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exo-9,9-Diphenyltetracyclo[4.2.1.$1^{2,5}$.$0^{1,6}$]decan-*anti*-10-ol. Photolytic Conversion of a Pyrazoline to a Propellane[1]

James W. Wilt* and Rein Niinemae[2]

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

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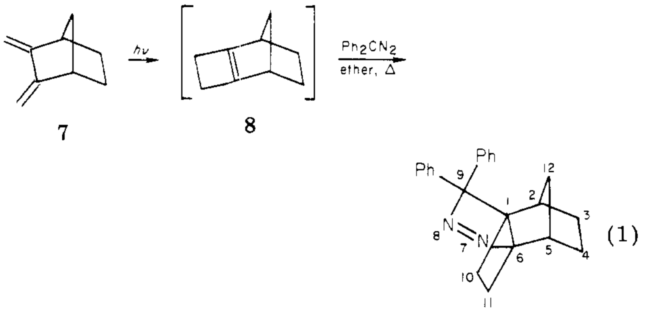
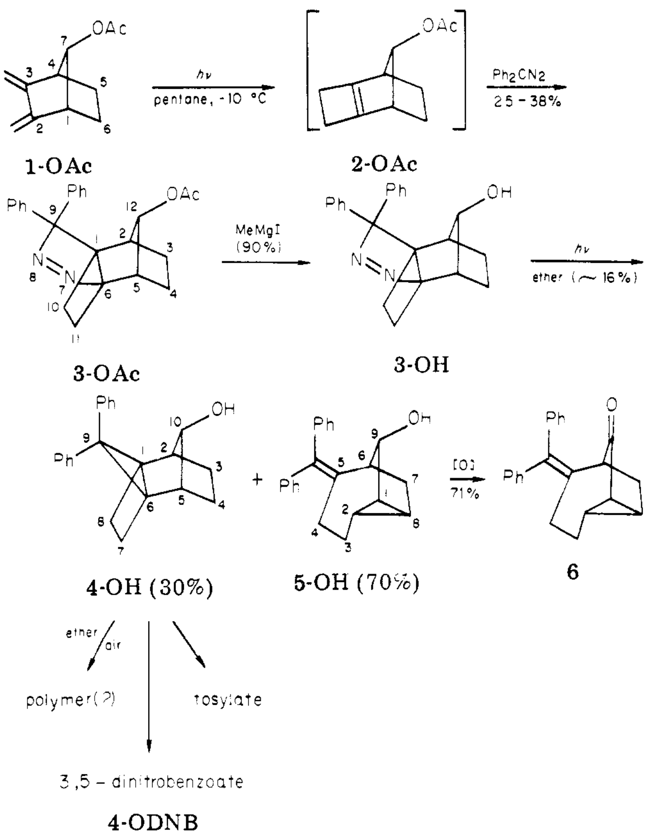
Our interest in long-range aryl migration (LRAM) coupled with electrocyclic cyclopropyl ring opening (ERO)[3] led us to synthesize alcohol **4-OH**. Although the alcohol was obtained in very low yield, the sequence developed in its synthesis seemed of sufficient interest to be communicated separately, involving as it did a rare tetracyclic ring system formed in an uncommonly used approach to propellane synthesis and the rearrangement which attended it. The sequence employed to construct alcohol **4-OH** is shown in Scheme I.

The procedure of Tanida and co-workers[4] used to prepare **1-OH** was modified somewhat, and the details are given in the Experimental Section. Photocyclization of **1-OAc** to **2-OAc** was effected as described by Aue[5] for a related case. No isolation of **2-OAc** was attempted. Rather, the photocyclized material was introduced into a diphenyldiazomethane solution directly and warmed. The pyrazoline adduct **3-OAc** was isolated in 25–38% yield over a series of such runs. The parent diene **7** was also successfully employed (eq 1).

