(a). The unreacted halide was equal to 4.23 ml. of AgNO$_3$, [b − x]. Substitution into $k = \dfrac{2.303}{b-a} \log \dfrac{a\,[b-x]}{b\,[a-x]}/t$ gave $k = 1.44 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$.

With those runs containing water, 1 ml. of water was added to the 10 ml. of lithium halide–DMF solution in the main body of the reaction flask. Concentrations were corrected for the volume increase. The reaction time for those runs containing water was 60–75 min.

For the extensive study of the rate of reaction of lithium iodide with methyl tosylate, the reaction vessel consisted of two 100-ml. round-bottom flasks joined by a bent adaptor fitted with two $^{24}/_{40}$ standard tapered male joints. Fifty ml. of lithium iodide–DMF solution was placed in one flask and methyl tosylate in the other; 5-ml. aliquots were removed and titrated with AgNO$_3$.

After vacuum transfer of the remainder of the extensive reaction to free it of the nonvolatile salts, the remainder was vapor chromatographed. Only three substances were observed—methyl iodide, DMF, and methyl tosylate. The retention times were identical with those obtained from a synthetic mixture. The yield of methyl iodide was 82% of theoretical.

Preparation of n-Butyl Chloride.—To a solution of lithium chloride (8.2 g., 0.195 mole) in 90 ml. of DMF at room temperature in a 250-ml. erlenmeyer flask, n-butyl iodide (31.0 g., 0.168 mole) was added all at once and stoppered. All of the n-butyl iodide did not dissolve immediately but did so after shaking for 15 min. About this time, evolution of heat was noticed and the flask was cooled in ice for 5 min. and then returned to the air. After an hour the contents were added to 150 g. of ice and the organic phase separated without aid of a solvent, washed with three 10-ml. portions of water, and dried over calcium chloride.

TABLE IV

EXTENSIVE REACTION OF LITHIUM IODIDE WITH METHYL TOSYLATE IN DMF AT 0°

[LiI]$_0$ = 0.1871 M = 8.48 ml.^{a}; [MeTos]$_0$ = 0.3709 M = 16.81 ml.^{a}

t, sec.	[LiI]^a	[MeTos]^a	$10^3 k_{obsd}$, l. mole^{-1} sec.$^{-1}$
0	8.48	16.81	. . .
955	6.94	15.27	0.596
1840	5.98	14.31	.557
3070	4.90	13.23	.548
3880	4.40	12.73	.531
8110	2.48	10.81	.529
10840	1.78	10.11	.528
14470	1.15	9.48	.537
24 hr.	0.00	. . .	
		Av.	0.546

^{a} Concentration in ml. of 0.1096 N AgNO$_3$ per 4.965-ml. aliquot.

The yield of crude n-butyl chloride was 98% (15.0 g., 0.165 mole, n^{25}D 1.4025, lit.^{30} n^{25}D 1.3995). Analysis of the n-butyl chloride by v.p.c. showed n-butyl iodide to be present to an extent less than 1%.

(30) R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949).

The Mechanism of the Barton Reaction[1a]

BY M. AKHTAR[1b] AND M. M. PECHET

A non-"cage," free-radical mechanism for the Barton reaction (Scheme I) has been proposed on the basis of the following experiment. Photolysis of a mixture of the nitrites (N^{15}-III) and (N^{14}-II) followed by rearrangement and oxidation gave a mixture of the ketonitriles VI and VII; the ratio N^{15}:N^{14} in these ketonitriles is 1:1.22 and 1:1.21 (in isooctane), respectively. Evidence for the existence of alkoxy radicals in the photolysis of nitrites is also presented.

Following the discovery by Barton and his co-workers of an intramolecular exchange reaction[2] of the type indicated in Scheme I (X = NO), the principle underlying this reaction has been used in the synthesis of a number of organic molecules hitherto available only with difficulty.[3] The Barton reaction involving the photolysis of a suitably constituted organic nitrite results in an intramolecular exchange of the NO of the nitrite residue with a hydrogen atom attached to a carbon atom in the γ-position. The C-nitroso compounds thus formed can be isolated as the corresponding nitroso dimers or, after isomerization, as the oximes. We report studies relating to the mechanism of this reaction.

