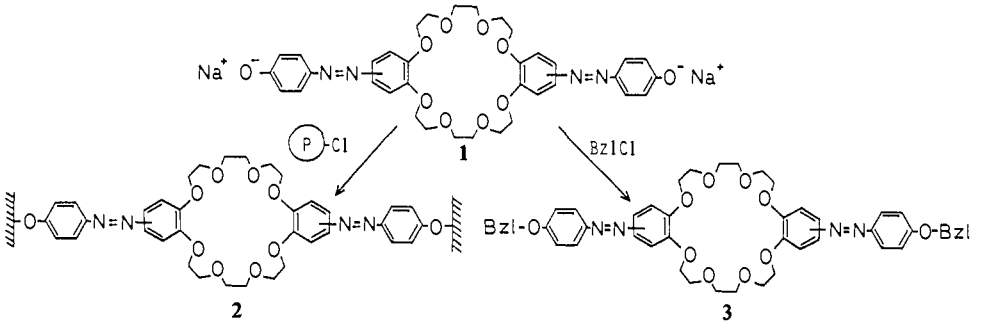
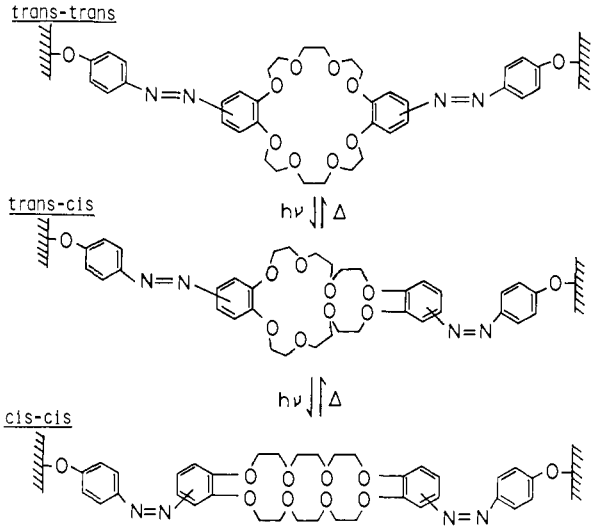
Scheme I



Scheme II



high-pressure Hg lamp (no filter), which induces the trans-to-cis isomerization of the azobenzene moiety, the concentration of cesium *p*-nitrobenzoate increased gradually and reached a new equilibrium where only 5% of Cs^+ was bound to **2**. On the other hand, when **2** in DMF was photoirradiated for 1 h and then mixed with the DMF solution of cesium *p*-nitrobenzoate in the dark, the absorbance of cesium *p*-nitrobenzoate decreased slowly and reached an equilibrium that was comparable with that attained in the dark (i.e., 17% binding). The time dependence which was also approximated by a first-order rate equation with $k = 0.0142$ min^{-1} is thus assumed to reflect the thermal cis-to-trans isomerization of the azobenzene moiety immobilized in the polymer support. It is of interest that the rate constant for the thermal isomerization in the polymer support (0.0142 min^{-1}) is very similar to that of the monomeric analogue (**3**) in the homogeneous solution (0.0101 min^{-1}). Finally, we photoirradiated **2** in DMF for 1 h and kept photoirradiating after mixing with the DMF solution of cesium *p*-nitrobenzoate. The decrease of OD_{270} was very slow (data not shown in Figure 1) and reached an equilibrium comparable with that of the final stage of the first experiment (i.e., 5% binding). The same photoirradiation effect was obtained when the concentration of cesium ion in the DMF solution was followed by an atomic absorption spectrophotometer.

The foregoing results consistently suggest that, as shown in Scheme II, the photoinduced trans-to-cis isomerization of the azobenzene moiety is capable of changing the conformation of the crown ether into a more stretched one which has poor ion-binding ability relative to the normal crown ether. Therefore, the binding ability of the crown ether immobilized as the azobenzene–crown–azobenzene bridge in the polymer support can be controlled by an on–off light switch. This conclusion suggests that the polymer support is useful as a "fixed point" to induce the conformational changes of immobilized functional molecules.[22] Since the surface of the polymer beads may be regarded as one side of the polymer membrane, we believe that this concept is applicable to the photocontrol of ion transport across the polymer membrane.

