an ethanol–ethyl acetate mixture gave an analytically pure sample: mp 169–170°; ν^{KBr} 1600 w, 1350 s, 1170 s cm^{-1}; nmr (δ^{CDCl_3}) 2.3 (s, three, CH_3), 4.56 (d, two, CH_2), 5.65 (t, one, CH), 6.6–7.9 ppm (m, 12, aryl).

1-Acetyl-1,2-dihydro-6-nitroquinoline (5g).—Sodium hydride (0.0255 mole), 5-nitro-N-acetylanthranilaldehyde (0.0255 mole), and 50 ml of anhydrous benzene were refluxed under a nitrogen atmosphere for 1.5 hr. After cooling the mixture to room temperature, vinyltriphenylphosphonium bromide (0.0255 mole) and 100 ml of dimethylformamide were added and the mixture was stirred at room temperature for 12 hr. Ether extraction was carried out as described above for compound **5a**. Evaporation of the ether extracts gave a yellow solid–oil mixture. Petroleum ether (bp 30–60°) was added to wash out the mineral oil and then decanted off. Methanol was then added and the mixture was heated slightly. Cooling and filtration gave 1.98 g of the crude compound **5g**, mp 95–102°. Several recrystallizations from methanol gave an analytically pure sample of yellow crystals: mp 105–106°; ν^{KBr} 1670 s, 1610 w, 1580 w cm^{-1}; nmr (δ^{CDCl_3}) 2.26 (s, three, CH_3), 4.45 (d, two, CH_2), 6.18 (m, one, $CH_2CH=$), 6.6 (d, one, $C_6H_3CH=$), 7.25–8.0 ppm (m, three, aryl).

N-*p*-Tolylsulfonylanthranilaldehyde.—The reaction of anthranilaldehyde with *p*-tolylsulfonyl chloride in pyridine, according to the general procedure of Vogel,[14] gave N-*p*-tolylsulfonylanthranilaldehyde which was recrystallized from ethanol to give an analytical sample: mp 135–136° (lit.[21] mp 203–205°); nmr (δ^{CDCl_3}) 2.35 (s, three, CH_3), 7.0–7.9 (m, eight, aryl), 9.8 (s, one, CHO), 10.76 ppm (s, one, NH).

Anal. Calcd for $C_{14}H_{13}NO_3S$: C, 61.06; H, 4.76; N, 5.10. Found: C, 61.10; H, 4.68; N, 5.20.

2-Amino-5-chloro-N-*p*-tolylsulfonylbenzophenone.—The reaction of 5-chloro-2-aminobenzophenone with *p*-tolylsulfonyl chloride in pyridine according to the general procedure of Vogel[14] gave light brown crystals of the desired product upon recrystallization from ethanol. Several recrystallizations gave an analytical sample: mp 121–122°; nmr (δ^{CDCl_3}) 2.3 (s, three, CH_3), 6.9–7.9 (m, twelve, aryl), 9.38 ppm (broad singlets, one, NH).

Anal. Calcd for $C_{20}H_{16}ClNO_3S$: N, 3.63. Found: N, 3.65.

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Some Reactions of Steroidal α-Bromo Ketones[1]

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16α-Bromoandrostan-3β-ol-17-one (I) is converted by methoxide ion into the dimethyl ketal of 3β-16α-dihydroxyandrostan-17-one (II). The 16β-bromo epimer Ia and the 5,6-dehydro analog Ib undergo the same transformation. The structure of the ketal II was apparent from its hydrolysis to 16α-hydroxy-17-ketone (III), its acetylation, its reduction to the 16α,17β-diol (VI), and its nmr spectra. The reaction of bromo ketone I with ethoxide takes a different course. The stereochemical results of the reaction of methoxide with I and Ia are discussed assuming 17β-methoxy-16α,17β-epoxyandrostan-3β-ol (VIII) as an intermediate. Some ring-opening reactions of acetoxy epoxides are discussed.