Random observations made during the application of the Barton reaction to various syntheses[4] strongly suggested that irradiation of a nitrite A leading to D (Scheme I) involves three discrete steps: first, the photochemical cleavage of the O–N bond to furnish the

alkoxy radical B and NO; second, the intramolecular abstraction of hydrogen to furnish the alkyl radical C; and finally, the combination of C with NO to furnish the product D. Quantum yield studies (ϕ = 0.25)[5] and the nitrite concentration effects indicate that the free-radical reactions are not of a chain nature. The initial photochemical dissociation is illustrated by reaction 1, and the fact that the quantum yield is less than unity[5] is explicable in terms of reversibility of reaction 1. The mechanism of the nitrite photolysis leading to the exchange reaction A → D, (X = NO, Scheme I) involves at least three possibilities.

Mechanism 1.—The two fragments, alkoxy radical and NO, initially formed remain bound within the solvent "cage"[6] until the completion of the exchange reaction, as illustrated in eq. 1 and 2. In this case, the NO group present in the final product D must originate from the NO group present in the parent molecule A.

Mechanism 2.—One may assume that in the reaction A ⇌ B (Scheme I), the reversible recombination of the alkoxy radical and NO takes place after the two species have broken out of their original environment, as illustrated by eq. 3. Then the product D, or its

(1) (a) This is Communication No. 26 from the Research Institute for Medicine and Chemistry. For No. 25 see P. A. Cruickshank and J. C. Sheehan, *Anal. Chem.*, in press; (b) Department of Physiology and Biochemistry, The University of Southampton, Southampton, England.

(2) (a) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *J. Am. Chem. Soc.*, **82**, 2640 (1960); (b) *ibid.*, **83**, 4076 (1961).

(3) (a) D. H. R. Barton and J. M. Beaton, *ibid.*, **83**, 4083 (1961); (b) **84** 199 (1962); (c) M. Akhtar and D. H. R. Barton, *ibid.*, **84**, 1496 (1962); (d) M. Akhtar, D. H. R. Barton, J. M. Beaton, and A. G. Hortmann, *ibid.*, **85**, 1512 (1963).

(4) The intermediacy of alkoxy radicals of the type B in the photolysis of organic nitrites is suggested by an experiment of A. L. Nussbaum, R. Wayne, E. Yuan, O. Zagneetko, and E. P. Oliveto, *ibid.*, **84**, 1070 (1962), and that of alkyl radicals of the type C by a number of rearrangements reported in references 3a, 3b, and 3d and by H. Reimann, A. S. Capomaggi, T. Strauss, E. P. Oliveto, and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 4481 (1961); also, M. Akhtar and D. H. R. Barton, unpublished work.
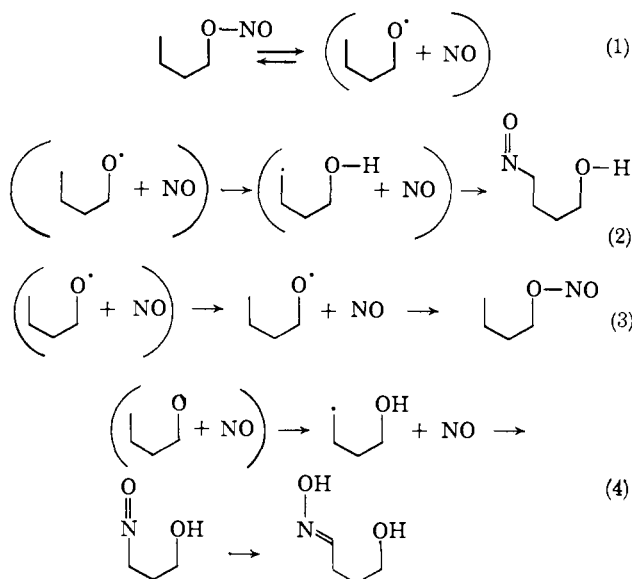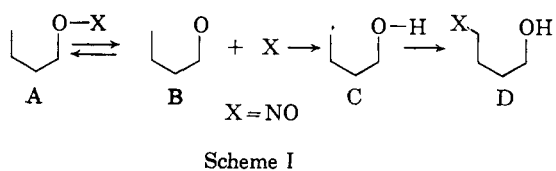
(5) P. Kabasakalian and E. R. Townley, *J. Am. Chem. Soc.*, **84**, 2711 (1962).