Acknowledgment. This research was supported by a grant from the Ministry of Education of Japan (No. 56850214).

Registry No. 1·2Na, 81456-74-8; **3**, 81456-75-9; cesium *p*-nitrobenzoate, 81456-99-7.

(22) A referee raised a question whether the 3.2% cross-linked polymer really acts as a "fixed point". Several our subsequent experiments support that the answer is yes: (i) the binding of K^+ in DMF is not subject to the photoirradiation effect; (ii) the photoirradiation effect appears clearly in DMF (not a good solvent for polystyrene resin) but is not clear in good solvents (e.g., *o*-dichlorobenzene and tetrahydrofuran); (iii) the photoirradiation effect is reproducible more clearly in highly cross-linked polystyrene resins; (iv) the solvent extraction of Cs^+ with monomeric **3** is scarcely affected by photoirradiation.

Generation and Rearrangement of the 2-Oxobicyclo[2.2.1]heptane-6,7-diyl Diradical via Nitrogen Extrusion from the Azoalkane 2,3-Diazatricyclo[4.3.0.0^{4,9}]non-2-en-8-one

Waldemar Adam,* Ottorino De Lucchi,† and Karlheinz Hill

Institut für Organische Chemie, Universität Würzburg Am Hubland, D-8700 Würzburg, West Germany and Departamento de Quimica, Universidad de Puerto Rico Rio Piedras, Puerto Rico 00931

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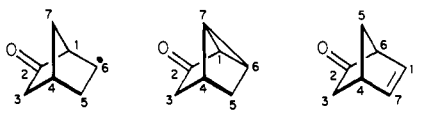
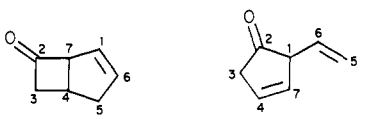
The diradical 2-oxobicyclo[2.2.1]heptane-6,7-diyl (**1**) has the



1 **2** **3**



4 **5**

options of cyclizing into tricyclo[3.2.0.0^{2,7}]heptan-3-one (**2**), of rearranging into 2-norbornenone (**3**) and bicyclo[3.2.0]hept-2-en-7-one (**4**), respectively, via C-1 to C-6 and C-1 to C-7 acyl 1,2-shifts, or of fragmenting into 2-vinylcyclopent-3-enone (**5**).[1] Presently we report on the generation of diradical **1** via the thermal and photochemical denitrogenation of azoalkane **6** (eq 1) and show that diradical **1** indeed affords the isomeric ketones **2**–**4**. The

* Universität Würzburg.

† On leave of absence from the University of Padova, Italy.

(1) Schuster, D. I. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 167–279.

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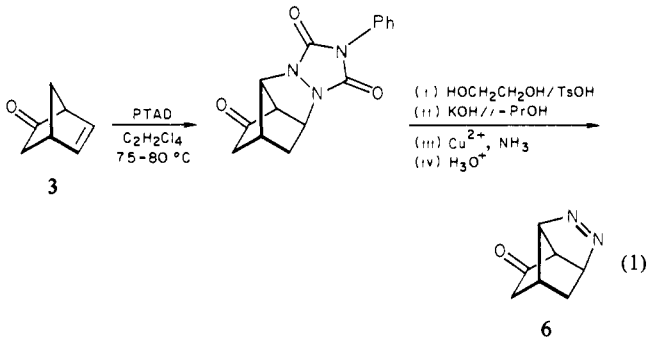

3 (1)

6

mechanistic implications of diradical **1** in the photochemical transformation of norbornenone (**3**) into the isomeric ketones **2** and **4**,[2] via the well-known oxadi-π-methane (ODPM) rearrangement,[1] is discussed.

