New Furoxan Chemistry. 1. Synthesis of Diacylfuroxans by Reaction of Ethynyl Acetates with Nitrosyl Fluoride/Nitrosonium Tetrafluoroborate†

David R. Brittelli* and George A. Boswell, Jr.

Central Research and Development Department, E. I. du Pont de Nemours and Co., Wilmington, Delaware 19898

Received July 25, 1980

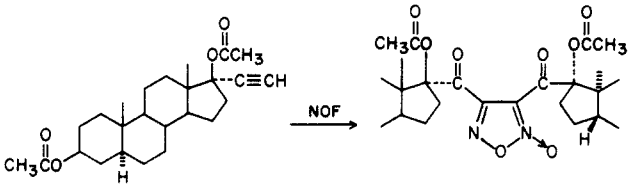
The reaction of α-ethynyl acetates with $NOF/NOBF_4$ yields 3,4-bis[(acetoxycycloalkyl)carbonyl]furoxans. The presence of the α-acetoxy substituent is necessary for the reaction to proceed. The course of the reaction is rationalized by invoking the intermediacy of a nitroacetylene, which dimerizes with rearrangement to afford the observed product.

The reaction of nitrosyl fluoride (NOF) with olefins leads to nitroso fluoride dimers or with olefins in which nitroso dimer formation is sterically prohibitive to α-fluoro nitrimines (1). Hydrolysis of the nitrimine function by chromatography on alumina completes a convenient synthesis of α-fluoro ketones **2** (Scheme I).[1]

The reaction of NOF with simple terminal acetylenes, on the other hand, leads to a complex mixture of products. In this report we describe the profound effect on the course of this reaction produced by the presence of an α-acetoxy substituent.

Results and Discussion

When 17α-ethynyl-5α-androstane-3β,17β-diol diacetate (**3**) was treated with excess NOF in CH_2Cl_2 at 20 °C and



3 **4**

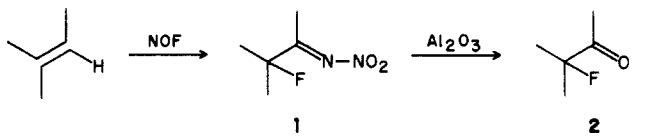
the mixture stirred several hours, a crystalline product, **4**, was obtained which analyzed for $C_{25}H_{35}NO_6$, i.e., addition of the elements of NO_2 to and loss of a proton from the starting material.

The infrared spectrum no longer displayed ethynyl hydrogen or C≡C bands but did have the acetate carbonyl and a new intense peak at 1613 cm^{-1}. Molecular weight determination by mass spectrometry also indicated the $C_{25}H_{35}NO_6$ (*m/e* 445) composition for the product. Other molecular weight determinations (cryoscopic in benzene and ebullioscopic in dichloroethane) gave molecular weights of 983 and 937, respectively, pointing to a dimer of $C_{25}H_{35}NO_6$. The ^1H NMR spectrum at 60 MHz showed two peaks of equal intensity at 62.0 and 64.5 Hz, indicative of two different C-18 angular methyl groups, and two peaks of unequal intensity (approximately 3:1) at 119.4 and 120.4 Hz, indicative of different acetate methyl groups.

These data are explicable on the basis of the furoxan structure **4** in which the C-18 angular methyl and 17β-acetate methyl groups become magnetically nonequivalent because of the asymmetry of the furoxan ring.[2]

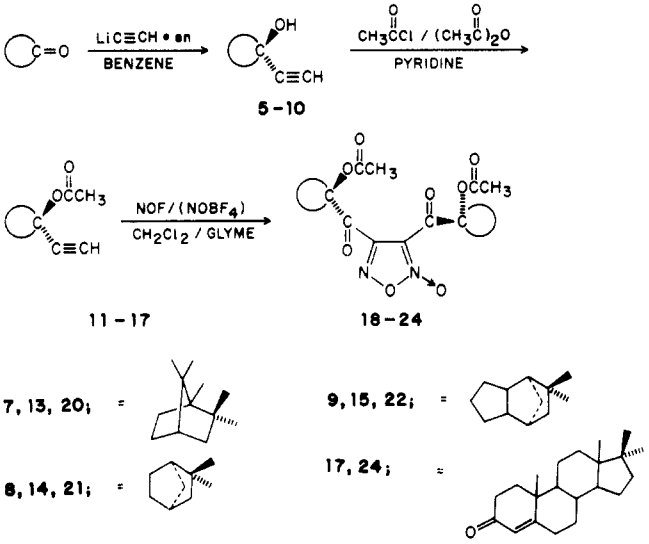
The IR and UV data are also characteristic of diacyl furoxans,[3,4] e.g., 3,4-diacetylfuroxan, which was reported[5] to have a strong band at 1605 cm^{-1} (furoxan ring) and a maximum in the UV at 275 nm (log ε 3.62).