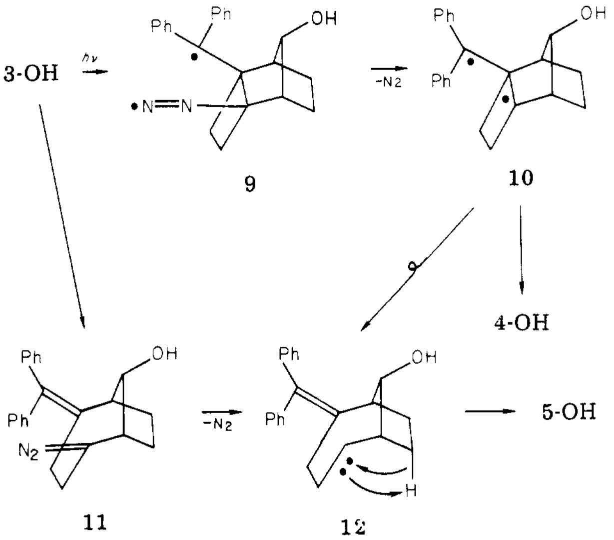


(1)

Scheme I



Scheme II



Because pyrolysis of **3-OAc** (and **3-H**) gave evidence of a complex product mixture,[6] photolysis of **3-OAc** was carried out instead.[7] No one of a variety of solvents was especially effective, so ether was ordinarily employed. Crude **4-OAc** and **5-OAc** were isolated in low yield (~11% and 26%, respectively), and purification was quite difficult from the tarry material formed in major amounts. Photolysis of alcohol **3-OH**, obtained by hydrolysis of acetate **3-OAc**, was poorer in terms of yield but better in terms of ease of purification. The major characterized product (11% yield) was alcohol **5-OH** (mp 127–128 °C) whose structure was determined spectrally (IR, UV, ^{1}H and ^{13}C NMR, lanthanide shift study). The desired alcohol **4-OH** (5% yield) was similarly characterized (see Experimental Section), and its symmetry was manifested in its four sets of geminally coupled doublets and one singlet for its bridgehead protons in its LSR ^{1}H NMR spectrum, as well as in its high melting point (185–188 °C).

To our knowledge all-carbon propellanes have not been synthesized before from pyrazolines.[8] Alcohol **4-OH**

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[1] Electrocyclic Effects in Solvolysis. 4. Part 3: J. W. Wilt, J. Kurek, and W. N. Roberts, *J. Org. Chem.*, **45**, 4243 (1980).

[2] Taken from the Dissertation of R.N., Loyola University of Chicago, June 1977; Loyola University Fellow, 1976–1977.

[3] J. W. Wilt, T. P. Malloy, P. K. Mookerjee, and D. R. Sullivan, *J. Org. Chem.* **39**, 1327 (1974).

[4] T. Tsuji, H. Ishitobi, and H. Tanida, *Tetrahedron Lett.*, 3083 (1972). We thank Dr. Tanida for correspondence on this synthetic sequence.

[5] (a) D. H. Aue and R. N. Reynolds, *J. Am. Chem. Soc.*, **95**, 2027 (1973). (b) We acknowledge with gratitude the help from Professor Aue regarding the demanding conditions of this photocyclization.

[6] It might be noted that pyrolysis of pyrazolines obtained by additions to norbornenes produces tricyclo[3.2.1.$0^{2,4}$]octane derivatives cleanly.[3] Clearly the strain engendered in propellane formation from 3-OAc and 3-H is significant and allows competitive side reactions to dominate.

[7] N. Filipescu and J. R. DeMember, *Tetrahedron*, **24**, 5181 (1968). These authors reported that photolysis and pyrolysis of a pyrazoline somewhat related to 3-H proceeded differently, the former affording the cyclopropyl ring containing product. G. Ege, *Tetrahedron Lett.*, 1667 (1963), reported that structurally similar pyrazolines behaved differently in photolysis. These reports illustrate the sensitivity of the process of pyrazoline decomposition both to experimental conditions and to the structure of the pyrazoline involved.

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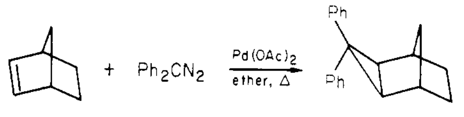
represents a functionalized representative of the rare and highly strained tetracyclo[4.2.1.1^{2,5}.0^{1,6}]decane ring system,[10] and its formation by such a pathway is noteworthy. Ether solutions of 4-OH underwent decomposition in air upon standing.[11] Studies on the solvolytic properties of 4-OH were thwarted by this inherent ease of oxidation and by the extreme lability of its tosylate. A 3,5-dinitrobenzoate, 4-ODNB, was obtained, however, for further characterization. Alcohol 5-OH also represents a little-studied ring system.[12] It was easily oxidized to ketone 6 in keeping with its secondary alcohol structure.

