1730 and 1680 cm^{-1}; nmr spectrum, 49 (18 methyl), 67 (triplet, J = 7.0 cps, methyl of N-ethyl), 121.5 (17 acetate), and 170–290 cps (complex multiplets).

Anal. Calcd for $C_{20}H_{31}NO_4$: C, 68.74; H, 8.94. Found: C, 68.65; H, 8.73.

Methyl 17β-Hydroxy-2,4-diaza-2-phenyl-1,2-seco-5α-estran-3-on-1-oate (1h).—A solution of acetamide **1c** (350 mg) in methanol (40 ml) was treated with concentrated hydrochloric acid (15 ml) and the solution was refluxed for 16 hr. Most of the methanol was evaporated in a stream of nitrogen and the mixture was diluted with water. The neutral fraction (105 mg) was removed by extraction with ethyl acetate, then the aqueous phase was made basic by the addition of concentrated ammonium hydroxide (15 ml). The acid-soluble fraction was recovered with ether and washed with water. Evaporation of the solvents gave 145 mg of an oil which resisted crystallization.

The above oil was dissolved in dry methylene chloride (5.0 ml) and phenyl isocyanate (0.13 ml) was added. After 1.5 hr water was added and the steroid was recovered with chloroform. The crude material was then chromatographed on a tlc silica plate [ethyl acetate–benzene (3:1)] to yield 130 mg of urea **1h**. Repeated recrystallization from methanol–ethyl acetate gave colorless crystals: mp 202–204°; ν_{max} 3340, 1730, 1670, 1590, 1640, and 1495 cm^{-1}; nmr spectrum (in deuteriodimethyl sulfoxide), 39.5 (18 methyl), 213 (carbomethoxy), 266 (doublet, J = 5.0 cps, 17 hydroxyl hydrogen), 359.5 (doublet, J = 9.0 cps), (4-NH), and 504 cps (2-NH).

Anal. Calcd for $C_{23}H_{32}N_2O_4$: C, 68.97; H, 8.05; N, 7.00. Found: C, 68.87; H, 7.92; N, 7.45.

1,17β-Dihydroxy-5β-amino-1,5-seco-2,3,4-trisnorestrane (2c).—Acetamide **1c** (840 mg) was hydrolyzed in methanol (80 ml) with concentrated hydrochloric acid (35 ml) as above to yield 580 mg of acid-soluble oil.

The oil was dissolved in tetrahydrofuran (30 ml) and ether (20 ml), lithium aluminum hydride (1.0 g) was added and the mixture was refluxed for 16 hr. The excess hydride was destroyed by cautiously adding water. The steroids were extracted into ether, then washed with 2 N sodium hydroxide and water. Removal of the solvent gave 400 mg of crystalline amine, which was recrystallized from methanol–ethyl acetate to mp 152–154°; ν_{max} 3390, 3280, 3160, 1130, 1075, 1065, 1040, and 1020 cm^{-1}.

Anal. Calcd for $C_{15}H_{27}NO_2$: C, 71.10; H, 10.74. Found: C, 71.23; H, 10.45.

17β-Acetoxy-4-acetyl-4-aza-2-oxa-5α-estrane (3e).—A mixture of amine **2c** (150 mg) and paraformaldehyde (18.5 mg) in benzene (10 ml) was heated at reflux for 20 hr. The water formed during the reaction was removed by a Dean-Stark tube. The benzene was removed by a stream of nitrogen and the insoluble residue was acetylated as usual. Work-up of the acetylation mixture gave 90 mg of residue which was chromatographed on a tlc silica plate [chloroform–ethyl acetate (1:1)]. The most mobile zone gave crystalline **3e**, which was recrystallized from ethyl acetate–pentane to mp 166–168°; ν_{max} 1725 and 1640 cm^{-1}; nmr spectrum, 48.5 (18 methyl), 121.5 (17 acetate), 126 (N-acetyl), 197 and 209 (pair of doublets, J = 9.5 cps, 2 hydrogens), 248.5 (quartet, J = 5.0 cps, 1 hydrogen), and 285.5 and 305.5 (pair of doublets, J = 11.0 cps, 2 hydrogens).

Anal. Calcd for $C_{20}H_{31}NO_4$: C, 68.74 H, 8.94. Found: C, 68.58; H, 8.78.

