Reaction of Perchloryl Fluoride with Testosterone Enol Diacetate[1]

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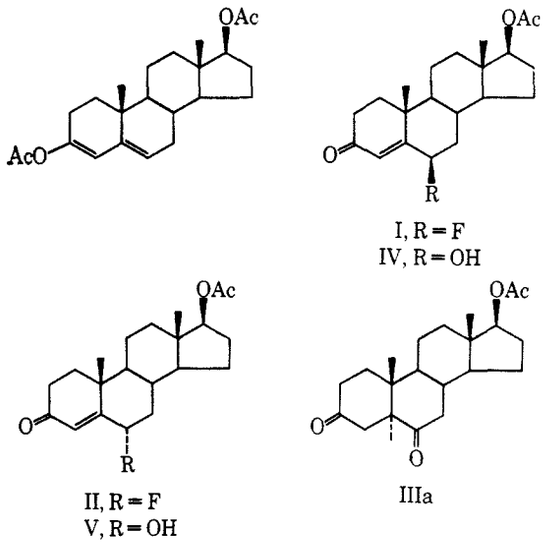
Reaction of perchloryl fluoride with testosterone enol diacetate, in the presence of aqueous dioxane, afforded, as the major products, 6α- and 6β-fluorotestosterone acetate and, as the minor products, 6α- and 6β-hydroxytestosterone 17-acetates and 17β-hydroxyandrostane-3,6-dione acetate. The axial products predominated in the 6-fluoro series, as well as in the 6-hydroxy series, implying that both reactions involved electrophilic attack at C-6.

As part of a general program of this laboratory,[3] we have studied the reaction of perchloryl fluoride with testosterone enol diacetate, aqueous dioxane serving as the reaction medium.[4] The reaction was of interest to us *per se* and also as a model for the reaction in the 19-nortestosterone series. In studying the corresponding reaction of 19-nortestosterone enol diacetate, the complete range of products could not be detected because of difficulties encountered in the attempted isolation.

Electrophilic C fluorinations by perchloryl fluoride of steroidal enamines,[5] enamides,[6] enol ethers,[7] and enol esters[8] have been utilized in several synthetic studies.[9] The variety of reaction media in which these fluorination reactions took place covered a considerable range of basicities, and included mixtures of water with methanol,[3,9b] with dioxane,[8,4] and with tetrahydrofuran.[9e] Initial findings suggested the following generalization concerning the point of electrophilic attack on enol derivatives of steroidal 4-en-3-ones: the enamines afforded products of mono- and difluorination uniquely at C-4;[9a] in contrast, the enol ethers[7] as well as the enol esters[8] afforded 6-fluoro derivatives. That enamines of 4-en-3-ones are fluorinated at C-4 has been confirmed.[3,9b,e] The recent finding of Magerlein, *et al.*,[9e] that the enol ether of a 4-en-3-one afforded, in addition to 6-fluoro-4-en-3-ones, also a 4-fluoro-5-en-3-one, indicates that fluorination at C-4 is not uniquely confined to enamines, as was thought earlier.[9a]

In our experiments, the reaction of perchloryl fluoride with testosterone enol diacetate, dissolved in aqueous dioxane, afforded five products. The major reaction products were 6-fluoro-4-en-3-ones, isolated in a total yield of 42%; the axial 6β-fluorotestosterone acetate (I, 30%) predominated over the equatorial 6α epimer II (12%). The remaining three products contained no halogen. They were identified as 6β-hydroxytestosterone 17-acetate (IV, 10% yield), 6α-hydroxytestosterone 17-acetate (V, 5% yield), and 17β-hydroxy-5α-androstane-3,6-dione acetate (IIIa, 2.5% yield). Thus,



stereoselectivity was evident in the predominant formation of the axial 6β-fluoro compounds,[10] and to a lesser degree in the formation of the axial 6β-hydroxy compounds.[11] These findings are suggestive of stereoelectronic control in the electrophilic substitutions at C-6. The diketone IIIa can be regarded as an isomerization product derived from either or both of the 6-hydroxy compounds (IV and V).[12] In the reaction of 19-nortestosterone enol diacetate with perchloryl fluoride under analogous reaction conditions, a mixture of products was obtained, from which 6β-hydroxy-19-nortestosterone 17-acetate was isolated in 15% yield.