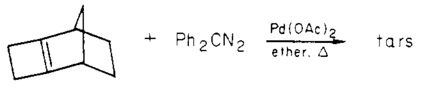
The formation of these alcohols in photolysis may be rationalized as shown in Scheme II, a sequence analogous to that advanced by others for pyrazoline photolyses.[13] The intermediacy of diazoalkene 11 was inferred from the transient pink color formed in these photolyses.[14] In the hope that the pathways to 4-OH and 5-OH might differ in spin multiplicity, photosensitized photolysis of 3-OH was performed. No formation of 4-OH was observed, however. It is therefore possible that a (presumably singlet[15]) diradical such as 10 served as the precursor to *both* 4-OH and 5-OH. Ring closure would form the former, and rearrangement[13a,e] to the carbene 12 followed by insertion would form the latter. Because the diazoalkene 11 apparently formed (pink color mentioned earlier), a companion route to 5-OH from 11 seems likely. The diazoalkene precursor is unknown, but it could be 3-OH itself[14b] or 9.

Metal salt promoted addition of the "diphenylcarbene" moiety was modestly successful on norbornene to form 13 by using the method of Kottwitz and Vorbrüggen,[16] but attempts to use the method on the tricyclic 8 (from photocyclization of 7) led only to tars (eq 2 and 3). The reported catalysis of pyrazoline decomposition to cyclopropanes by copper fluoroborate[17] was also attempted on pyrazoline 3-OH. Only alcohol 5-OH was detected, however.



(2)

13 (20%)



(3)

8

Future work will attempt to improve the sequence to propellane 4-OH and to find some measure of its behavior in the LRAM-ERO process.

Experimental Section

Melting points were taken on a calibrated Fisher-Johns block. Thin-layer chromatography (TLC) was done on Eastman silica gel plates with and without fluorescent indicator. Strips of dimensions 1 in. × 3 in. were used. The instruments used were as follows: IR, Perkin-Elmer 700A spectrophotometer; UV, Cary Model 14 spectrophotometer; NMR, Varian A-60A, CFT-20, and FT-80 spectrometers. The NMR spectra were taken in CDCl$_3$ containing 1% Me$_4$Si. Only portions of IR spectra are reported. Microanalyses were conducted by Micro-Tech Laboratories.

2,3-Dimethylene-*anti*-7-norbornanol (1-OH). This alcohol was obtained by starting from cyclopentanone and using the route described by Tanida and co-workers.[4] Some modifications are noted briefly. Ketalization of cyclopentanone was better achieved with *p*-toluenesulfonic acid rather than sulfuric acid[19] as catalyst. Bromination of the above ketal on a large scale by direct addition of bromine[20] rather than pyridinium bromide perbromide[21] was preferred. The absolute ethanol solvent volume had to be ≥10-fold that of the ketal for a good yield of high-purity product. Dehydrobromination of the dibromo ketal so formed was carried on for a 10-fold longer time than reported.[21] This ensured the absence of the dibromo ketal in subsequent reactions. Otherwise, purification of the various later intermediates was difficult. The ditosylation step of the sequence[4] required addition of the diol *to* the *p*-toluenesulfonyl chloride in dry pyridine, otherwise another product (from its spectra a cyclized ether[22]) formed. Elimination to form the diene from the ditosylate required a reaction time twice that reported.[4] Finally, reduction of **2,3-dimethylene-7-norbornanone** to 1-OH [mp 37–39 °C (lit.[4] mp 38–39 °C)] was best accomplished with lithium tri-*tert*-butoxyaluminum hydride (LTBAH) in tetrahydrofuran rather than with sodium borohydride.[4] The ratios of syn to anti alcohols formed were 1:2 (NaBH$_4$), 7:1 (L-Selectride), and 1:8 (LTBAH). The small amount of syn alcohol [mp 82–83 °C (lit.[4] mp 82–83 °C)] present in 1-OH in the last case was removed by dry column chromatography on Florisil with 40:60 ether–hexane.