Scheme I



1 **2**

Scheme II



5-10 **11-17** **18-24**

Further structural proof is the thermal reversion of the furoxan to two molecules of a β-acetoxy-α-oxo nitrile oxide, which can be trapped in situ with dipolarophiles as described in the following paper.

The generality of this novel acetylene-to-diacylfuroxan transformation was illustrated by preparation of several other 3,4-bis[(acetoxycycloalkyl)carbonyl]furoxans from cyclic ketones in the three-step synthesis summarized in Scheme II.

Starting cyclic ketones were ethynylated by using the commericially available lithium acetylide–ethylenediamine complex.[6] The stereochemistries of the ethynyl alcohols obtained from disymmetric ketones were assigned as de-

† Contribution No. 2808 from the Central Research and Development Department.

(1) G. A. Boswell, Jr., *J. Org. Chem.*, **33**, 3699 (1968).
(2) The ^1H NMR spectrum at 100 MHz confirmed that these were methyl groups having different chemical shifts rather than methyl resonances split due to spin–spin coupling.
(3) N. E. Boyer, G. M. Czerniak, H. S. Gutowsky, and H. R. Snyder, *J. Am. Chem. Soc.*, **77**, 4238 (1955).
(4) J. H. Boyer, G. A. Storer, and V. Toggweiler, *J. Am. Chem. Soc.*, **79**, 1748 (1957).
(5) L. I. Peterson, *Tetrahedron Lett.*, 1727 (1966).
(6) Available from Foote Mineral Co.

0022-3263/81/1946-0312$01.00/0

Table I

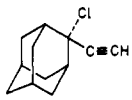
starting ketone	ethynyl alcohol	yield, %	ethynyl acetate	yield, %	furoxan	yield, %
adamantan-2-one	5	80	11	88	18	78
cyclohexanone	6[a]		12	85	19	53
d-(+)-camphor	7[b]		13	97[c]	20	44
bicyclo[2.2.1]heptan-2-one	8[b]		14	70[d]	21	39
tricyclo[5.2.1.$0^{2,6}$]decan-8-one	9	98	15	81	22	85
3-cholestanone	10	43 (β-OH)	16	51	23	62
testosterone			17		24	49

[a] Commercially available. [b] Not isolated. [c] From camphor. [d] From the ketone.

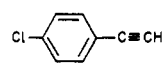
picted in Scheme II by several methods. The alcohol function of the product 7 obtained by ethynylation of *d*-(+)-camphor was shown to be exo by the nuclear Overhauser technique applied to the derived acetate 13; irradiation at the frequency of the acetate methyl absorption gave an enhancement of the signal strength in *two* of the absorptions of the methyl groups attached to the camphor ring. Ethynyl groups in the alcohols produced by ethynylation of bicyclo[2.2.1]heptane-2-one and tricyclo[5.2.1.$0^{2,6}$]decan-8-one (alcohols 8 and 9, respectively) were assumed to be exo from the known propensity of reagents to add to these systems from the less-hindered β face. The ethynylation of 3-cholestanone yielded a mixture of α and β alcohols. These were separated by fractional crystallization. The major isomer, which was then carried through the remainder of the sequence, was found to be the β alcohol 10 by virtue of the higher (1040 cm^{-1}) IR carbon–oxygen stretching absorption.[7] Acetate 17 derived from testosterone is well-known to be the β-substituted isomer.

