Synthesis of *exo-* and *endo*-Tetracyclo[5.4.0.0²,⁴.0³,⁶]undeca-1(7),8,10-trien-5-ol and Related Derivatives[1]

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Both *exo-* and *endo*-tetracyclo[5.4.0.0²,⁴.0³,⁶]undeca-1(7),8,10-trien-5-ol were synthesized by stereospecific pathways involving the photochemically induced rearrangement of appropriately substituted benzonorbornadienes. Derivatives of the tetracyclic compounds were prepared and some of the chemistry of this system is reported.

Our recently reported[2] synthesis of *endo*-tricyclo-[3.2.0.0²,⁷]heptan-6-ol (**1a**) and subsequent investigation[3] of the remarkable solvolytic reactivity of some of


1a, X = H; Y = OH
  b, X = OH; Y = H
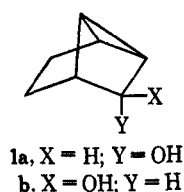
its derivatives have spurred our interest in related systems incorporating the essential features of **1**. We became especially interested in determining the exo/endo rate ratio for the 6-substituted tricyclic system (*i.e.*, **1a** and **1b**).

The reported[4] sensitized photorearrangement of benzonorbornadiene (**2**, X = Y = H) to the benzotricyclic hydrocarbon **3** (X = Y = H) has been suggested to proceed through a diradical intermediate **4** (X = Y = H).[5] This pathway suggests a potential stereospecific approach to both *exo-* and *endo*-tetracyclo[5.4.0.-0²,⁴.0³,⁶]undeca-1(7),8,10-trien-5-yl derivatives (*i.e.*, **3**).


2   **4**

3
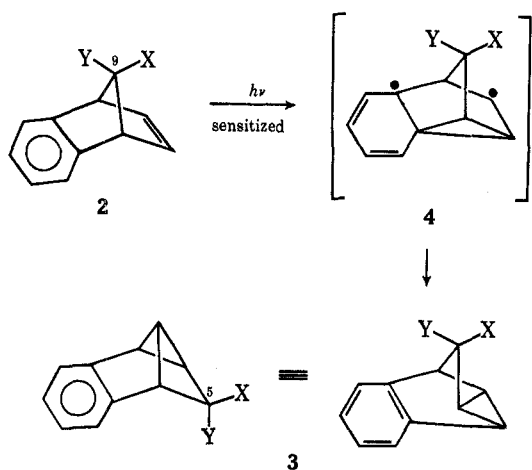
The observed[4b] stereospecificity of the photorearrangement of the dideuteriobenzonorbornadiene **5** to **6** is expected on the basis of a diradical corresponding to **4**. Moreover, such stereospecificity in related photo-

rearrangements is well precedented.[6] These results suggest that an effective route to *exo-* and *endo*-tetra-

5   **6**
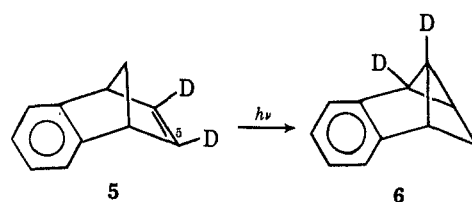
cyclo[5.4.0.0²,⁴.0³,⁶]undeca-1(7),8,10-trien-5-yl derivatives would involve photorearrangement of the appropriate 9-substituted benzonorbornadiene, **2**. Thus, the acetophenone-sensitized photorearrangement of *anti*-9-acetoxybenzonorbornadiene (**7**) is expected to afford exo benzotricyclic acetate **8**, while *syn*-9-ace-

7   **8**

9   **10**
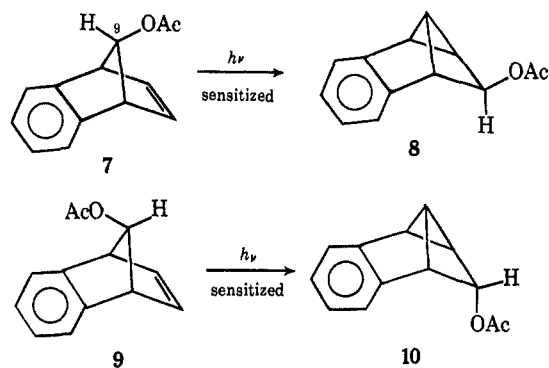
toxybenzonorbornadiene (**9**) should give endo benzotricyclic acetate **10**. We set out to confirm these predictions.

