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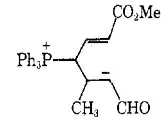

30

from **21** + **27**, because of its inferior leaving group,[1a] resulting in reversion to reactants and slower but productive formation of **25**. We would favor the alternative mechanism proposed in the text on the basis of the typical preference of Wittig reagents for 1,2 addition to enones and enals.

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Synthesis and Reactions of 5-Cyclononynone

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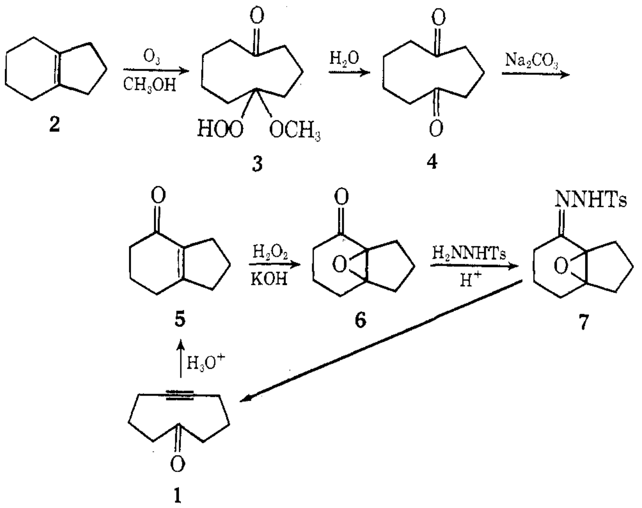
The previously unknown 5-cyclononynone (1) has been synthesized in an overall yield of 20% from 4,5,6,7-tetrahydroindan (2). As part of the synthesis, a very effective method of preparing bicyclo[4.3.0]-1(6)-nonen-2-one (5) has been developed. Fragmentation of the tosylhydrazone of the α,β-epoxy ketone 6 gave directly the strained cycloalkynone 1. A number of reactions of 1 have been investigated, including partial hydrogenation to yield *cis*-5-cyclononenenone (10), which in turn could be converted by photoisomerization to *trans*-5-cyclononenenone (11). A Diels–Alder reaction of 1 with 2,5-dimethyl-3,4-diphenylcyclopentadienone (12) resulted in the formation of the novel adduct 13. Acid-catalyzed transannular cyclization of 1 gave the bicyclic ketone 5 as the only product. All attempts to show that the optically active *l*-menthydrazone of 1 was a mixture of two diastereomers, because of the restricted rotation in the nine-membered ring, were unsuccessful.

A recent review[1] on the synthesis of cycloalkynes of medium sized rings indicated that no cyclononynone had yet been reported although 5-cyclodecynone had been prepared[2] and a Diels–Alder adduct of the very reactive 2-cyclooctynone had been isolated.[3] This report outlines the synthesis of the strained 5-cyclononynone (1) and describes a number of its reactions.

Synthesis of 5-Cyclononynone (1). The synthetic approach employed the well-known fragmentation reaction of the tosylhydrazone of an α,β-epoxy ketone.[2] The required ketone (6) was prepared from 4,5,6,7-tetrahydroindan (2) as outlined in Scheme I. Ozonolysis of 2 in methanol would be expected to yield hydroperoxide 3 which upon treatment with water would hydrolyze to 4, analogous to the ozonolysis of 9,10-octalin in methanol as reported by Criegee.[5-7] After this ozonolysis procedure no attempt was made to purify diketone 4 as previous reports[8] indicated it very readily underwent intramolecular aldol condensation. Thus, treatment of our hydrolyzed ozonolysis product with aqueous sodium carbonate solution gave the unsaturated ketone 5 in 50% yield from 2. This preparation of 5 is superior both in availability of starting material and overall percentage yield to those procedures previously reported.[9]

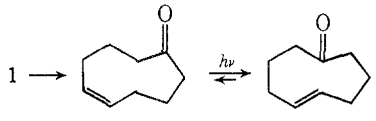
Epoxy ketone 6 was readily prepared from 5 by treatment with alkaline hydrogen peroxide.[10] Reaction of 6 with tosylhydrazine in acetic acid–methylene chloride at −20° followed by warming to room temperature gave 5-cyclononynone (1) in 56% yield. All the spectral properties are consistent with this structure (see Experimental Section). In the infrared spectrum of 1 no absorption for –C≡C–

Scheme I



stretching is found in the 2200-cm^{-1} region because of the symmetry of the molecule[11] but the reactions to be discussed leave no doubt that a triple bond is present. The sequence described accomplishes in an overall yield of 20% from **2** the synthesis of the previously unknown 5-cyclononynone (**1**). Unlike 2-cyclooctynone,[3] this strained system is stable at room temperature. Possibly 4-cyclooctynone could be prepared using the same approach and it would be of interest to ascertain if this compound were as unstable as the 2 isomer.