The product ethynyl alcohols were routinely acetylated by an acetyl chloride/acetic anhydride/pyridine treatment. The resulting ethynyl acetates were converted to furoxans in improved yields through the agency of NOF/$NOBF_4$; $NOBF_4$ had previously been found to improve the conversion of olefins to α-fluoro nitrimines.[8] Yields for the conversion of several cyclic ketones to the corresponding furoxan derivatives via this sequence are tabulated in Table I.

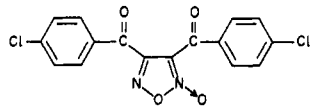
The course of the reaction with other terminal acetylenes proved fruitless. Reaction of 2-chloro-2-ethynyladamantane (25) with NOF/$NOBF_4$ resulted in recovery of starting material unchanged.



25



26



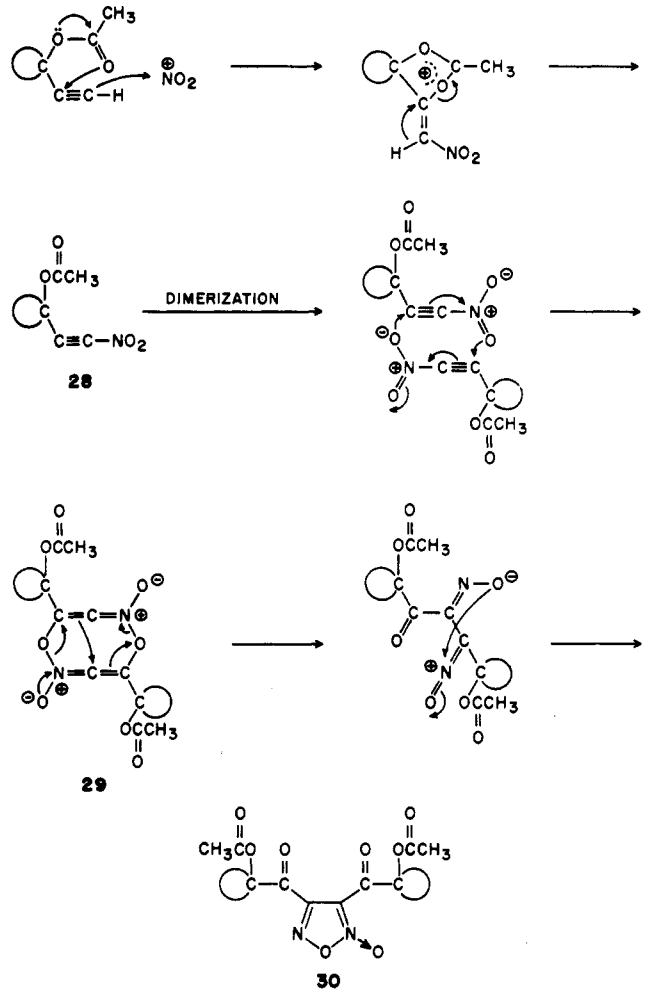
27

Similar results were obtained with *p*-chlorophenylacetylene (26); only a small percentage of the starting acetylene was consumed. Comparison of the reaction mixture from 26 and NOF/$NOBF_4$ with an authentic sample of furoxan 27[9] showed no detectable formation of the expected 27.

These results indicate that the α-acetoxy group plays an active role in this reaction. Although no mechanistic studies have been done, the following rationalization of the observed results can be offered (Scheme III).

With activation by the α-acetoxy group, the acetylenic moiety attacks a nitronium ion; NO_2^+ is known to be readily formed by reaction of NOF with glass, etc.[10]

Scheme III



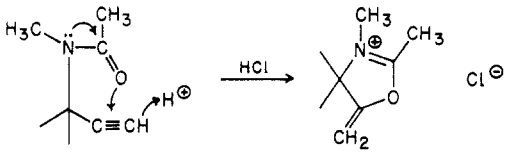
28

29

30

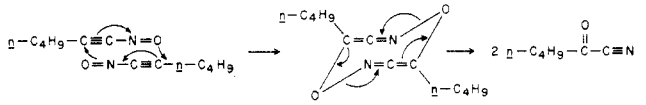
Consistent with this hypothesis is the conversion of ethynyl acetate 11 to 18 in 89% yield by treatment with NO_2BF_4; the scope of this interesting observation is currently under investigation. There is ample precedent for participation of acyl groups in such nucleophilic reactions of terminal acetylenes.[11-13] For example, Easton and co-workers[11] found that the acetamide 31 reacted with HCl in just such a fashion to afford a product comparable to the postulated intermediate.