(6) J. Frank and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934); R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 2042 (1955), and the references cited therein; R. K. Lyon and D. H. Levy, *ibid.*, **83**, 4290 (1961); L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961); C.–H. S. Wu, G. S. Hammond, and M. Wright, *ibid.*, **82**, 5386 (1960); C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 76; G. A. Russell and R. F. Bridger, *Tetrahedron Letters*, 737 (1963); J. F. Garst and R. S. Cole, *ibid.*, 679 (1963).

equivalent, will correspond to a situation where the over-all reaction has taken place by a non-"cage," free-radical reaction mechanism.

Mechanism 3.—The reversible reaction A ⇌ B (Scheme I) initially conforms to a geminate recombination, as illustrated in eq. 1, but in subsequent stages B → C → D, the partners are separated as illustrated in eq. 4. In this case the end product D, or its equivalent, will not show a "cage" effect, and the net result will be similar to that expected in mechanism 2 (*vide supra*). The experimental evidence to be presented in this paper strongly supports mechanism 3.

The experiments disproving mechanism 1 are: A mixture of two 6β-nitrites (II)[7] (androstane series) and III (cholestane series) differing in their substitution patterns at C_{17} was photolyzed. The nitrite II contained ordinary N in its –O–NO moiety, while the nitrite III contained N^{15} (98.3%) in the nitrite ester group. A mixture of the oximes IV and V was obtained from this photolysis reaction and oxidized to a mixture of the ketonitriles VI and VII with chromium trioxide–pyridine reagent and subjected to mass spectrometric analysis[8] using the pure ketonitriles (VI with N^{14}) and (VII with N^{14}) for comparison.[9]

the reaction solvent shows that the ratio $N^{15}:N^{14}$ (1 : 1.32) in the androstane series (VI) is comparable to that (1 : 1.25) of the cholestane series (VII). Similar results were obtained using isooctane as the solvent; the $N^{15}:N^{14}$ ratios for the nitriles in the androstane series (VI) and in the cholestane series (VII) are 1 : 1.22 and 1 : 1.21, respectively. These results indicate that in the conversion from A to D free radicals are involved and that the over-all process does not take place within a solvent "cage."

These results eliminate mechanism 1 and also any other mechanism using a direct bond-switching process to explain the Barton reaction; however, they do not permit a choice between mechanisms 2 and 3. To distinguish between these latter mechanisms, we have photolyzed a mixture of N^{14}-nitrite VIII in the pregnane series and N^{15}-nitrite III in the cholestane series to half-completion to determine the degree of scrambling in the reversible step A ⇌ B. The mixture of nitroso dimers thus obtained was rearranged into a mixture of oximes. The pure oxime V, which was obtained from the reaction mixture by chromatography, was further oxidized to the ketonitrile VII. Mass spectrometric

A   B   X = NO   C   D

Scheme I

(1)

(2)

(3)

(4)