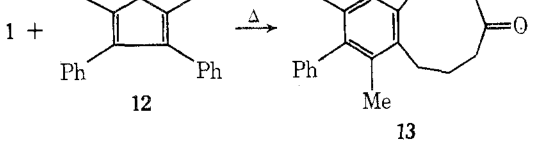
Reactions of 5-Cyclononynone (1). Hydrogenation of **1** in the presence of 5% Pd on charcoal resulted in the uptake of 2 mol of hydrogen and the formation of cyclononanone as the only product, thus confirming the carbon skeleton of **1**. When Brown's nickel boride (P2) catalyst[12] was used the rate of hydrogen uptake decreased sharply after the addition of 1 mol and *cis*-5-cyclononenone (**10**) was obtained in high yield. Uv irradiation of **10** with a 300-nm source resulted in the establishment of a photoequilibrium mixture consisting of 80% *trans*-5-cyclononenone (**11**) and 20% **10**. The ir spectra were particularly useful in distinguishing between the two compounds as the cis isomer had two medium intensity absorptions at 710 and 735 cm^{-1} while the trans isomer had strong absorptions at 975 and 990 cm^{-1}. Similar cis–trans isomerizations have been noted upon irradiation of *cis*-4-cyclooctenone[13] and *cis*-5-cyclodecenone.[14] Carlson reported[15] the formation of both **10** and **11** upon irradiation of 2-cyclopropylcyclohexanone. Compounds **10** and **11** can be separated by column chromatography using silica gel impregnated with silver nitrate[15] or by gas chromatography (gc) and thus the partial hydrogenation–photoisomerization approach provides a facile route to both of these medium ring enones from **1**.



10 **11**

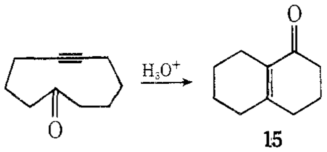
A particularly striking feature of the mass spectra of **10** and **11** is the high intensity of the M − H_2O peak (>90% of the base peak while in cyclononanone this peak is <10% of the base peak). A number of mechanisms could be proposed to account for the enhanced M − H_2O peak but it must be related to the fact that the hydrogens γ to the keto group are allylic and thus abstraction of these by the carbonyl oxygen would be a lower energy process than in the case of cyclononanone. A Dreiding model of the cis enone (**10**) shows that the carbonyl oxygen can come closer than 1.8 Å to these γ hydrogens and so hydrogen abstraction processes such as the McLafferty rearrangement should be possible.[16] In the trans isomer (**11**) this oxygen–γ-hydrogen distance is greater than 1.8 Å but the similarity of the mass spectra of the two isomers (see Experimental Section) suggests that there may be significant isomerization of **11** to **10** upon introduction into the spectrometer. Deuterium labeling experiments would obviously be necessary to gain further insight into the mechanism of these transformations.

Diels–Alder adducts are obtained upon reaction of either alkene[17] or alkyne[18] dienophiles with 2,5-dimethyl-3,4-diphenylcyclopentadienone (**12**).[19] In the alkyne reactions the adduct normally loses a molecule of carbon monoxide to give a substituted *o*-terphenyl system. Reaction of **1** with **12** in refluxing toluene gave adduct **13** in 42% yield. The novel aromatic ketone exhibited only one methyl resonance (τ 8.0) in its nmr spectrum, consistent with the symmetrical nature of the molecule. Formation of **13** is further evidence for the presence of an alkyne linkage in **1**. Dreiding models suggested there might be a possibility of an electronic interaction between the fully substituted benzene ring of the *o*-terphenyl system and the carbonyl group (or an appropriate derivative). The 2,4-dinitrophenylhydrazone (2,4-DNP) of **13** was prepared and its visible spectrum compared with that of the 2,4-DNP of cyclononanone.[20] No difference in the 300–500-nm region of the two spectra was noted and thus there was no indication of an intramolecular charge-transfer interaction between the hexasubstituted benzene ring (donor) and the dinitrosubstituted ring (acceptor).