***exo*-Tetracyclo[5.4.0.0²,⁴.0³,⁶]undeca-1(7),8,10-trien-5-yl Acetate.**—Benzonorbornadiene[7] was converted into *anti*-9-*tert*-butoxybenzonorbornadiene (**11**)[8a] as reported. Acid-catalyzed ether cleavage of **11** in acetic acid–acetic anhydride[8] containing perchloric acid affords *anti*-9-acetoxybenzonorbornadiene[8a,9] (**7**) in 80% yield. The nmr spectrum of **7** is in accord with that reported.[8a] A 1% solution of anti acetate **7** in hexane was photolyzed in the presence of acetophenone to give exo benzotricyclic acetate **8** (95% yield).

(1) We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) J. J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Commun.*, 1202 (1967).

(3) J. J. Tufariello and R. J. Lorence, *J. Amer. Chem. Soc.*, **91**, 1546 (1969).

(4) (a) J. P. Edman, *ibid.*, **88**, 3454 (1966); (b) J. R. Edman, *ibid.*, **91**, 7103 (1969).

(5) It is clear that this rearrangement may be concerted in nature: R. B. Woodward and R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(6) (a) H. Hart and R. K. Murray, Jr., *J. Amer. Chem. Soc.*, **91**, 2183 (1969); (b) R. C. Hahn, L. V. Rothman, *ibid.*, **91**, 2409 (1969); (c) H. E. Zimmerman and C. O. Bender, *ibid.*, **91**, 7516 (1969), and references cited therein; (d) M. G. Waite, G. A. Sim, C. R. Orlander, R. J. Warnet, and D. M. S. Wheeler, *ibid.*, **91**, 7763 (1969).

(7) G. Wittig and E. Knauss, *Chem. Ber.*, **91**, 895 (1958); (b) L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963); (c) T. F. Mich, E. J. Nienhouse, T. F. Farina, and J. J. Tufariello, *J. Chem. Educ.*, **45**, 272 (1968).

(8) (a) M. E. Brennan and M. A. Battiste, *ibid.*, **33**, 324 (1968); (b) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(9) S. J. Cristol and G. W. Nachtigall, *ibid.*, **32**, 3727, 3738 (1967).

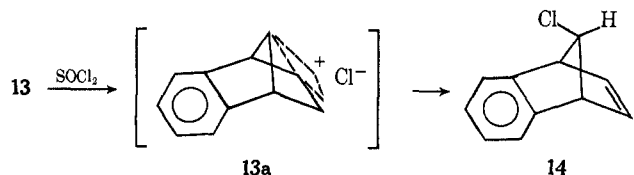The exo-5-substituted benzotricyclic system was also obtained by conversion of the anti *tert*-butyl ether 11 to the corresponding anti alcohol 12 using the method of Brennan and Battiste,[8a] followed by photolysis to afford exo benzotricyclic alcohol 13 (Scheme I). This