The results of two photolysis experiments carried out in toluene and in isooctane are shown in Table I. Although N^{15} was originally present in the nitrite III, analysis of the mixture of ketonitriles using toluene as
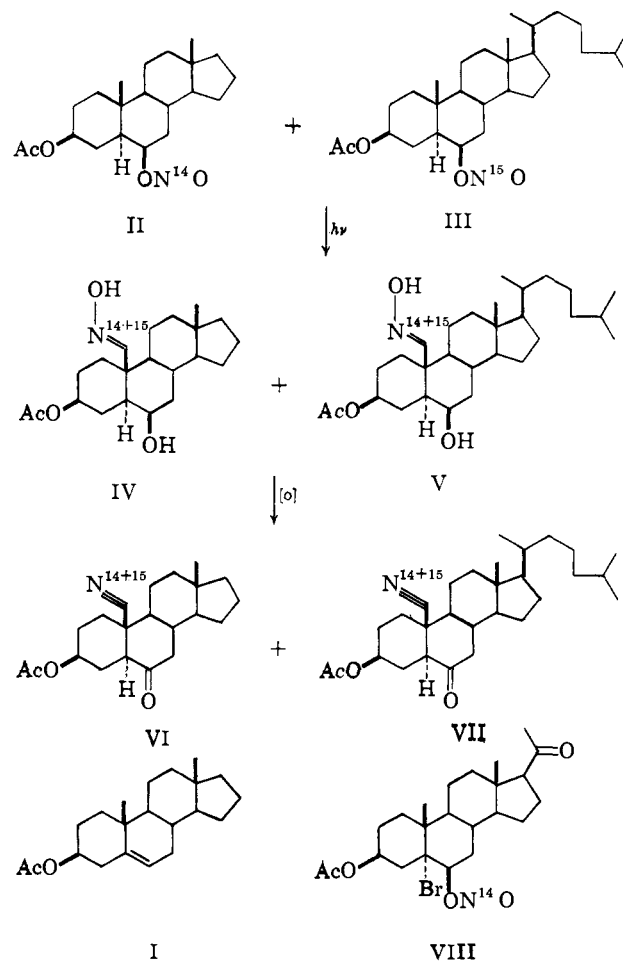

II   III

IV   V

VI   VII

I   VIII

analysis of the ketonitrile VII showed the ratio of $N^{15}:N^{14}$ as 1.15 : 1.00.[10] The mother liquor from the above partial photolysis was chromatographed on alumina to afford a pure sample of the unchanged nitrite III which, following further photolysis and con-

(7) A synthetic sequence leading to the nitrite II from Δ⁵-3β-acetoxy-androstane (I) is described in the Experimental section.

(8) Full details on the mass spectrometric aspects of this problem will be published separately by Prof. K. Biemann and Dr. A. L. Burlingame; also see K. Biemann, "Mass Spectrometry," McGraw–Hill Series in Advanced Chemistry, 1962, p. 312.

(9) Mass spectrometric analysis of the pure ketonitrile (VI, with N^{14}) shows a strong M-60 peak due to loss of acetic acid at m/e 283, accompanied by an isotope peak at m/e 284. The pure ketonitrile (VII, containing N^{14}) shows a strong M-60 peak (loss of acetic acid) at m/e 395 and the expected isotope peak at m/e 396. The corresponding N^{15}-ketonitriles in the androstane and cholesterol series have the M-60 peaks at m/e 284 and 396, respectively. In the ketonitriles V and VII containing a mixture of N^{14} and N^{15}, the peaks at m/e 284 and 396 contain a substantial contribution from the isotope peaks corresponding to m/e 283 and 395. In evaluating the amount of N^{15} in the mixture, the contribution of these isotope peaks has been subtracted by a simple mathematical calculation.

(10) There is a lesser degree of scrambling in the pair N^{14}-VIII and N^{15}-III as compared with the pair N^{14}-II and N^{15}-III. This may be due to the presence of the 5α-bromine substituent in the nitrite VIII which alters its rate of decomposition. Although N^{14}-II and N^{15}-III would appear to be a better pair for the experiment, nevertheless, the separation of the pure nitrite using this pair is very difficult. Since the relative ratio of $N^{15}:N^{14}$ is the determinative factor, the use of the pair N^{14}-VIII and N^{15}-III suffices.

TABLE I

	Nitrites photolyzed	Solvent, temp., °C.	Ratio of N^{15}:N^{14} in the ketonitriles
1	N^{14}-II + N^{15}-III[a]	Toluene, 4	VI, 1.0:1.32; VII, 1.0:1.25[b]
2	N^{14}-II + N^{15}-III	Isooctane, 30	VI, 1.0:1.22; VII, 1.0:1.21[b]
3a	N^{14}-VIII (1.0 mole)		
	N^{15}-III (1.0 mole)	Toluene, 4	VII, 1.0:0.87
3b	Photolysis of the nitrite III recovd. after half reacn. time from expt. 3a	Isooctane, 30	VII, 1.0:0.00
4	N^{14}-t-butyl nitrite (8.5 moles) + N^{15}-III (1.0 mole)	Carbon tetrachloride, 30	VII, 1.0:3.45

