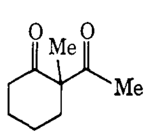
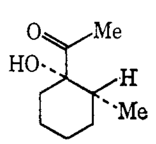
chemistry of **1** we employed triangular wave cyclic voltammetry, a simple and powerful technique for the investigation of organic electrode processes.[5] At the hanging drop mercury electrode in acetonitrile with tetraethylammonium bromide as supporting electrolyte, **1** showed a redox couple having a well-defined cathodic wave at −2.8 V (*vs.* saturated calomel electrode) and a small but definite anodic wave at −2.6 V. The relative height of the anodic wave increased with increasing scan rate, indicating that the reduced species, although apparently unstable, had a lifetime of the order of seconds under these conditions.



1



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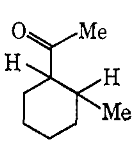

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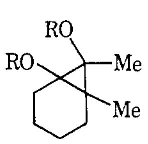
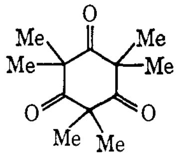


4a, R = H
b, R = Ac

Attempts to isolate cyclopropanediols from controlled potential electrolyses of **1** at a stirred mercury pool cathode were without useful issue until the solvent was changed from acetonitrile to tetrahydrofuran. Using tributylethylammonium tetrafluoroborate as supporting electrolyte[6] and employing acetic anhydride as a trapping agent for reactive anions, we obtained a mixture of products containing *inter alia* up to 33% of the two stereoisomers of **4b**. The isomers were separated from the mixture by glpc in approximately equal amounts. Analytical figures were in agreement with the formula $C_{13}H_{20}O_4$. Both isomers showed strong acetate absorption at 1749 and 1230 cm^{-1} in the ir. Isomer A (a liquid) showed singlets in the nmr at δ 2.00, 1.00, and 1.37 (intensity ratio 2:1:1). Isomer B (a crystalline solid, mp 36–38°) showed similar absorption at δ 1.96, 1.94, 1.45, and 0.95. Mass spectra of the two isomers were superimposable except for a small molecular ion at 240 in isomer A which was absent in B. Prominent peaks occurred at *m/e* 180 (loss of acetic acid), 43 (CH_3CO^+), and 138 (loss of acetic anhydride or equivalent). Treatment of each isomer with methanolic acid led to **2** (24% yield from isomer A, 66% from isomer B). The weight of evidence clearly supported structure **4b**.[7]



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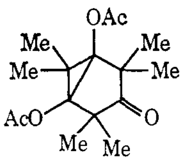
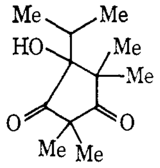


6



7

A similar electrolysis of trione **5** in acetonitrile led in 71% yield to diacetate **6**, mp 125–126°. Again analytical data supported this structure, as did ir (1750, 1240, 1210, 1060 cm^{-1}) and mass spectra (peaks at *m/e* 43 for CH_3CO^+ and 194 for loss of acetic anhydride or equivalent). The nmr spectrum of **6** in 1:1 carbon tetrachloride–benzene solution showed five clearly visible groups of methyls occurring as singlets at δ 1.87 (two methyls), 1.35 (two methyls), 1.19 (one methyl), 1.15 (two methyls), and 1.02 (one methyl). Acid hydrolysis of **6** gave in 48% yield the hydroxydione **7**, identical with material prepared[8] by Clemmensen reduction of **5**.

Examination of the cyclic voltammetry curves of **5** in the presence and absence of acetic anhydride suggested that the reduction of this molecule was proceeding by sequential electron and acetic anhydride additions. Electrolysis of **5** in the cavity of an esr spectrometer produced a radical showing a single broad line.[9] Although this may be the anion radical of **5**, the absence of any fine structure made identification uncertain, and consequently no light was shed on the intriguing possibility of a delocalized structure for such a radical.

Besides adding further support for the intermediacy of cyclopropanediols in the abnormal Clemmensen reductions of 1,3-diketones, our work opens a convenient synthetic route to derivatives of a novel class of compounds. Work in progress indicates that the chemistry of these substances holds some interesting surprises. We plan to report these results in the near future.[10]

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(5) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964), and references therein.