SCHEME I
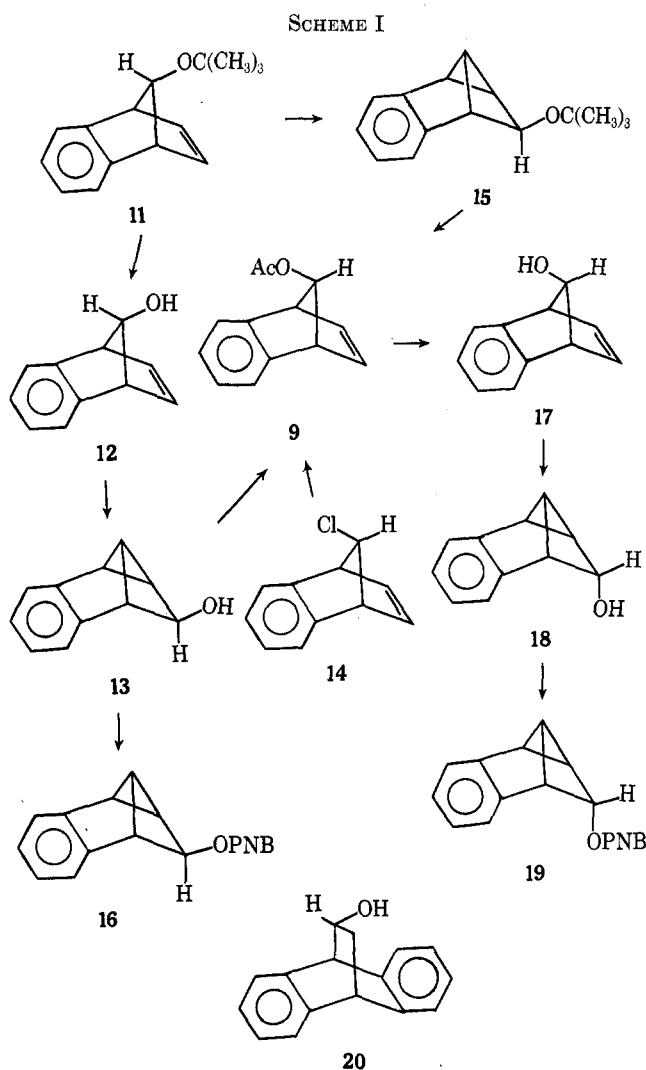
alcohol was also prepared by lithium aluminum hydride reduction of the exo acetate 8.

The nmr spectrum of benzotricyclic hydrocarbon 3 (X = Y = H) contains a doublet (J = 2.5 Hz) for the endo hydrogen (*i.e.*, Y in 3) when decoupled at the frequency of the exo proton (*i.e.*, X in 3). In addition, studies of 8,11-disubstituted tetracyclo[5.4.0.0²,⁴.0³,⁶]-undeca-1,8,10-trienes reveal a similar value (J = 2.7 Hz) for this coupling constant.[6d] The exo benzotricyclic acetate 8 exhibited the expected doublet for H-5 (J = 4 Hz) at δ (CCl₄, TMS) 4.07 ppm.

The exo acetate 8 was reduced to the corresponding exo benzotricyclic alcohol 13, which in turn was transformed into the known *syn*-9-chlorobenzonorbornadiene[10] (14) with thionyl chloride in ether. The ob-

served stereospecificity of this reaction is explicable on the basis of an exclusive collapse of the presumed ion-pair intermediate 13a to give the observed syn chloride 14. Cristol and Nachtigall[10] have shown that carbonium ions such as 13a undergo nucleophilic attack to afford syn products exclusively.

The syn chloride 14 was transformed into the *syn*-9-acetoxybenzonorbornadiene (9) by solvolysis in acetic acid containing potassium acetate.[10] The spectral and physical properties of 14 and 9 are in accord with those previously reported[8a,9,10] as is the observed stereospecificity of the 14 → 9 transformation. In addition, the exo benzotricyclic alcohol 13 can be directly transformed into syn acetate 9 by treatment with acetic anhydride in acetic acid containing perchloric acid.

The acetophenone-sensitized photolysis of *anti*-9-*tert*-butoxybenzonorbornadiene (11) in hexane affords exo *tert*-butyl ether 15. Rearrangement of 15 in acetic acid (*cf.* Experimental Section) gave syn acetate 9 in good yield. This latter process (*i.e.*, 11 → 15 → 9) provides a most convenient and efficient means of obtaining the syn acetate 9. In addition, this brief sequence, involving a tricyclic intermediate, appears to be a remarkably facile means for bridging the anti and syn benzonorbornadienyl series.