17β-Acetoxy-4-aza-2-oxa-3-oxo-5α-estrane (3f).—To a olution of **2c** (210 mg) in pyridine (2 ml) and chloroform (10 ml) a saturated solution of phosgene in benzene (4 ml) was added and the mixture was stored for 16 hr at room temperature. The steroids were recovered as described for **3c** to yield 150 mg of an acid-insoluble (neutral) residue. The residue was chromatographed on plates, [silica, benzene–ethyl acetate (1:1)]. The product of intermediate mobility (30 mg) was acetylated to yield **3f**. Crystallization from ethyl acetate–pentane gave a sample: sintering occurred at 250° dec; ν_{max} 3300, 1735, 1710, 1670, and 1250 cm^{-1}. Mass spectrum showed a molecular ions at 321 ($C_{18}H_{27}O_4N$, 321.40).

17β-Hydroxy-2-aza-2-benzyl-3ζ-methyl-1-oxo-A-norestr-5(10)-ene (4).—A solution of acid **1a** (100 mg) in benzylamine (1.1 ml) was heated at reflux for 18 hr. The reaction was cooled, diluted with ether, and washed with 2 N hydrochloric acid, water, saturated sodium bicarbonate solution, and water. Removal of the solvent gave 80 mg of crystalline product **4**, which was recrystallized from ethyl acetate–pentane to mp 192–197°; ν_{max} 3420, 1660, and 710 cm^{-1}; λ_{max}^{MeOH} end absorption with a shoulder at 240 mμ; nmr spectrum, 47.5 (18 methyl), 69.5 (doublet, J = 7.0 cps, C-3 methyl), and 238.5 and 302 (pair of doublets, J = 15.0 cps, methylene of N-benzyl).

Anal. Calcd for $C_{24}H_{31}NO_2$: C, 78.86; H, 8.55. Found: C, 78.82; H, 8.17.

17β-Hydroxy-2-aza-2-benzyl-1,3-dioxo-A-nor-5α-estrane (5).—A solution of diacid[1] **1i** (100 mg) in benzylamine (1.1 ml) was refluxed for 17 hr. The solution was diluted with ether–chloroform (3:1) and washed with 2 N hydrochloric acid, water, sodium bicarbonate, and water. Evaporation of the solvents gave a yellow residue which was chromatographed on a tlc silica plate [ethyl acetate–benzene (1:1)]. The most mobile zone was eluted to give 33 mg of imide **5**. Repeated recrystallizations from acetone gave an analytical sample: mp 183–186°; ν_{max} 3550, 1770, and 1700 cm^{-1}; nmr spectrum, 45 (18 methyl), 274.5 (methylene of N-benzyl), and 435.5 cps (aromatic hydrogens).

Anal. Calcd for $C_{23}H_{29}NO_3$: C, 75.17; H, 7.95. Found: C, 75.30; H, 7.77.

N,N′-Dibenzyl-17β-acetoxy-1,4-*seco*-2,3-bisnor-5α-estradioic Diamide (6b).—The least mobile zone from the above experiment was eluted to give 75 mg of hydroxy diamide **6a**. Attempts to recrystallize this material resulted in gels. The compound was acetylated as usual to **6b**, which was recrystallized from chloroform–acetone to mp 241–242°; ν_{max} 3300, 1730, 1635, and 1540 cm^{-1}.

Anal. Calcd for $C_{32}H_{40}N_2O_4$: C, 74.39; H, 7.80. Found: C, 73.92; H, 7.53.

Photochemical Cycloaddition Reactions with Norbornene

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The photochemical addition of dimethyl maleate, dimethyl fumarate, and maleic anhydride to norbornene has been studied. Stereochemistry has been deduced for the adducts and a revised structure has been assigned the one isomer recorded by Hara, Odaira, and Tsutsumi.[2]

Direct irradiation of a solution of norbornene in dimethyl maleate has been reported to yield a single 1:1 adduct assigned the structure 2.[2] The *exo* nature of the cyclobutane ring was securely established by degradation of the adduct to the known *exo*-2,3-bishydroxymethylbicyclo[2.2.1]heptane, while the assignment of the *cis,trans,cis*-substitution pattern of the