[a] The N^{15}-nitrite III used in this study contained 98% of its nitrogen as N^{15}.   [b] Assuming 100% chemically pure for the two nitrites II and III for complete scrambling, the expected ratio of N^{15}:N^{14} in experiments 1 and 2 would have been 1.0:1.05 and 1.0:1.08, respectively.   It is noteworthy that the N^{15}-nitrite III was prepared by a method (see Experimental section) which, though very convenient for introducing N^{15}, does suffer from the disadvantage that the nitrites thus prepared are slightly contaminated with the starting alcohols.

version into the ketonitrile VII, gave a ratio of N^{15}:N^{14} as 1.00:0.00.

These results indicate that in the photolysis of nitrites involving a transformation of the type A → D, the initial reversible reaction A ⇄ B resulting in the formation of the nitrite from alkoxy radical and NO proceeds via geminate recombination.   Therefore, it is apparent that non-"cage" collisions occur only in the subsequent stages of the reaction.   These experiments provide evidence for mechanism 3 as an explanation of the Barton reaction.   It should be emphasized that N^{15} experiments do not eliminate a free-radical chain mechanism.   Such a mechanism is excluded on the basis of quantum yield studies [1] (vide supra).

Though in the normal photochemical transformation of a nitrite A into D the initial reversible step A ⇄ B does not result in any significant non-"cage" collisions, this situation can be changed under forcing conditions. During our studies on the photochemistry of organic nitrites, it was observed that the addition of t-butyl nitrite to a nitrite photolysis reaction (for example, photolysis of III) strongly inhibits its conversion to the corresponding oxime.   The addition of t-butyl nitrite results in an excess of NO in the reaction mixture, and consequently the reversible reaction A ⇄ B becomes the main path for consuming alkoxy radicals.   When the N^{15}-nitrite III was photolyzed in carbon tetrachloride in the presence of an excess of N^{14}-t-butyl nitrite for 12 min., the starting nitrite III could be recovered in high yield.   This nitrite, after photolysis and conversion into the ketonitrile VII, showed a very high incorporation of N^{14}.   The N^{15}:N^{14} ratio was 1.0:3.45 (see Experimental section and Table I).   This experiment provides evidence in support of the existence of alkoxy radicals in the photolysis of organic nitrites.[12]

In conclusion, the Barton reaction is best explained in terms of a mechanism involving a non-"cage," free-radical process.   The possibility that scrambling might have occurred in the initial reversible step A ⇄ B has been eliminated.   Under special "forcing conditions" the existence of alkoxy-free radicals in the photolysis of organic nitrites can be demonstrated.

Experimental

Microanalyses were performed by Dr. Alfred Bernhardt, Max Planck Institute, Mulheim (Ruhr), Germany.   Infrared spectra were determined using an Infracord Model 137 spectrophotometer; melting points were taken on a Kofler-type hot stage. Merck acid-washed alumina was used for all chromatograms unless otherwise specified.

3β-Acetoxy-Δ⁵,⁶-androstene.—Dehydroepiandrosterone (20 g.) in ethylene glycol (400 cc.), KOH (40 g.), and hydrazine (9.6 cc.) at 200° for 16 hr. by the method of Huang-Minlon gave 3β-

(11) From a mechanistic viewpoint another important feature of the Barton reaction is the intramolecular hydrogen abstraction step (B → C). This is discussed by P. Kabasakalian, E. R. Townley, and M. D. Yudis, J. Am. Chem. Soc., 84, 2716 (1962); also see E. J. Corey and W. R. Hertler, ibid., 82, 1657 (1960); S. Wawzonek and T. P. Culbertson, ibid., 81, 3367 (1959); C. Walling and A. Padwa, ibid., 85, 1597 (1963).

(12) Also see G. R. McMillan, ibid., 84, 4007 (1962), and references cited therein; A. L. Nussbaum and C. H. Robinson, Tetrahedron, 17, 35 (1962).

hydroxy-Δ⁵,⁶-androstene, which on acetylation furnished the 3-acetate (17.8 g.), m.p. 98–102° (lit.[13] m.p. 91–93°).