(6) T. J. Curphey and J. H. Williams, unpublished results. Tributylethylammonium tetrafluoroborate is easily prepared from tributylamine and triethyloxonium tetrafluoroborate, has none of the explosive hazard of the more commonly used quaternary ammonium perchlorates, and has exceptionally good solubility in media of low polarity. It appears to be a useful and convenient electrolyte for electrochemical investigations in nonaqueous solvents.

(7) Based on the slight difference in nmr spectra, isomer A has been assigned the structure with *cis* acetoxy groups and isomer B that with *trans* groups. This assignment rests on rather tenuous arguments which will not be presented here and is to be regarded as provisional.

(8) T. J. Curphey and R. L. McCartney, *J. Org. Chem.*, in press.

(9) We thank Sr. Mary Hertrich for help in performing this experiment.

(10) By using zinc powder in acetic anhydride saturated with hydrogen chloride as the reducing agent [see S. Yamamura and Y. Hirata, *J. Chem. Soc.*, *C*, 2887 (1968)], we have succeeded in synthesizing **4b** (isomer A) and **6** from **1** and **5**, respectively. Yields were high in both cases. This reduction and the related abnormal Clemmensen reduction of unsaturated ketones [for examples and references see B. R. Davis and P. D. Woodgate, *ibid.*, 2006 (1966)] are being investigated as general routes to cyclopropanediol and cyclopropanol derivatives.

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Received February 10, 1969

The Photolysis of Azine Monoxides. A Novel Electrocyclic Reaction[1]

Sir:

A vast amount of work has been reported within the past couple of years dealing with the photochemical transformations of various aromatic amine N-oxides.[3] In all cases, the only reactions which were reported, other than simple deoxygenation processes, were those in which the oxygen initially migrated to an adjacent carbon atom, ostensibly *via* an oxaziridine intermediate.

Most recently Kumler and Buchardt showed[4] that

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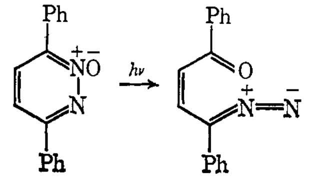
(1) Thermal and Photochemical Rearrangements of Azine Oxides. II. For paper I, see ref 2.

(2) W. M. Williams and W. R. Dolbier, Jr., *J. Org. Chem.*, **34**, 155 (1969).

(3) (a) B. Singh, *J. Am. Chem. Soc.*, **90**, 3893 (1968); (b) O. Buchardt and B. Jensen, *Acta Chem. Scand.*, **22**, 877 (1968); (c) O. Buchardt, B. Jensen, and I. K. Larsen, *ibid.*, **21**, 1841 (1967); (d) O. Buchardt, C. Lohse, A. M. Duffield, and C. Djerassi, *Tetrahedron Letters*, 2741 (1967).

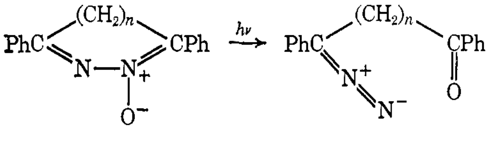
(4) P. L. Kumler and O. Buchardt, *J. Am. Chem. Soc.*, **90**, 5640 (1968).

3,6-diphenylpyridazine N-oxide, **1**, was converted photolytically to the diazoketone **2**.



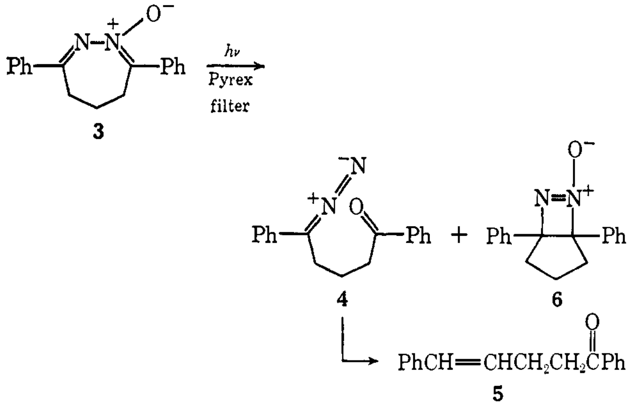
1 **2**

In view of these results, the photolysis of saturated cyclic azine monoxides might be expected to provide a route to the yet unexplored β-, γ-, and δ-diazo ketones. Indeed acyclic azine monoxides have been shown to



fragment upon irradiation to produce 1 equiv each of diazo compound and carbonyl compound.[5]

Our development of an improved synthetic method[2] for azine monoxides enabled us to prepare that cyclic azine oxide, **3**, which upon photolysis should fragment to the δ-diazo ketone **4**.