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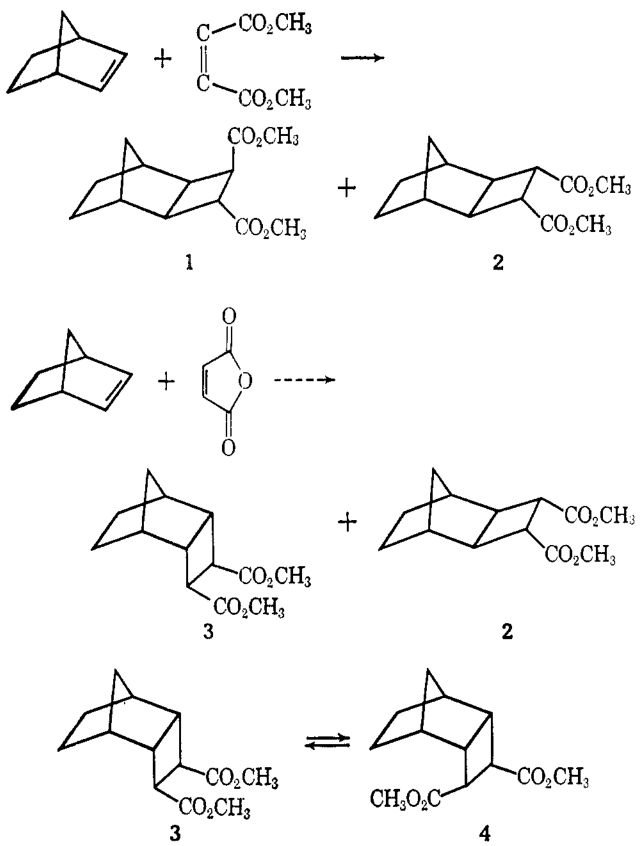
(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) M. Hara, Y. Odaira, and S. Tsutsumi, *Tetrahedron*, **22**, 95 (1966).

cyclobutane ring rested on nmr evidence. We have examined the photochemical cycloaddition of dimethyl maleate, dimethyl fumarate, and maleic anhydride to norbornene. We report here that photoaddition of dimethyl maleate to norbornene yields *trans*-3,4-dicarbomethoxy-*exo*-tricyclo[4.2.1.$0^{2,5}$]nonane (**1**) as the major product along with a lesser amount of *cis,endo*-3,4-dicarbomethoxy-*exo*-tricyclo[4.2.1.$0^{2,5}$]nonane (**2**). Further, we have shown that photoaddition of maleic anhydride to norbornene yields, after hydrolysis and esterification, **2** and *cis,exo*-3,4-dicarbomethoxy-*endo*-tricyclo[4.2.1.$0^{2,5}$]nonane (**3**) (Scheme I).

SCHEME I



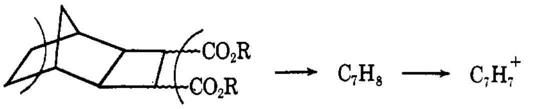
Direct irradiation of a solution of norbornene in dimethyl maleate yielded after distillation a mixture of products which deposited crystals of **1** upon standing. The physical properties of the purified crystals correspond to those reported[2] by the Japanese workers for their 1:1 adduct. In addition, however, a second product was identified in the gas-liquid partition chromatogram (glpc) and constituted nearly 15% of the distillate.

Base-catalyzed equilibration of either of the two purified diesters led to the same 4:1 mixture of the two found in the photochemical experiment; in addition a third component (1%) appeared and was presumed to be the third isomer of the *exo* series, **5**. This equilibration, the mass spectra and the previous demonstration of the *exo* ring fusion[2] clearly establish that the two photoproducts differ only in being epimeric about the ring carbomethoxyl bonds.

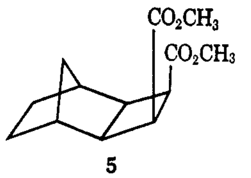
Final assignment of structure, **1** for the major product and **2** for the minor product, is based on evidence presented below.

Entry into the *endo* series of compounds was provided by the photochemical addition of maleic anhydride to norbornene. The 1:1 adduct was hydrolyzed, esterified with diazomethane, and purified by glpc. Two isomeric diesters (molecular weight determined by mass spectroscopy) were obtained in nearly equal amounts. The first compound eluted was identified as the minor product of the dimethyl maleate–norbornene irradiation (**2**), but the second compound (**3**) had not previously been observed. Base-catalyzed equilibration of this new diester led to a 65:35 mixture of isomeric diesters **4** and **3**. Since these are 1:1 adducts and since two (and probably all three) of the *exo*-fused compounds have already been identified, these must be two of the corresponding *endo* isomers.

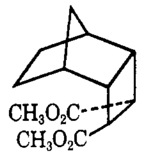
The mass spectra obtained from each of the four diesters (**1**–**4**) are essentially identical, thus providing further evidence for the structural similarity of the four compounds.[3] Each spectrum exhibited the parent ion, a low-intensity peak, at *m/e* 238, and peaks of considerable intensity at *m/e* 207, 206, 179, 178, 119, and 91. The first five fragmentation peaks correspond to loss of OCH_3, H + OCH_3, $COOCH_3$, H + $COOCH_3$, and H + $2COOCH_3$, respectively. This behavior is well documented for vicinal diesters.[4] The peak at *m/e* 91 provides an unusual verification of the assigned structures since decomposition under electron impact as shown below can lead to the C_7H_8 molecule and $C_7H_7^+$ ion.[5]



Having ascertained the gross structure of the four diesters as well as the *exo* or *endo* fusion of the cyclobutane ring, we addressed the question of the *cis* or *trans* disposition of the carbomethoxyl groups. Of the six possible isomers, assuming *cis* fusion of cyclobutane to norbornane nucleus, two diesters, the *exo,cis,exo* isomer **5** and the *endo,cis,endo* isomer **6**, are expected to be considerably less stable than the others because of molecular crowding, and thus present in the appropriate equilibrium mixture in very small amounts.



