puckering with minima 32° from a planar structure.[9] The pucker angle in this study of 41.9° may be larger than that of the other compounds cited because of the bulky phenyl groups tending toward equatorial conformation. The measured torsional angles of this study are O-S-C-1-C-4 = 95.7° and O-S-C-3-C-10 = 98.8° indicating the twist of C-1 and C-3. The atoms in the benzene ring C-4-C-9 have a maximum deviation from planarity of 0.04 Å and those in the ring C-10-C-15 have a maximum deviation of a 0.02 Å.

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Registry No. *cis*-2,4-Diphenylthietane *trans*-1-monoxide, 24605-73-0.

Supplementary Material Available. The atomic coordinates, anisotropic temperature factors, and a packing diagram will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-246.

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Photochemistry of 4-Cyclooctenone[1a]

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In a preliminary communication we reported on the photochemistry of *cis*-4-cyclooctenone (1), emphasizing the unusual nature of its transformation to 3-vinylcyclohexanone (2).[2] The present report reveals that 1 is reversibly isomerized to the trans isomer 3 upon $n-\pi^*$ irradiation, whereas higher energy light is required for the formation of 2.

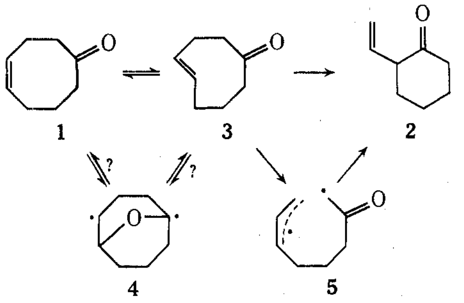
Irradiation of a cyclohexane solution of 1 with a 450-W Hanovia source through a Pyrex filter for 20 hr gave a mixture of 1 and its trans isomer 3 as the only products. Similar results were also obtained with a benzene solution irradiated through a Vycor filter. The identical 60:40 mixture of 1:3 was achieved starting from either isomer in small-scale photolyses conducted in a Rayonet reactor using 3100-Å lamps. Under these conditions prolonged irradiation of an acetone solution of 1 did not result in appreciable reaction. On the other hand, 30 min of irradiation with the Hanovia source directly through a *quartz* probe converted 1 predominantly into cyclohexanone 2. A minor product (6%) in this photolysis had the same glpc characteristics as 3. Irradiation of identical samples of 1 and 3 through quartz test tubes in the Rayonet reactor with 2537-Å bulbs for 15 min resulted in 17% conversion of 3 to 2 but only 3% of 1 to 2. The 3 to 1 isomerization was also more rapid than the conversion of 1 to 3. Cyclohexanone 2 gave only photoreduction to a mixture of isomeric cyclohexanols upon irradiation of a cyclohexane solution with the Pyrex-filtered Hanovia source.

Isolation of a 95% pure sample of 3 was effected by selective extraction into 5% aqueous $AgNO_3$ and preparative glpc at <130°. The assignment of structure 3 follows from the photoequilibration studies and its spectral properties: ir 5.88, 6.09, and 10.1 μ;[3] nmr δ 5.9 (1, m), 5.1 (1, m), and 3.0-1.8 (10, m). A spin-decoupling experiment indicated a 16-Hz coupling constant between the two olefinic hydrogens, consonant only with a trans double bond.[4] The mass spectra of 1 and 3 were similar but not identical. The uv spectrum of 3 was unusual in that exceptional low-wavelength absorption was observed in addition to normal $n-\pi^*$ absorption: λ_{max} 222 nm (ϵ 1000) and 280 nm (24) in ethanol and λ_{max} 287 (11), ϵ_{220} 1120 in cyclohexane. The cis isomer shows λ_{max} 285 nm (ϵ 16) and ϵ_{222} 268 in ethanol and λ_{max} 287 (11), ϵ_{220} 206 in cyclohexane. This feature of 3 is probably attributable to its structural rigidity, which holds the two π systems in close proximity to each other. Many β,γ-unsaturated ketones show such abnormality in their uv spectra.[5]

There was a slow disappearance of 3 upon refluxing in xylene leading to both 1 and uncharacterized higher molecular weight materials, but no 2 was thus produced. Exposure to *p*-toluenesulfonic acid in benzene solution for 4 days did not appreciably transform 3 to either 1 or 2.