2,3-Dimethylene-*anti*-7-norbornyl Acetate (1-OAc). Alcohol 1-OH (12.5 g, 92 mmol), benzene (300 mL), and acetic anhydride (18 g, 180 mmol) were refluxed 36 h under nitrogen. The cooled solution was washed with sodium bicarbonate (5%, 3 × 100 mL), water, and then brine and dried (Na$_2$SO$_4$). Removal of the benzene left an oil which was distilled: 13.7 g (83%); bp 50–55 °C (0.1 mm); IR (neat) 1740 (CO), 880 (=CH$_2$) cm^{-1}; NMR δ 5.31 4.98 (2 s, 4 H, =CH$_2$), 4.71 (br s, 1 H, H-7), 2.88 (dd, J = 1 Hz, 2 H, H-1, H-4), 2.03 (s, 3 H), OCOCH$_3$), 2.00–1.10 (m, 4 H, H-5, H-6). The acetate gummed up rapidly in air. It was used quickly in the next step or stored at −5 °C in the presence of hydroquinone.

***anti*-12-Acetoxy-*exo*-9,9-diphenyl-7,8-diazatetracyclo[4.3.2.1^{2,5}.0^{1,6}]dodec-7-ene (3-OAc).**[5b] Into an Ace glass photoreactor modified for low-temperature irradiation under dry, oxygen-free nitrogen[18] was placed 1-OAc (1.5 g, 8.4 mmol) dissolved

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[8] The commonly employed routes to isolable all-carbon propellanes involve photochemical [2 + 2] cycloaddition (intramolecularly with dienes or intermolecularly with an alkene and an enone), cyclopropanation via carbenes or carbenoids, ring contraction via diazo ketones or α-halosulfones, thermal [4 + 2] cycloaddition of dienes to strained olefins, and Dieckmann, Michael, and acyloin ring closures.[9]

[9] For leading references, cf. D. Ginsburg, *Acc. Chem. Res.*, **2**, 121 (1969); **5**, 249 (1972).

[10] The parent hydrocarbon is the only other reported example we know of. It was prepared by D. H. Aue and R. N. Reynolds [*J. Org. Chem.*, **39**, 2315 (1974)] by reaction of 8 with diazomethane in the presence of copper(I) bromide. No pyrazoline intermediate was apparent, and the reaction is probably a carbenoid addition process. We thank Professor Aue for a preprint of this work and for unpublished further information on his studies of 8.

[11] [3.2.1]Propellane has been reported to react rapidly with oxygen to form a copolymer: K. B. Wiberg, *Angew. Chem., Int. Ed. Engl.*, 11, 332 (1972).

[12] C. Lam and J. M. Mellor, *J. Chem. Soc., Perkin Trans. 2*, 865 (1974); M. Hartmann, *Justus Liebigs Ann. Chem.*, **729**, 8 (1969).

[13] (a) M. Franck-Neumann, *Tetrahedron Lett.*, 2979 (1968); (b) D. H. White, P. D. Condit, and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 1348 (1972); (c) R. A. Keppel and R. G. Bergman, *ibid.*, **94**, 1350 (1972); (d) D. F. Eaton, R. G. Bergman, and G. S. Hammond, *ibid.*, **94**, 1351 (1972); (e) P. G. Gassman and W. J. Greenlee, *ibid.*, **95**, 980 (1973).

[14] (a) A pink color ascribed to a transient diazoalkene was also observed in a related system by Gassman and Greenlee.[13e] (b) Isolation of a diazoalkene from photolysis of a pyrazoline was reported: M. Franck-Neumann and C. Buchecker, *Tetrahedron Lett.*, 2659 (1969).

[15] The deleterious effect of photosensitization on the process agrees with this viewpoint. Because the photolyses were carried out with >300-nm light (Pyrex filter), intervention of triplet diradicals seems less likely. It has been claimed that light of <300 nm can produce triplet species from pyrazolines: S. D. Nowacki, P. B. Do, and F. H. Dorer, *J. Chem. Soc., Chem. Commun.* 273 (1972).

[16] J. Kottwitz and H. Vorbrüggen, *Synthesis*, 636 (1975).

[17] D. S. Wolfman and R. S. McDaniel, Jr., *Tetrahedron Lett.*, 4523 (1975).

[18] For complete details, cf. ref 2.

[19] J. Boeseken and F. Tellegen, *Recl. Trav. Chim. Pays-Bas*, **57**, 133 (1938).

[20] E. L. Allred and C. Anderson, *J. Org. Chem.*, **32**, 1874 (1967).

[21] P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, **87**, 2769 (1965).