(7) R. N. Jones and G. Roberts, *J. Am. Chem. Soc.*, 80, 6121 (1958).
(8) W. C. Ripka (to Du Pont), U.S. Patent 3641006 (1972).
(9) N. E. Boyer and H. R. Snyder, *J. Am. Chem. Soc.*, 77, 4233 (1955).
(10) R. Schmutzler, *Angew. Chem., Int. Ed. Engl.*, 7, 440 (1968). In many cases chemistry derived from NO_2^+ is observed in NOF reactions. It is a consistent observation that NOF bubbled into CCl_4, CH_2Cl_2, or glyme initially produces a blue color (attributable to NO) which when the mixture is allowed to stand gives rise to the characteristic brown fumes of NO_2.
(11) N. R. Easton, D. R. Cassady, and R. D. Dillard, *J. Org. Chem.*, 27, 2927 (1962).
(12) K. Sisido, K. Hukuoka, M. Tuda, and H. Nozaki, *J. Org. Chem.*, 27, 2663 (1962).
(13) E. Farkas and J. A. Swallow, *J. Med. Chem.*, 7, 739 (1964).



31

Loss of a proton from the initial adduct would yield a nitroacetylene, **28**.[14] Dimerization of the nitroacetylene, again possibly with participation of the neighboring α-acetoxy group, would lead to the cyclic dimer **29**, rearrangement of which leads to the observed product furoxan **30**. Just such an intermediate as **29** was invoked by Tedder[15] to account for the formation of butyryl cyanide from nitrosohexyne, viz.:



An analogous breakdown of **29** would lead to two molecules of the β-acetoxy-α-oxo nitrile oxide. Attempts to detect an intermediate nitrile oxide by trapping with dipolarophiles have been unsuccessful; thus it is proposed that the dimer rearranges directly to furoxan rather than splits into two nitrile oxides, recombination of which could yield the furoxan.

Thermal reversion of bis[(acetoxycycloalkyl)carbonyl]-furoxans to acyl nitrile oxides at elevated temperatures has been found and is the subject of the next paper in this series.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded in KBr disks or neat by using a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were taken in absolute ethanol by using a Cary 14 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as the internal reference.

Preparation of Ethynyl Alcohols. General Procedure. Ketones were routinely converted to ethynyl alcohols by the following modification of the method of Beumel and Harris.[16] To 20.05 g (0.22 mol) of lithium acetylide–ethylenediamine complex[6] in a 500-mL flask with acetylene flowing through at a moderate rate was added dropwise over the period of 0.5 h a solution of 0.20 mol of the appropriate ketone in 500 mL of benzene, rapid stirring being initiated after 100 mL of solution had been added. The mixture was heated at 55 °C for 18 h after the addition was complete and then poured into 250 mL of 5% aqueous NaCl solution. The resulting mixture was extracted with two 250-mL portions of ether, the combined organic layers were dried ($MgSO_4$), and the solvent was removed in vacuo to afford the crude alcohol.

2-Ethynyl-2-hydroxyadamantane (5). From 20.05 g of the lithium acetylide complex and 30 g of 2-adamantanone there was obtained 28.2 g (80%) of **5** after crystallization of the crude product from pentane at −78 °C: mp 104.5–106 °C; ν_{max} ($CHCl_3$) 3580, 3540, 3300, 2100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.4–2.3 (m, 14 H, ring H), 2.50 (s, 1 H, OH), 2.52 (s, 1 H, C≡CH).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.71; H, 9.15.

2α-Ethynyl-2β-hydroxybornane (7). From 15 g of the acetylide complex and 23 g of camphor there was obtained 27.0 g (100%) of product: mp 63.5–64.5 °C (from pentane); ν_{max} ($CHCl_3$) 3600, 3300, 2100 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.87 (s, 3 H, CH_3), 0.93 (s, 3 H, CH_3), 1.05 (s, 3 H, CH_3), 1.2–2.2 (br m, 7 H, bornyl ring H), 2.50 (s, 1 H, OH), 2.54 (s, 1 H, C≡H).

Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.05; H, 10.39.

8β-Ethynyl-8α-hydroxytricyclo[5.2.1.0^{2,6}]decane (9). Reaction of 20.05 g of the acetylide complex with 30 g of 8-oxotricyclo[5.2.1.0^{2,6}]decane yielded 34.7 g (98%) of **9**: mp 108.5–109 °C (from pentane): ν_{max} ($CHCl_3$) 3600, 3400, 3300, 2100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.8–2.8 (br m, 14 H, tricyclodecane ring H), 2.05 (s, 1 H, OH), 2.47 (s, 1 H, C≡CH).

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.54; H, 9.17.

3α-Ethynyl-3β-cholestanol (10). From 18.8 g of 3-cholestanone[17] and 7.5 g of lithium acetylide–ethylenediamine complex there was obtained 19.9 g (99%) of a mixture of α and β alcohols. Fractional crystallization from ethanol–methanol yielded 8.6 g (43%) of **10**: mp 164–165 °C (lit.[18] mp 167 °C); ν_{max} ($CHCl_3$) 3650, 3300, 2100, 1040 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.67 (s, 3 H, 18-CH_3), 0.8–2.2 (br m, 31, steroid ring and side-chain H), 0.89 (d, J = 7 Hz, 9 H, 21-, 26-, and 27-CH_3), 2.32 (s, 1 H, OH), 2.50 (s, 1 H, C≡CH).

Preparation of Ethynyl Acetates. General Procedure. Ethynyl alcohols were routinely acetylated by the following method. To 0.184 mol of the ethynyl alcohol were added 15 mL of acetic anhydride, 15 mL of pyridine, and 8 mL of acetyl chloride (in that order). The mixture was heated under reflux for 1.0 h, poured into a suspension of 100 g of ice in 400 mL of acetone, and stirred for 2.0 h. The resulting solution was diluted with 200 mL of water and extracted with two 300-mL portions of ether. The combined ethereal extracts were dried ($MgSO_4$) and evaporated in vacuo to yield the crude ethynyl acetates.

2-Ethynyl-2-acetoxyadamantane (11). From 52.8 g of **5** there was obtained 57.47 g (88%) of **11** after recrystallization from pentane at −78 °C: mp 65.5–67 °C; ν_{max} ($CHCl_3$) 3300, 2100, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.65 (s, 1 H, C≡CH), 2.05 (s, 3 H, $OCOCH_3$), 1.4–2.6 (br m, 14, adamantane ring H).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.77; H, 8.34.

2-Ethynyl-2-acetoxycyclohexane (12). From 124 g of **6** (Air Reduction Co.) there was obtained 141.6 g (85.5%) of **12**: bp 90 °C (12 mm); n^{20}_D 1.4632 (lit.[19] n^{20}_D 1.4635); ν_{max} (liquid film) 3300, 2100, 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.7 (br m, 10 H, ring H), 1.97 (s, 3 H, $OCOCH_3$), 2.75 (s, 1 H, C≡CH).

2α-Ethynyl-2β-acetoxybornane (13). From 29.6 g of **7** there was obtained 32.9 g (97%) of **13**: bp 80 °C (0.2 mm); ν_{max} (liquid film) 3300, 2100, 1740; ^{1}H NMR $CDCl_3$) δ 0.8–2.5 (br m, 9 H, ring H), 0.87 (s, 3 H, CH_3), 0.90 (s, 3 H, CH_3), 1.00 (s, 3 H, CH_3), 2.00 (s, 3 H, $OCOCH_3$), 2.50 (s, 1 H, C≡CH).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.05; H, 9.18.

2β-Ethynyl-2α-acetoxynorbornane (14). Norcamphor (11.0 g) was converted by sequential application of the general ethynylation and acetylation procedures into 12.5 g (70% overall) of **14**: bp 43 °C (1.0 mm); n^{20}_D 1.4783 (lit.[20] n^{20}_D 1.4778); ν_{max} (liquid film) 3300, 2200, 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1–2.4 (br m, 9 H, ring H), 1.97 (s, 3 H, $OCOCH_3$) , 2.78 (s, 1 H, C≡CH), 2.85 (s, 1 H, bridgehead H).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.15; H, 8.11.