All the exo benzotricyclic derivatives (*i.e.*, the *tert*-butyl ether 15, acetate 8, and *p*-nitrobenzoate 16), with the exception of the alcohol, exhibit a doublet assignable to the endo-5 hydrogen. In the alcohol this signal is complicated by the presence of further coupling of the hydroxyl proton to H-5. Observation of models indicates that the endo-5 hydrogen in the exo-alcohol 13 is shielded as a result of the anisotropic effect of the benzene ring in 13 and consequently appears at higher field (δ 3.52 ppm) than that observed for the corresponding exo-5 hydrogen in the endo alcohol 18 (δ 4.22 ppm).

endo-Tetracyclo[5.4.0.0²,⁴.0³,⁶]undeca-1(7)8,10-trien-5-yl Acetate.—The acetophenone-sensitized photorearrangement of *syn*-9-acetoxybenzonorbornadiene (9) gives endo benzotricyclic acetate 10 in 92% yield. Reduction of the acetate 10 with lithium aluminum hydride affords the endo alcohol 18, which was converted into its *p*-nitrobenzoate 19. The nmr spectrum of the acetate displayed the exo-5 hydrogen as the anticipated quartet[11] at δ (CCl₄, TMS) 5.19 ppm (J = 7.5 Hz, J = 4 Hz). The *p*-nitrobenzoate exhibited the corresponding quartet at δ (CCl₄, TMS) 5.47 ppm (J = 6.8 Hz, J = 3.3 Hz). An alternative procedure employed for the synthesis of the endo alcohol 18 involves the complex metal hydride reduction of the syn acetate 9 to the corresponding alcohol 17, which may then be photolyzed as usual to give 18.

The structures of the exo and endo alcohols, 13 and 18 respectively, were further confirmed by the results of intramolecular hydrogen-bonding studies in the first overtone region for hydroxyl stretching in the near infrared. For those compounds which exhibit two absorptions in this region, the absorption at the shorter wavelength (ca. 14100 Å) is attributable to free hydroxyl while that at longer wavelength may be fairly safely attributed to intramolecularly hydrogen-bonded hydroxyl provided that B_1/B_2 < 1 and $\Delta\nu/2$ > 26 cm⁻¹ (*cf.*

(10) S. J. Cristol and G. W. Nachtigall, *J. Amer. Chem. Soc.*, **90**, 7132, 7133 (1968).

(11) (a) H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966); (b) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966).

<div style="text-align:center">

TABLE I

HYDROGEN-BONDING STUDIES[a]

</div>

Compd[b]	λ_{max}, Å	B, cm mol^{-1} [c]	B_1/B_2[d]	$\Delta\nu/2$,[e] cm^{-1}
Exo alcohol 13	14158	59.2	2.30	25
	14257	27.7		
Endo alcohol 18	14150	32.0	0.57	36
	14306	56.5		
Dienol 20	14161	51.0	0.57	37
	14310	90.4		

[a] The procedure used is described in the Experimental Section (*cf.* ref 12). [b] All compounds were studied over a range in concentrations (*i.e.*, 10^{-1} to 10^{-3} *M*) in carbon tetrachloride. [c] The areas of the peaks were determined by using $B = \epsilon \times \Delta\nu_{1/2}$, where ϵ (cm^2 mol^{-1}) is the extinction coefficient and $\Delta\nu_{1/2}$ is the peak width at half-height in reciprocal centimeters. [d] The ratio of the peak areas (B_1/B_2) was determined by inserting the area of the lowest wavelength absorption in the numerator. [e] The peak separation $\Delta\nu/2$ includes the factor 2 since we are dealing with the first overtone region for hydroxyl stretching.

Table I).[12] These criteria are clearly met for the endo alcohol **18** where intramolecular hydrogen bonding to the proximate benzene ring is expected to occur, especially on comparison with dibenzobicyclo[2.2.2]octadienol **20**. In the case of the exo alcohol **13**, where the aforementioned criteria are not met, the possibility of intramolecular hydrogen bonding can not be distinguished from that where the two absorptions are due to the presence of two (or more) conformations involving the hydroxyl group, each conformation having a somewhat different hydroxyl stretching frequency.[12] Thus, while it is tempting to postulate a weak hydrogen-bonding interaction to the cyclopropane ring in the exo isomer **13**, this conclusion is not warranted.