3β-Acetoxy-6-nitro-Δ⁵,⁶-androstene.—The preceding acetate (17.8 g.) in nitric acid (370 cc.) was treated during 1 hr. with sodium nitrite (13.1 g.).   Stirring was continued for 10 min. The reaction mixture was cooled, diluted with cold water, and extracted with ether–petroleum ether, 1:1, and worked up as usual.   Crystallization from methylene chloride–methanol gave the 6-nitro compound (5.4 g.), m.p. 152–161°; after recrystallization, m.p. 158–160.5°, $[\alpha]^{21}$D − 123° (CHCl₃, c 1.702).

Anal.   Calcd. for $C_{21}H_{31}O_4N$: C, 69.77; H, 8.64; O, 17.70; N, 3.88.   Found: C, 69.68; H, 8.91; O, 17.87; N, 3.99.

3β-Acetoxy-6β-hydroxyandrostane.—A solution of the preceding nitro compound (5.2 g.) in acetic acid (120 cc.) and water (12 cc.) was treated with zinc dust during 1.5 hr.   The reaction was worked up to yield the 6-ketone (4.08 g.), m.p. 105–114°; after recrystallization from methylene chloride–methanol, m.p. 115–118°, $[\alpha]^{22}$D −51.3° (CHCl₃, c 1.21).

Anal.   Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70; O, 14.44. Found: C, 75.46; H, 9.62; O, 14.79.

The latter (4.08 g.) in methanol (100 cc.) was cooled to 10° and was carefully treated with sodium borohydride (1.5 g.).   After 45 min. the reaction mixture was worked up as usual.   Chromatography of the residue on acid-washed alumina, followed by crystallization from ether–hexane, gave the 6β-alcohol (2.2 g.), m.p. 130.5–132.5°, $[\alpha]^{21}$D −37.5° (CHCl₃, c 1.537).

Anal.   Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25; O, 14.35. Found: C, 75.32; H, 10.15; O, 14.61.

3β-Acetoxyandrostan-6β-yl Nitrite (II).—The preceding alcohol (600 mg.) in pyridine (10 cc.) at 0° was treated with an excess of nitrosyl chloride and worked up as usual.   Crystallization from methylene chloride–hexane gave the 6β-nitrite II (500 mg.), m.p. 135–138°, $[\alpha]^{28}$D −63.3° (CHCl₃, c 1.07).

Anal.   Calcd. for $C_{21}H_{33}O_4N$: C, 69.39; H, 9.15; O, 17.61; N, 3.85.   Found: C, 69.77; H, 9.39; O, 17.20; N, 3.80.

Photolysis of the Preceding Nitrite and Its Conversion to 3β-Acetoxy-19-nitriloandrostan-6-one.—The preceding nitrite (70 mg.) in toluene (2 cc.) was photolyzed in a Pyrex test tube at 4° using a 200-w. Hanovia high-pressure mercury arc lamp.   After 15 min. the nitroso dimer was filtered off and washed with toluene. The dimer was refluxed in isopropyl alcohol (5 cc.) for 1 hr. Evaporation of the solvent furnished a noncrystalline oxime. The latter in pyridine (2 cc.) was treated with chromium trioxide (200 mg.) in pyridine (7 cc.) at room temperature overnight and worked up as usual.   Crystallization from methylene chloride–methanol gave the nitrile (25 mg.), m.p. 230–236°, $[\alpha]^{25.5}$D −54.3° (CHCl₃, c 0.6525).

Anal.   Calcd. for $C_{21}H_{29}O_3N$: C, 73.43; H, 8.51; O, 13.98; N, 4.08.   Found: C, 73.22; H, 8.45; O, 14.07; N, 4.35.

3β-Acetoxy-19-nitrilocholestan-6-one was prepared by the oxidation of the corresponding oxime[2b] (500 mg.) in pyridine (10 cc.) with chromium trioxide (1 g.) in pyridine (10 cc.) at room temperature overnight, as described in the preceding experiment. Crystallization from methylene chloride–methanol gave the nitrile (320 mg.), m.p. 241–244°, $[\alpha]^{24}$D −25° (CHCl₃, c 0.974).