8β-Ethynyl-8α-acetoxytricyclo[5.2.1.0^{2,6}]decane (15). From 32.25 g of **9** there was obtained 32.2 g (81%) of **15**: bp 75 °C (0.25 mm); ν_{max} (liquid film) 3300, 2150, 1750 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.8–2.65 (br m, 14 H, ring H), 1.94 (s, 3 H, $OCOCH_3$), 2.42 (s, 1 H, C≡CH).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.28; H, 8.46.

3α-Ethynyl-3β-cholestanyl Acetate (16). From 8.6 g of **10** there was obtained 9.9 g of crude **16**, which was purified by

(14) V. Jäger and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, 8, 273 (1969).
(15) E. Robson, J. M. Tedder, and D. J. Woodcock, *J. Chem. Soc. C*, 1324 (1968).
(16) O. F. Beumel, Jr., and R. F. Harris, *J. Org. Chem.*, **29**, 1872 (1964).
(17) "Organic Syntheses", Collect. Vol II, Wiley, New York, 1943, p 139.
(18) A. M. Giroud, A. Rassat, P. Witz, and G. Ouissan, *Bull. Soc. Chim. Fr.*, 324 (1964).
(19) D. Papa, F. J. Villani, and H. F. Ginsberg, *J. Am. Chem. Soc.*, **76**, 4446 (1954).
(20) B. Guilich and G. Hildebrandt, *Chem. Ber.*, **91**, 2388 (1958).

chromatography on silica gel with benzene to yield 4.7 g (51%) of **16**: mp 116–118 °C; ν_{max} ($CHCl_3$) 3300, 2100, 1740; ^1H NMR ($CDCl_3$) δ 0.7–2.5 (br m, 46 H, steroid ring protons), 2.03 (s, 3 H, $OCOCH_3$), 2.60 (s, 1 H, C≡CH); mass spectrum (70 eV), calcd *m/e* 454.3811, found *m/e* 454.3812.

Reaction of Ethynyl Acetates with NOF/$NOBF_4$. General Procedure. To 12 g (0.10 mol) of nitrosonium tetrafluoroborate in 250 mL of 1,2-dimethoxyethane at 0 °C was added over the period of 1.0 h a solution of 0.06 mol of ethynyl acetate in 300 mL of methylene chloride while 20 g (0.41 mol) of nitrosyl fluoride was simultaneously bubbled into the solution. The resulting mixture was stirred at 0 °C for 4.0 h, poured into water, and extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated in vacuo to yield the crude furoxan.

3,4-Bis[(3β,17β-diacetoxy-5α-androstan-17α-yl)carbonyl]furoxan (4). From 6.7 g of 17α-ethynyl-3β,17β-diacetoxy-5α-androstane (**3**)[21] and 5.5 g of NOF there was obtained a viscous liquid which was purified by chromatography on 200 g of activity 3 alumina with 1:1 hexane–benzene. Fractions of 11–25 were recrystallized from ether–methanol to yield 1.21 g (16%) of **4**: mp 226–230 °C; $[\alpha]^{24}_D$ +9° (*c* 2.69 g/100 mL, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.82 (s, 6 H, C-19 CH_3's), 1.03 (s, 3 H, C-18 CH_3), 1.08 (s, 3 H, C-18′ CH_3), 2.00 (s, 12 H, $OCOCH_3$); λ_{max} (C_2H_5OH) 275 nm (ε 3700); ν_{max} (KBr) 1736, 1615, 1240 cm^{-1}; mol wt 983 (cryoscopic, benzene), 977 (ebullioscopic, benzene), calcd for $C_{50}H_{78}N_2O_{12}$ 891.08.

Anal. Calcd for $C_{50}H_{70}N_2O_{12}$: C, 67.39; H, 7.92; N, 3.14. Found: C, 67.34; H, 8.05; N, 2.95.

