Unsaturated Heterocyclic Systems. LXXIX. The Alkali Metal Reduction of Oxepins[1]

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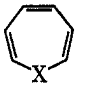
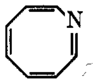
The alkali metal reduction of 2,7-dimethyloxepin and 3-benzoxepin was investigated for comparison with 2-methoxyazocines which undergo ready conversion to azocinyl dianions. In agreement with MO theory, these oxepins do not give rise to oxepinyl dianions. 2,7-Dimethyloxepin was found to give initially octa-4,6-dien-2-one which with excess potassium was further reduced to 4-octen-2-one. Under analogous conditions, 3-benzoxepin afforded equimolar mixtures of *o*-ethyl- and *o*-ethynylphenylacetaldehydes. Whereas the former substance is a reduction product, the latter arises from base-induced ring cleavage of the oxepin ring. The divergent behavior of π-excessive and π-equivalent heterocyclic analogs of cyclooctatetraene on reduction is briefly discussed.

An understanding of the chemical reactivity of monoheterocyclic eight-π-electron systems isoelectronic with cyclooctatetraene has received considerable attention in the recent literature. Such 4nπ molecules, which obviously do not satisfy the Hückel rule, are recognized to be divisible into two general classes. In the case of oxepin (**1a**), azepine (**1b**), thiepin (**1c**), and their derivatives, the eight π electrons are potentially delocalizable over seven atoms, a condition which is clearly π excessive.[3,4] In contrast, azocine (**2**) and its congeners are endowed with the capability for π-electron delocalization over eight atoms and may therefore be termed π-equivalent analogs of the parent hydrocarbon.[5]



1a, X = O
b, X = NH
c, X = S



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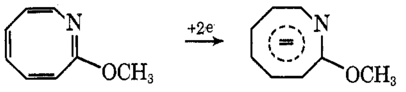
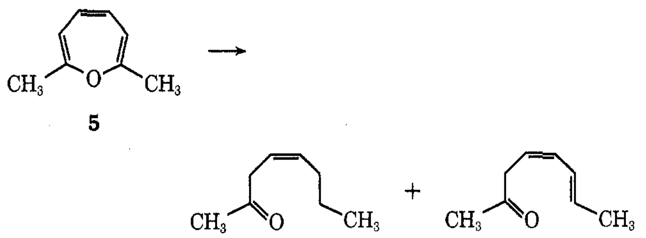
The classification is readily seen to be more than a formalistic distinction. In molecular orbital terms, the fourth MO of the heterotropylidines (**1**) can be shown to possess little bonding character.[6] Accordingly, localization of the π electrons is prevalent, a condition which fosters comparatively facile oxidation.[7] An important consideration for the present study is the realization that the fifth MO in such systems is unequivocally antibonding. The situation with regard to azocine (**2**) is quite different,[8] as attested to experimentally, for example, by the ready two-electron reduction of 2-methoxyazocines (*e.g.*, **3**) to stable aromatic azocinyl dianions (*e.g.*, **4**).[8,9] Similar reduction of heterotropylidines to their dianions was not considered possible on the basis of the above theoretical considerations. However, the manner in which such heterocyclic polyenes would interact with alkali metals was not readily predictable. The present study has concerned itself with an examination of the reactivity of two representative oxepins toward potassium metal reduction. The selection of 2,7-dimethyloxepin (**5**) and 3-benzoxepin (**12**) was dictated by the knowledge that these derivatives exhibit little tendency for valence isomerization to their respective arene oxide forms.[3]



3 **4**

Incremental addition of small pieces of potassium metal to cold (−70°) solutions of 2,7-dimethyloxepin (**5**) in anhydrous liquid ammonia–tetrahydrofuran (5:1) resulted in the formation of a reddish brown heterogeneous mixture. Although this complication caused difficulty in estimation of the "end point" (persistent blue coloration), approximately 3 g-atom equiv of the alkali metal were seen to be required. Addition of water and subsequent vpc analysis of the volatile product mixture revealed the formation of **6** (75%) and **7** (20%), together with a third minor substance of unknown composition.