Anal.   Calcd. for $C_{29}H_{45}O_3N$: C, 76.43; H, 9.95; O, 10.53; N, 3.07.   Found: C, 76.37; H, 9.77; O, 10.64; N, 3.18.

3β-Acetoxycholestan-6β-yl Nitrite (N^{15}-III).—The alcohol (110 mg.) in hot acetic acid (2.5 cc.) was treated with $KN^{15}O_2$ (60 mg.; N^{15}, 98%; KNO_2, 85%) at 50° for 20 sec.   The reaction was then diluted with water (0.2 cc.) and the resulting crystalline nitrite filtered, washed successively with water, aqueous sodium bicarbonate, and water, and dried.   This gave 90 mg., m.p. 144–149°.

Photolysis of the Nitrites II and III in Toluene at 4°.—A solution of the nitrites II (54 mg., 0.149 mole) and III (70 mg., 0.147 mole; N^{15}, 98%) in toluene (1.6 cc.) was irradiated at 4° with a

(13) A. Butenandt and L. A. Suranyi, Ber., 75B, 591 (1942).

200-w. Hanovia lamp for 15 min. The resulting mixture of nitroso dimers was removed by filtration and converted into the mixture of ketonitriles VI and VII, as described before. Crystallization from methylene chloride–hexane gave 21 mg. Mass spectrometric analysis showed $N^{15}:N^{14}$ 1:1.32 and 1:1.25 in the ketonitriles VI and VIII, respectively.

Photolysis of the Nitrites N^{14}-II and N^{15}-III in Isooctane at 30°.—A solution of the nitrites II (27 mg., 0.0743 mole) and III (m.p. 151–153° recrystallized, 24 mg., 0.0713 mole; N^{15}, 98%) in isooctane was photolyzed and treated as above to yield a mixture of ketonitriles VI and VII; 6.7 mg. Mass spectrometric analysis showed $N^{15}:N^{14}$ 1:1.22 and 1:1.21 in the ketonitriles VI and VII, respectively.

Photolysis of Mixed Nitrites N^{15}-III and N^{14}-VIII.—A mixture of 3β-acetoxy-6β-hydroxycholestane N^{15}-nitrite (III) (122.3 mg.) and 3β-acetoxy-6β-hydroxy-5α-bromo-pregnan-20-one N^{14}-nitrite (VIII) (124.6 mg.) in anhydrous toluene (2.8 ml.) was photolyzed for 10 min. at 5° using the 200-w. lamp. The precipitate (42 mg.) was filtered and treated as described below; the mother liquors were diluted with hexane (3 ml.) and chromatographed on Florisil (5 g.) to give the nitrite III (51.2 mg.), m.p. 150–152°.

The precipitate (42 mg.) was heated to reflux with isopropyl alcohol (4 ml.), evaporated to dryness, dissolved in benzene, and chromatographed on acid-washed alumina (800 mg.) to give, with 1% methanol in methylene chloride, the oxime V, which was oxidized with pyridine (7 ml.) and chromium trioxide (350 mg.) at room temperature overnight. Addition of water, extraction with ether, and crystallization from methanol–methylene chloride gave the nitrile VII (11 mg.), which on mass spectrometric analysis showed $N^{15}:N^{14}$ as 1.00:0.87.

The recovered nitrite III (51.2 mg.) in isooctane (3 ml.) was photolyzed for 25 min. at room temperature using a 200-w. lamp. The precipitate was rearranged and oxidized as above to give the ketonitrile VII (14 mg.), which on mass spectrometric analysis showed $N^{15}:N^{14}$ as 1.0:0.0.

Photolysis of the Nitrite N^{15}-III and N^{14}-t-Butyl Nitrite.—3β-Acetoxycholestan 6β-yl nitrite-N^{15} (75 mg.) and t-butyl nitrite (0.15 cc.) in carbon tetrachloride (4 cc.) were photolyzed for 12 min. using the 200-w. lamp. Solvent was then removed, and the residue was crystallized from ether–methanol to yield 3β-acetoxycholestan-6β-yl nitrite (45 mg.).