3,4-Bis[(2-acetoxy-2-adamantyl)carbonyl]furoxan (18). From 21.8 g of **11**, 34 g of $NOBF_4$, and 34 g of NOF there was obtained 20.4 g (78%) of **18** after crystallization of the crude product from pentane: mp 174–176 °C; ν_{max} ($CHCl_3$) 1740, 1612 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–2.8 (br m, 28 H, ring H), 2.12 (s, 3 H, $OCOCH_3$), 2.13 (s, 3 H, $OCOCH_3$); λ_{max} (C_2H_5OH) 273 nm (ε 3710).

Anal. Calcd for $C_{28}H_{34}N_2O_8$: C, 63.87; H, 6.51; N, 5.32. Found: C, 64.02; H, 6.62; N, 5.55.

3,4-Bis[(1-acetoxycyclohexyl)carbonyl]furoxan (19). From 33.2 g of **12**, 34 g of $NOBF_4$, and 33.2 g of NOF there was obtained 48.1 g of a liquid, which was purified by chromatography on silica gel with $CHCl_3$. Fractions 12–21 (32.4 g) were recrystallized from pentane to yield 22.0 g (53%) of **19**: mp 90–92 °C; ν_{max} ($CHCl_3$) 1740, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.5 (br m, 20 H, ring H), 2.12 (s, 6 H, $OCOCH_3$); λ_{max} (C_2H_5OH) 273 nm (ε 3340).

Anal. Calcd for $C_{20}H_{26}N_2O_8$: C, 56.87; H, 6.20; N, 6.63. Found: C, 56.78; H, 6.37; N, 6.69.

3,4-Bis[(2β-acetoxy-2α-bornyl)carbonyl]furoxan (20). From 24.8 g of **13**, 21 g of $NOBF_4$, and 30 g of NOF there was obtained 30.1 g of a liquid, which was chromatographed on silica gel with $CHCl_3$. Fractions 26–36 were combined and crystallized from pentane to yield 14.1 g (44%) of **20**: mp 171–173 °C; ν_{max} ($CHCl_3$), 1740, 1615 cm^{-1}; λ_{max} (C_2H_5OH) 273 nm (ε 4200), 330 (228); ^1H NMR ($CDCl_3$) δ 0.9–3.0 (br m, 14 H, ring H), 0.90 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3), 1.08 (s, 6 H, CH_3), 2.10 (s, 3 H, $OCOCH_3$), 2.13 (s, 3 H, $OCOCH_3$).

Anal. Calcd for $C_{28}H_{38}N_2O_8$: C, 63.38; H, 7.22; N, 5.28. Found: C, 63.62; H, 7.49; N, 5.48.

3,4-Bis[(2-acetoxy-2-norbornyl)carbonyl]furoxan (21). From 10.5 g of **14**, 12 g of $NOBF_4$, and 20 g of NOF there was obtained 15.8 g of a liquid, which was purified by chromatography on silica gel with $CHCl_3$. Fractions 13–25 were crystallized from pentane to afford 5.2 g (39%) of **21**: mp 108.5–109.5 °C; ν_{max} ($CHCl_3$) 1740, 1600 cm^{-1}; λ_{max} (C_2H_5OH) 275 nm (ε 3300); ^1H NMR ($CDCl_3$) δ 1.0–3.0 (br m, 20 H, ring H), 2.00 (s, 3 H, $OCOCH_3$), 2.02 (s, 3 H, $OCOCH_3$).

Anal. Calcd for $C_{22}H_{26}N_2O_8$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.23; H, 5.99; N, 6.25.

3,4-Bis[(8-acetoxy-8-tricyclo[5.2.1.$0^{2,6}$]decyl)carbonyl]furoxan (22). From 29.7 g of **22**, 23 g of $NOBF_4$, and 24.7 g of NOF was obtained 39.0 g of a liquid, which was chromatographed on silica gel with $CHCl_3$. Fractions 17–44 were combined and crystallized from pentane to give **22**: 30.6 g (85%); mp 153–154 °C; ν_{max} ($CHCl_3$) 1745, 1600 cm^{-1}; λ_{max} (C_2H_5OH) 274 nm (ε 3550); ^1H NMR ($CDCl_3$) δ 0.8–2.9 (br m, 28 H, tricyclodecane ring H), 2.03 (s, 3 H, $OCOCH_3$), 2.08 (s, 3 H, $OCOCH_3$).