5



6

Of the remaining four diesters, two, **1** and **2** from dimethyl maleate addition, are already known to possess the *exo* ring fusion, and **3** and **4** have the *endo* cyclobutane. Since the stereochemistry of the ring fusion has already been assigned in each compound,

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(3) We wish to thank Professor A. L. Burlingame and Dr. H. K. Schnoes for obtaining mass spectra of these compounds for us.

(4) R. Ryhage and E. Stenhagen, "Mass Spectrometery of Organic Ions," T. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, pp 444–451.

(5) This mode of decomposition has been noted in dimers of norbornene-(pentacyclo[8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]tetradecanes). The detailed pattern of fragmentation was established by deuterium labeling.[6]

(6) G. G. Meisels and D. R. Arnold, to be published, as cited in D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).

determination of the *cis* or *trans* nature of the carbomethoxy groups will complete the structural assignment. Careful study of the high-resolution 100-Mc/sec nmr spectrum of each diester provided evidence sufficient to distinguish between *cis* and *trans* isomers in each pair. In both series the *cis* isomers possess an element of symmetry (a mirror plane) that will interchange the two carbomethoxy groups. In the absence of any long-range coupling, a single, sharp peak should appear for the OMe resonance. No such element of symmetry exists for the two *trans* isomers so that each of these isomers should exhibit two different OMe resonances. In fact, one compound in each series, **1** and **4**, exhibited two OMe resonances separated by less than 1 cps and one compound in each series, **2** and and **3**, exhibited one sharp single resonance (width at half-height of 0.4 cps). These observations, summarized in Table I, allow a complete assignment of the stereochemistry of the four isomers.

TABLE I

TRICYCLIC DIESTERS FROM NORBORNENE

Compd	Mp, °C	Nmr OMe resonances, δ	% at equilibrium
1	78–79	3.648, 3.639	80
2	84–85	3.630	20
3	Liquid	3.579	35
4	100–101	3.590, 3.579	65

In summary, photoaddition of dimethyl maleate to norbornene yields two isomeric diesters, both having the cyclobutane ring fused *exo* to the norbornane nucleus. In the major product, mp 78–79°, the carbomethoxyl groups are *trans* (**1**) and in the minor product, mp 84–85°, these groups are *cis* and *anti* to the norbornane nucleus (**2**). Sensitized addition of maleic anhydride to norbornene provides, after hydrolysis and esterification, diester **2** and the *endo*-fused *cis* diester **3**. Base-catalyzed equilibration of either **1** or **2** gave a mixture containing 80% of **1** and 20% of **2**. Equilibration of **3** provided a mixture of diesters **3** and **4**, 35 and 65%, respectively.

The relative amounts of diesters **1** and **2** in the photo product and at equilibrium are the same. Similar mixtures were also obtained from direct irradiation of norbornene and dimethyl fumarate and from sensitized irradiation of norbornene and dimethyl maleate.[7]

The formation of the *endo*-fused product by addition of maleic anhydride and the absence of such products in either direct or sensitized addition of dimethyl maleate may indicate involvement of a charge transfer complex.[8]

Experimental Section[9]

Irradiation of Norbornene and Dimethyl Maleate.—A solution of 24.1 g of norbornene in 60 ml of dimethyl maleate was irradiated in a quartz apparatus with a 450-w mercury arc (Hanovia, Type L) for 9.5 hr. Unchanged dimethyl maleate, dimethyl fumarate, and norbornene were removed by distillation at 0.25 mm, bp to 50°. After an intermediate fraction, bp 85–105° (0.5 mm), the product was obtained as a yellow distillate, bp 106–130° (0.8 mm), yield 4.9 g. Gas–liquid partition chromatographic (glpc) analysis of the product fraction (DEGS or silicone oil columns) showed the presence of two major products, **1** and **2**, in the ratio ~4:1. The two products comprise about 75% of total mixture. Small amounts of other products including dimethyl maleate and dimethyl fumarate as well as compounds presumed to be a dimer of norbornene and traces of **3** and **4** (based solely on retention times) were also found. Crude diester **1** crystallized from the distillate[10] and pure **1**, mp 78–79°, was obtained by collection (glpc), or by sublimation.