This photochemical system presents several noteworthy aspects. Irradiation into the $n-\pi^*$ band of the carbonyl group promotes clean cis-trans isomerization of the transannular double bond at the expense of the normally expected photochemistry of a nonconjugated, medium-ring ketone (Norrish type I and type II cleavages, reductions, etc.).[6] Nor is there any evidence for intramolecular photocycloaddition leading to oxetane formation.[7] More exacting physical studies will be required to demonstrate the mechanism for this conversion, but several potential pathways can be imagined. The photoequilibration of 1 and 3 could involve $n-\pi^*$ excitation, intersystem crossing, triplet-energy transfer from carbonyl to the double bond (either intra- or intermolecularly), and subsequent collapse of the triplet olefin to the isomeric cyclooctenones. This is a well-precedented mechanistic possibility.[6] However, intermolecular energy transfer (and possibly the intramolecular counterpart) is contradicted by the lack of reaction upon photolysis in acetone solution, since the triplet acetone generated under these conditions should also be effective at energy transfer and thus promote the 1 to 3 conversion. A detailed study[8] of the photobehavior of 5-hepten-2-one, an acyclic γ,δ-unsaturated ketone, has led to the conclusion that intramolecular singlet exciplex formation accounts for the nonquenchable oxetane formation and geometrical isomerization, exceptionally short-lived excited singlet, and lack of the normally expected Norrish type II reaction that have been found for this system.[9] A similar intermediate can be invoked for the interconversion of 1 and 3 in the present system, although there is some question regarding the compatibility of the severely restricted geometries of these medium-ring compounds with the necessary relationship of the two π units for intramolecular exciplex formation. Finally, reversible formation of a Schenck-type biradical such as **4** could also explain this isomerization.[10]

Not only is the photoisomerization to **2** a relatively unprecedented type of rearrangement, formally involving 1,3 migration of an acylmethylene group,[11] but reaction appears to require excitation into some higher excited singlet state. This fact indicates that there is some very fast diverting step leading ultimately to product, since this reaction must compete with rapid relaxation by internal conversion and intersystem crossing. The fact that **2** is formed more rapidly from the trans isomer **3** may reflect its additional strain or special conformation, but a more trivial explanation is related to the more efficient absorption of low-wavelength light for **3** relative to **1**. (At 2537 Å the trans isomer has roughly four times the absorptivity of the cis compound.) The two most likely mechanism for this conversion are concerted 1,3-sigmatropic rearrangement or the stepwise equivalent proceeding by photodissociation to biradical **5**, followed by reclosure to **2**.



Experimental Section

General. Nmr spectra were obtained on CCl_4 solutions with Varian A-60 or HA-100 instruments; infrared spectra (ir) were obtained on neat samples with Perkin-Elmer 137 and 137G spectrophotometers. Ultraviolet spectra (uv) were recorded on a Cary 14 spectrophotometer. Gas chromatogrpahy (glpc) was performed on Varian Aerograph A600, A1200 (analytical), and A90-P3 (preparative) instruments. The analytical column was 10 ft × 0.125 in. of 15% Carbowax 20M on 60–80 Chromosorb W and the preparative column was 20 ft × 0.375 in. of 15% Carbowax 20M on 60–80 Chromosorb W. Mass spectra were obtained at 70 eV on AEI-MS9 and Varian-MAT CH-7 instruments. Anhydrous magnesium sulfate was used for all drying operations. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind., and Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

***cis*-4-Cyclooctenone (1).** To a cooled, stirred solution of 70 g of 4-cyclooctenol[12] in 500 ml of acetone was added dropwise 160 ml of 8 *N* chromic acid. The addition required 1.5 hr, and stirring was continued for an additional 45 min at room temperature. The mixture was poured into 500 ml of water and extracted with five 150-ml portions of pentane. The pentane extracts were combined, washed twice with water, dried, and concentrated. The residue was distilled through an Annular Teflon spinning-band column to give 44 g (64%) of **1**: bp 80–85° (10 mm); ir 5.88, 6.09, 13.6, and 13.8 μ; uv (95% EtOH) end absorption ϵ_{222} 268, λ_{max} 285 nm (ϵ 16); uv (cyclohexane) end absorption ϵ_{220} 206, λ_{max} 287 nm (ϵ 11); mass spectrum *m/e* (rel intensity) 124 (24), 96 (59), 68 (92), 67 (92), 55 (57), 54 (97), 41 (65), 39 (100), 28 (46), 27 (81).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.27; H, 9.72.