Our recent studies of the rearrangement of 16-amino-17-keto steroids to 17β-hydroxy-16-keto steroids in the presence of water[2] led us to the investigation of other reactions in the D ring of these systems. A possible route to various 16-substituted 17-keto steroids could be the displacement of 16-bromo 17-ketones with amines and other bases, in particular since it is known that dehydrobromination or Favorski rearrangement of 16-bromo 17-ketones do not occur readily under basic conditions.[3]

It was of interest to establish whether the reaction of 16α-bromoandrostan-3β-ol-17-one with strong base would lead to substitution or to three-membered ring intermediates such as VIII or VIIIa. Stevens and coworkers[4] have shown that methoxy epoxides are intermediates in the reaction of α-bromo ketones with methoxide. We found that bromo ketone I reacted readily upon heating for short periods of time with potassium hydroxide in methanol to yield a product identified as 17,17-dimethoxyandrostane-3β,16α-diol (II, Scheme I). These results are analogous to those obtained in the estrone series by Mueller, *et al.*,[5] using anhydrous methoxide as a base. The structure of the dimethyl ketal II was proved by acid hydrolysis to the 16α-hydroxy 17-ketone III. The identity of the latter was apparent by conversion to its diacetate IIIa, by base isomerization of III to the more stable isomer IV, as well as by conversion of III and IV to the bisphenylhydrazone V. As expected, the ketal diol II was stable to lithium aluminum hydride, but formed a diacetate derivative IIa. The nmr spectrum of II indicates two distinct methoxy groups at τ 6.53 (H_3, singlet) and 6.65 (H_3, singlet), and a C-16 proton at 5.74 (triplet).

Stevens and co-workers[4] as well as Tchoubar, *et al.*,[6] have investigated the reaction of simpler α-bromo ketones with anhydrous methoxide and have shown it to lead to α-hydroxy ketals. The stereochemical results of the conversion of I to II require further comment.[7] Since the same product, namely II, is obtained whether one uses anhydrous methoxide or potassium hydroxide in methanol the 16α-hydroxy function could not have been derived by a displacement at C-16 but is most likely the result of ring opening of an α-epoxide such as VIII. In order to obtain a 16α,17α-epoxide, attack by methoxide ion on I must have taken place at C-17 from the β side, which is rather surprising in view of the well-established preferred attack from the α side in 17-keto steroids. The

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(2) A. Hassner and A. W. Coulter, *Steroids*, **4**, 281 (1964).

(3) W. S. Johnson and W. F. Johns, *J. Am. Chem. Soc.*, **79**, 2005 (1957).

(4) C. L. Stevens, W. Malik, and R. Pratt, *ibid.*, **72**, 4758 (1950); C. L. Stevens, J. Beereboom, and K. Rutherford, *ibid.*, **77**, 4590 (1955).