The synthesis of the exo and endo alcohols **13** and **18**, and their respective *p*-nitrobenzoate derivatives **16** and **19**, makes possible a study of their respective chemical reactivities.

Experimental Section

All melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-5a spectrophotometer and calibrated using the 6.238-μ bond of polystyrene. Proton nmr spectra were obtained using TMS as internal standard on a Varian A-60 or Varian HA-60 spectrometer.

Benzonorbornadiene (2, X = H; Y = H).—The previously described procedure[7b,c] was used for the preparation of benzonorbornadiene.[7a] Distillation of the crude reaction mixture through a 10-in. Vigreux column afforded benzonorbornadiene, bp 72–81° (10 mm) (40% yield) [lit.[7a] bp 82.5–83° (12 mm)]. Spectral properties are in accord with those previously reported.[7c]

Standard Photolysis Procedure.—Approximately 100 ml of 1–2% solution of the substrate was dissolved in reagent grade benzene (unless otherwise specified). The solution was placed in a Pyrex vessel and 5–12 drops (90–216 mg) of acetophenone was added, depending on the amount of substrate. The solution was purged with nitrogen for 15 min prior to, and then throughout, the irradiation. The irradiation was performed in a Rayonnet photochemical reactor equipped with a bank of 16 General Electric F8 T5-BLB lamps (3500 Å). The irradiation was continued overnight or until vinyl absorption was no longer visible in the nmr spectrum.

anti-9-**Acetoxybenznorbornadiene (7).**—The method of Story[8b] was adapted for the preparation of the title compound. From 22 g (0.1 mol) of *tert*-butyl ether **11** was obtained 15 g (75%) of the desired product bp 84–91° (0.15 mm). These physical and

spectral properties are in accord with those previously reported for this compound.[10,13]

anti-9-**Benznorbornadienol (12).** **A.**—The procedure of Tanida,[18] employing methylmagnesium iodide, was applied to the acetate **7**. Recrystallization from hexane gave 70% yield of the alcohol as colorless prisms, mp 104.5–106° (lit. mp 105–106,[18] 104–105° [8a]).

B.—The procedure of Brennan and Battiste[8a] was used. The ether **11**, 21.4 g (0.1 mol), 200 ml of THF, and 100 ml of 50% aqueous H$_2$SO$_4$ gave the anti alcohol **12** (13 g, 83%), mp 104.5–106° (lit. mp 105–106,[18] 104–106° [8a]).

exo-5-**Acetoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (8).**—Treatment of 1.08 g (5.4 mmol) of *anti*-9-acetoxybenzonorbornadiene in 108 ml of hexane with 4 drops of acetophenone, followed by photolysis under the standard photolysis conditions (*vide supra*), gave after solvent removal 1.03 g of crude product. Evaporative distillation (Kugelrohr oven) at 85–90° (0.05 mm) gave 0.91 g (85%) of exo acetate **8** whose purity (>99%) was confirmed by glpc analysis on a 4-ft silicone rubber column. The samples used for the spectral analysis were collected from 4-ft silicone rubber columns (glpc): ir (film) 3.29 (w), 5.78 (s), 8.10 (s), and 13.35 μ (s); nmr (CCl$_4$) δ 2.12 (m, 4), 2.57 (t, 1, J = 5.0 Hz), 3.24 (m, 1), 3.58 (m, 1), and 4.07 ppm (d, 1, J = 3.5 Hz); mass spectrum (70 eV) *m/e* 200 (molecular ion).