5 **6** **7**

The two ketones were identified by their elemental analyses and spectra. Thus, the infrared spectrum of **6** exhibits an intense carbonyl band at 1720 cm^{-1} which is characteristic of nonconjugated acyclic ketones. The nmr spectrum ($CDCl_3$) shows a narrow two-proton multiplet in the vinyl region (δ 5.56) confirming the location of the double bond at a nonconjugated site. Additionally, there was revealed absorption indicative of the presence of a $-CH_2CO-$ grouping (δ 3.14, d, J = 6 Hz), an acetyl methyl substituent (2.13, s), two allylic protons (2.00, m), and a terminal ethyl group (1.38, sextuplet, and 0.89, t, J = 7 Hz).

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[1] For the previous paper in this series, see L. A. Paquette and J. F. Kelly, *J. Org. Chem.*, **36**, 442 (1971).

[2] University Postdoctoral Fellow, 1969–1970.

[3] For recent reviews of heterotropylidine chemistry, see (a) L. A. Paquette in "Nonbenzenoid Aromatics," Vol. I, J. Snyder, Ed., Academic Press, New York, N. Y., 1969, pp 249–310; (b) E. Vogel and H. Günther, *Angew. Chem.*, **79**, 429 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).

[4] This terminology was originally proposed by A. G. Anderson, Jr., W. F. Harrison, and R. G. Anderson, *J. Amer. Chem. Soc.*, **85**, 3448 (1963).

[5] (a) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, *ibid.*, **93**, 152 (1971); (b) L. A. Paquette and T. Kakihana, *ibid.*, **90**, 3897 (1968); (c) L. A. Paquette and J. C. Philips, *ibid.*, **90**, 3898 (1968).

[6] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 280.

[7] R. W. Schmid, *Helv. Chim. Acta*, **45**, 1982 (1962).

[8] L. A. Paquette, J. F. Hansen, and T. Kakihana, *J. Amer. Chem. Soc.*, **93**, 168 (1971).

[9] L. B. Anderson, J. F. Hansen, T. Kakihana, and L. A. Paquette, *ibid.*, **93**, 161 (1971).

By comparison, the carbonyl stretching frequency of ketone **7** was also seen at 1720 cm^{-1}. Its nmr spectrum shows four vinyl protons in the δ 5.4–6.5 region, $-CH_2CO-$ absorption at 3.34 (d, $J = 7.5$ Hz), an acetyl methyl at 2.18, and an allylic methyl substituent at 1.82 (d, $J = 6$ Hz). The presence of four vinyl protons, the terminal methyl group, and the nonconjugated acetyl function is consistent only with structure **7**. In both **6** and **7**, the geometry of the double bonds has been tentatively assigned by spectral correlation with model compounds.

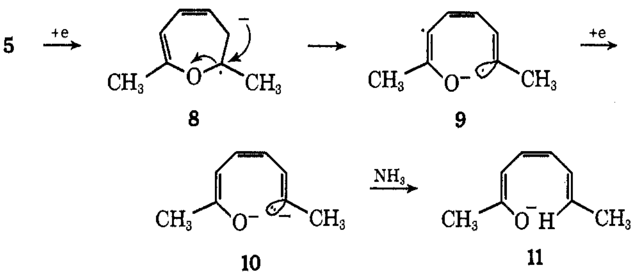
Final confirmation of these assignments was achieved by independent catalytic hydrogenation of **6** and **7** to 2-octanone.

Not unexpectedly, when the reduction was worked up by addition of deuterium oxide, the enone and dienone exhibited complicated patterns of deuterium incorporation as a result of base-catalyzed exchange of the α-carbonyl protons. For example, enone **6** was isolated as a mixture of d_1–d_7 species with the d_3 (24%), d_4 (37%), and d_5 (27%) forms predominating.

