added a solution of 7.4 g (0.05 mol) of EDSA[1] in 25 ml of ethanol. Ice cooling was needed to hold the temperature at 30–35°.

After an overnight stand at 25°, the mixture was flashed into a Dry Ice cooled trap at 5 mm and 25°. Glpc analysis of the volatiles indicated the presence of 0.048 mol of dimethyl sulfide and 0.080 mol of ethyl acrylate.

Distillation of the residue gave 9.8 g (69%) of triethyl 2-pentene-1,3,5-tricarboxylate, bp 106–109° (<1 mm) and $n^{25}D$ 1.4553, and 4.1 g of residue (21% yield calculated as **3**).

Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.7; H, 7.7. Found: C, 58.7; H, 7.8.

The nmr spectrum showed multiplets at δ 1.3 (9 H, $-CO_2CCH_3$), 2.0–2.7 (4 H, $C{=}C(CH_2)_2COOR$), and 3.9–4.4 (6 H, CO_2-CH_2–), a triplet at 7.0 (1 H, $-CH{=}CCOOR$), and a doublet at 3.4 (2 H, $-C{=}CCH_2COOR$).

Distillation of the residue gave material with bp 170–175° (<1 mm) in good recovery. It was shown by infrared analysis to be identical with compound **3** prepared below.

2-Pentene-1,3,5-tricarboxylic Acid.—A solution of 8.0 g (0.028 mol) of triester in 50 ml of concentrated hydrochloric acid was warmed on the steam bath for 4 hr and then allowed to stand overnight. Filtration of the resulting precipitate gave 3.4 g, mp 181–182°; concentration of the filtrate followed by crystallization from acetone gave another 0.5 g, mp 178–180° (70% combined yield). Recrystallization of the two crops gave product with mp 181–182°.

Anal. Calcd for $C_8H_{10}O_6$: C, 47.5; H, 5.0. Found: C, 47.8; H, 5.1.

The nmr spectrum showed a multiplet at δ 2.0–2.7 (4 H, $C{=}C(CH_2)_2COO$–), a doublet at 3.3 (2 H, $-O_2CCH_2C{=}C$–), a triplet at 6.9 (1 H; $-CH{=}C$–), and a singlet at 11.1 (3 H, –COOH).

Hydrogenation of the unsaturated acid was carried out in a Parr hydrogenator using 5% palladium-on-carbon catalyst, ethyl alcohol as solvent, and a pressure of 40 psi. One molar equivalent of hydrogen was absorbed in 0.5 hr to give 1,3,5-pentanetricarboxylic acid, mp 112–114°. A mixture melting point with an authentic sample (mp 113–115°)[3] was not depressed. The infrared spectra were identical.

Reaction of Carbethoxymethyl Dimethylsulfonium Bromide with Potassium Carbonate and Ethyl Acrylate.—A mixture of 22.9 g (0.10 mol) of sulfonium bromide,[1] 30.0 g of ethyl acrylate, 21 g of anhydrous potassium carbonate, and 100 ml of absolute ethanol was allowed to stir for 18 hr at 25°.

Filtration followed by Claisen distillation gave 15.3 g (40% yield) of relatively pure product, bp 174–187° (<1 mm) and $n^{25}D$ 1.4605. Redistillation through a small Vigreux column gave analytically pure triethyl 3-(2-ethoxycarbonylethyl)-1-pentene-1,3,5-tricarboxylate: bp 203–206° (1 mm), $n^{25}D$ 1.4616.

Anal. Calcd for $C_{19}H_{30}O_8$: C, 59.1; H, 7.8; mol wt, 386. Found: C, 59.4; H, 7.9; mol wt, 395 ± 12 (ebullioscopic, benzene).

The nmr showed multiplets at δ 1.3 (12 H, RCO_2CCH_3), 1.8–2.8 (8 H, $-CH_2$–), and 4.2 (8 H, RCO_2CH_2–) and doublets at 6.0 (1 H, $RO_2CCH{=}C$) and 7.1 (1 H, $RO_2C{-}C{=}CH$–).

Reaction of EDSA with Ethyl Crotonate.—A mixture of 11.4 g (0.10 mol) of ethyl crotonate, 7.4 g of EDSA (0.05 mol), and 50 ml of ethanol was held at room temperature for 4 days and then heated under reflux for 1 hr.