12 **13**

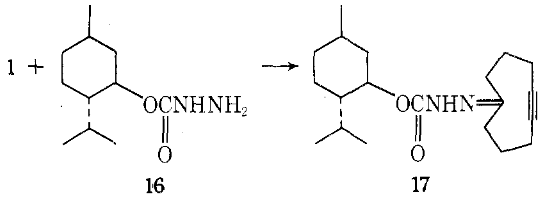
Two different investigations[21,22] showed that 5-cyclodecynone (**14**) underwent acid-catalyzed transannular cyclization to give bicyclo[4.4.0]-1(6)-decen-2-one (**15**) as the



14 **15**

only product. In the present case, treatment of **1** with dilute acid (2 *N* H_2SO_4) in aqueous ethanol gave cleanly the bicyclic ketone **5**. Presumably the mechanism for this cyclization *via* the vinyl cation is the same as that previously outlined for the conversion **14** → **15**.[21] Thus the same type of transannular reaction that was observed with the C_{10} 5-cycloalkynone occurs just as effectively with the C_9 homolog.

A Dreiding model of 5-cyclononynone (**1**) can be assembled but it is quite rigid with the carbonyl oxygen pointing in toward the center of the ring and either above or below the plane created by the triple bond and its adjacent carbon atoms. By preparing an appropriate optically active carbonyl derivative we postulated that it might be possible to separate the two diastereomers formed as a consequence of this rigidity or restricted rotation.[23] Toward this end, **1** was reacted with *l*-menthydrazide (**16**), an optically active reagent for carbonyl compounds developed by Woodward,[24] to give the *l*-menthydrazone (**17**),[25] $[\alpha]_D$ −42.2°. All attempts to separate the two proposed isomers either by tlc or fractional crystallization were unsuccessful. Apparently rotation in the ring is not restricted to the extent that it prevents interconversion between the two isomers. The nmr spectrum of **17** was determined at −50° to slow or stop this interconversion and the sharp methyl doublets of the methyl ring were examined. Again there was no indication of the existence of two compounds either because the interconversion is still too rapid or the chemical shifts of the methyl groups in the two compounds are not sufficiently different.[26]



16 **17**

In conclusion, we have outlined in this report an effective synthesis of 5-cyclononynone (1) from readily available starting materials and have described a number of reactions which support the proposed structure of 1 and also provide easy access to a number of novel medium ring structures.

Experimental Section

Melting points were determined on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman Model IR-5A infrared spectrophotometer, ultraviolet spectra on a Unicam SP 800 spectrophotometer, and mass spectra on a Varian Mat CH7 spectrometer operating at 70 eV. Nuclear magnetic resonance spectra were recorded on a Varian A-60A spectrometer using the internal standard tetramethylsilane (TMS, τ 10.0) and the following designations are used: s = singlet, d = doublet, and m = multiplet. Gas chromatographic (gc) analyses and collections were carried out on an Aerograph Autoprep Model A-700 using either of the following: column A, 20% Carbowax 20M on Chromosorb W, 60–80 mesh, 6 ft × 0.25 in.; column B, 20% OV-210 silicone fluid on Chromosorb W high performance, 80–100 mesh, 5 ft × 0.25 in. Peak areas were determined by triangulation and were not corrected for differences in thermal response. Thin-layer chromatography, tlc, and preparative-layer chromatography, plc, employed silica gel GF 254 in thicknesses of 0.25 and 0.75 mm, respectively. The solvent system used throughout was 1% ethyl acetate–chloroform. Optical rotations were determined at 25° on a Bendix-NPL Automatic Polarimeter, Type 143, using a 1-cm cell and absolute ethanol as solvent. Photochemical irradiations were performed in a Rayonet Model RPR 208 preparative reactor equipped with 300-nm lamps. Elemental analyses were performed by H. S. McKinnon, Chemistry Department, University of Guelph or A. B. Gygli, Microanalysis Laboratory, Toronto.