Azoalkane **6** was prepared (eq 1) in 2.5% overall yield from 2-norbornenone (**3**);[3] mp 121–124 °C (CCl_4/pentane), with satisfactory elemental composition for $C_7H_8N_2O$. The spectral data[4] are in accord with the proposed structure.

The results of the product compositions in the nitrogen extrusion of azoalkane **6** are summarized in Table I. Clearly, the expected isomeric ketones **2–4**, except for the fragmentation ketone **5**, are formed in the nitrogen extrusion of the azoalkane **6**. These products were identified by comparison of capillary gas chromatography (CGC) retention times and IR and NMR spectra with the authentic materials.

A number of control experiments had to be conducted to establish that the ketones **2–4** were primary products in the thermolysis and photolysis of azoalkane **6**. Thus, under the thermolysis conditions of **6** (ca. 300 °C) the ketones **2–4** were stable. Furthermore, all three ketones were photostable under the benzophenone-sensitization conditions (350 nm) of azoalkane **6** and TMD-chemienergization conditions, but under direct photolysis (350 nm) 2-norbornenone (**3**) was converted into ketone **4** to the extent of ca. 5–7%. Finally, in the presence of 1,3-cyclohexadiene as triplet quencher the yield of tricyclic ketone **2** was reduced in favor of the bicyclic ketones **3** and **4** in the direct photolysis (350 nm) of azoalkane **6**.

A number of important mechanistic features are borne out by the product data in Table I. For example, in the vacuum flash thermolysis (VFT) no tricyclic ketone **2** is formed, although this product is stable under VFT conditions. Presumably the singlet-state diradical **1** prefers to rearrange into the bicyclic ketones **3** and **4**, presumably via C-1 to C-6 and C-1 to C-7 acyl 1,2-shifts, respectively, rather than cyclize into the tricyclic ketone **2**. The stability order of these ketone products is clearly **3** > **4** > **2**, and thus the thermally equilibrated or "cold" diradical **1** appears to sense this stability order. The triplet-sensitized process, i.e., benzophenone sensitization[5] and TMD chemienergization,[6] affords appreciable yields (Table I) of tricyclic ketone **2**. The major product is still **3**, and a small amount of **4** is formed. Thus, the triplet-state diradical **1** also discriminates in favor of the thermodynamically preferred bicyclic ketone **3** vs. **4**, but a significant fraction (20–30%) is channeled toward tricyclic ketone **2** via cyclization.

Table I. Product Composition[a] of the Denitrogenation of Azoalkane **6**

denitrogenation cond	conversion, %	yields, %[b] 2	3	4
6, VFT (300 °C/22 torr)	100	[c]	87 ± 2	13 ± 1
6, $h\nu$ (350 nm, C_6H_6)[d]	40	7 ± 1	50 ± 2	42 ± 2
6; $h\nu$ (350 nm, 1,3-cyclohexadiene, C_6H_6)[e]	40	3.5 ± 1	43 ± 2	53 ± 2
6, $h\nu$/Ph_2C=O (350 nm, C_6H_6)[f]	60	28 ± 2	68 ± 2	4 ± 1
6, TMD (85 °C, C_6H_6)[g,h]	8	30 ± 2	59 ± 2	5 ± 1
3; $h\nu$/Ph_2C=O (366 nm, C_6H_6)	45	0.042[i]		0.006[i]

[a] Determined by CGC; 50-m OV-101 capillary column, operated at injector, column, and detector temperatures of 200, 90, and 200 °C. [b] Normalized to 100% conversion. [c] Stable toward VFT conditions. [d] Under these conditions ca. 7% of authentic **3** is transformed into **4**; the % yields have been appropriately corrected; [azo] = 0.0096 M; Rayonet photoreactor with 350-nm lamps. [e] Same conditions as in footnote *d*, except in the presence of 0.102 M 1,3-cyclohexadiene. [f] 15 mol benzophenone/mol of **6**. [g] 1 mol tetramethyl-1,2-dioxetane (TMD)/mol **6**. [h] Under these conditions ca. 5% of authentic **3** is transformed into **2**; ca. 6% unidentified products. [i] Quantum yields from ref 2a.