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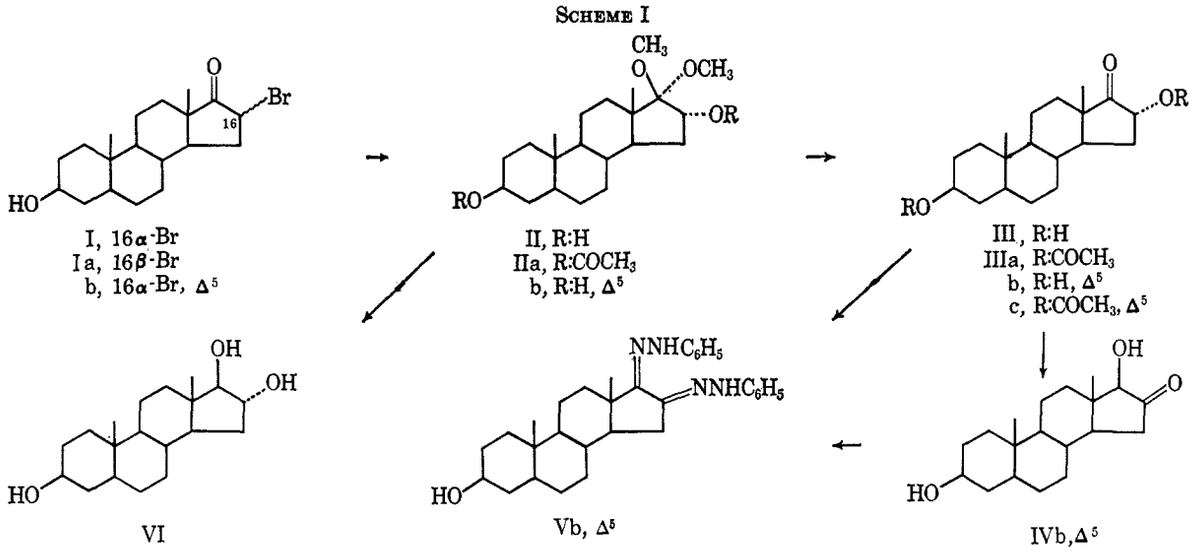
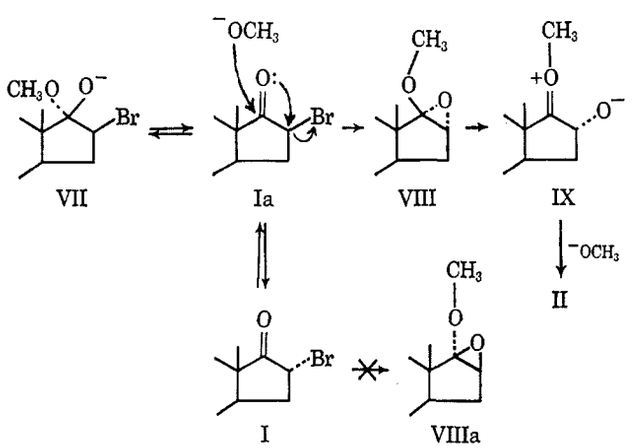
(7) These results and the analogous ones discussed earlier by Mueller and Johns[5] warrant a detailed analysis because the reaction product is not the one expected from direct displacement on I, from cleavage of the logical intermediate VIIIa, or from ring opening of intermediate VIII at the less hindered C-16.

SCHEME I



formation of 16α,17α-epoxide VIII also requires a precursor with a 16β-bromo substituent.

These facts were recognized earlier by Mueller and Johns[5] who postulated an equilibration between the 16α- and 16β-bromo ketones I and Ia followed by conversion of Ia to VIII. It is surprising that no products derived from VIIIa were found either by us or by previous workers.[5] Such a scheme requires preferential reaction of Ia over I with methoxide, which has an analogy in the sodium borohydride reduction of 16α-bromo 17-ketone I to the 16β-bromo 17β-alcohol[8] and which can be explained by relief of nonbonded interactions between the 16β-bromine and the 13β-methyl group in Ia. Reversible attack by methoxide at C-17 of Ia from the less hindered α side would lead to VII which cannot react further, whereas attack from the β side leads to epoxide VIII. In accordance with this hypothesis, we found that the 16β-bromo 17-ketone Ia also was converted by potassium hydroxide in



methanol to the ketal II. Although a methoxy epoxide has reportedly been isolated in D-homo steroids,[9] our attempts to isolate an intermediate epoxide VIII by exposing I to methoxide ions in ether or methanol, in the cold or at reflux, for 30 sec to 1 hr were unsuccessful and only starting material and/or ketal II were obtained. Exposure of bromo ketone I to refluxing ethanolic potassium hydroxide or to sodium ethoxide in ethanol did not lead to a diethyl ketal analogous to II but to ketol IV. Presumably ketol III is formed, which is known to rearrange under basic conditions to the isomeric ketol IV.[10] 16α-Bromo-5-androsten-3β-ol-17-one (Ib) reacted with methoxide ions like its 5,6-dihydro analog I to give ketal IIb, albeit in lower yield. On the other hand, 2α-bromo-3-cholestanone with methoxide ions gave an impure ketol rather than a hydroxy ketal, confirming earlier reports.[11]