***trans*-4-Cyclooctenone (3).** A solution of 12.0 g of **1** in 1200 ml of degassed cyclohexane was irradiated with a Pyrex-filtered 450-W Hanovia lamp for 20 hr. Glpc assay indicated a 60:40 mixture of **1** and **3** as the only important products. The photolysis solution was extracted with two 100-ml portions of 5% $AgNO_3$ solution. Each of these was washed with three 15-ml portions of ether and treated with excess NH_4OH. The resulting mixtures were each extracted with three 50-ml portions of ether, the ether solutions were dried, and the ether was removed. The first extraction gave 2.4 g of **3** as a colorless liquid containing 5% of **1**. The second gave 1.0 g of a mixture of **3** and **1** (85:15). Glpc collection on a 5 ft × 0.375 in. column of 20% Carbowax 20M with injector, detector, and collector temperatures at 130° and a column temperature of 120° gave 95% pure **3** (5% **1**): ir 5.88, 6.09, and 10.1 μ; nmr (neat) δ 5.9 (m, 1), 5.1 (m, 1), and 1.4–3.2 (m, 10); uv (95% EtOH) λ_{max} 222 nm (ϵ 1000), 280 (24); uv (cyclohexane) end absorption ϵ 1120, λ_{max} 285 nm (ϵ 15); mass spectrum *m/e* (rel intensity) 124 (11), 96 (41), 68 (68), 67 (73), 55 (32), 54 (100), 41 (55), 39 (91), 28 (68), 27 (73); exact mass 124.088 (calcd for $C_8H_{12}O$, 124.089).

Photolysis of 1 and 3 at 3100 Å through Pyrex. The following samples were prepared in Pyrex test tubes and irradiated at 3100 Å in a Rayonet reactor using a merry-go-round: (a) 14.7 mg of **1** (96%, no **3**) in 1.47 ml of cyclohexane; (b) 10.1 mg of **3** (95%, 5% **1**) in 1.01 ml of cyclohexane. Glpc analysis showed that after 4 hr both samples had just reached a 60:40 ratio of **1** to **3**.

Photolysis of 1 in Acetone. Irradiation of a dilute acetone solution of **1** in a Pyrex test tube with 3100-Å bulbs in the Rayonet apparatus for 45 hr gave at most 2% conversion to **3**.

Photolysis of 3. A solution of 0.30 g of **3** in 30 ml of cyclohexane was irradiated with 3100-Å lamps through a Pyrex test tube in a Rayonet reactor for 10 hr. Glpc indicated a 55:45 ratio of **1** and **3** with 7% of a much higher retention time component as the only detectable by-product. The residual **3** was extracted from the solution with 10 ml of 5% $AgNO_3$ solution. The cyclohexane solution was dried and the solvent was removed, yielding a product which gave ir and nmr data identical with those of **1**.

Photolysis of 1 in Benzene. A solution of 1.0 g of **1** in 110 ml of benzene was degassed and irradiated with a Vycor-filtered 450-W Hanovia lamp for 2 hr. Glpc assay showed a 54:46 ratio of **1** to **3**. Extraction of the benzene solution with 20 ml of 5% $AgNO_3$ solution followed by the above work-up procedure gave only 0.24 g of **3** containing 9% of **1**. Glpc analysis indicated a 79:21 ratio of **1** to **3** in the remaining benzene solution. Thus, the reaction in benzene gives a higher proportion of **3** more rapidly than the direct irradiation, but does not allow the ease of isolation of **3** observed in cyclohexane.

Low-Wavelength Photolysis of 1. A solution of 0.20 g of **1** (98% purity) in 100 ml of degassed cyclohexane was irradiated under N_2 for 30 min using a quartz probe for a 450-W Hanovia Type L lamp. Glpc analysis revealed one major product and several minor products. One minor product (6%) had the same glpc retention time as *trans*-4-cyclooctenone (**3**). Preparative glpc gave a pure sample of **2**: ir 3.24, 5.81, 6.1, 10.1, and 11.0 μ; nmr δ 5.75 (m, 1), 5.0 (m, 2), and 2.6–1.2 (m, 9); mass spectrum *m/e* (rel intensity) 124 (44), 96 (31), 81 (100), 80 (73), 67 (78), 55 (67), and 54 (70).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.13; H, 9.60.