Our finding that perchloryl fluoride, in aqueous dioxane, effects electrophilic hydroxylation as well as fluorination at C-6 of an enol acetate of a steroid 4-en-3-one is without counterpart in related studies.[7,8,9e] This finding is, however, in accord with our study of the reaction of indene, in aqueous dioxane, with perchloryl fluoride.[13] Indene afforded *cis*- and *trans*-1,2-dihydroxyindans, 2-indanone, as well as the main product of oxofluorination, 2-fluoroindanone, and the concomitant

(1) Supported by Grant P-265-F of the American Cancer Society.

(2) Postdoctoral Fellow, 1961–1962.

(3) M. Neeman and Y. Osawa, *Tetrahedron Letters*, 1987 (1962).

(4) M. Neeman and Y. Osawa, Abstracts of Papers, 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, p 45N.

(5) R. B. Gabbard and E. V. Jensen, *J. Org. Chem.*, **23**, 1406 (1958).

(6) S. Nakanishi and E. V. Jensen, *ibid.*, **27**, 702 (1962).

(7) S. Nakanishi, K. Morita, and E. V. Jensen, *J. Am. Chem. Soc.*, **81**, 5259 (1959).

(8) B. M. Bloom, V. V. Bogert, and R. Pinson, Jr., *Chem. Ind.* (London), 1317 (1959).

(9) For example, (a) S. Nakanishi, R. L. Morgan, and E. V. Jensen, *ibid.*, 1136 (1960); (b) R. Joly and J. Warnant, *Bull. Soc. Chim. France*, **28**, 569 (1961); (c) G. R. Allen, Jr., and N. A. Austin, *J. Org. Chem.*, **26**, 5245 (1961); (d) A. H. Goldkamp, *J. Med. Pharm. Chem.*, **5**, 1176 (1962); (e) B. J. Magerlein, J. E. Pike, R. W. Jackson, G. E. Vandenberg, and F. Kagan, *J. Org. Chem.*, **29**, 2982 (1964); (f) ref 3.

(10) The degree of stereoselectivity in the fluorination of enol ethers and esters of steroid 4-en-3-ones reported by different investigators vary considerably, reflecting reaction conditions as well as isolation procedures. Nakanishi, *et al.*,[7] obtained a single product, 6β-fluorocholest-4-en-3-one, in one case, and a mixture of 6β- and 6α-fluoroprogesterones in another. Under similar reaction conditions (enol ethers in pyridine solution, low temperature), Magerlein, *et al.*,[9e] observed low stereoselectivity. In the present study, a higher degree of stereoselectivity was evident, as in the findings of Bloom, *et al.*,[8] who employed similar reaction conditions (enol acetates, aqueous dioxane, ambient temperature).

(11) The stereoselectivity observed has a counterpart in the steric course of the per acid hydroxylation at C-6 of enol acetates [J. Romo, G. Rosenkranz, C. Djerassi, and F. Sondheimer, *ibid.*, **19**, 1509 (1954)] and of enol ethers (ref 23) of steroid 4-en-3-ones.

(12) The equatorial hydroxy compound V would be expected to afford the diketone IIIa more readily than the axial hydroxy compound IV, in view of its more facile enolization.

(13) M. Neeman and Y. Osawa, *J. Am. Chem. Soc.*, **85**, 232 (1963).

trans-2-chloroindanol. A benzylic carbonium ion, arising from electrophilic hydroxylation at C-2 of indene, was proposed as the common reactive intermediate that gave rise to the isolated three nonhalogenated reaction products.[13] Hydroxylation of indene,[13] as well as that of the enol acetates of a 4-en-3-one, observed in this study, is explicable if an electrophilic hydroxylating species is invoked in both cases.[14]

Experimental Section[15]

Reaction of Testosterone Enol Diacetate (3,17β-Diacetoxyandrosta-3,5-diene)[16] with Perchloryl Fluoride.—A slow stream of perchloryl fluoride was passed through a solution of 6.140 g of testosterone enol diacetate in 90 ml of 95% aqueous dioxane at 22° for 4 hr, during which period a total of 52.5 ml of water was added to the reaction mixture in portions of 5.1, 5.4, 6.3, 15.3 and 20.4 ml at 0.5-hr intervals; thus a final concentration of 60% aqueous dioxane was produced. Nitrogen was bubbled through the reaction mixture for 10 min, and the solvent was flash evaporated at 22° to afford 8.642 g of a yellow oil. The product was chromatographed on a column of 70 g of Florisil by the gradient elution method, using 2 l. of 1:10[3] acetone–benzene as the recipient, and 400 ml of 3:7 acetone–benzene as the donor solvent, giving two fractions. The eluent from 50 to 1250 ml afforded fraction A, 4.950 g of oil, λ_{max} 234–237 mμ, and the eluent from 1350 to 2000 ml gave fraction B, 0.955 g of oil, λ_{max} 241 mμ. Fraction A was rechromatographed on a column of 70 g of Florisil, eluting first with 700 ml of benzene, and then, by the gradient elution method, with 2 l. of benzene as the recipient and 300 ml of 1:4 acetone–benzene as the donor solvent. Four fractions were obtained: fraction 1 was eluted with benzene, 2.105 g of oil, λ_{max} 234–237 mμ; eluent from 300 to 1140 ml of the gradient elution gave fraction 2, 1.101 g of oil, λ_{max} 237 mμ; eluent from 1250 to 1840 ml afforded fraction 3, 0.753 g of solid, which showed no peak in the ultraviolet region; fraction 4 was obtained from 1900 to 2300 ml of eluent, 0.972 g of oil, λ_{max} 237 mμ.