It has already been shown that the evidence for the structure II is consistent with ring opening of intermediate VIII at C-17. It is noteworthy that methoxide enters not only at the more substituted carbon but also at a clearly more hindered position in the molecule (C-17 is a neopentyl-type carbon). These results, which are consistent with those observed by other workers,[4-6] indicate that methoxide does not attack VIII in a bimolecular displacement but more likely reacts with a form such as IX, produced directly from VIII. Possibly, in the reaction of I with ethoxide, ketol III could be formed from decomposition of the ethyl analog of IX because formation of a diethyl ketal at C-17 would be sterically less favorable than formation of a dimethyl ketal. It is unlikely that a diethyl analog of II forms first and decomposes in hot base since the dimethyl ketal II was shown to be stable to refluxing sodium ethoxide in ethanol. We were also unable to find evidence for formation of ethylene which might have resulted from a concerted abstraction by the oxygen at C-16 of a β proton from the ethyl group in a diethyl analog of II.

Opening of epoxides such as VIII or X should be able to proceed either by epoxide C–O bond rupture (*e.g.*, VIII–IX) or by substituent C–O bond rupture (*e.g.*, X–XI, since acetate is a good leaving group). An example of the latter case is probably the conversion of epoxide X to acetoxy ketone IIIa on heating or on chromatography.[12] The intermediacy of XI and XII would account for the observed results inasmuch as IIIa, rather than its less stable 16β epimer[10] is expected

(8) J. Fajkos, *Collection Czech. Chem. Commun.*, **20**, 312 (1955).
(9) D. A. Prins and D. W. Shoppee, *J. Chem. Soc.*, 494 (1946).
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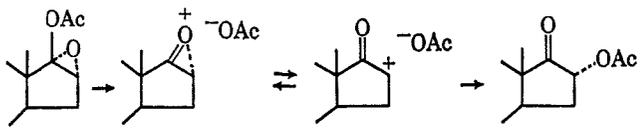
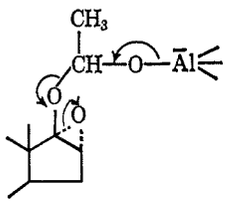
(12) N. S. Leeds, D. K. Fukushima, and T. F. Gallagher, *J. Am. Chem. Soc.*, **76**, 2943 (1954).



X XI XII IIIa

to result from XII. The above pathway is also consistent with the formation of 16α-bromo-17-keto steroids from 17β-bromo-16α,17α-epoxy steroids on heating.[13]

In connection with these studies it was of interest to examine the hydride reduction of acetoxy epoxides such as X. Direct hydride opening of the epoxide in X should proceed from the β side and lead either to a 17β-alcohol (attack at C-16) or to a 16α,17α-diol (attack at C-17). On the other hand, coordination of the epoxide with lithium aluminum hydride should lead to ring opening to a 17-ketone, so that the ultimate reduction product would be the 16α,17β-diol VI. The product of lithium aluminum hydride reduction of X is indeed diol VI.[12] However, since epoxide X, like most epoxides is stable to sodium borohydride, a better explanation of the above results might be that reduction of the acetate function precedes opening of the epoxide to a 17-ketone as shown in XIII. In



XIII

any case it appears that hydride, like methoxide, does not open negatively substituted epoxides such as VIII or X in a bimolecular reaction but that epoxide opening occurs before reaction with the nucleophile.

Experimental Section[14]

17,17-Dimethoxyandrostane-3β,16α-diol (II). A. From 16α-Bromoandrostan-3β-ol-17-one (I).—A solution of 0.5 g of bromo ketone (I)[15] in 15 ml of warm anhydrous methanol was poured into a solution of sodium methoxide prepared from 1 g of sodium and 30 ml of methanol. The mixture was heated under reflux for 10 min and then poured into ice–water. The resulting precipitate was washed with water and dried (410 mg). Recrystallization from methanol gave ketal II, mp 179–180°. The nmr spectrum, in addition to the common peaks, shows two methoxy singlets at τ 6.53 and 6.65, two angular methyls as singlets at 9.23 and 9.0, and the 16α hydrogen as a triplet at 5.74; the infrared spectrum shows ν_{max} 3400 cm^{-1} (OH).