Anal. Calcd for C$_{13}$H$_{12}$O$_2$: C, 77.98; H, 6.04. Found: C, 77.86; H, 6.04.

anti-9-*tert*-**Butoxybenzonorbornadiene (11).**—The procedure of Brennan and Battiste[8a] was used for the preparation of the title compound. Benzonorbornadiene (142 g, 1.0 mol), benzene (360 ml), cuprous bromide (300 mg), and *tert*-butyl perbenzoate (76 g, 0.39 mol) afforded after two distillations 26 g (32%) of *tert*-butyl ether **11**, bp 72–80° (0.2 mm). Pure *tert*-butyl ether was obtained upon redistillation through a 24-in. stainless steel spinning-band column, bp 78–80° (0.23 mm). Recrystallization from hexane gave colorless crystals, mp 48–49° (lit.[8a] mp 48–49°). The spectral characteristics of **11** are identical with those previously reported.[8a]

endo-5-**Acetoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (10).**—Treatment of 3.1 g (15.5 mmol) syn acetate **9** in 400 ml of hexane with 20 drops of acetophenone, followed by photolysis under the standard conditions, gave after solvent removal and evaporative distillation at 90° (0.04 mm) 2.93 g (95%) of clear, pure (glpc analysis, 4-ft silicone rubber column) liquid: ir (film) 3.25 (w), 5.77 (s), 8.07 (s,), and 13.30 μ (s); nmr (CCl$_4$) δ 1.40 (s, 3), 2.35 (m, 1), 2.64 (t, 1, J = 5.0 Hz), 3.07 (m, 1), 3.93 (m, 1), 5.19 (q, 1, J = 7.5 Hz), 6.93–7.52 (m, 4); mass spectrum (70 eV) *m/e* 200 (molecular ion).

Anal. Calcd for C$_{13}$H$_{12}$O$_2$: C, 77.98; H, 6.04. Found: C, 77.90; H, 5.84.

exo-**Tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-trien-5-ol (13).** **A.**—To a stirred suspension of 2.0 g (52.5 mmol) of lithium aluminum hydride in 50 ml of anhydrous ether was added slowly, over a 20-min period, a solution of 6.7 (33.5 mmol) of *exo*-acetate **8** in 50 ml of anhydrous ether. The reaction mixture was stirred for an additional 45 min and the excess lithium aluminium hydride was decomposed by the careful (dropwise) addition of water. The resulting salts were removed by filtration. The solvent was removed at reduced pressure and the crude product was distilled at 94–95° (0.03 mm) in a Kugelrohr oven. There was obtained 4.2 g (80%) of a clear viscous oil which crystallized upon standing: mp 61.5–63.7°; ir (film) 3.0 (s), 9.32 (m), 13.45 μ (s); nmr (CCl$_4$) δ 1.89 (m, 1), 2.45 (t, 1, J = 6.0 Hz) 3.08 (m, 1), 3.53 (m, 2), 5.00 (s, 1), 6.83–7.50 ppm (m, 4).

B.—Treatment of 1.0 g (6.3 mmol) of *anti*-9-benzonorbornadienol (**12**) in 100 ml of benzene with 5 drops of acetophenone under the standard photolysis conditions gave 0.76 g of exo alcohol **13** (76%) as a white solid (mp 61.5–63.5°) after evoporative distillation in a Kugelrohr oven at 90° (0.04 mm). The exo-alcohol **13** prepared in this manner is identical in physical and spectral properties with that described above (A).

The exo alcohol **13** (0.90 g, 5.7 mmol) was converted into the corresponding *p*-nitrobenzoate **16** using 4 ml of pyridine and 1.13 g (6.1 mmol) of *p*-nitrobenzoyl chloride.[14] The *p*-nitrobenzoate was obtained as yellow crystals (1.00 g, 65%): mp 88–89°; ir (Nujol mull) 5.83 (s), 6.53 (s), 7.80 (s), 14.0 μ (s); nmr (CDCl$_3$)

(12) (a) R. J. Piccolini and S. Winstein, *Tetrahedron Lett.*, No. 13, 4 (1959); (b) R. J. Piccolini, Ph.D. Dissertation, UCLA, Los Angeles, Calif., 1960.

(13) H. Tanida, and T. Tsuji, *J. Org. Chem.*, **29**, 849 (1964).

(14) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 736.

δ 2.24 (m, 1), 2.67 (t, 1, J = 5.0 Hz), 3.44 (m, 1), 3.69 (m, 1), 4.38 (d, 1, J = 4.0 Hz), 7.05–7.60 (m, 4), 8.20 ppm (s, 4).