Claisen distillation gave 7.5 g (75%) of diethyl 3-methylglutaconate, bp 65–66° (<1 mm), $n^{25}D$ 1.4488 (lit.[4] *cis*, bp 131° (9 mm), $n^{20}He$ 1.452; *trans*, bp 127° (12 mm), $n^{20}He$ 1.452).

Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1. Found: C, 59.9; H, 8.1.

Nmr analysis indicated an approximately 1:1 mixture of *cis* and *trans* isomers showing a triplet at δ 1.2 (6 H, RCO_2CCH_3), two doublets at 2.0 and 2.2 (3 H, $C{=}C{-}CH_3$), two singlets at 3.2 and 3.7 (2 H, $C{=}C{-}CH_2{-}COOR$), a quartet at 4.2 (4 H, RCO_2CH_2–), and a multiplet at 5.8 (1 H, $-HC{=}C$–).

Saponification by aqueous ethanolic sodium hydroxide gave an 86% yield of isomers, mp 95–110°. Recrystallization from benzene afforded a mixture with constant mp 111–115°.[5]

Anal. Calcd for $C_6H_8O_4$: C, 50.0; H, 5.6; neut equiv, 72. Found: C, 50.3; H, 5.7; neut equiv, 72.

(3) R. P. Mariella, R. Clutter, and H. G. Ebner, *J. Org. Chem.*, **20**, 1702 (1955).

(4) "Dictionary of Organic Compounds," Vol. 4, Oxford University Press, New York, N. Y., 1965, p 2311.

(5) For a discussion of these *cis* and *trans* isomers, see L. M. Jackman and R. H. Wiley, *Proc. Chem. Soc.*, 196 (1958).

Nmr analysis indicated an approximately 2:1 ratio of *cis–trans* isomers (COOH–CH_2COOH): a pair of doublets at δ 2.0 and 2.2 (3 H, $C{=}C{-}CH_3$), a doublet at 3.3 (J = 1–2 cps), and a singlet at 3.7 in the ratio of 2:1 (2 H, $-C{=}C{-}CH_2{-}COO$–), a singlet at 4.7 (2 H, –COOH), and a multiplet at 5.9 (1 H, $-CH{=}C$–).

Triethyl Aconitate.—The reaction was carried out as above using 34.4 g (0.20 mol) of diethyl fumarate and 14.8 g (0.10 mol) of EDSA in 75 ml of ethanol.

After 18 hr the mixture was Claisen distilled to give 17.1 g (0.10 mol) of recovered diethyl fumarate, bp 60–70° (<1 mm), and 22.5 g (87%) of triethyl aconitate, bp 97–99° (<1 mm), $n^{25}D$ 1.4515 (lit.[6] bp 165° (12 mm), $n^{20}D$ 1.4556).

Glpc analysis indicated a 70:30 mixture of *trans–cis* isomers.[7] The early emerging peak was confirmed as the *trans* isomer by saponifying and then reesterifying Pfizer technical grade triethyl aconitate (all *trans*). The Pfizer triester and the 70:30 mixture showed nearly identical infrared spectra.

An nmr analysis was carried out on the 70:30 product showing multiplets at δ 1.3 (9 H, RCO_2CCH_3) and 4.2 (6 H, RCO_2CH_2–) and singlets at 3.9 (2 H, $-C{=}CCH_2{-}CO_2R$) and 6.9 (1 H, $RO_2CH{=}C$–). A minor multiplet at 2.5 indicated the presence of a small amount of impurity. The latter was not resolved by glpc analysis.

Registry No.—**1**, 5697-31-4; **2**, 15649-51-1; $C_8H_{10}O_6$, 15717-32-5; **3**, 15649-53-3; **4** (*cis*), 15649-54-4; **4** (*trans*), 1466-21-3; $C_6H_8O_4$ (*cis*), 15649-56-6; $C_6H_8O_4$ (*trans*), 372-42-9.

(6) Reference 4, Vol. 1, p 33.

(7) J. Casanova, Jr., and D. A. Rutolo, Jr. (*Chem. Commun.*, 1224 (1967)) have reported the formation of *trans*-trimethyl aconitate from the reaction of methyl (dimethylsulfuranylidene)acetate with dimethyl fumarate in methanol solution.