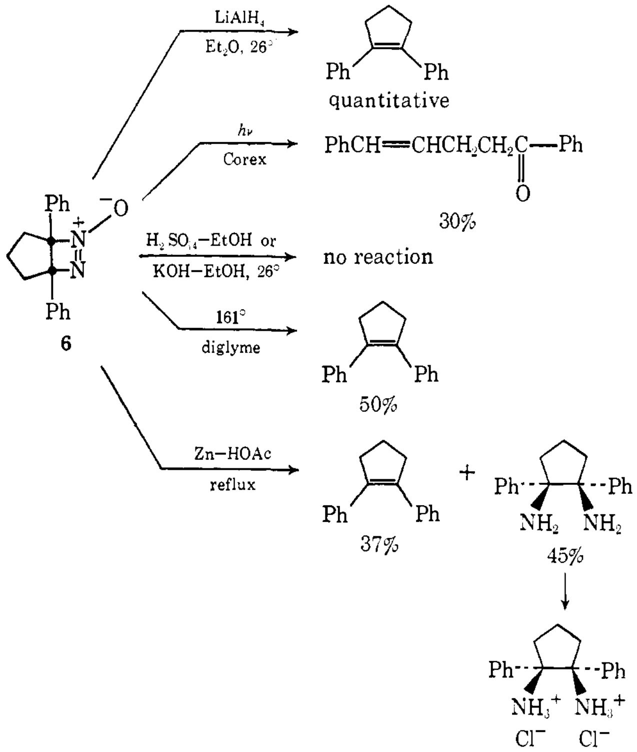


Irradiation of **3**[6] resulted in the formation of two products, one in 44% yield which could be shown to be 1,5-diphenyl-4-penten-1-one, **5**. The structure of **5** was consistent with its ir, uv, nmr, and mass spectra, and the ir and nmr were identical with those of an authentic sample.[7] Formation of **5** most likely arose from decomposition of the δ-diazo ketone **4** whose presence was suggested by the formation of a transient pink-colored solution which had a characteristic λ_{max}, 508 mμ.[8]

In addition to **5**, a solid, white compound (mp 135°), isomeric with **3**, could be isolated in 24% yield by elution chromatography.[9] All spectroscopic data are consistent with the azoxy structure **6**. The compound showed a dominant peak in the ir (KBr) at 1550 cm^{-1}, a uv spectrum with λ_{max} 210 mμ (ε 17,800), a mass spectrum with a base peak at *m/e* 220 (parent − N_2O) in addition to the parent ion at *m/e* 264,[10] and a 60-MHz proton nmr spectrum with a singlet at δ 7.14 (10 H) and a complex multiplet centered at δ 2.20 (6 H).[11] The ^{13}C nmr spectrum gave five absorptions (86.5, 117.5, 158.3, 16.18, and 171.0 ppm upfield from CS_2 as external standard) of equal intensity which were indicative of two different quaternary and three different secondary aliphatic carbon atoms in the molecule.

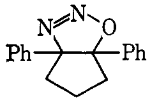
The chemistry of **6**, as shown in Scheme I, further

Scheme I



substantiates our assignment of structure.

No four-membered-ring azo compound could be detected from the deoxygenation[13] of **6** with $LiAlH_4$, the only isolable product being 1,2-diphenylcyclopentene which was identical in all respects with an authentic sample.[7] Although continued irradiation through a Pyrex filter (cutoff 280 mμ) resulted in no further change in **6**, if Corex (cutoff 260 mμ) was substituted, conversion of **6** to the unsaturated ketone **5** occurred, most likely *via* the azine monoxide **3**, which could have been regenerated by a reversal of the initial electrocyclic process. Th isolation of the 1,2-diphenylcyclopentane-1,2-diamine as its dihydrochloride from the reduction of **6** with Zn–HOAc verified that both nitrogens are carbon bonded in **6** and ruled out the alternative 1,2,3-oxadiazoline structure, **7**.