This nitrite was dissolved in a mixture of toluene (1 cc.) and isooctane (3 cc.) and photolyzed for 15 min. using the 200-w. lamp. The resulting precipitate was filtered, rearranged to the oxime with isopropyl alcohol as usual, and then oxidized to the corresponding ketonitrile VII (7 mg.). Mass spectrometric analysis showed ratio of $N^{15}:N^{14}$ as 1:3.45.

Appendix

Table II

Analytical Data

		m/e	Intensity
N^{14}-Ketonitrile VI	M-60 peak	282	5.6
		283	100
	Isotope peak for M-60 peak	284	24.1
N^{14}-Ketonitrile VII	M-60 peak	395	100
	Isotope peak for M-60 peak	396	31
Expt. 2 (see Table I)			
Analysis of the mixture Androstane series	Isooctane solvent, temp. 30°	282	8
	M-60 N^{14}	283	131
	M-60 N^{15} + isotope peak for m/e 283	284	134
	Isotope peak for m/e 284	285	24

Ratio of $N^{15}:N^{14}$

Intens. of M-60 peak for N^{15} cmpd. $= 134 - \dfrac{24.1 \times 131}{100} = 102.43$

Intens. of M-60 peak for N^{14} cmpd. $= 131 - \dfrac{102.43 \times 5.6}{100} = 125.27$

Ratio of $N^{15}:N^{14}$ = 102.43:125.27 = 1:1.22

Cholestane series	Isooctane solvent temp. 30°		
	M-60 peak N^{14}	395	88
	M-60 peak for N^{15} cmpd. + isotope peak for m/e 395	396	100
	Isotope peak N^{15}	397	26

Intens. of M-60 peak for N^{15} cmpd. $= 100 - \dfrac{31 \times 88}{100} = 72.72$

Ratio of $N^{15}:N^{14}$ = 72.72:88 = 1:1.21

Expt. 1 (see Table I)

Analysis of the mixture Androstane series	Toluene solvent temp. 4°	282	6.5
	M-60 N^{14}	283	100
	M-60 peak for N^{15} cmpd. + isotope peak for m/e 283	284	97
	Isotope peak for N^{15}	285	21.6

Ratio of $N^{15}:N^{14}$

Intens. of M-60 peak for N^{15} cmpd. $= 97 - \dfrac{24.1 \times 100}{100} = 72.9$

Intens. of M-60 peak for N^{14} cmpd. $= 100 - \dfrac{72.9 \times 5.6}{100} = 95.92$

Ratio of $N^{15}:N^{14}$ = 72.9:95.92 = 1:1.32

Cholestane series	Toluene solvent temp. 4°		
	M-60 N^{14}	395	90
	M-60 peak for N^{15} cmpd. + isotope peak for m/e 395	396	100
	Isotope peak	397	26

Ratio of $N^{15}:N^{14}$

Intens. of M-60 peak for N^{15} cmpd. $= 100 - \dfrac{31 \times 90}{100} = 72.1$

Ratio of $N^{15}:N^{14}$ = 72.1:90 = 1:1.25

Expt. 3 (see Table I)

(a) Photolysis of N^{15}-III (1.0 mole) and N^{14}-VIII (1.0 mole) to half-completion, isolation of the oxime V corresponding to III and its conversion to the ketonitrile VII

	M-60 peak for N^{14} cmpd.	395	100
	M-60 peak for N^{15} cmpd. + isotope peak for m/e 395	396	145
	Isotope peak	397	45

Ratio of $N^{15}:N^{14}$ = 114:100 = 1:0.87

(b) Photolysis of the nitrite (III) recovd. from the above expt. and its conversion to the ketonitrile VII

	M-60 peak for N^{14} cmpd.	395	2
	M-60 peak for N^{15} cmpd. + isotope peak for m/e 395	396	100
	Isotope peak	397	30

Ratio of $N^{15}:N^{14}$ = 1:0.0

Expt. 4 (see Table I)

Photolysis of N^{15}-III (1 mole) and N^{14}-t-butyl nitrite (8.5 moles), recovery of the nitrite III and its conversion to VII

	M-60 peak for N^{14} cmpd.	395	100
	M-60 peak for N^{15} cmpd. + isotope peak for m/e 395	396	60
	Isotope peak	397	12.5

Ratio of $N^{15}:N^{14}$ = 29:100 is 1:3.45