The direct photolysis (excitation of the $n\rightarrow\pi^*$ azochromophore) gives a considerably higher yield of bicyclic ketone **4**, a small amount of the tricyclic ketone **2**, and 2-norbornenone (**3**) as major product (Table I). If a vibrationally excited or "hot" singlet diradical **1** is invoked for this direct photolysis, then the product distribution **3** ~ **4** > **2** can be readily rationalized. The small yield of tricyclic ketone **2** could be the result of a triplet path, i.e., intersystem crossing at the excited azoalkane **6** stage. Indeed, in the presence of 1,3-cyclohexadiene as triplet quencher (Table I), the yield of tricyclic ketone **2** was reduced in favor of the bicyclic ketones **3** and **4**.

Our present results on the behavior of diradical **1** have some interesting and significant bearings on the mechanism of the oxadi-π-methane (ODPM) rearrangement of the bicyclic ketones **3** and **4** into the tricyclic ketone **2**.[2a] Despite the mechanistic controversy on this problem,[2] diradical **1** appears to be the logical precursor to the ODPM product **2**, formed via an acyl 1,2-shift from C-6 to C-1 in excited **3** or from C-7 to C-1 in excited **4**. Therefore, the ODPM processes **3** → **2** + **4** and **4** → **2** and the presently reported nitrogen extrusion reaction **6** → **2** + **3** + **4** appear to be connected through the common diradical intermediate **1**.

Indeed, the experimental data (Table I) of the benzophenone-sensitization reactions for these two processes support this mechanistic conclusion. For example, as the quantum yield data[2a] for the ODPM process of **3** (Table I, sixth entry) and the product yields for the nitrogen extrusion of **6** (Table I, fourth entry) show, the product ratio of tricyclic ketone **2** and bicyclic ketone **4** are within the experimental error the same, i.e., ca. 7. Unfortunately, no quantum yield data for the ODPM process of **4** are available, and it was not possible to show that **4** gives also **3** besides **2** because 2-norbornenone (**3**) rearranges into **2** considerably more efficiently than **4** into **2**.[2a] However, the fact that the diradical **1**, derived by nitrogen extrusion from azoalkane **6**, does give **3**, indeed as major product, implies that in the photochemistry of **4** ketone **3** must also be formed. Mechanistically more significant, the photochemical isomerization of **3** into **4**, formally an acyl 1,3-shift,[1] may involve for 2-norbornenone (**3**) the two successive **3** → **1** and **1** → **4** acyl 1,2-shifts.

In summary, for the specific case of the ODPM rearrangement of 2-norbornenone we conclude that: (a) The photochemical isomerization of the ketones **2–4** and the nitrogen extrusion of azoalkane **6** are interconnected through the common diradical intermediate **1**. (b) The overall acyl 1,3-shift in 2-norbornenone may proceed via the two successive 1,2-shift **3** → **1** → **4**. (c) The

(2) (a) Schexnayder, M. A.; Engel, P. S. *Tetrahedron Lett.* **1975**, 1153. (b) Ipaktschi, J. *Chem. Ber.* **1972**, *105*, 1840. (c) Bays, D. E.; Cookson, R. C. *J. Chem. Soc. B* **1967**, 226. (d) Schuster, D. I.; Axelrod, M.; Auerbach, J. *Tetrahedron Lett.* **1963**, 1911. (e) Schenck, G. O.; Steinmetz, R. *Chem. Ber.* **1963**, *96*, 520.

(3) Adam, W.; De Lucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806.