[22] Other cases of cyclized ether formation upon attempted ditosylation are known: ref 9; B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **28**, 1388 (1963).

in purified pentane (500 mL). By means of a circulating pump, cold (−30 °C) methanol from a refrigerated reservoir served as a bath to keep the pentane solution at ∼−10 °C for the 72-h duration of the irradiation from a 450-W Hanovia lamp through a Vycor filter under an atmosphere of dry nitrogen. The photolysate was then forced by nitrogen pressure into a solution of diphenyldiazomethane[23] (1.7 g, 8.7 mmol) in dry, purified hexane (100 mL). The solution was refluxed under nitrogen for 48 h and then reduced in volume to 30–50 mL. Upon cooling, the solution deposited white prisms. Addition of ether changed these prisms to fluffy needles which were collected: 0.8–1.2 g (over a number of runs; 25.5–38% yield); mp 107–111 °C dec upon several recrystallizations from chloroform–ether; IR (KBr) 1725 (CO), 1550 (N=N) cm^{-1}; NMR δ 7.80–7.20 (m, 10 H, Ar H), 3.81 (m, 1 H, H-12), 2.85 (m, 1 H, H-5), 2.51 (m, 1 H, H-2), 2.40–1.40 (m, 8 H, H-3, H-4, H-10, H-11), 1.80 (s, 3 H, $OCOCH_3$). The compound readily formed solvates upon repeated recrystallization from ether alone or methylene chloride, in which forms it was shelf stable. Anal. Calcd for $C_{24}H_{24}N_2O_2 \cdot 3(C_2H_5)_2O$: C, 76.61; H, 6.93. Found: C, 76.49; H, 7.01. Calcd for $C_{24}H_{24}N_2O_2 \cdot CH_2Cl_2$: C, 72.92; H, 6.20. Found: C, 73.49; H, 6.37.

***anti*-12-Hydroxy-*exo*-9,9-diphenyl-7,8-diazatetracyclo[4.3.2.1^{2,5}.0^{1,6}]dodec-7-ene (3-OH).** Pyrazoline **3**-OAc (2.6 g, 7 mmol) was dissolved in dry tetrahydrofuran (25 mL) and added dropwise over 15 min to a stirred solution of ethereal methylmagnesium iodide (25 mL, prepared from 41 mmol of magnesium) at 5 °C. The material was stirred at room temperature for 3 h and cooled. The complex formed was decomposed with wet ether, and the layers were separated. The flask was washed with ethyl acetate (2 × 100 mL) and water (100 mL). The ethyl acetate phase was combined with the reaction ether phase and dried (Na_2SO_4). Removal of the solvent left **3**-OH: 2.1 g (90%); mp 145–146 °C dec (as white crystals from chloroform–hexane; little heat, short time); IR (KBr) 3375 (OH), 1550 (N=N) cm^{-1}; NMR δ 7.70–7.10 (m, 10 H, Ar H), 3.03 (m, 1 H, H-12), 2.58 (m, 1 H, H-5), 2.40–1.20 (m, 10 H, remaining H's). Anal. Calcd for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71. Found: C, 79.64; H, 6.84.

Photolysis of Alcohol 3-OH. Pyrazoline alcohol **3**-OH (500 mg, 1.51 mmol) in oxygen-free dry ether (250 mL) was added slowly to further oxygen-free dry ether (500 mL) at −20 °C as the latter was irradiated by a Pyrex-filtered 450-W Hanovia lamp for 2 h. The materials were stirred during irradiation by a nitrogen bubbler. The irradiation was continued for 1 h after the addition. The ether was removed by rotary evaporation. The residues (much tar) *from eight such runs* were combined and chromatographed with 5% ether–hexane on Florisil (500 g) containing fluorescent indicator in a 4.5 × 80 cm nylon tube. The separated bands were observed with a "Mineralite" (Ultra-Violet Products, Inc.), and the tube cut at the appropriate points. The compounds were then eluted with ethyl acetate from these sections and obtained after removal of the solvent.

The faster eluting compound (TLC R_f 0.33 in 10% ethyl acetate–hexane) was ***exo*-9,9-diphenyltetracyclo[4.2.1.1^{2,5}.0^{1,6}]decan-*anti*-10-ol (4-OH)**: 190 mg (average yield per run 4.8%); white solid; mp 185–188 °C (from ether–hexane followed by ethanol–water); IR (KBr) 3250 (OH), 3000, 2950, 1600, 1490, 1465, 1450, 1285, 1155, 1070, 1030, 1000, 925, 740, 708, 700 cm^{-1}; other spectra below. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 86.98; H, 7.52.