Preparation of Bicyclo[4.3.0]-1(6)-nonen-2-one (5). A suspension of 8.0 g (66 mmol) of 4,5,6,7-tetrahydroindan (2)[4] in 60 ml of absolute methanol was stirred rapidly at −70° while a stream of ozone from a Welsbach generator (200 W) was bubbled through the reaction for 30 min. The suspension had cleared and the characteristic blue color of excess ozone was evident. A solution of 5 g of potassium iodide in 20 ml of water was added to destroy the peroxide formed in the hydrolysis and the reaction was allowed to warm to room temperature at which time the iodine color was discharged with a solution of sodium thiosulfate. To this crude ozonolysis mixture was added 6 g of sodium carbonate and sufficient water to give a total of 60 ml of water added overall. The reaction solution was heated to reflux for 1.5 hr, cooled, and extracted with chloroform. The organic phase was washed with water and brine and dried ($MgSO_4$). Removal of the solvent and distillation gave 4.48 g (50%) of 5 as a colorless liquid which was >95% pure by gc analysis (column B, 170°): bp 49–52° (0.3 mm); ir (neat) 1665, 1640 cm^{-1};[8] uv λ_{max} (EtOH) 250 nm (ϵ 10,600);[8,9] 2,4-DNP derivative, mp 247–247.5 (lit.[8] mp 250°).

The *l*-menthydrazone of 5[27] was prepared using the general procedure previously described[24] with a reflux period of 7 hr to give pale yellow needles from aqueous ethanol: mp 158–158.5°, uv λ_{max} (EtOH) 268 (ϵ 26,000); $[\alpha]_D$ −48.6° (*c* 1.23).

Preparation of 10-Oxatricyclo[4.3.1.0]-2-decanone (6). To a stirred solution of 9.8 g (72 mmol) of 5 in 22 ml of 30% hydrogen peroxide and 70 ml of methanol at 15° was added dropwise over a period of 15 min a solution of 2.1 g of potassium hydroxide in 9 ml of water. After stirring at 20–25° for 3 hr the reaction mixture was poured into 150 ml of brine and this aqueous phase was extracted with ether. The organic phase was washed with brine and dried ($MgSO_4$). Removal of the solvent and distillation gave 7.75 g (71%) of 6 which exhibited only one peak on gc analysis (column A, 182°): bp 61–65° (0.6 mm); ir (neat) 2920, 1700, 1370, 1090, 915, 880, 790 cm^{-1}; nmr (CCl_4) τ 7.4–8.7 (m). *Anal.* Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found C, 71.20; H, 8.22.

Preparation of 5-Cyclononynone (1). To a solution of 6.88 g (45.2 mmol) of 6 in 75 ml of glacial acetic acid and 75 ml of methylene chloride at −20° was added 8.48 g (45.5 mmol) of *p*-toluenesulfonylhydrazine. The solution was stirred for 0.5 hr at this temperature during which time a white precipitate formed. The reaction was stirred at 0° for 2 hr then at room temperature for 3 hr to give a clear yellow solution. Solid sodium carbonate was added to neutralize the acetic acid and water was added to dissolve any solid present. To two phases were separated and the aqueous phase was extracted with methylene chloride. The combined organic phases were washed with saturated sodium bicarbonate solution and brine and dried ($MgSO_4$). Removal of the solvent and distillation yielded 3.44 g (56%)[28] of 1 which gc analysis (column A, 182°) showed to be >95% pure: bp 46–48° (0.2 mm); ir (neat) 2930, 1695, 1430, 1340, 1190, 1095 cm^{-1}; nmr (CCl_4) τ 7.5–8.1 (m); mass spectrum *m/e* (rel intensity) 136 (18, M$^+$), 135 (19), 108 (47), 79 (100).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.32; H, 8.89.

The *l*-menthydrazone of 1[27] was prepared using the general procedure previously described[24] with a reflux period of 40 hr to yield colorless needles from aqueous methanol: mp 167–167.5°; uv λ_{max} (EtOH) 232 (ϵ 10,100); nmr ($CDCl_3$) τ 9.18 (3 H, d), 9.12 (6H, d, *J* = 5.5 Hz), 7.4–9.3 (21 H, m), 5.3 (1 H, m), 2.5 (1 H, broad s); $[\alpha]_D$ −42.2° (*c* 1.19). All attempts to isolate another derivative from the mother liquors or to separate this product into two compounds by fractional crystallization with aqueous methanol or aqueous ethanol or by tlc failed.