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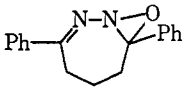

8

(5) L. Horner, W. Kirmse, and H. Fernekess, *Chem. Ber.*, **94**, 279 (1961).

(6) The photolysis is carried out for 35 min in CH_2Cl_2 utilizing a Hanovia 450-W medium-pressure Hg lamp (679-A).

(7) We are grateful to Professor M. A. Battiste of the University of Florida and Professor A. Padwa of the State University of New York at Buffalo for copies of ir and nmr spectra of 1,2-diphenylcyclopentene and 1,5-diphenyl-4-penten-1-one, respectively.

(8) Phenylmethyldiazomethane has λ_{max} 520 mμ: D. G. Farnum, *J. Org. Chem.*, **28**, 270 (1963).

(9) Satisfactory elemental analyses were obtained for all new compounds described here.

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(10) The p − 16 peak, characteristic of mass spectra of azine oxides, oxaziridines, and, usually, azoxy compounds, is significant by its absence.

(11) A 220-MHz proton nmr spectrum revealed that this multiplet consisted of at least 31 peaks.[12]

(12) We thank Dr. Leroy Johnson of Varian Associates, Palo Alto, Calif., for running the 220-MHz proton and ^{13}C nmr spectra of the azoxy compound **6**.

(13) G. M. Badger and G. E. Lewis, *J. Chem. Soc.*, 2147 (1953).

Imine oxaziridine structure **8** is especially ruled out by the spectroscopic data[14] as well as the observed chemistry of **6**. The $LiAlH_4$ and thermal reactions as well as the unusual stability of **6** in acid are inconsistent with the expected properties of an oxaziridine structure.[3,16]

The remarkable thermal stability of **6** (12-hr half-life in refluxing diglyme) and its inability to revert thermally to **3** are consistent with the qualitative predictions of Woodward and Hoffmann for systems such as this.[17]

The formation of the four-membered-ring azoxy compound from this photolysis of an azine monoxide represents the *first authentic example* of an electrocyclic, ring-forming reaction in a diazabutadiene system. No analogous reactions of cyclic or acyclic azines have thus far been able to be detected.

Acknowledgment. We are pleased to acknowledge support of this work by the Petroleum Research Fund (Grant No. 3521-A1,4), administered by the American Chemical Society, and by the Research Corporation.

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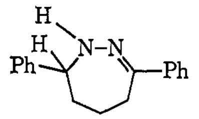
(14) The uv spectrum of compound i,[15] which is a reasonable model



i

λ_{max} 290 mμ (ϵ 5370)

structure for **8**, is inconsistent with the observed uv spectrum of compound **6**.

(15) C. G. Overberger and J. G. Lombardino, *J. Am. Chem. Soc.*, **80**, 2317 (1958).

(16) For a summary of oxaziridine properties see E. Schmitz, "Dreiringe Mit Zwei Heteroatomen," Springer-Verlag, Berlin, 1967.

(17) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

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exo-2-Phenyl-1-aza-7-oxabicyclo[2.2.1]heptane, a Novel Heterobicyclic Ring System

Sir:

The present paper reports the synthesis of the title compound by a new mechanisticly significant mode of intramolecular 4 + 2 cycloaddition of a nitrone to a double bond. Slow fractional distillation, or refluxing in xylene (10% w/v) for 24 hr, of N-1-buten-3-yl-*anti*-benzaldoxime (**1a**)[1-3] afforded a basic product (bp 88–92° (0.005 mm), 72%) from which was isolated a crystalline picrate (mp 139–140°, $CHCl_3$, 87.3%).[2] Treatment of the picrate with aqueous sodium carbonate gave a colorless liquid isomer of **1a**.[2,7] The ir spectrum of this material indicated no olefin absorption and lacked the characteristic nitrone bands at 1585 and 1150 cm^{-1}.[8] The nmr spectrum (100 MHz) showed two low-field hydrogens expected of structure **3** but not of **4**. A broad triplet at δ 4.88 (J = 4.8 Hz) is assignable to H_A which should be coupled nearly equally to the *exo* hydrogens at C_3 and C_5 and negligibly to the *endo* hydrogens.[9] The expected doublet of doublets for H_B is observed at δ 3.80 (J = 5.2, 8.0 Hz). A 13-line multiplet centered at δ 2.99 is assigned to the methylene hydrogens at C_6 since this is not coupled to H_A or H_B according to spin-decoupling experiments. The eight-line multiplet centered at δ 1.56 is assigned to H_C (*endo*-C_5) since this signal collapses to a broad doublet ($J \sim$ 11 Hz) and a broad quartet ($J \sim$ 11, 7.5 Hz) when the δ 2.99 multiplet is irradiated at its center and at the center of its low-field half, respectively. A first-order approximation assuming coupling constants summarized in Table I is remarkably similar (eight lines allowing for superpositions) to the observed pattern for H_C.