Anal. Calcd for $C_{28}H_{34}N_2O_8$: C, 63.87; H, 6.51; N, 5.32. Found: C, 64.26; H, 6.58; N, 5.52.

3,4-Bis[(3β-acetoxy-3α-cholestanyl)carbonyl]furoxan (23). From 4.5 g of **16**, 3.4 g of $NOBF_4$, and 3.8 g of NOF there was obtained 4.5 g of crude crystalline product, which was purified by chromatography on silica gel with $CHCl_3$ to give 3.1 g (62%) of **23** recrystallized from ethanol: mp 186.5–188 °C; ν_{max} ($CHCl_3$) 1740, 1600 cm^{-1}; λ_{max} (C_2H_5OH) 273 nm (ε 3680); ^1H NMR 0.5–2.3 (steroid ring, side chain H), 2.04 (s, 6 H, $OCOCH_3$); mass spectrum (70 eV), *m/e* 499 ($C_{27}H_{46}(O_2CCH_3)COC{\equiv}N{\rightarrow}O$).

Anal. Calcd for $C_{62}H_{98}N_2O_8$: C, 74.51; H, 9.88; N, 2.80. Found: C, 74.62; H, 10.18; N, 2.84.

3,4-Bis[(3-oxo-17β-acetoxy-4-androsten-17α-yl)carbonyl]furoxan (24). From 7.30 g of 17α-ethynyl-17β-acetoxy-4-androsten-3-one (**17**)[22] and 3 g of NOF was obtained a yellow liquid which was chromatographed on 150 g of activity 3 alumina with petroleum ether and then with benzene. Fractions 12–17 were recrystallized from acetone–hexane to give 2.07 g (25%) of **24**: mp 253–255 °C (from CH_3OH); $[\alpha]^{24}_D$ ($CHCl_3$) +71° (*c* 2.19 g/100 mL); ν_{max} (KBr) 1740, 1678, 1625, 1615, 1260, 1240, 1235 cm^{-1}; λ_{max} (C_2H_5OH) 238 nm (ε 17 100), 280 (sh, 1670).

Anal. Calcd for $C_{23}H_{29}NO_5$: C, 69.15; H, 7.32; N, 3.51. Found: C, 68.62; H, 7.21; N, 3.16.

Reaction of 11 with NO_2BF_4. To 1.11 g of NO_2BF_4 in 20 mL of 1,2-dimethoxyethane under nitrogen at −5 °C was added dropwise a solution of 0.61 g of **11** in 20 mL of methylene chloride. The temperature was then allowed to rise to 22 °C and the mixture was stirred for 18 h. The resulting mixture was poured into water and extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated in vacuo to yield 0.64 g (87%) of crystalline **14**, mp 172–174 °C; the IR spectrum of this material was identical with that of authentic **14** from **11** and NOF/$NOBF_4$.

Registry No. **3**, 27741-55-5; **4**, 75782-43-3; **5**, 70887-49-9; **6**, 78-27-3; **7**, 75828-06-7; **9**, 13380-92-2; **10** (isomer 1), 75828-07-8; **10** (isomer 2), 75828-08-9; **11**, 75782-44-4; **12**, 5240-32-4; **13**, 75782-45-5; **14**, 75782-46-6; **15**, 13380-93-3; **16**, 75782-47-7; **17**, 2542-26-9; **18**, 75768-47-7; **19**, 75768-46-6; **20**, 75768-37-5; **21**, 75782-48-8; **22**, 75782-49-9; **23**, 75782-50-2; **24**, 75768-35-3; lithium acetylide–ethylenediame complex, 39990-99-3; 2-adamantanone, 700-58-3; *d*-(+)-camphor, 464-49-3; 8-oxotricyclo[5.2.1.$0^{2,6}$]decane, 13380-94-4; 3-cholestanone, 15600-08-5; norcamphor, 497-38-1; nitrosonium tetrafluoroborate, 14635-75-7; nitrosyl fluoride, 7789-25-5; cyclohexanone, 108-94-1; testosterone, 58-22-0.

(21) L. Ruzicka and K. Hoffman, *Helv. Chim. Acta*, **20**, 1280 (1937).

(22) L. Ruzicka and H. F. Meldahl, *Helv. Chim. Acta*, **21**, 1760 (1938).