6β-Fluorotestosterone Acetate (I).—Crystallization of fraction 1 from *n*-hexane gave 0.870 g of crude 6β-fluorotestosterone acetate (I), mp 103–115°. A 0.217-g portion of this material was purified by gradient elution chromatography on 50 g of Woelm neutral alumina containing 4% water, 1.8 l. of benzene being employed as the recipient and 400 ml of 3:7 diethyl ether–benzene as the donor solvent. Thus was obtained 0.056 g of needles, mp 103–109°, and 0.001 g of needles, mp 164–177° dec, undepressed on admixture with 6α-fluorotestosterone acetate (II), mp 175–177° dec, described below. Recrystallization of the main product from aqueous ethanol gave needles of I: mp 112–116°; λ_{max} 234 mμ (log ε 4.08); λ_{max} 5.81, 5.94 μ; RD (*c* 0.10), $[\alpha]_{700}$ −12°, $[\alpha]_{589}$ −7°, shoulder $[\alpha]_{375-380}$ −480°, trough $[\alpha]_{365}$ −597°, inflection $[\alpha]_{350}$ −255°, peak $[\alpha]_{310}$ +1008°, $[\alpha]_{290}$ +915°.[17] The amount of I in fraction 1, calculated from its ultraviolet absorption on the basis of that of the pure compound, respresented a yield of 30% from testosterone enol diacetate.

Anal. Calcd for $C_{21}H_{29}FO_3$: C, 72.38; H, 8.39; F, 5.5. Found: C, 72.07; H, 8.43; F, 5.3.

All mother liquors from the isolation and purification of I were combined and the solvents were removed by evaporation. The syrupy material thus obtained was used in acid-catalyzed epimerization experiment described in the next paragraph.

6α-Fluorotestosterone Acetate (II).—(A) Crystallization of fraction 2 from ethanol gave 0.090 g of 6α-fluorotestosterone acetate (II),[18] mp 164–172° dec. This product was recrystallized from ethanol and showed mp 175–177° dec, undepressed on admixture with another specimen of the 6α epimer II of mp 175–177° described below (obtained by acid-catalyzed epimerization of the 6β epimer I). The infrared spectra and RD curves of both specimens of II were identical. The amount of II in fraction 2, calculated from its ultraviolet absorption based on that of the pure compound, corresponded to a yield of 12% from testosterone enol diacetate. (B) Dry hydrogen chloride was passed for 1 hr into a solution of 1.521 g of the syrupy material from the mother liquors of I (described above) in 50 ml of acetic acid cooled to 15–18°.[19] After an additional hour at 22° the reaction mixture was diluted with 500 ml of water, and the product was extracted with diethyl ether. The extracts were washed with water, with saturated sodium chloride solution, with 5% sodium carbonate solution, and with water and dried over anhydrous sodium sulfate. The solvent was removed by evaporation, and the product was chromatographed on 40 g of Florisil. Elution with 1 l. of 1:33 diethyl ether–benzene and 2 l. of 1:20 diethyl ether–benzene afforded 0.270 g of 6α-fluorotestosterone acetate (II), mp 172–176° dec. Recrystallization from ethanol gave a pure specimen of II: mp 175–177° dec; λ_{max} 237 mμ (log ε 4.13); λ_{max} 5.81, 5.94 μ; RD (*c* 0.10), $[\alpha]_{700}$ +45°, $[\alpha]_{589}$ +70°, peak $[\alpha]_{420-470}$ +115°, trough $[\alpha]_{372}$ −135°, peak $[\alpha]_{363}$ −60°, trough $[\alpha]_{356}$ −104°, inflection $[\alpha]_{340}$ +408°, $[\alpha]_{315}$ +1600°.[20]