Anal. Calcd for $C_{21}H_{36}O_4$: C, 71.55; H, 10.30. Found: C, 71.77; H, 10.12.

The ketal II was also obtained by heating I with 5% potassium hydroxide in methanol under reflux for 4 hr. Exposure of I to methanolic hydroxide or to anhydrous methoxide at room temperature overnight or at reflux for 1 min resulted in the isolation of starting material in 80–90% yield.

B. From 16β-bromoandrostan-3β-ol-17-one (Ia).—A solution of 690 mg of Ia[7] in 50 ml of methanol containing 1.5 g of potassium hydroxide was refluxed for 3.5 hr. The yellow solution was poured into ice–water and extracted with four portions of chloroform. The organic layer was washed with water, dried with magnesium sulfate, and evaporated to yield an oily solid, which on recrystallization from methanol gave 230 mg of ketal II identical by infrared spectrum and melting point with the product isolated by method A.

17,17-Dimethoxyandrostane-3β,16α-diol Diacetate (IIa).—Acetylation of diol II with an excess of acetic anhydride and pyridine gave diacetate IIa, mp 143–144°, in 85% yield: ν_{max} 1725 and 1240 cm^{-1}.

Anal. Calcd for $C_{25}H_{40}O_6$; C, 68.77; H, 9.24. Found: C, 69.07; H, 9.43.

Reaction of Bromo Ketone I with Ethanolic Potassium Hydroxide or Sodium Ethoxide.—Bromo ketone I (3 g) was dissolved in 300 ml of ethanol containing 6 g of potassium hydroxide. The mixture was heated on a steam bath for 4 hr and one-half of the solvent was removed on the rotovac. Dilution with water and acidification with dilute hydrochloric acid gave a white precipitate which, when washed and dried, weighed 1.670 g. Recrystallization from methanol–water yielded 1.1 g of IV, mp 213–215°. The infrared spectrum of this material was identical with that of authentic androstane-3β,17β-diol-16-one (IV).[16]

When bromo ketone I (200 mg), dissolved in 15 ml of warm anhydrous ethanol, was added to a solution of sodium ethoxide (1 g of sodium in 30 ml of ethanol) and heated under reflux for 12–15 min, then poured into ice–water, extracted with ether, and worked up as above, 60 mg of an oil was isolated. After two crystallizations with methanol–water, ketol IV was obtained: mp 208–212°.

Hydrolysis of Ketal II to Ketone III.—17,17-Dimethoxyandrostan-3β-ol-17-one (II, 1 g) was dissolved in 100 ml of methanol containing 5 ml of concentrated hydrochloric acid. The mixture was heated under reflux for 4 hr. Then, one-half of the solvent was removed under reduced pressure and the rest was diluted with water. The white precipitate was collected by filtration, washed, and dried: yield 480 mg. Crystallization from acetone–petroleum ether (bp 60–90°) gave 380 mg of III: mp 184–186°; ν_{max} 3395, 3280 (OH), and 1735 cm^{-1} (C=O).

Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87. Found: C, 74.52; H, 9.95.

3β,16α-Diacetoxyandrostan-17-one (IIIa).—Acetylation of ketol III with acetic anhydride and pyridine at room temperature afforded IIIa, mp 182–184°, identical by infrared spectrum with an authentic sample.

Anal. Calcd for $C_{23}H_{34}O_5$: C, 70.74; H, 8.72. Found: C, 70.90; H, 8.86.