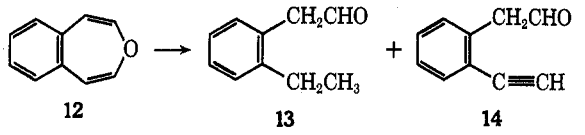
Repetition of the reduction with one-half the previous amount of potassium led to a substantially different product composition. Under these conditions, **7** was the major component (70%), accompanied by lesser amounts of **6** (10%), unreacted oxepin (15%), and the same unknown minor constituent (5%). The obvious inference that **7** is the first-formed product and that this dienone undergoes reduction to give **6** under the reaction conditions was substantiated as follows. Resubmission of a product mixture rich in **7** to reduction with excess potassium in liquid ammonia–tetrahydrofuran led almost exclusively (~95%) to **6**.

To account for these results, it is suggested that the reduction of **5** proceeds initially by one-electron addition to the oxepin nucleus leading to radical anion **8**. The instability of this species results in ring cleavage to give vinyl radical **9**, which can reasonably be expected to accept a second electron.[10] Protonation of the resulting dianion (**10**) at the vinylic center by the ammonia provides the enolate of **7** (Scheme I). The reduction of **7** to enone **6** would seem to be possible not only from the neutral molecule (established by independent experiment), but also by electron transfer to **11**.

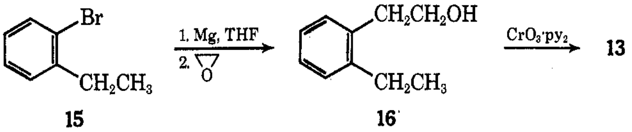
Scheme I

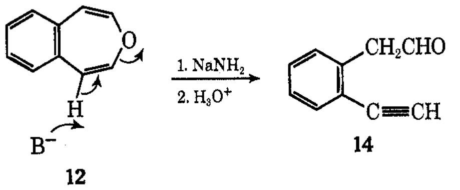


Similar reduction of 3-benzoxepin (**12**) at −70° likewise resulted in the appearance of a brownish suspension. Approximately 2.5 g-atom equiv of potassium metal were required to produce a permanent blue coloration. Work-up led in 30% yield to a mixture of two aldehydes ($\nu_{max}^{CCl_4}$ 1727 cm^{-1}) that resisted separation by preparative vpc and tlc methods, as well as fractional crystallization of their semicarbazones. The mass spectrum of the mixture showed two substances to be present, one isomeric with **12** (parent ion at m/e 144) and the other a tetrahydro product (parent ion at m/e 148). The nmr spectrum suggested the mixture to consist of approximately equimolar amounts of **13** and **14**. These assignments were subsequently confirmed by independent synthesis.



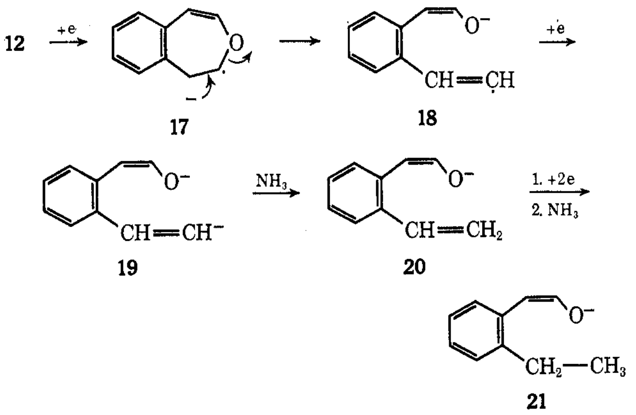
Starting with *o*-bromoethylbenzene (**15**), alcohol **16** was prepared by reaction of the derived Grignard reagent with ethylene oxide. Controlled oxidation of **16** with Collins reagent[11] conveniently afforded **13**. The unequivocal preparation of **14** was founded on the mechanistic rationalization of its formation, *viz.*, base-induced ring cleavage of **12**. In point of fact, exposure of **12** to sodium amide in liquid ammonia–tetrahydrofuran (5:1) at −33° led to **14** in a straightforward way. When a composite of the nmr and ir spectra of these two aldehydes was made, it was found to be indistinguishable from the spectra of the mixture isolated in the reduction experiments.