Anal. Calcd for $C_{18}H_{13}NO_4$: C, 70.36; H, 4.23; N, 4.56. Found: C, 70.67; H, 4.08; N, 4.38.

syn-9-Chlorobenzonorbornadiene (14).—To a stirred solution of 1.90 g (12.0 mmol) of exo alcohol 13 in 20 ml of anhydrous ether was added slowly by syringe 1.44 g (12.0 mmol) of thionyl chloride in 2.5 ml of anhydrous ether over a 5-min period. The reaction mixture was stirred overnight at room temperature. The reaction mixture was then washed successively with cold water and saturated $NaHCO_3$ solution and then dried $(MgSO_4)$. The solution was then filtered and the solvent was removed at reduced pressure, to leave a yellow liquid which was evaporatively distilled in a Kugelrohr oven at 80–85° (0.05 mm) to afford a white solid (1.71 g, 82%), whose physical and spectral properties are in accord with those reported by Cristol and Nachtigall.[9,10]

exo-5-tert-Butoxytetracyclo[5.4.0.0²,⁴.0³,⁶]undeca-1(7),8,10-triene (15).—Treatment of 1.1 g (5.14 mmol) of *anti*-9-*tert*-butoxybenzonorbornadiene in 100 ml of benzene with 5 drops of acetophenone under the standard photolysis conditions gave, after evaporative distillation in a Kugelrohr oven, 0.87 g (79%) of 15 as a viscous liquid which solidified on cooling. Recrystallization from hexane gave an analytical sample: mp 71–72°; ir (Nujol mull) 8.36 (m), 9.27 (s), 13.35 μ (s); nmr $(CDCl_3)$ δ 1.21 (s, 9), 1.85 (m, 1), 2.50 (m, 1), 3.13 (m, 1), 3.37 (d, 1, J = 7.6 Hz), 3.63 (m, 1), 6.90–7.60 (m, 4).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.11; H, 8.41. Found: C, 84.04; H, 8.69.

syn-9-Acetoxybenzonorbornadiene (9).—The exo *tert*-butyl ether 15 (4.3 g, 20.0 mmol) was dissolved in 32 ml of glacial acetic acid containing 5.9 ml of acetic anhydride. The solution was cooled to a temperature just above its freezing point and was then added rapidly, with vigorous swirling, to a flask containing 4.1 g of 70% perchloric acid at 0°. The reaction flask was swirled in an ice bath for 4 min, then poured into 200 ml of a 1:1 ice-water mixture and extracted with chloroform. The chloroform solution was washed with a saturated $NaHCO_3$ solution and dried over anhydrous K_2CO_3. The solution was filtered and the solvent was removed at reduced pressure. The resulting pale yellow liquid was distilled [74–76° (0.04 mm)] in a Kugelrohr oven to give 3.2 g (81%) of syn acetate 9: ir (film) 5.74 (s), 8.08 (s), 9.55 (s), 13.51 (s), 14.36 μ (s); nmr (CCl_4) δ 1.55 (s, 3), 3.80 (q, 4, J = 5.0 Hz, J = 2.0 Hz), 4.83 (t, 1, J = 2.4 Hz), 6.60 (t, 2, J = 2.4 Hz), 6.77–7.28 $(A_2B_2, 4)$.

The product obtained (*i.e.*, 9) exhibits physical and spectral properties identical with those reported by Cristol and Nachtigall.[10]

syn-9-Hydroxybenzonorbornadiene (17).—To a stirred solution of 0.59 g (15.5 mmol) of lithium aluminum hydride in 25 ml of anhydrous ether was added slowly, over a 2-hr period, a solution of 3.13 g (15.6 mmol) of *syn*-9-acetoxybenzonorbornadiene (9) in 25 ml of anhydrous ether. The reaction was stirred for an additional 30 min. The excess lithium aluminum hydride was decomposed by the dropwise addition of water and the salts were removed by filtration. The solvent was distilled at reduced pressure, leaving 2.14 g (84%) of a clear viscous liquid which solidified on standing to give, upon recrystallization from hexane: white needles; mp 89–92.5°; ir (film) 2.92 (m), 9.35 (s), 13.68 (s), 14.43 μ (s); nmr (CCl_4) δ 3.17 (s, 1), 3.58 (q, 2, J = 5.0