Isomerization of ketol IIIa to ketol IV in the presence of sodium hydroxide was accomplished as previously described.[12]

Androstane-3β-ol-16,17-dione Bisphenylhydrazone (V).—To a solution of 1 mmole of 3β,17β-dihydroxyandrostan-16-one (III) or of 1 mmole of 3β,16α-dihydroxyandrostan-17-one in 30 ml of glacial acetic acid was added 3 mmoles of phenylhydrazine, and the solution was allowed to stand at room temperature for 12–15 hr. The product was precipitated by pouring the solution into cold water. Crystallization (twice) from methanol–acetone gave V, mp 228–230°.

Anal. Calcd for $C_{31}H_{40}N_4O$: C, 76.82; H, 8.32. Found: C, 77.00; H, 8.20.

17,17-Dimethoxy-5-androstene-3β,16α-diol (IIb).—A solution of 5 g of bromo ketone Ib[17] in 50 ml of warm anhydrous methanol was poured into a solution of sodium methoxide, prepared from 3.5 g of sodium and 50 ml of methanol. The mixture was heated under reflux for 35 min, poured into ice–water, and extracted with ether. After drying the organic layer with magnesium sulfate and removal of the solvent, 3.1 g of product was obtained after recrystallization from acetone.

Since the infrared spectrum showed a small peak in the carbonyl region, 2 g of this compound was reheated in a solution of sodium methoxide (100 ml of methanol and 2 g of sodium) for 10 hr. The solution was poured into ice–water and the product (no carbonyl in the infrared spectrum) was recrystallized from acetone to yield 1.43 g of ketal IIb, mp 177–179°,

Anal. Calcd for $C_{21}H_{34}O_4$: C, 71.96; H, 9.78. Found: C, 71.43; H, 9.54.

Hydrolysis of Ketal IIb to Ketol IIIb.—By the procedure described for the hydrolysis of II, 0.5 g of 17,17-dimethoxy-5-

(13) Unpublished results from this laboratory.

(14) All melting points were taken on a Fisher-Johns melting point block and are uncorrected. Infrared spectra were obtained in KBr disks on a Beckman IR-5 spectrometer, whereas nmr spectra were run in 10% solutions of chloroform on a Varian A-60 spectrometer using tetramethylsilane as a standard. Elemental analysis were performed by A. Bernhardt, Mülheim, Germany.

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androstene-3β,16α-diol (IIb) was hydrolyzed with hydrochloric acid in methanol to give 280 mg of ketol IIIb after recrystallization from aqueous methanol. One more crystallization brought the melting point to 177–180° (lit.[18] 177–181°). Its infrared spectrum shows absorption bands at 3400 (OH) and 1750 cm^{-1} (C=O).

3β,16α-Diacetoxy-5-androsten-17-one (IIIc).—Acetylation of ketol IIIb with acetic anhydride and pyridine at room temperature over night yielded IIIc, mp 167–168° (lit.[18] 166–168°).

Isomerization of Ketol IIIb to Ketol IVb.—A solution of 40 mg of 5-androstene-3β,16α-diol-17-one (IIIb) in 25 ml of aqueous methanol containing 150 mg of potassium hydroxide was let stand for 10 hr at room temperature. The mixture was poured into water, extracted with ether, washed, and dried to yield crude product (35 mg). Crystallization from aqueous ethanol gave ketol IVb. Its infrared spectrum and melting point were identical with those of an authentic sample prepared according to Stodola, *et al.*[19]

5-Androsten-3β-ol-16,17-dione Bisphenylhydrazone (Vb). From Ketol IIIb or IVb.—Following the procedure for V there was prepared the osazone Vb from 3β,16α-dihydroxy-5-androsten-17-one (IIIb) or from 3β,17β-dihydroxy-5-androsten-16-one (IVb). Recrystallization from ethanol water brought yellow crystals, mp 233–237°.