A grossly reasonable mechanism for the formation of **13** (Scheme II) parallels exactly that advanced

Scheme II



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(10) For an excellent discussion of dissolving metal reductions, see H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, Chapter 3.

(11) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

earlier for **6**. Reductive cleavage of a C–O bond leads *via* **17** to **18**. This transient intermediate undergoes further reduction and protonation to afford the styrene alkoxide **20** which undergoes ultimate conversion to **21**, the enolate of **13**.

The formation of **14** by base-induced ring opening of 3-benzoxepin (**12**), although somewhat unusual, has some analogy in the cleavage reactions of 3-benzofuryllithiums.[12,13] Since no potassium amide was employed directly in the reduction, the source of base was necessarily the amide ion released upon protonation of **19** and its dihydro counterpart, or alkoxides **20**, **21**, and the like. The fact that no acetylenic material was isolated from the reduction of **5** is presumably a reflection of either the diminished acidity of its β protons relative to those in **12**, or the susceptibility of the internal acetylene so generated to reduction. We favor the first alternative. The position that **13** may possibly result from further reduction of first-formed **14** is not tenable, since terminal acetylenes are known to be inert to the action of alkali metals.[14]

In conclusion, we note the inability of oxepins to undergo reduction to 10-π-electron oxepinyl dianions in agreement with MO theory and contrast such behavior with the ready passage of azocines to azocinyl dianions.[8,9] Thus, the divergent chemical properties of π-excessive and π-equivalent heterocyclic analogs of cyclooctatetraene are made particularly evident in such electron-transfer reactions.[15]

Experimental Section

In all experiments involving liquid ammonia, predrying was achieved by stirring with sodium metal for 1 hr at −70°, followed by direct distillation into the predried reaction vessel under anhydrous conditions.

Reduction of 2,7-Dimethyloxepin (5). A. Potassium (3 Equiv).—To a stirred solution of 344 mg (2.82 mmol) of **5**[16] in 30 ml of liquid ammonia and 6 ml of anhydrous tetrahydrofuran (freshly distilled from $LiAlH_4$), cooled in a Dry Ice–acetone bath, was slowly added small pieces of potassium metal. The solution developed a turbid brown-red color which darkened with progressive addition of the metal (3 g-atom equiv were added). The addition required approximately 2 hr, at which time the blue color persisted for more than 5 min. The cooling bath was removed and the ammonia was allowed to evaporate under a gentle dry nitrogen stream. With stirring, water (6 ml) was added and the resulting dark brown solution was extracted with ether. The combined ether layers were washed well with brine, dried, and evaporated to yield 196 mg of a brown oil. This material was seen to consist of three components (ratio of 5:75:20) on vpc analysis (10% SE-30 at 85°). Preparative vpc isolation was successful in separating the two major components.

The major component (80 mg) was identified as **6**:[17] $\nu_{\max}^{\mathrm{CCl_4}}$ 1720 cm^{-1}; $\delta_{\max}^{\mathrm{CDCl_3}}$ 5.56 (m, 2, vinyl), 3.14 (d, J = 6 Hz, 2, CH_2CO), 2.13 (s, 3, CH_3CO), 2.0 (m, 2, allyl), 1.38 (sextuplet, 2, CH_2CH_3), and 0.89 (t, J = 7 Hz, CH_3CH_2).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.10; H, 11.11.

The minor product was subsequently identified as **7**.