Ethyl (Dimethylsulfuranylidene)acetate. III. Reaction with α-Bromo Acrylic Compounds

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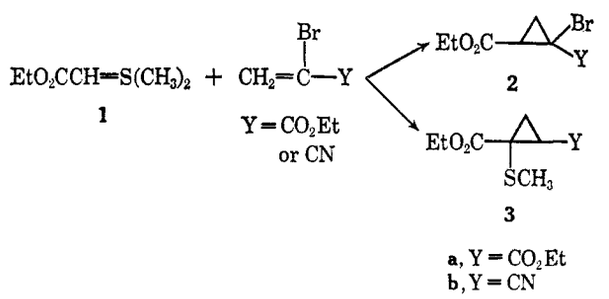
Earlier reports have described the synthesis[1] of ethyl (dimethylsulfuranylidene)acetate (**1**, EDSA), its reaction with α,β-unsaturated compounds in aprotic solvents to produce cyclopropanes,[1] and its reaction with α,β-unsaturated esters in ethanol solution to give esters of acyclic polybasic acids.[2]

The reactions of EDSA with 2-bromoacrylonitrile and ethyl 2-bromoacrylate were carried out with the expectation that bromocyclopropanes **2** might be produced.



a, Y = CO_2Et
b, Y = CN

Whereas **2a** was indeed produced (36% yield) from the reaction of EDSA with ethyl 2-bromoacrylate at room temperature *in benzene solution*, very little was

(1) G. B. Payne, *J. Org. Chem.*, **32**, 3351 (1967).

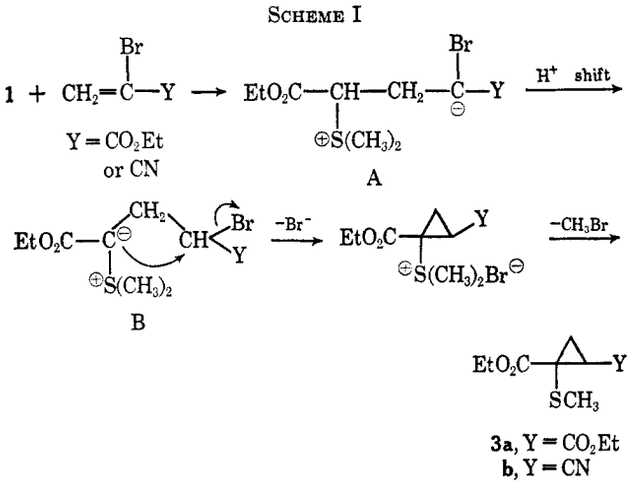
(2) G. B. Payne, *ibid.*, **33**, 1284 (1968).

formed using acetone as solvent. In the latter case, the predominant product (52% yield) was the methylthio compound **3a** (a 25% yield of **3a** was also observed in the reaction carried out in benzene).

Interestingly, very little **2b** appeared to be formed from EDSA and 2-bromoacrylonitrile irrespective of the solvent used. Thus, with acetone the yield of **3b** was 50% based on EDSA, whereas with benzene **3b** and **2b**[3] were obtained in 29 and 6% yields, respectively.

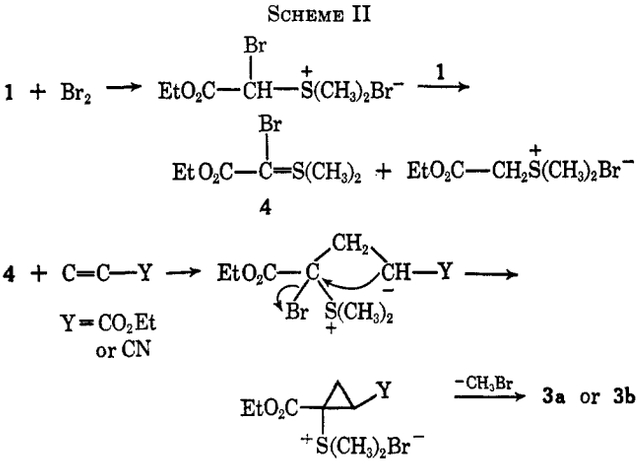
The formation of **3a** and **3b** has been rationalized according to Scheme I. The relatively polar solvent acetone apparently facilitates the prototropic shift to produce new ylide B at the expense of direct ring closure of A to give **2**.

SCHEME I



Structures **3a** and **3b** were assigned on the basis of elemental, infrared, and nmr analyses and subsequently confirmed by alternate syntheses according to Scheme II.