Hydrogenation of 1. (a) With Pd/C. A suspension of 0.50 g (3.7 mmol) of 1 and 50 mg of 5% Pd on charcoal in 25 ml of ethyl acetate under 1 atm of hydrogen at 25° was stirred vigorously until 185 ml (7.5 mmol) had been consumed and the uptake had ceased. The catalyst was filtered and the solvent was removed leaving 0.48 g of a product which was identical in every respect (gc retention time, ir and mass spectrum) with an authentic sample of cyclononanone.[29]

(b) With Nickel Boride (P2) Catalyst.[12] To a stirred solution of 249 mg (1.0 mmol) of nickel acetate tetrahydrate in 8 ml of 95% ethanol under hydrogen was added a solution of 38 mg (1.0 mmol) of sodium borohydride in 7 ml of 95% ethanol to give a finely divided black catalyst. To this stirred catalyst suspension under 1 atm of hydrogen at 25° was added 0.50 g (3.7 mmol) of 1 in 3 ml of ethanol and the gas uptake was followed. After 1 hr 93 ml (3.8 mmol) of hydrogen had been consumed and the uptake had essentially ceased. The catalyst was filtered and the solvent was removed to give 0.46 g of a colorless liquid. Gc analysis (column A, 170°) indicated 91% of 10 (retention time 3.9 min) and 9% of 1 (retention time 7.5 min). An analytical sample of 10 was isolated by preparative gc: ir (neat) 3010, 2930, 1700, 735, 710 cm^{-1}; nmr (CCl_4) τ 7.5–8.4 (12 H, m), 4.4–4.8 (2 H, m); mass spectrum *m/e* (rel intensity) 138 (14, M$^+$), 120 (90), 82 (63), 67 (100), 55 (96), 54 (98); uv λ_{max} (EtOH) 219 (ϵ 640), 278 (26). *Anal.* Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.19; H, 10.30.

Formation of 11 by Photoisomerization. A solution of 100 mg (0.74 mmol) of 10 in 10 ml of spectroquality benzene was placed in a Pyrex tube and degassed with dry, oxygen-free nitrogen. The tube was sealed with a serum cap and placed in a water-cooled immersion well and the sample was irradiated with 300-nm lamps. Aliquots were withdrawn every few hours and the extent of photoisomerization was monitored by gc (column A, 148°). After 30 hr irradiation the reaction mixture consisted of 80% of 11 (retention time 7.3 min) and 20% of 10 (retention time 7.8 min) and continued irradiation did not change this ratio. An analytical sample of 11 was isolated by preparative gc: ir (neat) 3010, 2930, 1695, 1125, 990, 975 cm^{-1}; nmr (CCl_4) τ 7.5–8.3 (12 H, m), 4.6–4.9 (2 H, m); mass spectrum *m/e* (rel intensity) 138 (14, M$^+$), 120 (94), 82 (68), 67 (100), 55 (76), 54 (82); uv λ_{max} (EtOH) 219 (ϵ 560), 278 (28). *Anal.* Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.11; H, 10.17.

Preparation of Adduct 13. A solution of 200 mg (1.47 mmol) of 1 and 382 mg (1.47 mmol) of the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone (12)[19] in 2.5 ml of toluene was heated to reflux for 16 hr during which time the reddish-orange solution changed to a cloudy yellow mixture.[30] The solvent was removed and the residue was triturated with hot hexane leaving a powdery white solid which was discarded. The hexane solution was reduced to a volume of *ca.* 10 ml and upon cooling gave 225 mg (42%) of crystalline product. Recrystallization from hexane gave colorless needles of adduct 13: mp 204–205°; ir (CCl_4) 3040, 3020, 2940, 1705, 1600, 1490, 1440, 700 cm^{-1}; nmr (CCl_4) τ 8.0 (6 H, s), 7.5–8.0 (8 H, m), 7.0–7.3 (4 H, m), 2.8–3.3 (10 H, m); uv λ_{max} (EtOH) 218 (sh, ϵ 24,300), 228 (ϵ 25,900); mass spectrum *m/e* (rel intensity) 368 (100, M$^+$), 335 (63), 297 (37), 283 (30), 269 (32); 2,4-DNP derivative, mp 241–242°.[27] *Anal.* Calcd for $C_{27}H_{28}O$: C, 88.00; H, 7.66. Found: C, 88.07; H, 7.65.

Acid-Catalyzed Cyclization of 1. A solution of 84 mg (0.62 mmol) of 1 in 1 ml of 4 *N* H_2SO_4 and 1 ml of 95% of ethanol was left at room temperature for 12 hr. The solution was then poured into 5 ml of water and extracted with ether. The organic extract was washed with saturated sodium bicarbonate solution and brine and dried ($MgSO_4$). Removal of the solvent left 80 mg of a yellow oil which was shown by gc analysis (column B, 176°) to be a mixture of 97% of **5** and 3% of **1**. The identity of the major peak was confirmed by isolation and comparison of its spectral properties with an authentic sample of **5**.