The infrared spectrum of this material was identical with that of the bisphenylhydrazone prepared from bromo ketone Ib.[18]

Attempted Reaction of 2α-Bromo-3-cholestanone with Methoxide.—2α-Bromo-3-cholestanone (1 g) was added to a solution of sodium methoxide prepared from 2 g of sodium and 100 ml of methanol. The mixture was heated under reflux for 45 min. Then it was poured into ice–water and worked up as for IIb. The crude product was obtained as an oily solid (850 mg), which resisted attempts of purification by chromatography or crystallization. The infrared spectrum of this compound indicated the presence of hydroxyl at 3500 and carbonyl at 1730 cm^{-1}. The nmr spectrum indicated that methoxy groups were absent. The same product mixture was obtained by heating the bromo ketone with potassium hydroxide in methanol.

Acknowledgment.—This investigation was supported by U. S. Public Health Service Grant CA-04474 from the National Cancer Institute. One of us (A. H.) also wishes to thank the Council on Research and Creative Work, University of Colorado, for a Faculty Fellowship.

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The Alkyl Nitration of Active Methylene Compounds. IV. The Mononitration of Ketones

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The mononitration of cycloalkanones with alkyl nitrates in the presence of potassium *t*-butoxide affords not only α-nitrocycloalkanones (A) but also ω-nitrocarboxylic esters (B). The latter arise from a fragmentation reaction which occurs (except in the case of cyclopentanone) during the nitration step and not during subsequent acidification, but cleavage is not caused by direct alkoxide attack except in the case where the resulting nitro ketone is tertiary. The relative amounts of compounds A and B formed vary with ring size, the fragmentation being most pronounced in the "middle ring region" and with α,α′-disubstituted cycloalkanones. Fragmentation also takes place with aliphatic and aryl alkyl ketones. Infrared, nmr, and ultraviolet spectra of α-nitrocyclanones and their potassium salts are reported. Spectral data of the six-, eight-, and ten-membered α-nitrocycloalkanones indicate a high degree of enolization.

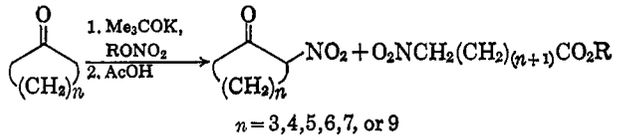
In continuation of our studies of the alkyl nitrate nitration of active methylene compounds,[2] we are now reporting on its application to the preparation of α-mononitro ketones.

Other general methods which have been employed for preparing α-nitro ketones are oxidation of the appropriate nitro alcohols[3] and the reaction between acyl cyanides and alkanenitronates, and of enol acetates or enol ethers with nitryl chloride.[4]

Attempts by Wieland and co-workers to prepare α-nitrocyclopentanone by treating cyclopentanone with ethyl nitrate in the presence of potassium ethoxide led only to the formation of dipotassium 2-ketocyclopentane-1,3-dinitronate; however, with cyclohexanone a low yield of 2-nitrocyclohexanone was obtained in addition to the dinitro compound.[5]

It has now been found that the procedure which led to high yields in the dinitration of ketones[2a] can be readily adapted to their mononitration by employing equivalent amounts of nitrate ester and ketone and a 50% excess of sublimed potassium *t*-butoxide in tetrahydrofuran (THF), and by acidifying the reaction mixture with glacial acetic acid prior to work-up.

However, the reaction did not only lead to α-nitro ketones but also to cleavage products which in the case of cyclic ketones were identified as ω-nitro carboxylic esters. Since it became apparent that the



amount of cleavage reaction was dependent on the structure of the starting ketone, a number of ketones were nitrated and the results are summarized in Table I.

(1) Dow Chemical Corp. Fellow, 1963–1964.

(2) For previous publications, see (a) H. Feuer, J. W. Shepherd, and C. Savides, *J. Am. Chem. Soc.*, **78**, 4364 (1956); (b) H. Feuer and C. Savides, *ibid.*, **81**, 5826 (1959); (c) H. Feuer and B. F. Vincent, Jr., *J. Org. Chem.*, **29**, 939 (1964).

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