SCHEME II



Bromo ylide **4**[4] was prepared *in situ* by adding 1 molar equiv of bromine to 2 of EDSA in chloroform at ice temperature. On completion of the addition, the cold mixture was treated immediately[5] with either ethyl acrylate or acrylonitrile to give **3a** and **3b** in 59 and 80% yields, respectively. Compound **3b** was again formed as virtually the sole product, whereas **2a** was obtained as a by-product to **3a** in 7% yield. The preferential displacement of bromide ion relative to dimethyl sulfide observed in the present study is in accord with earlier work.[6]

(3) An analytical sample of this minor component was not secured; its identification must therefore be considered tentative.

(4) See K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1689 (1966), for a discussion of the reactions of bromine and iodine with some resonance-stabilized sulfonium ylides.

(5) Infrared analysis of a chloroform solution of the bromo ylide indicated it to have a half-life of less than 1 hr at room temperature.

Experimental Section[7]

Ethyl 2-Bromoacrylate and 2-Bromoacrylonitrile.—To 26 g (0.10 mol) of ethyl 2,3-dibromopropionate (Columbia Organic Chemicals) held in a 200-ml distillation flask was added 13 g (0.10 mol) of quinoline. The mixture was allowed to warm to about 75–80° for 10 min and then vacuum distilled from the quinoline salt. The yield of ethyl 2-bromoacrylate, bp 50–60° (10 mm) and $n^{25}D$ 1.4710, was 16 g (90%). Redistillation from hydroquinone at 10 mm gave purified ester, bp 50–53° and $n^{25}D$ 1.4672 (lit.[8] bp 76–77° (33 mm), $n^{25}D$ 1.4678), in 70% yield over-all.

Application of the above procedure to 2,3-dibromopropionitrile (Columbia) gave 2-bromoacrylonitrile, bp 40–45° (40 mm), $n^{25}D$ 1.4717 (lit.[9] bp 116° (740 mm)), in 84% yield. It was used immediately without further purification.

Reaction of EDSA with 2-Bromoacrylonitrile.—To a stirred solution of 14.8 g (0.10 mol) of EDSA in 100 ml of dry acetone was added dropwise at 30–35° over 0.5 hr a solution of 13.2 g (0.10 mol) of 2-bromoacrylonitrile in 50 ml of acetone. The mixture was stirred 3 hr longer and allowed to stand overnight.

Filtration gave 1.3 g (5%) of carbethoxymethyl dimethylsulfonium bromide, mp and mmp 80–82° dec. Vacuum concentration of the filtrate followed by Claisen distillation gave 9.4 g (50% yield) of a mixture of *cis*- and *trans*-ethyl 2-cyano-1-methylthiocyclopropanecarboxylate, bp 88–93° (<1 mm). The purity (two isomers) was 95% by glpc analysis.

Redistillation using a 0.7 × 50 cm glass spiral packed column gave the two isomers with bp 97–98° (1 mm), $n^{25}D$ 1.4901. The relative amounts were 25:75, early to late emerging peaks.[10]

Anal. Calcd for $C_8H_{11}O_2NS$: C, 51.7; H, 6.0; S, 17.3. Found: C, 51.4; H, 6.0; S, 16.6.

The infrared spectrum showed significant bands at 5.83, 7.92, 8.90, and 10.0 μ. Nmr analysis showed triplets at δ 1.4 (3 H, CO_2CCH_3) and 2.6 (1 H, C–C–CHCN), a multiplet at 1.8 (2 H, cyclopropyl protons), a singlet at 2.4 (3 H, SCH_3), and a quartet at 4.2 (2 H, CO_2CH_2).

Reaction of EDSA with Ethyl 2-Bromoacrylate.—To a stirred solution of 35.8 g (0.20 mol) of ethyl 2-bromoacrylate in 100 ml of dry acetone was added dropwise at 25–30° over 0.5 hr a solution of 14.8 g of EDSA (0.10 mol) in 50 ml of acetone.

After stirring for 3 hr and then standing overnight, the mixture was filtered, concentrated, and Claisen distilled to give 15.4 g of product with bp 75–88° (0.2 mm). By glpc analysis the material contained 12.2 g (53% yield) of diethyl 1-methylthio-1,2-cyclopropanedicarboxylate and 0.8 g (3% yield) of diethyl 1-bromo-1,2-cyclopropanedicarboxylate.

Redistillation through the packed column gave analytically pure methylthio compound, bp 87–90° (<1 mm), $n^{25}D$ 1.4754, as a single isomer by glpc.