Acknowledgments. The authors acknowledge the financial assistance of the National Research Council of Canada and the capable technical assistance of Mr. Richard Shum. We thank Dr. M. J. Nye for several helpful discussions and for providing a sample of 2,5-dimethyl-3,4-diphenylcyclopentadienone.

Registry No.—**1**, 52920-58-8; **2**, 695-90-9; **5**, 22118-01-0; **5** *l*-menthydrazone, 52920-61-3; **5** 2,4-DNPH, 52920-62-4; **6**, 39746-31-1; **10**, 52920-63-5; **11**, 52920-64-6; **12**, 26307-17-5; **13**, 52920-59-9; **13** 2,4-DNPH, 52920-65-7; **17**, 52920-60-2.

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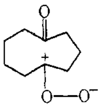

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(20) Note that in **13** the carbonyl group is part of a nine-membered ring.
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(23) **1** itself has a plane of symmetry and is achiral, but replacement of >C═O by >C═N̈– introduces the possibility of chirality into the structure *if* the rotation is sufficiently restricted.
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(25) The *l*-menthydrazone of ketone **5** was also prepared for comparison to establish that during the preparation of the derivative of **1** acid-catalyzed cyclization did not occur to ultimately give the derivative of **5** instead.
(26) A referee has suggested that the ready bending of the sp–sp^3 linkage would make **1** considerably less strained than Dreiding models indicate, *e.g.*, E. Kloster-Jensen and J. Wirz, *Angew. Chem., Int. Ed. Engl.* **12**, 671 (1973).
(27) The C, H, and N analysis for this derivative was within the usually acceptable limits of ±0.3%.
(28) If the crude product was purified by silica gel column chromatography, in addition to the isolation of **1** (eluted with 50% ether–petroleum ether), a 20% yield of the tosylhydrazone of **1**,[27] mp 144–145°, was also obtained (eluted with 2% ethyl acetate–ether). Apparently **1** was being formed before the reaction of tosylhydrazine with **6** was complete, but even when the reaction was maintained at 0° overnight before warming to room temperature the yield of **1** was not improved.
(29) Obtained from Aldrich Chemical Co.
(30) The reaction was followed by tlc with adducts **13** and **12** having R_f 0.55 and 0.65, respectively. The crude product could also be purified by plc.

Synthesis and Reactions of 4-Substituted 2-Azaadamantanes

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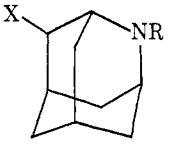
The synthesis of a series of 4-substituted 2-azaadamantyl compounds is reported. The ring system of these compounds was obtained *via* a closure reaction brought about by spontaneous intramolecular opening of an epoxide, at the former double-bond site of N-substituted bicyclo[3.3.1]non-6-en-3-ylamine (6), by the amide nitrogen. This unexpectedly facile closure, resulting from the unusual proximity of the amide nitrogen to the back side of the epoxide-bearing ring carbon, is one of several herein described examples of enhanced reactivity at the former double-bond site of this endo-substituted bicyclo[3.3.1]nonane ring system. Acetolysis of the *p*-toluenesulfonate ester of *N*-benzoyl-2-azaadamantan-*anti*-4-ol (8) was effected in buffered solution. The only product was anti acetate 14. Rate measurements demonstrated a slight rate retardation when compared to 2-adamantyl *p*-toluenesulfonate, the analogous carbocyclic system. Attempts to obtain the epimeric syn alcohol 18 by reduction, equilibration, and displacement are described.

As part of a continuing effort in our laboratories to synthesize hetero analogs of rigid carbocyclic systems[3–5] and in conjunction with our interest in adamantane chemistry,[6–7] we initiated a program of research directed toward the synthesis of adamantyl analogs in which the molecular framework has been altered through replacement of a bridge carbon by a nitrogen. It was our intent, then, to synthesize compounds illustrated by structures **1**. The β-amino and β-amido sulfonate esters could then be subjected to solvolytic conditions to assess the effects of the β nitrogen upon ionization.



1, R = PhCO, $PhCH_2$, H, CH_3; X = OH, OTs

We wish to report here the synthesis of this new class of compounds and our preliminary results on the solvolysis of one of them, *N*-benzoyl-2-azaadamantan-*anti*-4-ol.