The 3,5-dinitrobenzoate ester **4**-ODNB was prepared in the usual manner:[24] 40% yield; mp 240–245 °C dec (from benzene–acetone). Anal. Calcd for $C_{29}H_{24}O_6N_2$: C, 70.15; H, 4.87. Found: C, 69.84; H, 4.94. Attempts to prepare its tosylate were unrewarding. Although small amounts of apparent tosylate were obtained on occasion, not enough of the seemingly labile substance for analysis or other purposes was accumulated. Alcohol **4**-OH, though air stable when crystalline, underwent decomposition when an ether solution of it was exposed to air overnight. The nature of the gummy residue was not investigated.

The slower eluting product (TLC R_f 0.25 in 10% ethyl acetate–hexane) was **5-(diphenylmethylene)tricyclo[4.2.1.0^{2,8}]nonan-*anti*-9-ol (5-OH)**: 440 mg (average yield per run 11%); white solid; mp 127–128 °C (from ether–hexane); IR (KBr) 3260, 3100, 3040, 2930, 2860, 1495, 1445, 1320, 1260, 1025, 980, 760, 735, 700; UV (EtOH) λ_{max} 245 nm (ϵ 13600); other spectra below. Anal. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33. Found: C, 87.34; H, 7.43. The alcohol was oxidized at 0 °C to **5-(diphenylmethylene)tetracyclo[4.2.1.0^{2,8}]nonan-9-one (6)** on a 100-mg scale with chromium trioxide (0.5 g) in dry pyridine (8 mL). After 12 h the material was processed by addition to water and ice (200 mL) and extraction with ethyl acetate (3 × 50 mL). The extracts were washed with hydrochloric acid (10%, 50 mL) and saturated aqueous sodium bicarbonate (50 mL) and dried (Na_2SO_4). Removal of the solvent left **6** which was recrystallized from ethanol: 70 mg (71%); mp 122–122.5 °C. Anal. Calcd for $C_{22}H_{20}O_2$: C, 87.96; H, 6.71. Found: C, 87.98; H, 6.76.

Other photolyses (acetone solvent, or in the presence of benzophenone in ether or benzene or azulene in ether) yielded essentially no **4**-OH.

Photolysis of Acetate 3-OAc. Pyrazoline acetate **3**-OAc (250 mg, 0.67 mmol) was dissolved in tetrahydrofuran (10 mL) and added to hexane (90 mL). Nitrogen was bubbled through the solution for 30 min after which time the solution was irradiated as mentioned above at 0 °C for 30 min. Processing the reaction material by chromatography as described led to crude samples of **4**-OAc and **5**-OAc, 25 mg (11%, TLC R_f 0.3, 3% ether–hexane) and 60 mg (26%, TLC R_f 0.45, 3% ether–hexane), respectively. The tar accompanying the products was less easily removed in these cases. Neither acetate was obtained pure enough for analysis, but certain spectra were taken. For **4**-OAc: IR (KBr) 1720 cm^{-1}; NMR δ 7.7–7.0 (m, 10 H, Ar H), 4.36 (m, 1 H, H-10), 2.59 (m, 2 H, H-2, 5), 2.55–1.2 (m, 6 H, H-3, H-4, H-7x, H-8x), 1.83 (s, 3 H, $OCOCH_3$), 1.30 (d, J = 8 Hz, 2 H, H-7n, H-8n). For **5**-OAc: NMR δ 7.4–7.0 (m, 10 H, Ar H), 5.18 (s, 1 H, H-9), 2.91 (m, 1 H, H-6), 1.91 (s, 3 H, $OCOCH_3$), 2.5–0.8 (m, 9 H, remaining H's).

Photolysis of **3**-OAc was performed also in toluene, benzene, acetonitrile, tetrahydrofuran, isopropyl alcohol, and ether. No significant improvement in the overall process was observed in any case.

Lanthanide Shift NMR Studies. The method of Crumrine and Yen[25] was followed closely. Framework Molecular Orbital (Prentice-Hall; FMO) models of alcohols **4**-OH and **5**-OH associated with Eu(fod)$_3$ were built, from which the r and θ values for use in the McConnell–Robertson equation were measured. Good correlation between the calculated and observed shifts in the presence of Eu(fod)$_3$ was observed.