3-Vinylcyclohexanone (2). To a stirred, cooled solution of 32 g of $Hg(OAc)_2$ in 200 ml of 50% aqueous THF was added dropwise 10.9 g of 4-vinylcyclohexene. The yellow color disappeared before all the olefin had been added. The resulting colorless solution was stirred for an additional 45 min. To this solution was slowly added 100 ml of 3 *M* sodium hydroxide followed by 100 ml of 0.5 *M* sodium borohydride in 3 *M* sodium hydroxide. The resulting mixture was diluted with 100 ml of water and washed with four 100-ml portions of pentane. The combined extracts were washed twice with water, dried, and concentrated. The residue was distilled to give 8 g of a mixture of three components in a ratio of 65:20:15, bp 40–45° (3 mm).

To a cooled, stirred solution of 8 g of this mixture of alcohols in 100 ml of acetone was added 20 ml of 8 *N* chromic acid. The ice bath was removed and stirring was continued for 30 min. The reaction mixture was poured into 150 ml of water and extracted with four 100-ml portions of pentane. The pentane extracts were washed with water, dried, and concentrated. Distillation gave 6 g of a mixture of ketones in a ratio of 62:21:17, bp 45–50° (15 mm). Isolation by glpc gave 3-cyclohexen-1-yl methyl ketone[13] [ir 3.28, 5.88, 6.05, and 11.7 μ; nmr δ 5.6 (m, 2), 2.7–1.4 (m, 7), and 2.1 (s, 3)], 3-vinylcyclohexanone, and 4-vinylcyclohexanone:[14] ir (CCl_4) 3.3, 5.82, 6.1, 10.1, and 11.0 μ; nmr δ 6.2–4.8 (m, 3) and 2.6–1.3 (m, 9); mass spectrum *m/e* (rel intensity) 124 (40), 81 (25), 68 (29), 55 (100), 54 (35).

Photolysis of 2. Photolysis of a 1.0-g sample of **2** in 110 ml of cyclohexane for 10 hr led to formation of two products plus starting material. The solvent was removed and the residue was vacuum transferred (0.1 mm) to give 0.75 g of crude product. Glpc gave bicyclohexyl (25%), starting material (36%), and a third fraction collected as a 30:70 mixture of two components (39%) which was identified as *trans*- and *cis*-3-vinylcyclohexanols: ir 3.0, 3.24, 6.1, 9.6, 10.1, and 11.0 μ; nmr δ 5.7 (m, 1), 4.9 (m, 2), 3.85 (s, 1), 3.5 (m, 1), and 2.3–0.8 (m, 8).

Lithium Aluminum Hydride Reduction of 2. To a cooled, stirred slurry of 250 mg of lithium aluminum hydride in 20 ml of ether was added dropwise 250 mg of **2** in 15 ml of ether. The resulting mixture was stirred at room temperature for 2 hr. Hydrolysis was effected by addition of aqueous HCl. The layers were separated and the aqueous layer was extracted with ether. The ether extract was washed with water and dried, and the solvent was removed by distillation to give 250 mg of a crude mixture of *trans*- and *cis*-3-vinylcyclohexanols identical with the material obtained from photolysis of **2** in cyclohexane. Glpc analysis indicated that the two isomers were present in ratio of 10:90.

Photolysis of 1 and 3 at 2537 Å. The following samples were prepared in quartz test tubes and irradiated at 2537 Å in a Rayonet reactor using a merry-go-round: (a) 10.4 mg of **1** (98%, no **3**) in 1.04 ml of cyclohexane, and (b) 13.0 mg of **3** (96% + 4% **1**) in 1.30 ml of cyclohexane. After 15 min, glpc analysis revealed that 17% of **3** had been converted to **2**, while only 3% of **1** had been converted to **2**. Conversion of **3** to **1** was also more rapid than the conversion to **1** to **3**. The difference in per cent of **2** in these reactions increased until it reached 25% (1 hr), after which time **2** decreased as the per cent of **3** reached the same level in both samples.

Acid-Catalyzed Reaction of 3. A solution of 25 mg of **3** and 3 mg of *p*-toluenesulfonic acid in 2 ml of benzene was allowed to stand for 4 days at 25°. Glpc indicated a decrease of ~20% in the amount of **3** present, but no increase in **1**.

Pyrolysis of 3. A solution of 15 mg of **3** in 1 ml of xylene was heated in reflux for 1 hr. No **2** was observed by glpc, but **1** increased relative to **3**. Quantitative glpc revealed that the increase in **1**, as well as the increase in a higher retention time product, resulted from transformation of **3** both to these compounds and to products not detectable by glpc (presumably polymers). The loss of **3** was divided about evenly between these two processes.