Hz, J = 2.0 Hz), 4.08 (t, 1, J = 2.0 Hz), 6.60 (t, 2, J = 2.0 Hz), 6.90–7.42 ppm $(A_2B_2, 4)$.[15]

endo-Tetracyclo[5.4.0.0²,⁴.0³,⁶]undeca-1(7),8,10-trien-5-ol (18). **A.**—To a solution of 0.10 g (7.2 mmol) of lithium aluminum hydride in 10 ml of anhydrous ether at 0° was added dropwise a solution of 0.5 g (2.5 mmol) of endo acetate 10 in 5 ml of anhydrous ether over a 15-min period. After the mixture was stirred for an additional 10 min, the excess lithium aluminum hydride was decomposed by the dropwise addition of water. The solution was filtered, dried (K_2CO_3), and filtered again, and the solvent was removed under reduced pressure. Evaporative distillation of the residue in a Kugelrohr oven at 83° (0.06 mm) afforded 0.29 g (76%) of endo alcohol 18 as a viscous oil: ir (film) 2.90 (m), 9.17 (s), 13.2 μ (s); nmr (CCl_4) δ 1.20 (s, 1), 2.23 (m, 2), 2.73 (m, 1), 4.16 (m, 1), and 7.08 ppm (m, 4).[15]

B.—Treatment of 1.08 g (6.8 mmol) of syn alcohol 17 in 100 ml of benzene with 6 drops of acetophenone under the standard photolysis conditions gave, after evaporative distillation in a Kugelrohr oven at 71° (0.07 mm), 0.75 g (75%) of endo alcohol 18. On some occasions we have found the endo alcohol to undergo substantial isomerization to its syn isomer 17 upon distillation. Therefore, we ordinarily used the crude endo alcohol without purification for the further chemical transformations.

endo-Tetracyclo[5.4.0.0²,⁴.0³,⁶]undeca-1(7),8,10-trien-5-ol *p*-Nitrobenzoate (19).—The endo alcohol 18 (0.10 g, 0.63 mmol) was dissolved in 2 ml of carbon tetrachloride containing 0.05 ml of dry pyridine and cooled to 0° in an ice bath. *p*-Nitrobenzoyl chloride (0.11 g, 0.59 mmol) was added to the solution in one portion and the reaction vessel was immediately stoppered and placed in the refrigerator overnight. The white crystals which had formed were removed by filtration and the solvent was distilled at reduced pressure to give a yellow oil which solidified. Recrystallization from hexane gave 0.09 g (44%) of yellow needles: mp 166–168° dec; ir (Nujol mull) 5.82 (s), 6.57 (s), 7.88 (s), 13.39 (s), 13.90 μ (s); nmr (CCl_4) δ 2.33–2.72 (m, 2), 3.05 (m, 1), 3.95 (m, 1), 5.47 (q, 1, J = 7.0 Hz, J = 3.2 Hz), 6.75–8.20 ppm (m, 8).

Anal. Calcd for $C_{18}H_{13}NO_4$: C, 70.36; H, 4.23. Found: C, 70.50; H, 4.22.

Hydrogen-Bonding Studies.[12]—The hydrogen-bonding studies were restricted to the first overtone region for hydroxyl stretching in the near-infrared (15600–13900 Å) using a Cary Model 14 automatic recording spectrophotometer at the following settings: speed, 5 Å sec⁻¹; chart, 5 in. min⁻¹; slit control, 20. Matched 1-cm, 5-cm, and 10-cm quartz cells were used. Carbon tetrachloride was used as solvent. Concentrations of substrates varied from 10^{-1} to 10^{-3} *M* in all cases.

The areas of the absorption peaks (*B* values) were determined by multiplying the extinction coefficients of the bands by their bandwidth at half-height (in reciprocal centrimeters). These values are tabulated in Table I (*cf.* text).

(15) This compound was not subjected to carbon–hydrogen combustion analysis since it decomposed upon standing.