B. Potassium (1.5 Equiv).—Treatment of 183 mg (1.5 mmol) of **5** for 1 hr with 89 mg (2.2 mg-atoms) of potassium as above provided, after work-up, a brown oil which consisted (vpc analysis) of 15% unreacted **5**, 10% **6**, and 70% **7**.

Approximately 85% of this material was subjected to preparative vpc purification. In addition to 4 mg of **6**, there was obtained 25 mg of **7**:[18] $\nu_{\max}^{\mathrm{CCl_4}}$ 1720 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.4–6.5 (m, 4, vinyl), 3.34 (d, J = 7.5 Hz, 2, CH_2CO), 2.18 (s, 3, CH_3CO), and 1.82 (d, J = 6 Hz, 3, methyl).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.24; H, 9.47.

The remaining portion of the brown oil was further reduced with 70 mg of potassium in liquid ammonia–tetrahydrofuran (5:1) for 1 hr. The principal product (∼95%) was enone **6**.

Reduction of 3-Benzoxepin (12).—To a pale yellow suspension of **12**[19] (295 mg, 2.05 mmol) in 20 ml of liquid ammonia and 4 ml of anhydrous tetrahydrofuran was added slowly approximately 200 mg (2.5 mg-atom equiv) of potassium metal with stirring under nitrogen at −70°. The ammonia was evaporated under a gentle stream of nitrogen, water (10 ml) was added, and the mixture was thoroughly extracted with ether. The combined ether extracts were washed with brine, dried, and evaporated to give a brown oil which showed one peak on vpc analysis. Preparative vpc afforded 88 mg (30%) of an inseparable mixture of **13** and **14**, $\nu_{\max}^{\mathrm{CCl_4}}$ 1727 cm^{-1}. The physical properties of these aldehydes are presented in the ensuing paragraphs.

1-Ethyl-2-(2-hydroxyethyl)benzene (16).—A solution of 6.23 g (37.7 mmol) of *o*-bromoethylbenzene in 20 ml of dry tetrahydrofuran was added under nitrogen to a stirred suspension of magnesium turnings (1 g, 41.5 mg-atoms) in 20 ml of the same solvent, to which had previously been added a crystal of iodine and 0.1 g of ethylene dibromide. The resulting mixture was refluxed for 45 min and cooled to 0°, and ethylene oxide (25 g, tenfold excess) was distilled directly into the flask. After being stirred at 0° for 3 hr and at room temperature for 12 hr, the mixture was treated with 100 ml of 30% aqueous ammonium chloride solution and extracted with ether. Processing of the ether extract and distillation furnished 2.8 g (56%) of **16** as a colorless oil: bp 65–70° (2.3 mm); $\nu_{\max}^{\mathrm{film}}$ 3200–3300 cm^{-1}; $\delta_{\max}^{\mathrm{CDCl_3}}$ 7.12 (br s, 4, aryl), 3.75 (t, J = 7 Hz, 2, CH_2OH), 2.96 (br s, 1, OH), 2.85 (t, J = 7 Hz, 2, CH_2CH_2OH), 2.64 (q, J = 7.5 Hz, 2, CH_2CH_3), and 1.20 (t, J = 7.5 Hz, 3, methyl).

The 3,5-dinitrobenzoate of **16** was obtained as small white needles, mp 138.5–139°, from ethanol.

Anal. Calcd for $C_{17}H_{16}N_2O_6$: C, 59.30; H, 4.68; N, 8.14. Found: C, 59.23; H, 5.06; N, 8.11.

***o*-Ethylphenylacetaldehyde (13).**—Alcohol **16** (400 mg, 2.67 mmol) was stirred at 20° for 16 hr with a suspension of $CrO_3 \cdot py_2$[11] (7 g, approximate tenfold excess) in 50 ml of methylene chloride. The red suspension was filtered, the filtrate evaporated, and the residue taken up in ether. The ether extract was washed with 5% hydrochloric acid solution and brine, dried, and evaporated. The residual yellow oil was purified by preparative vpc to give 60 mg (15%) of **13** as a colorless oil: $\nu_{\max}^{\mathrm{CCl_4}}$ 1725 cm^{-1}; $\delta_{\max}^{\mathrm{CDCl_3}}$ 9.63 (t, J = 2.5 Hz, 1, CHO), 7.0–7.3 (m, 4, aryl), 3.65 (d, J = 2.5 Hz, 2, CH_2CHO), 2.60 (q, J = 7.5 Hz, 2, CH_2CH_3), and 1.18 (t, J = 7.5 Hz, 3, methyl).

