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]

ROBERT L. AUGUSTINE, RUSSELL F. BELLINA,[2] AND ALFEN J. GUSTAVSEN

Department of Chemistry, Seton Hall University, South Orange, New Jersey 07079

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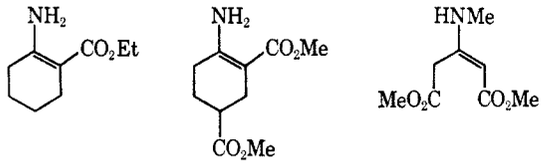
The hydrogenation of the double bond of most enol derivatives of β-dicarbonyl compounds (vinylogous carboxylic acid derivatives) generally takes place readily at low temperatures and pressures using a palladium catalyst.[3,4] However, hydrogenolysis is favored by more drastic conditions as well as by 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.

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(2) NDEA Predoctoral Fellow, 1965–present.

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Experimental Section[10,11]

Ethyl 3,4,5,6-tetrahydroanthranilate (1) was prepared following the procedure of Prelog and Geyer,[12] mp 73–74.5 (lit.[12] mp 72–73.5). The product amino ester from the hydrogenation was isolated as the HCl salt, mp 128–129° (lit.[8] mp 131–133°).

Methyl 4-carbomethoxy-3,4,5,6-tetrahydroanthranilate (2) was prepared in quantitative yield from 2,4-dicarbomethoxycyclohexanone[13] by the procedure described by Becker,[14] mp 58–60.5° (hexane–benzene–ether, 10:1:1).

Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33; H, 7.09; N, 6.57. Found: C, 56.22; H, 7.22; N, 6.74.

Dimethyl β-N-Methylamino Glutaconate (3).—In a three-necked flask equipped with a gas inlet tube, mechanical stirrer, and a Dean–Stark water separator was placed 17.4 g (0.1 mol) of dimethyl acetone–dicarboxylate dissolved in 250 ml of dry benzene. The solution was heated to 60–70° and methylamine gas was bubbled in slowly. The temperature of the reaction mixture was kept between 70–75° and the gas flow continued until the theoretical amount of water was trapped in the water separator. The benzene was removed under reduced pressure giving a viscous oil which slowly crystallized. After washing thoroughly with anhydrous ether 14 g of white crystals, mp 83–90°, was obtained. Repeated recrystallization from ether gave a mixture of *cis* and *trans* isomers, mp 92–99°.

Anal. Calcd for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.18; H, 6.86; N, 7.49.

The product amino diester, dimethyl β-N-methyl glutarate, was purified as its 3,5-dinitrobenzamide, mp 86–88° (pentane–chloroform).

Anal. Calcd for $C_{15}H_{17}N_3O_9$: C, 46.98; H, 4.47; N, 10.97. Found: C, 47.07; H, 4.67; N, 11.01.

Recommended Procedure for the Hydrogenation of Vinylogous Urethans. The Hydrogenation of 2.—To 8 g of 5% palladium on charcoal was added, carefully, 35 ml of dry dioxane so that the catalyst was thoroughly moistened with the solvent. To this paste was added, carefully, 65 ml of absolute methanol. (Direct addition of methanol to a dry hydrogenation catalyst can result in severe fires.[3]) This mixture was poured into the hydrogenation apparatus and 12.5 g of the vinylogous urethan 2 in 125 ml of methanol added. The hydrogenation was run for 18–24 hr at 85° and 1000–1500 psi. After this time the reaction mixture was cooled, the catalyst filtered off, and the solvent removed under reduced pressure at 30–35°. The cloudy residue was taken up in ether and filtered. Evaporation of the ether from the filtrate gave 11.25 g (90%) of the product amino diester as a colorless oil. The 3,5-dinitrobenzamide had mp 175–176° (ether–methanol).

Anal. Calcd for $C_{17}H_{19}N_3O_9$: C, 49.88; H, 4.68; N, 10.26. Found: C, 49.77; H, 4.93; N, 9.99.

Registry No.—2, 15649-59-9; 3,5-dinitrobenzamide of hydrogenated 2, 15649-60-2; 3 (*cis*), 15649-63-5; 3,5-dinitrobenzamide of hydrogenated 3, 15717-42-7; 3 (*trans*), 15983-53-6.