Anal. Calcd for $C_{10}H_{16}O_4S$: C, 51.7; H, 6.9; S, 13.8. Found: C, 51.8; H, 6.9; S, 13.6.

The infrared spectrum showed significant bands at 5.81, 7.95, 8.45, 8.88, 9.70, and 11.6 μ. Nmr analysis showed triplets at δ 1.3 (6 H, CO_2CCH_3) and 2.7 (1 H, C–C–CHCOOR), a multiplet at 1.7 (2 H, cyclopropyl protons), a singlet at 2.2 (3 H, SCH_3), and a quartet at 4.2 (4 H, CO_2CH_3).

(6) See J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 167.

(7) Boiling points are uncorrected. Nmr spectra were obtained in $CDCl_3$ with a Varian A-60 spectrometer using tetramethylsilane as an internal standard. Glpc analyses were done on an F & M Model 720 instrument using a 10-ft column packed with 5% of X-1150 on Chromosorb W.

(8) "Dictionary of Organic Compounds," J. R. A. Pollock and R. Stevens' Ed., Oxford University Press, New York, N. Y., 1965, Vol. 1, p 417.

(9) H. Brintzinger and A. Scholz, *Chem. Ber.*, **83**, 141 (1950).

(10) The two isomers could not be separated by glpc trapping; no attempt was made to determine the stereochemistry of any of the products obtained in this study.

The reaction was repeated using *benzene* in place of acetone. Claisen distillation gave 15.5 g of mixture, bp 82–87° (<1 mm). Glpc analysis indicated the presence of 38% of diethyl 1-methylthio-1,2-cyclopropanedicarboxylate (25% yield based on EDSA) and 62% of diethyl 1-bromo-1,2-cyclopropanedicarboxylate (36% yield). The latter was isolated by glpc trapping as a single isomer.

Anal. Calcd for $C_9H_{13}O_4Br$: C, 40.8; H, 4.9. Found: C, 40.9; H, 5.2.

Significant bands in the infrared were located at 5.83, 7.94, 8.44, and 8.89 μ. Nmr analysis showed triplets at δ 1.3 (6 H, CO_2CCH_3) and 2.6 (1 H, C–C–CHCOOR), a doublet at 1.9 (2 H, cyclopropyl protons), and a quartet at 4.2 (4 H, CO_2CH_2).

Reaction of Acrylonitrile with the Bromo Ylide from EDSA.—To a stirred solution of 14.8 g (0.10 mol) of EDSA in 100 ml of chloroform was added dropwise at 5–10° a solution of 8.0 g (0.05 mol) of bromine in 25 ml of chloroform. There was then added immediately 5.3 g (0.10 mol) of acrylonitrile and the mixture was allowed to warm slowly to room temperature over 18 hr.

After vacuum concentration at 25°, the residue was treated with acetone and filtered to give 8.5 g (74% yield) of carbethoxymethyl dimethylsulfonium bromide, mp and mmp 80–82° dec. The filtrate was reconcentrated and then Claisen distilled to give 7.4 g (80% yield) of ethyl 2-cyano-1-methylthiocyclopropanecarboxylate, bp 80–85° (<1 mm), as a 38:62 mixture of isomers. The purity was 99% (two isomers) and the product was shown to be the same (except for slight variation in ratio of isomers) as that prepared from EDSA and 2-bromoacrylonitrile by glpc, infrared, and nmr comparisons.

Reaction of Ethyl Acrylate with the Bromo Ylide from EDSA.—The above reaction was repeated, substituting 10.0 g (0.10 mol) of ethyl acrylate for acrylonitrile. Claisen distillation gave 9.0 g, bp 55–80° (<1 mm). Glpc analysis indicated the presence of 76% by weight of diethyl 1-methylthio-1,2-cyclopropanedicarboxylate and 11% of diethyl 1-bromo-1,2-cyclopropanedicarboxylate. These compounds correspond to yields of 59 and 7%, respectively, based on EDSA.

Glpc trapping gave a pure sample of the methylthio compound; its infrared spectrum was identical with that of the product prepared from EDSA and ethyl 2-bromoacrylate.

Registry No.—**1**, 5697-31-4; **2a**, 15619-29-1; **3a**, 15619-30-4; **3b**, 15619-31-5.