The semicarbazone of **13** was obtained as lustrous white sheetlets, mp 164–165°, from ethanol–water (2:3).

Anal. Calcd for $C_{11}H_{15}N_3O$: C, 64.36; H, 7.37; N, 20.47. Found: C, 64.24; H, 7.52; N, 20.42.

***o*-Ethynylphenylacetaldehyde (14).**—To a suspension of sodium amide (prepared from 500 mg of sodium and a crystal of hydrated ferric nitrate) in 30 ml of liquid ammonia at −33° was added a solution of 330 mg (2.3 mmol) of 3-benzoxepin (**12**)[19] in 5 ml of anhydrous tetrahydrofuran. The mixture was stirred for 3.5 hr

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(12) (a) H. Gilman and D. S. Melstrom, *J. Amer. Chem. Soc.*, **70**, 1655 (1948); (b) A. S. Angeloni and M. Tramontini, *Boll. Sci. Fac. Chim. Ind. Bologna*, **21**, 243 (1963); *Chem. Abstr.*, **60**, 15808 (1964).

(13) The formation of open anions from dihydrooxepin also bears some similarities: H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **89**, 667 (1970).

(14) (a) Reference 10, p 72; (b) N. A. Dobson and R. A. Raphael, *J. Chem. Soc.*, 3558 (1955).

(15) The alkali metal reduction of 1,2,7-trimethylazepine [L. A. Paquette, D. E. Kuhla, J. H. Barrett, and R. J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969)] has been examined in a preliminary way. Dianion formation was again not evidenced. However, product characterization was seriously thwarted because of the extreme lability of the products to hydrolysis and air oxidation.

(16) L. A. Paquette and J. H. Barrett, *Org. Syn.*, **49**, 62 (1969).

(17) An isomer of 4-octen-2-one has been prepared earlier by A. P. Meshcheryakov, L. V. Petrova, and A. D. Petrov: *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 98 (1960). However, stereochemical and spectral details are lacking.

(18) Two stereoisomers of octa-4,6-dien-2-one have previously been synthesized, but no stereochemical details are available in either instance: (a) J. Wiemann and H. Danechpejouh, *C. R. Acad. Sci.*, **266**, 1165 (1968); (b) F. Hoffmann-La Roche and Co., A.-G., Belgian Patent 660,099 (Aug 23, 1965); *Chem. Abstr.*, **63**, 19706*e* (1965).

(19) G. R. Ziegler, *J. Amer. Chem. Soc.*, **91**, 446 (1969).

at this temperature and subsequently treated with solid ammonium chloride. Evaporation of the ammonia was followed by the addition of water and ether extraction. The customary work-up afforded a yellow oil, purification of which by preparative vpc (10% SE-30, 150°) afforded 56 mg (17%) of **14**: $\nu_{max}^{CCl_4}$ 1727 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 9.66 (t, J = 2 Hz, 1, CHO), 7.0–7.7 (m, 4, aryl), 3.82 (d, J = 2 Hz, 2, CH_2CHO), and 3.30 (s, 1, $C{\equiv}CH$).

The semicarbazone of **14** was obtained as a fawn-colored solid, mp 183–184° dec, from ethanol.

Anal. Calcd for $C_{11}H_{11}N_3O$: C, 65.67; H, 5.51; N, 20.88. Found: C, 65.40; H, 5.47; N, 20.58.