Hydrolysis of Diester 1.—A mixture of 149 mg (0.636 mmole) of diester **1** and 4.0 ml of 10% sodium hydroxide solution was refluxed for 17.5 hr. The cooled solution was acidified. The resulting solid was collected by filtration, washed with water, and dried, yield 93 mg, mp 207–208°. The melting point of the diacid from diester **1** was not changed when the melt was allowed to solidify and the melting point was redetermined.[2]

Addition of Maleic Anhydride to Norbornene.—A solution of 1.17 g of maleic anhydride, 5.0 g of norbornene, and 576 mg of benzophenone in 130 ml of methylene chloride was irradiated as above, but with a Pyrex filter, for 4.5 hr. The solvent was removed and the residue was boiled overnight with 70 ml of 4% sodium carbonate solution. The neutral compounds were extracted into ether and the aqueous solution was acidified with aqueous sulfuric acid. Extraction of the aqueous mixture with ether, followed by drying and evaporation gave 712 mg of crystals, mp 159–160°. Sublimation at 0.3 mm of a small portion gave an analytical sample, mp 159–159.5°.

Anal. Calcd for $C_{11}H_{14}O_4$ (210.22): C, 62.84; H, 6.71. Found: C, 62.90; H, 6.66.

Treatment of the crystalline products with diazomethane gave a mixture of diesters **2** and **3** in approximately equal amounts. In a large-scale experiment diester **2** crystallized from the mixture after the solvent was removed. Pure **2**, mp 84–85°, was then obtained by recrystallization from cyclohexane. Pure diester **3**, a liquid, was obtained by collection (glpc) after most of the **2** had been removed by crystallization.

Irradiation of Norbornene and Dimethyl Fumarate.—A solution of 5.0 g of norbornene and 5.0 g of dimethyl fumarate in 70 ml of methylene chloride was irradiated (quartz) for 4.5 hr. The solvent was removed at reduced pressure. Glpc analysis of the residue showed, in addition to dimethyl fumarate and dimethyl maleate, diester **1** and other as yet unidentified products.

Sensitized Irradiation of Norbornene and Dimethyl Maleate.—A solution of 14.0 g of norbornene, 5.0 g of dimethyl maleate, and 3.3 g of benzophenone in 65 ml of methylene chloride was irradiated (Pyrex filter) for 11.3 hr. The solvent was removed at reduced pressure. The residue deposited crystals of dimethyl fumarate and the oxetane formed by addition of benzophenone to norbornene,[11] mp 102–125°, which were removed by filtration. Glpc analysis of the filtrate showed that the major product was diester **1**.

Equilibration of Diesters 1, 2, and 3.—A solution of sodium methoxide was prepared by dissolving a small piece of sodium in 10 ml of dry methanol. One-milliliter aliquots of this solution were added to each of three Pyrex tubes containing 25 mg of **1**, **2**, and **3**, respectively, and the tubes were sealed. The tubes were heated at 65 ± 5° for 20 hr. The tubes were opened, water was added, and the solutions were extracted with ether. The ether extracts were dried and concentrated. The analysis of each product by glpc is shown in Table II.

TABLE II

Starting material	Products	Ratio
Pure **1**	**1** + **2** + **5**	80:19:1
Pure **2**	**1** + **2** + **5**	84:15:1
Pure **3**	**3** + **4**	35:65

Isolation of Diester 4.—Collection of diester **4** obtained in the equilibrium experiment provided sufficient material, mp 100–101°, for mass spectral and nmr analysis.

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[7] These facts indicate that the mechanism of addition is probably more complicated than the simultaneous formation of two carbon–carbon bonds. However, it was not our intention to study the mechanism of the photochemical reaction. The problem, in general, of how this type photochemical reaction proceeds is most recently set forth in A. Cox, P. de Mayo, and R. W. Yip, *J. Am. Chem. Soc.*, **88**, 1043 (1966).

[8] R. Robson, P. W. Grubb, and J. Barltrop, *J. Chem. Soc.*, 2153 (1964).

[9] The high-resolution nmr spectra were obtained with a Varian HA-100 nmr spectrometer on solutions of 5–10% concentration in carbon tetrachloride solution. We are grateful to the National Science Foundation for funds under Grant GP-3761, for partial purchase of this instrument.

[10] This compound is identical with the "*exo,cis,trans,cis*" compound obtained previously.[2]

[11] H. D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963).