For **4**-OH the values used were Eu–O distance = 3 Å and Eu–O–C angle = 180°; for **5**-OH the values were Eu–O distance = 3 Å and Eu–O–C angle = 130°, with the Eu atom equidistant and anti to the phenyl rings. The data are gathered in Table I.

Other NMR Studies. Alcohols **4**-OH and **5**-OH were further characterized by ^1H and ^{13}C NMR determinations.[26] The data are collected in Table II.

***exo*-9,9-Diphenyl-7,8-diazatetracyclo[4.3.2.1^{2,5}.0^{1,6}]dodec-7-ene (3-H).** $\Delta^{2,5}$-Tricyclo[4.2.1.0^{2,5}]nonene (**8**) was prepared as described by Aue and Reynolds.[5a] The olefin was not isolated but rather was treated with diphenyldiazomethane as described above for **3**-OAc (10-mmol scale). The mixture was heated for 6 h and reduced in volume, whereupon crystalline adduct precipitated (1.1 g, TLC R_f 0.6 in 10% ethyl acetate–hexane). The hexane was then removed, and the residual yellow oil was chromatographed in a 3 × 60 cm nylon column of Florisil (150 g) with 10% ether–hexane with observation by a Mineralite. The tube was cut at the appropriate points and the adsorbed material was removed with ethyl acetate. Evaporation of the solvent left further adduct (270 mg). The combined adduct was recrystallized from hexane: 1.2 g (39%); mp 125–126 °C dec; IR (KBr) 1545 (N=N); NMR δ 7.80–7.10 (m, 10 H, Ar H), 2.80 (m, 1 H, H-5), 2.50 (m, 1 H, H-2), 2.25–1.20 (m, 8 H, H-3, H-4, H-10, H-11), 0.73 (d, J = 10 Hz, 1 H, anti H-12), 0.36 (d, J = 10 Hz, 1 H, syn H-12). Anal.

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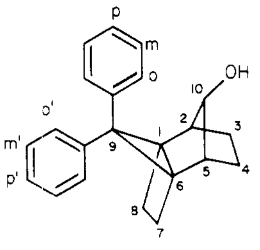
(23) J. B. Miller, *J. Org. Chem.*, 24, 560 (1959).

(24) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 5th ed., Wiley, New York, 1964.

(25) D. S. Crumrine and H.-H. B. Yen, *J. Org. Chem.*, 41, 1273 (1976). We are grateful to Professor Crumrine for his assistance in this portion of the work.

(26) The ^{13}C spectrum of **5**-OH was kindly determined for us on a Varian CFT-20 instrument at Purdue University. We thank Mr. James C. Pomes for this assistance.

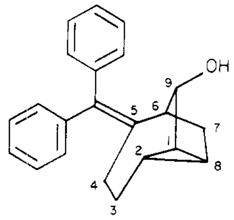
Table I. Lanthanide Shift Data



4-OH

proton	chemical shift, ppm calcd[a]	chemical shift, ppm obsd[b]	multiplicity (*J*, Hz)
10	12.9	9.0	s
3x, 4x	10.5	4.65	d (8)
2, 5	9.5	4.6	s
3n, 4n	5.4	2.65	d (8)
7n, 8n	2.7	1.9	d (8)
7x, 8x	2.5	1.5	d (8)
o	2.2	1.85	
m	1.2	0.55	
p	0.77	0.55	
o'	2.1	1.2	
m'	1.0	0.55	
p'	0.8	0.55	

correlation coefficient:[c] aliphatic H's, 0.992; aliphatic and aromatic H's, 0.984



proton	chemical shift, ppm calcd[a]	chemical shift, ppm obsd[b]	multiplicity (*J*, Hz)
9	12.8	20	s
6	11.2	14.4	d (9)
1	9.3	11.9	t (7)
7x	6.6	11.2	m
7n	4.4	6.3	m
3x	4.2	6.3	m
4x	3.4	3.4	m
8	3.0	3.6	m
3n	2.9	3.1	m
4n	2.5	3.4	m
2	2.0	3.1	m
aromatics[d]	0.8-2.8	2.7, 0.9	m

correlation coefficient:[c] 0.985

[a] $10^3(3 \cos \theta - 1)/r^3$. [b] $\Delta\delta$/(moles of LSR/moles of alcohol). The value of the denominator used to extrapolate to a 1/1 complex was 1.55 for 4-OH and 0.8 for 5-OH. [c] The CHOH pair of protons did not correlate well, as expected,[25] and was omitted from the calculation. [d] The aromatic protons were too complex for secure assignment. The LSR study of 4-OH and 5-OH showed clearly the symmetry of the former and the dissymmetry of the latter.