Registry No.—**5**, 1487-99-6; **6**, 28362-73-4; **7**, 28362-74-5; **12**, 264-13-1; **13**, 28362-76-7; **13** semicarbazone, 28362-77-8; **14**, 28362-78-9; **14** semicarbazone, 28362-79-0; **16**, 22545-12-6; **16** 3,5-dinitrobenzoate, 22532-40-7.

Acknowledgment.—The authors are indebted to the National Institutes of Health for partial financial support of this research.

Thermally Disallowed Valence Tautomerization of an Indano[1,2-*b*]aziridine to an Isoquinolinium Imine[1a,b]

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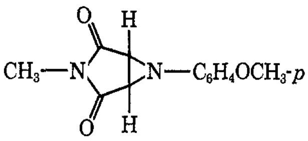
1-Cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine (**4**) at 135° in toluene undergoes conversion to an aromatic valence tautomer, the red isoquinolinium imine **5**, despite the geometrical restrictions imposed by the molecule on the formally required conrotatory opening. Both the thermal and analogous photochemical isomerizations are reversible. The chemistry of **5** is discussed, in particular its trapping as an azomethine ylide in a series of 1,3-dipolar cycloadditions.

The thermal conrotatory opening of the cyclopropyl anion to the allyl ion predicted by the Woodward–Hoffman rules[2] has yet to receive experimental verification. However, Huisgen and his coworkers have convincingly demonstrated both the expected thermal conrotatory and photochemical disrotatory opening of examples of the isoelectronic analog aziridine to azomethine ylides.[3] Subsequent 1,3-dipolar cycloadditions of the azomethine ylide intermediates to homomultiple and heteromultiple bonds to give a variety of heterocycles are firmly established by several groups of workers.[4] When the aziridine ring is constrained in a bicyclic structure of medium size (five-or six-membered ring) at the 2,3 bond, disrotatory photochemical opening is allowed, but thermal conrotatory ring opening is not permitted by the geometry of the system. The latter reaction is therefore a disallowed process. In agreement with this prediction Huisgen reported[5] that the bicyclic aziridine **1**, while it undergoes facile photochemical disrotatory opening to species **2** which was subsequently trapped with dimethyl acetylenedicarboxylate to give **3** in 70% yield, was totally unreactive when heated to temperatures of even 180°.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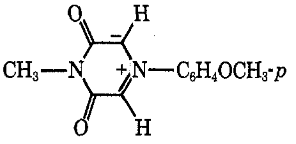
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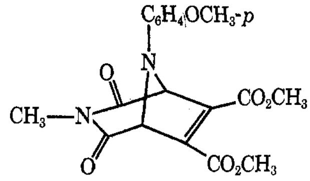
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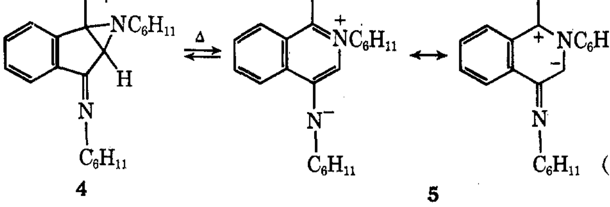
Oida and Ohki similarly recognized that in a bicyclic aziridine closely related to **1**, while photochemical disrotatory opening is allowed, thermal conrotatory ring opening is disallowed.[4j]

We report the thermally disallowed valence tautomerization of 1-cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine **4** to the isoquinolinium imine **5** (see eq 1) and subsequent trapping of the latter as an azomethine ylide in a series of cycloadditions. The phenylindano[1,2-*b*]aziridine[6] is a white


4 **5** (1)

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[1] (a) A preliminary report of this work has appeared previously: J. W. Lown and K. Matsumoto, *Chem. Commun.*, 692 (1970). (b) We are indebted to the National Research Council of Canada (Grant A2305) for financial aid. (c) National Research Council of Canada Postdoctoral Fellow, 1969–present.

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