17β-Hydroxyandrostane-3,6-dione Acetate (IIIa).—Crystallization of fraction 3 from ethanol gave 0.140 g of 17β-hydroxyandrostane-3,6-dione acetate (IIIa),[21] which melted at 178–182° after recrystallizations from the same solvent. This product was found to be identical with another specimen of 17β-hydroxyandrostane-3,6-dione acetate described below, which was prepared from 6β-hydroxytestosterone 17-acetate (IV) by isomerization with base followed by reacetylation, of mp 186.5–188.5° undepressed on admixture with the product IIIa. The infrared spectra and rotatory dispersion of both specimens were identical.

6β-Hydroxytestosterone 17-Acetate (IV).—Crystallization of fraction 4 from diethyl ether–*n*-hexane afforded 0.522 g of 6β-hydroxytestosterone 17-acetate (IV),[16] mp 193–197°, which was recrystallized twice from benzene–*n*-hexane: mp 203–206°; λ_{max} 237 mμ (log ε 4.17); λ_{max} 2.76, 5.81, 5.97, 6.15 μ; RD (*c* 0.10), $[\alpha]_{700}$ +3°, $[\alpha]_{589}$ +6°, peak $[\alpha]_{450}$ +23°, trough $[\alpha]_{370}$ −148°, peak $[\alpha]_{367}$ −136°, trough $[\alpha]_{357}$ −295°, peak $[\alpha]_{348}$ −113°, trough $[\alpha]_{343}$ −154°, shoulder $[\alpha]_{327-330}$ +194°, inflection $[\alpha]_{317}$ +466°, peak $[\alpha]_{305}$ +579°, $[\alpha]_{275}$ +440°.[22] The amount of IV in fraction 4, calculated from its ultraviolet absorption based on that of the pure compound, corresponded to a yield of 10% from testosterone enol diacetate.

6α-Hydroxytestosterone 17-Acetate (V).—Fraction B, obtained in the first chromatographic separation of the reaction mixture, crystallized partly after a period of 1 week. This material was triturated with diethyl ether, and 0.028 g of needles, mp 202–212°, were collected by filtration. Recrystallization of this product from benzene–*n*-hexane afforded 0.019 g of 6α-hydroxytestosterone 17-acetate (V):[23] mp 216–218°; λ_{max} 241 mμ (log ε 4.19); λ_{max} 2.76, 5.81, 5.99, 6.14 μ; RD (*c* 0.10), $[\alpha]_{700}$ +50°, $[\alpha]_{589}$ +69°, peak $[\alpha]_{410-430}$ +135°, trough $[\alpha]_{368}$ −156°, peak $[\alpha]_{360}$ −101°, trough $[\alpha]_{353}$ −219°, shoulder $[\alpha]_{338-342}$ +289°, inflection $[\alpha]_{325}$ +1045°, $[\alpha]_{280}$ +2268°.[24] The amount of V in fraction B, calculated from its ultraviolet absorption on the basis of that of the pure compound, corresponded to a yield of 5% from testosterone enol diacetate.

17β-Hydroxy-5α-androstane-3,6-dione (IIIb).—(A) To a solution of 0.206 g of IV, mp 193–197°, in 10.0 ml of methanol was

(14) An obvious mechanism giving rise to an electrophilic hydroxylating species is not readily apparent from the available evidence, in view of the uncertainty whether perchloryl fluoride itself, or a secondary product derived from it, is involved in this reaction.

(15) Melting points of analytical specimens were determined on a Hershberg melting point apparatus and are corrected for stem exposure. Ultraviolet spectra were determined with a Cary Model 14 recording spectrophotometer, 95% ethanol being used as the solvent. Infrared spectra were determined on a Baird Model AB 2 double-beam infrared recording spectrophotometer, methylene chloride being used as the solvent. Optical rotatory dispersion measurements were made with a Rudolph photoelectric spectropolarimeter Model 200 AS/80Q/650, dioxane being employed as the solvent.

(16) See J. Romo, *et al.*, reference in footnote 11.

(17) C. Djerassi, J. Osiecki, R. Riniker, and B. Riniker [*J. Am. Chem. Soc.*, **80**, 1216 (1958)] reported the rotatory dispersion of 6β-fluorotestosterone. The rotatory dispersion of I was in agreement with these data.

