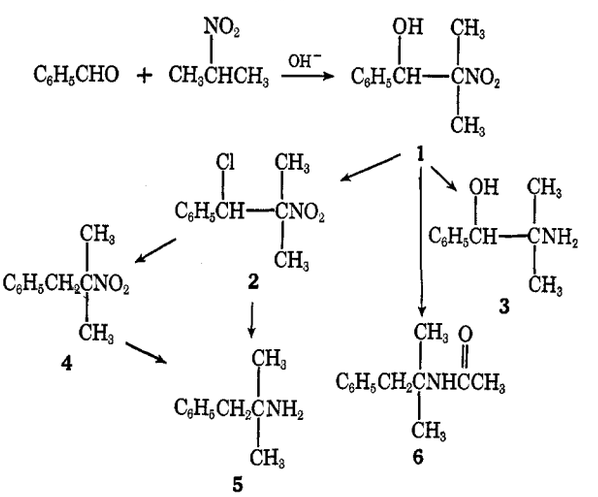
Received October 14, 1971

The pharmacological properties of the derivatives of α,α-dimethylphenethylamine (phenthermine) (**5**) have created considerable interest in the large-scale preparation of these compounds. The usual synthesis involves a Ritter reaction[1,2] between hydrogen cyanide and α,α-dimethylphenethyl alcohol or β,β-dimethylstyrene, to form the *N*-formyl derivative of **5**, and the hydrolysis of this intermediate. This reaction sequence is admirably suited for small-scale work, but, due to the hazards inherent in the use of hydrogen cyanide and in carrying out the Grignard reactions which lead to the alcohol or the styrene, it is not ideal for large-scale preparations. In view of these objections, a synthesis on the basis of a catalytic reduction, similar to those used for the derivatives of the less substituted phenethylamine[3] and α-methylphenethylamine (amphetamine),[4] would appear to be desirable.

The basic starting material for our work was α-(1-methyl-1-nitroethyl)benzyl alcohol (**1**), which can be prepared easily by the condensation of 2-nitropropane and benzaldehyde.[5] Palladium was used in all cases as hydrogenation catalyst, due to its well documented inactivity toward aromatic rings and its high effectiveness for the hydrogenolysis of benzyl groups and the reduction of aliphatic nitro groups.[6a] The variation of other reaction parameters resulted in rather selective reductions (Scheme I), which prompts us to report these in the present communication.

SCHEME I



The hydrogenation of the nitro alcohol **1** in ethanolic acetic acid over 10% palladium on charcoal yielded only the amino alcohol **3**,[7] as had already been reported by Zenitz, *et al.*[5] This is not an abnormal result, since the stabilization of a benzylic alcohol by a vicinal amino group is a well-known fact,[6b] which had already led Rosenmund and Kung[4] to the development of the tech-

(1) (a) J. J. Ritter and J. Kalish, *J. Amer. Chem. Soc.*, **70**, 4048 (1948); (b) J. J. Ritter and J. Kalish, *Org. Syn.*, **44**, 44 (1964).
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(4) K. W. Rosenmund and E. Kung, *Ber.*, **75**, 1850 (1942).
(5) B. L. Zenitz, E. B. Macks, and M. L. Moore, *J. Amer. Chem. Soc.*, **70**, 955 (1948).
(6) (a) P. N. Rylander, "Catalytic Hydrogenation Over Platinum Metals," Academic Press, New York, N. Y., 1967, p 320; (b) 152.
(7) The nature of all the products, except **4**,[9] can be deduced unequivocally from the elemental analysis data and the nmr and ir spectra given in the Experimental Section.