Hydrogenation of β-Amino-α,β-Unsaturated Esters[1]

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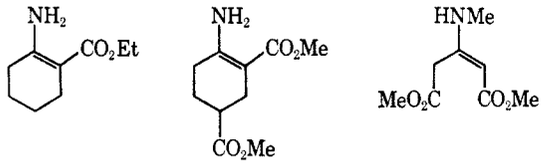
The hydrogenation of the double bond of most enol derivatives of β-dicarbonyl compounds (vinylogous carboxylic acid derivatives) generally takes place readily at low temperatures and pressures using a palladium catalyst.[3,4] However, hydrogenolysis is favored by more drastic conditions as well as by the use of platinum catalysts.[3–5] Overreduction of β-amino-α,β-unsaturated ketones (vinylogous amides) is observed under all conditions.[6]

From the limited amount of data reported on the hydrogenation of β-amino-α,β-unsaturated esters (vinylogous urethans), it is apparent that these compounds are more difficult to hydrogenate than are the other vinylogous carboxylic acid derivatives[7a] and, if care is not taken, extensive hydrogenolysis can take place.[7b] It has recently been shown by Liska,[8] however, that saturation of the double bond of 3,4,5,6-tetrahydroanthranilic ester (**1**) could be accomplished by the use of rhodium on alumina at 85° and 500 psi.

Our interest in this problem was aroused when it was found that under these conditions methyl 4-carbomethoxy-3,4,5,6-tetrahydroanthranilate (**2**) was completely inert to hydrogenation. This difficulty observed in the hydrogenation of the 4-carboxy compound **2** coincides with the lack of reactivity reported for the hydrogenation of the double bond of 3-cyclohexene carboxaldehydes.[9] Whereas it was apparent that more drastic conditions would be required for the hydrogenation of **2**, it was also necessary that they be chosen so as to minimize hydrogenolysis.



1 **2** **3**

Thus, in order to find the optimum conditions for the hydrogenation not only of **2**, but also of other vinylogous urethans, a thorough study of the reaction was made. Compounds **1** and **2** and dimethyl β-methylaminoglutaconate (**3**) were hydrogenated under a variety of conditions. It is interesting to note that with platinum oxide in glacial acetic acid the β-keto ester from which the vinylogous urethan was formed was the only isolable product. Since the solvent was carefully dried before use it is quite probable that this "hydrolysis" occurred by way of a Michael addition of the solvent to the unsaturated ester followed by elimination of the amine group and then hydrolysis of the resulting enol derivative during work-up. The use of the Liska[8] conditions gave satisfactory results in the hydrogenation of **3** as well as **1**.

However, with a 5% palladium-on-charcoal catalyst at 85° and 1000–1500 psi excellent yields of the saturated amino esters were obtained. With **2**, which was resistant to hydrogenation under practically all other conditions, the saturated product was obtained in 80–90% yield by this procedure. Since these conditions did give such superior results, their use is recommended for the hydrogenation of all vinylogous urethans. Temperature control in this reaction is critical, however, since at room temperature no reaction occurred and at higher temperatures (120°) extensive deamination was observed.

(1) Supported by Grants NH-10107 from the National Institutes of Health and 2474 from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgement is made of this support.

(2) NDEA Predoctoral Fellow, 1965–present.

(3) R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, Inc., New York, N. Y., 1965.

(4) P. N. Rylander and S. Starrick, *Engelhard Ind. Tech. Bull.*, **7**, 106 (1966).

(5) Pl. A. Plattner, A. Fürst, and J. Hellerbach, *Helv. Chim. Acta*, **30**, 100 (1947); B. D. Astill and V. Boekelheide, *J. Amer. Chem. Soc.*, **77**, 4079 (1955); R. H. Baker and P. C. Weiss, *ibid.*, **66**, 343 (1944).

(6) C. P. Rader, G. E. Wicks, R. L. Young, Jr., and H. S. Aaron, *J. Org. Chem.*, **29**, 2252 (1964).

(7) (a) B. R. Baker, R. E. Schaub, M. V. Querry, and J. H. Williams, *ibid.*, **17**, 97 (1952); (b) R. H. Baker and A. H. Schlesinger, *J. Amer. Chem. Soc.*, **68**, 2009 (1946).

(8) K. J. Liska, *J. Pharm. Sci.*, **53**, 1427 (1964).

(9) I. N. Nazarov, G. P. Kugatova, and G. A. Laumenskas, *Zh. Obshch. Khim.*, **27**, 2450 (1957); H. E. Hennis and W. B. Trapp, *J. Org. Chem.*, **26**, 4678 (1961).