(18) A. Bowers, L. C. Ibanez, and H. J. Ringold, *Tetrahedron*, **7**, 138 (1959).

(19) J. A. Edwards, H. J. Ringold, and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 2321 (1960).

(20) The rotatory dispersion of II was in agreement with that reported for 6α-fluorotestosterone (see reference in footnote 17).

(21) S. H. Eppstein, P. D. Meister, H. M. Leigh, D. H. Peterson, H. C. Murray, L. M. Reineke, and A. Weintraub, *ibid.*, **76**, 3174 (1954).

(22) The rotatory dispersion of IV agreed with that reported for 6β-hydroxytestosterone: C. Djerassi, R. Riniker, and B. Riniker, *ibid.*, **78**, 6377 (1956).

(23) J. D. Dusza, J. P. Joseph, and S. Bernstein, *J. Org. Chem.*, **27**, 4046 (1962).

(24) The rotatory dispersion of V corresponded closely with that reported for 6α-hydroxycholest-4-en-3-one (see Romo, *et al.*, reference in footnote 11).

added 1.0 ml of 20% aqueous potassium hydroxide, and the reaction mixture was refluxed for 45 min under nitrogen. It was diluted with 200 ml of water and the product was extracted with chloroform. The extract was washed with water and dried over anhydrous sodium sulfate. The solvent was flash evaporated. The residue crystallized and triturated with aqueous methanol. The product, 0.174 g of needles, mp 223–228°, was purified by chromatography on 30 g of Florisil by gradient elution, 1.1 l. of benzene being used as the recipient and 200 ml of 3:7 acetone–benzene as the donor solvent. The eluent from 915 of 1185 ml gave 0.075 g of 17β-hydroxy-5α-androstane-3,6-dione (IIIb):[25] mp 232–235°; λ_{max} 2.76, 5.87 μ.

Acetylation of 30 mg of IIIb with acetic anhydride in pyridine yielded 21 mg of 17β-acetoxy-5α-androstane-3,6-dione (IIIa):[21] mp 186.5–188.5°; λ_{max} 5.80, 5.86 μ; RD (*c* 0.10), $[\alpha]_{700}$ −7°, $[\alpha]_{589}$ −6°, trough $[\alpha]_{350-420}$ −38°, peak $[\alpha]_{322}$ +152°, trough $[\alpha]_{314}$ +10°, peak $[\alpha]_{306}$ +120°, trough $[\alpha]_{302}$ +45°, peak $[\alpha]_{298}$ +106°, $[\alpha]_{290}$ −9°.

(B) To a solution of 2.8 mg of V, mp 216–218°, in 1.0 ml of methanol, was added 0.3 ml of 20% aqueous potassium hydroxide and the reaction mixture was refluxed for 15 min under nitrogen. It was diluted with 30 ml of water and the product was extracted with chloroform. The extracts were washed with water and dried over anhydrous sodium sulfate, and the solvent was evaporated to give 2.1 mg of needles, mp 223–227°. Recrystallization of the product from benzene–diethyl ether afforded 1.5 mg of colorless needles, mp 229–231°, undepressed on admixture with 17β-hydroxy-5α-androstane-3,6-dione (IIIb), mp 232–235°, obtained from IV as described above; the infrared spectra of both specimens were identical.

(25) F. Sondheimer, S. Kaufmann, J. Romo, H. Martinez, and G. Rosenkranz, *J. Am. Chem. Soc.*, **75**, 4712 (1953).

6β-Hydroxy-19-nortestosterone 17-Acetate.—A solution of 1.320 g of 19-nortestosterone enol diacetate[26] in 30 ml of 95% aqueous dioxane was treated with perchloryl fluoride, as described above for testosterone enol diacetate and worked up in the same manner, affording 1.272 g of a yellow syrup: λ_{max} 236 mμ; λ_{max} 2.75, 5.82, 5.96 μ. The product was chromatographed on a column of 50 g of Florisil by the gradient elution method using 2 l. of 1:2 × 10^3 acetone–benzene as the recipient and 300 ml of 3:17 acetone–benzene as the donor solvent. The first peak, eluted with 1800 ml of eluent, represented a mixture which could not be separated into identifiable products. The eluent from 1800 to 2200 ml gave a fraction, 0.340 g of solid, which was recrystallized from diethyl ether–*n*-hexane to afford 0.185 g (15% yield) of 6β-hydroxy-19-nortestosterone 17-acetate, mp 162–164°. Recrystallization from the same solvent mixture gave an analytical specimen: mp 166°; λ_{max} 237 mμ (log ε 4.17); λ_{max} 2.76, 5.82, 5.96 μ; RD (*c* 0.10), $[\alpha]_{700}$ −46°, $[\alpha]_{589}$ −62°; trough $[\alpha]_{371}$ −736°, peak $[\alpha]_{367}$ −705°, trough $[\alpha]_{357}$ −830°, shoulder $[\alpha]_{342-346}$ −391°, inflection $[\alpha]_{326-328}$ +225°, peak $[\alpha]_{307}$ +545°, $[\alpha]_{282}$ +39°.

Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.33; H, 8.52.

Registry No.—I, 2627-94-3; II, 855-55-0; IIIa, 745-43-7; IIIb, 899-39-8; IV, 13096-48-5; V, 13573-36-9; perchloryl fluoride, 7616-94-6; testosterone enol diacetate, 1778-93-4; 6β-hydroxy-19-nortestosterone 17-acetate, 13573-37-0.

(26) British Patent 755,129 (1956); *Chem. Abstr.*, **51**, 10601e (1957).

Photolytic Reaction of Ethyl Azidoformate with Enol Acetates

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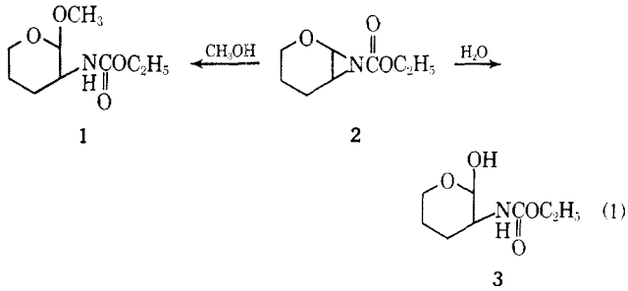
Irradiation of a dilute dichloromethane solution of ethyl azidoformate and isopropenyl acetate or 1-acetoxycyclohexene leads to the corresponding very reactive N-carbethoxyaziridine which upon water treatment affords an α-carbethoxyamino ketone in modest yield. Products derived from C–H insertion of the likely intermediate, carbethoxynitrene, are also observed to a lesser extent.

Our interest in the photolysis of ethyl azidoformate[1] in the presence of enol acetates stems from a search for a new general synthesis of N-protected α-aminocarbonyl groupings (Scheme I) which could be used in connection with the synthesis of some natural products.

Brown and Edwards[2] have studied the related photochemical reaction of ethyl azidoformate with dihydropyran and have isolated in good yield the reactive aziridine **2**. Subsequent reaction of this substance with water produced urethan **3**, while with methanol urethan **1** was obtained along with some **3** (eq 1).



1 2 3 (1)

(1) W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963); W. Lwowski and T. W. Mattingly, Jr., *ibid.*, **87**, 1947 (1965); W. Lwowski and T. J. Maricich, *ibid.*, **87**, 3630 (1965); K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Letters*, 3953 (1964).

We wish to report the results of our studies on the photodecomposition of ethyl azidoformate in the presence of somewhat less than 1 equiv of either isopropenyl acetate or 1-acetoxycyclohexene in dichloromethane solution.[3,4]

Results and Discussion

Removal of the solvent at 25° under vacuum after photolysis of a solution of ethyl azidoformate and isopropenyl acetate in dichloromethane afforded a clear pale yellow oil. The nmr and infrared spectra of this oil[5] were consistent with the presence of a large pre-

(2) I. Brown and O. E. Edwards, *Can. J. Chem.*, **43**, 1266 (1965).

(3) The photodecomposition of isopropenyl acetate and 1-acetoxycyclohexene could in principle be a serious side reaction. However, Mazur[4] has shown that ultraviolet irradiation of a dilute solution of isopropenyl acetate or 1-acetoxycyclohexene in cyclohexane for 24 hr or longer resulted in recovery of much starting enol acetate, accompanied by less than a 30% yield of rearranged products. While we have not directly observed such rearranged products in our experiments, they may well be present in minor amounts.

(4) A. Yogev, M. Gorodetsky, and Y. Mazur, *J. Am. Chem. Soc.*, **86**, 5208 (1964).

(5) Aziridines **4** and **9** were not stable to vapor phase chromatography or column chromatography. Vacuum distillation was accompanied by ta r formation. Nmr spectra of the distillates indicated that only slight enrichment of the aziridines had been effected. Consequently, the oily mixture rich in aziridine as obtained directly from the photolysis experiments was used for spectral determinations and chemical transformations.