(4) IR (CCl_4) ν (cm^{-1}) 3000, 2884, 1760; ^1H NMR (CCl_4, $SiMe_4$) δ 0.85 (1 H, H_5, A part AB system split in d, $J_{A,B}$ = 12.9 Hz, J = 6.0 Hz); 1.25 (1 H, H_5, B part of AB system split into d, J = 3.9 Hz); 2.15–2.60 (4 H, m); 5.03 (1 H, m); 5.39 (1 H, br s); ^{13}C NMR ($CDCl_3$, $SiMe_4$) δ 28.45 (t), 29.63 (d), 48.26 (t), 65.73 (d), 76.25 (d), 86.32 (d), 208.14 (s); λ_{max} 342 nm (ϵ 215). Experimental details will be given in the full report.

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(6) Adam, W. *Pure appl. Chem.* **1980**, *52*, 2591.

tricyclic ketone **2** is principally triplet-state derived. (d) The bicyclic ketone **4** is principally singlet-state derived.

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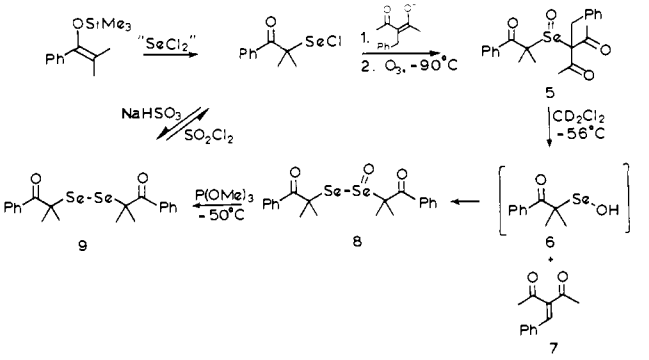
Registry No. 1, 81447-74-7; **2**, 37939-83-6; **3**, 694-98-4; **4**, 54074-60-1; **6**, 81447-75-8.

Scheme I



Organoselenium Chemistry. Characterization of Reactive Intermediates in the Selenoxide Syn Elimination: Selenenic Acids and Selenolseleninate Esters

Hans J. Reich,* Carl A. Hoeger, and William W. Willis, Jr.

McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

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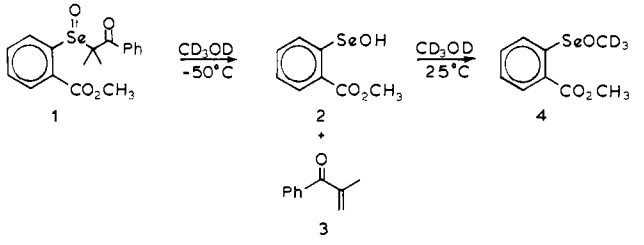
Selenenic acids (RSeOH) and their derivatives are presumed intermediates in a number of important reactions: selenoxide syn eliminations,[1,2] [2.3]sigmatropic rearrangements of allylic and propargylic selenoxides,[3] oxidation of selenols and diselenides,[1b,4] reduction of seleninic acids ($RSeO_2H$).[5,6] A selenenic acid may also be at the active site of the redox selenoenzyme glutathione peroxidase[7] as part of a selenocysteine residue. With the exception of a series of *o*-nitrobenzene and anthraquinone derivatives,[6] selenenic acids are unstable and disproportionate to diselenides and seleninic acids.

We have examined the syn elimination of several selenoxides to establish whether selenenic acids could be observed and their chemistry studied. Compound **1**[8] was chosen as a precursor to



the selenenic acid **2**. There was reason to believe that **2** might be stable, since *o*-benzoylbenzeneselenenic acid has been reported.[6b] The decomposition of selenoxide **1** at −50 °C in CD_3OD followed first-order kinetics ($t_{1/2} \approx 13$ min), giving only two products, the enone **3** and a compound we believe to be the selenenic acid **2**. The ^{77}Se NMR chemical shift of **2** (1091 ppm)[10] is different from that of the related seleninic acid (1220) and diselenide (458) and quite similar to the chemical shift of the stable[6a] *o*-nitrobenzeneselenenic acid (1053).[11] Compound **2** is stable in methanol below 25 °C but does react slowly at 25 °C ($t_{1/2}$ = 2 h) with solvent to give the methyl selenenate ester **4**. The identity of the selenenate ester was confirmed by carrying out the elimination of selenoxide **1** in protiomethanol. Solvent removal and dissolution in methanol-d_4 allowed observation of the ^1H NMR spectrum (δ 4.07, $^3J_{Se-H}$ = 7 Hz), in which the OCH_3 signal gradually disappeared as transesterification replaced methoxy with deuteriomethoxy. Selenenic acid **2** was much less stable in CD_2Cl_2 than in CD_3OD solvent.[12]