Calcd for $C_{22}H_{22}N_2$: C, 84.04; H, 7.05. Found: C, 83.89; H, 7.18.

Addition of palladium(II) acetate (trimer, Alfa, ~15 mg) to an ethereal solution of the diphenyldiazomethane-photocyclized material prior to the 6-h heating period, followed by the above isolation procedure, led to ill-defined tarry material with no spectral evidence of either propellane product or **3**-H. This contrasted with the palladium(II) acetate promoted reaction[16] of diphenyldiazomethane to norbornene, from which was isolated hydrocarbon **13**[27] in 20% yield, along with benzophenone-azine (20%).

Table II. ^1H and ^{13}C NMR Data

alcohol	position	δ_H (*J*, Hz)	δ_C
4-OH	1, 6		28.1
	2, 5	2.20 br s	45.2
	3, 4	2.05 m	24.1
	7, 8	2.46 d (8),[a] 1.25 d (8)[b]	20.4
	9		35.9
	10	3.56 br s	77.6
	OH	1.20 br s	
	Ar	7.33-7.16 m	144.6-125.6[c]
5-OH	1	*d*	29.6
	2	*d*	21.4
	3	*d*	24.6
	4	*d*	32.0
	5	*d*	143.8
	6	2.92 d (8.5)	50.6
	7	*d*	30.0
	8	*d*	18.0
	9	4.30 s	78.7
	$Ph_2C=$		137.5
	OH	*d*	
	Ar	7.40-7.10 m	140.7-120.0[e]

[a] Exo. [b] Endo. [c] Eight resonances in this range, mostly unassigned. [d] Complex multiplet, δ 2.6-0.8. [e] Complex, with not all eight resonances assigned.

Pyrolysis Studies. A solution of pyrazoline alcohol **3**-OH (1 mmol) in benzene (10 mL) was refluxed in the presence of copper(II) fluoborate[17] (Alfa, ~3 mg) until the evolution of nitrogen stopped. Analysis of the evaporated reaction material by TLC showed **5**-OH as the only identifiable product. No **4**-OH was detected.

Pyrolysis of pyrazoline **3**-H as a neat solid led to a very complex mixture which was not extensively investigated. Reaction of **3**-H (200 mg) in xylene (15 mL) under reflux for 30 min led to nitrogen evolution (92%). Removal of the xylene and elution of the residue through Florisil (10 g) with hexene followed. Evaporation of the hexane left a solid consisting of a major and very minor compounds by TLC. The mixture showed a complex NMR spectrum and clearly contained no propellane. The matter was not pursued intensively, but the provisional structural assignment of 5-(diphenylmethylene)bicyclo[4.2.1]non-2-ene [δ 5.63 (d, *J* ≃ 5 Hz), 5.41 (d, *J* ≃ 1.5 Hz, vinyl H's)] was given to the major product.

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Registry No. *anti*-1-OH, 38680-07-8; *syn*-1-OH, 38680-08-9; 1-OAc, 75347-89-6; 3-OH, 75347-82-9; 3-OAc, 75347-83-0; 4-OH, 75347-84-1; 4-OAc, 75347-85-2; 4-ODNB, 75347-86-3; 5-OH, 75347-87-4; 5-OAc, 75365-49-0; 6, 75347-88-5; 2,3-dimethylene-7-norbornane, 38680-06-7; diphenyldiazomethane, 883-40-9.

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(27) J. W. Wilt and T. P. Malloy, *J. Org. Chem.*, 38, 277 (1973).

A Facile Route to 1,3,5,7-Tetraaminoadamantane. Synthesis of 1,3,5,7-Tetranitroadamantane[†]

Gilbert P. Sollott* and Everett E. Gilbert

Chemistry Branch, Energetic Materials Division, U.S. Army Armament Research and Development Command, Dover, New Jersey 07801

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Stetter and Krause[1] have reported that they were unable to convert 1,3,5,7-tetrabromoadamantane (1) to acetamido

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