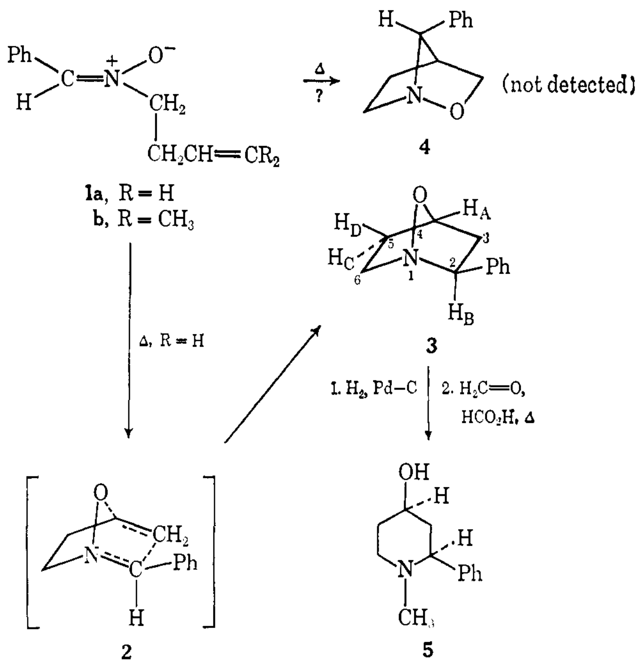

Table I. Summary of Coupling Constants (in Hertz) in Bicyclo[2.2.1]heptanes

	Bicyclo[2.2.1]-heptanes[9]	**3**[a,b]
$J_{endo-endo}$	8.9	8.0
$J_{endo-exo}$	2.3	5.2
J_{A-exo}	~4	4.8
J_{A-endo}	~0	~0
J_{CD}	12.0[9c]	~11

[a] Assumed equal to line spacings. [b] Sign not implied.

Final confirmation of structure **3** and *exo*-C_2 stereochemistry came from hydrogenolysis (Pd–C) followed by methylation with formaldehyde and formic acid to

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(1) Prepared in 42% yield by alkylation of the sodium salt of *anti*-benzaldoxime[4,5] with 1-iodo-3-butene.[6]

(2) Satisfactory microanalyses have been obtained for all new compounds reported herein.

(3) Bp 105–107° (0.01 mm); $\nu_{max}^{CHCl_3}$ 3060, 2950, 1640, 1585, 1150, 993, 943, 920 cm^{-1}; nmr^{DMSO-d_6} (δ ppm, TMS) 8.32 (2 H, m), 7.88 (1 H, s), 7.42 (3 H, m), 6.25–6.50 (3 H, m), 4.03 (2 H, t, J = 7Hz), 2.65 (2 H, m, J = 7 Hz).

(4) E. Buehler, *J. Org. Chem.*, **32**, 265 (1967).

(5) E. F. Schoenewaldt, R. B. Kinnel, and P. Davis, *ibid.*, **33**, 4270 (1968).

(6) L. Kaplan, *Chem. Commun.*, 754 (1968).

(7) Bp 90° (0.005 mm); $\nu_{max}^{CHCl_3}$ 2960, 1490, 1450, 1280, 995, 875, 830 cm^{-1}; mol wt (osmometric in benzene) 173, 176 (calcd 175.22).

(8) J. Thesing and W. Sirrenberg, *Chem. Ber.*, **92**, 1748 (1959).

(9) See: (a) J. Meinwald and Y. C. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963), for coupling constants in some bicyclo[2.2.1]heptane derivatives; (b) F. A. Anet, *Can. J. Chem.*, **39**, 789 (1961); (c) R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, **7**, 355 (1966).