(10) Infrared spectra were recorded on a Beckman IR-10 spectrophotometer. The extent of hydrogenation was determined in some cases by product isolation and in others it was estimated by observing the decrease in adsorption at 1655 ($NH_2C{=}CC(=O)OR$) and at 1620 cm^{-1} ($C{=}C$)[11] and the corresponding increase in adsorption at 1730 ($CH_2(O{=})COR$) as well as by tlc.

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Synthesis of *exo,exo*-5,6-Dideuterio-*syn*-7-acetoxynorbornene and *exo,exo*-5,6-Dideuterio-2-norbornene

B. FRANZUS, W. C. BAIRD, JR., AND J. H. SURRIDGE

Esso Research and Engineering Company, Central Basic Research Laboratory, Linden, New Jersey

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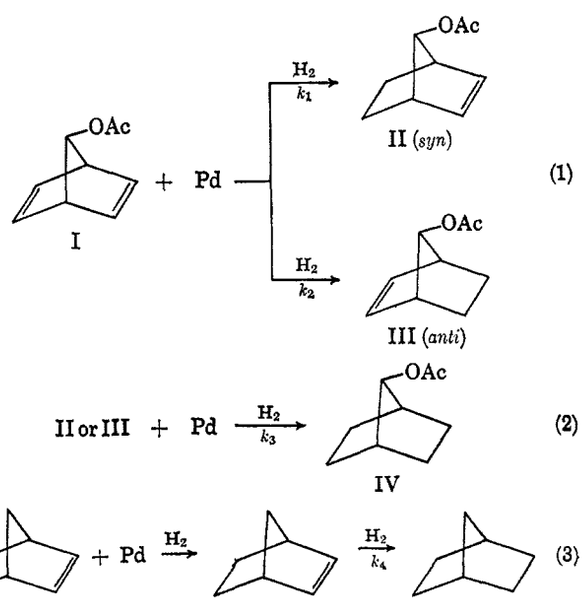
In a previous publication in which the synthesis of *syn*-7-acetoxynorbornene (II) by the platinum-catalyzed reduction of 7-acetoxynorbornadiene (I) was described, the isolated yield of *syn*-acetate was reported to be 22%.[1] During a subsequent study of reductions in the 7-substituted norbornadienyl system and the effect of various transition metal catalysts,[2] 7-acetoxynorbornadiene was hydrogenated over a palladium catalyst in the presence of an equal molar amount of norbornadiene.[3] The utilization of this technique increased the yield of *syn*-7-acetoxynorbornene (II) to ~40% (~70% by glpc). When deuterium was substituted for hydrogen in this reduction, a comparable yield of *exo,exo*-5,6-dideuterio-*syn*-7-acetoxynorbornene was realized. Furthermore, this method has led to a procedure for achieving the deuterium reduction of norbornadiene to *exo,exo*-5,6-dideuterionorbornene (V) with high selectivity and conversion. These useful synthetic procedures are presented in detail in the Experimental Section of this Note.

The significantly increased yield of the *syn*-acetate (II) is attributed to two factors that operate in this reduction. One of these is the preferential reduction of the less sterically hindered *anti* double bond of the dienyl acetate (I). The other is the competitive hydrogenation on the catalyst surface of the various diolefinic and monoolefinic species present in the reaction mixture. The relative amounts of the various reduction products as a function of per cent reduction are illustrated by Figure 1. It is apparent that norbornadiene is rapidly reduced to norbornene while the reduction of dienyl acetate (I) to the isomeric *syn*- (II) and *anti*-acetates (III) proceeds at a somewhat slower rate. The norbornene produced, however, which reduces more slowly than the dienyl acetate (I), is reduced more rapidly than either the *syn* (II) or the *anti* (III) isomer. This rate differential effectively suppresses the subsequent conversion of II and III to saturated acetate product (IV). The data of Figure 1 may be rationalized by consideration of eq 1–3. The



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(2) The results of this work will be fully described in forthcoming publications.

(3) This experiment was performed at the suggestion of Professor H. C. Brown in order to investigate several anomalies that had been observed regarding the stereochemistry of these reductions.[2] The synthetic utility of this reduction was not anticipated.