A second compound studied was the selenoxide **5**, a possible precursor to the aliphatic selenenic acid **6**. Compound **5** was prepared as shown in Scheme I. It decomposes at −52 °C in CD_3OD and at −60 °C in CD_2Cl_2 ($t_{1/2} \approx 18$ min). The reaction was followed by low-temperature NMR spectroscopy (−50 to −80 °C). In addition to the enedione **7**, only one other product was observed. It shows four methyl resonances (^1H: δ 1.80, 1.84, 1.94, 1.96; ^{13}C: δ 20.9, 24.3, 28.4, 29.37) in a 1:1:1:1 ratio, two sets of *ortho*-aryl protons at δ 7.72, 7.87, as well as ^{13}C resonances for two carbonyl groups (δ 200.6, 202.3) and two aliphatic quaternary carbons (δ 52.4, 76.5). The ^{77}Se NMR spectrum showed two signals at 862 and 540 ppm.[10] On the basis of this spectral information, in particular the observation of two sets of diastereotopic methyl groups (indicating the presence of a center of chirality) and the Se NMR shift (see below), we assign the selenolseleninate structure **8** to this species. Further supporting evidence is provided by the clean and quantitative reduction of **8** to the diselenide **9**[13] with trimethyl phosphite and its conversion to selenenamide **10**[13] on treatment with dimethylamine.[14] No

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(2) For recent reviews see: (a) Reich, H. J. "Oxidation of Organic Compounds, Part C"; Trahanovsky, W., Ed.; Academic Press: New York, 1978; p 1. (b) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22. (c) Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049.

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(7) For recent reviews see: Sunde, R. A.; Hoekstra, W. G. *Nutr. Rev.* **1980**, *38*, 265. Stadtman, T. C. *Adv. Enzymol.* **1979**, *48*, 1. Stadtman, T. C. *Annu. Rev. Biochem.* **1980**, *49*, 93.

(8) This selenoxide was prepared by the reaction of *o*-carbomethoxybenzeneselenenyl chloride[9] with the enolate of isobutyrophenone, followed by ozonization.

(9) Lesser, R.; Schoeller, A. *Chem. Ber.* **1914**, *47*, 2505. Lesser, R.; Weiss, R. *Chem. Ber.* **1913**, *46*, 2540.

(10) All ^{77}Se chemical shifts are reported in ppm downfield from Me_2Se.

(11) For previous studies of ^{77}Se NMR chemical shifts see: (a) McFarlane, W.; Wood, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1397. (b) Lardon, M. A. In "Organic Selenium Compounds: Their Chemistry and Biology"; Klayman, D. L., Günther, W. H. H., Eds.; Wiley-Interscience: New York, 1973; p 933. (c) Odom, J. D.; Dawson, W. H.; Ellis, P. D. *J. Am. Chem. Soc.* **1979**, *101*, 5815 and references therein. (d) Llabres, G.; Baiwir, M.; Piette, J.-L.; Christiaens, L. *Org. Magn. Reson.* **1981**, *15*, 152.

(12) Similar observations had been made for sulfenic acids: Shelton, J. R.; Davis, K. E. *Int. J. Sulfur Chem.* **1973**, *8*, 205.

(13) Selenium-77 NMR (CD_2Cl_2): δ **9**, 559, 25 °C; **10**, 986, −42 °C; **13**, 289, 25 °C.

(14) Compound **10** could also be prepared by reaction of the selenenyl chloride with dimethylamine. Benzeneselenenic acid reacts in situ with secondary amines to form selenenamides.[1b,15]

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