Registry No. 1, 31598-70-6; **2**, 1740-63-2; **3**, 43101-33-3; 4-cyclooctenol, 4277-34-3; 4-vinylcyclohexene, 100-40-3; 3-cyclohexen-1-yl methyl ketone, 7353-76-6; 4-vinylcyclohexanone, 1740-64-3; *trans*-3-vinylcyclohexanol, 43101-34-4; *cis*-3-vinylcyclohexanol, 43101-35-5.

References and Notes

(1) (a) Supported by a research grant from the NSF. (b) Alfred P. Sloan Fellow, 1968–1970; John Simon Guggenheim Fellow, 1970–1971. (c) NDEA Title IV Fellow, 1965–1968; NSF Trainee, 1968–1969. (d) PRF Predoctoral Fellow, 1968–1969.

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Deamination of 1-Adamantylamine

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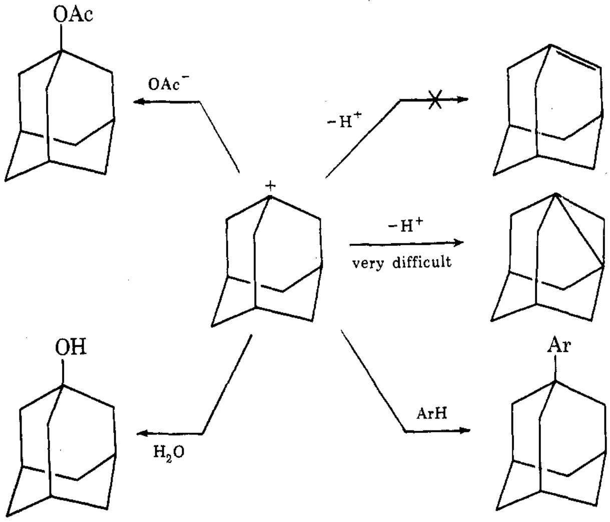
Kazanskii has reported[1] that the deamination of 1-adamantylamine by nitrous acid affords 1-adamantanol and adamantane in 20 and 80% yields, respectively. The adamantane must arise by hydride abstraction, and the necessary stoichiometry of such a process, with adamantane derivatives as the only possible hydride sources, makes the high yield of adamantane surprising. However, intermolecular hydride shifts are known for other adamantane systems[2-4] and therefore this reaction is of mechanistic interest. Accordingly, we decided to examine in detail the deamination of adamantylamines.

Two types of deamination reactions were studied: "normal," with aqueous acid and sodium nitrite;[5] and aprotic, employing isoamyl nitrite and 1 equiv of acetic acid.[6] The product analyses are contained in Table I.

Within our limits of detection (0.1%) no adamantane is formed under any conditions; the only products are 1-adamantanol and 1-adamantyl acetate. We must conclude that intermolecular hydride transfer is not an important reaction pathway in deamination, and therefore that the earlier results[1] are in error. This conclusion is strengthened by our observation that adamantane is not found even when deamination is carried out in the presence of the excellent hydride source, triphenylmethane (Table I).

In examining the literature on aprotic deaminations of alkylamines, one is struck by the minimal amount of alkylation of the aromatic solvents. Typically, only 0.5–2.5% of alkylbenzene is produced, the major products being alkene and cyclopropanes resulting from elimination and rearrangement, and alcohols or acetates.[6,7] Because the 1-adamantyl cation cannot lose a proton (Bredt's rule), and because incorporation of a cyclopropyl ring into the adamantane skeleton can be accomplished only with difficulty,[8] one might expect adamantylamine to yield significantly more alkylbenzenes than other alkylamines.



However, when the aprotic deamination of 1-adamantylamine is carried out in benzene solution, no phenyladamantane at all is detected among the products. When anisole is present, a trace (*ca.* 0.2%) of *p*-anisyladamantane is found. In each case, the only significant products are 1-adamantanol and 1-adamantyl acetate.

Friedman has suggested[9] that a tight diazonium ion-acetate ion pair is the principal intermediate in aprotic deamination in nonpolar solvents. The formation of a tight ion pair would seem to be the best explanation for our results also, with the difference that the cation is more likely the 1-adamantyl ion, because of the known ease of formation of this species.[10,11] We further suggest that the molecule of water formed along with the diazonium ion remains associated with the ion pair. Such an association is consistent with the formation of large amounts of alcohol in the absence of other intermolecular products,