quite similar product mixtures. Anodic oxidation of carboxylic acids at a carbon anode produces products from both radical and cationic intermediates, but the cationic pathway is the major one. With cycloalkyl systems, the cations undergo internal hydrogen rearrangements and competitive product formation similar to those from amine deaminations.

Registry No.—II, 25023-19-2: cyclooctanecarboxylic acid, 4103-15-5; dicyclooctylmercury, 21406-57-5.

Heterocyclic Studies. 33. 5-Methyl-6-phenyl-1,2-diazabicyclo[3.2.0]-2,6-heptadien-4-one. Thermolysis to 4-Methyl-5-phenylpyridazine[1]

EUGENE J. VÖLKER, MELVIN G. PLEISS, AND JAMES A. MOORE*

Department of Chemistry, University of Delaware, Newark, Delaware 19711

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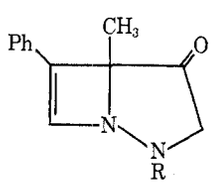
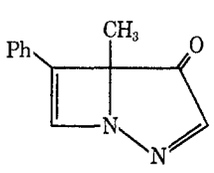
The preparation and properties of the title dienone **2** are described. The dienone is quite stable to hydrolysis; addition occurs with borohydride and methyllithium to give dienols. Thermolysis of **2** at 475° gives 4-methyl-5-phenylpyridazine; a mechanism involving a diazatropone intermediate is discussed. The thermal stability of **2** and the related diazabicyclo[3.2.0]-6-heptenone **1** and diazabicyclo[3.2.0]heptanone **19**, prepared by hydrogenation of **1** (R = Ac), are compared. The dimer of 2-methyl-3-phenylcyclopentadienone is described.

Part A

As previously reported,[2] the 1,2-diazabicyclo[3.2.0]-heptadienone **2** is obtained as a by-product in the photochemical preparation of **1a** and can be prepared by the base-catalyzed elimination of toluenesulfinic acid from **1b**. In this paper are described the details of the preparation and the chemical properties of **2**. This strained polyfunctional dienone appeared at the outset to offer possibilities for reactions of several types. Compounds containing the transoid cyclic unit –N=C–C=O are not well known, and the few examples that have been described are quite prone to solvolysis[3] or dimerization,[4] particularly in the absence of a substituent on the central carbon atom. The monomeric structure of **2**, which is consistent with the solubility and volatility of the compound, was confirmed by the mass spectrum, which contained no peaks above *m/e* 200 (P + 2).

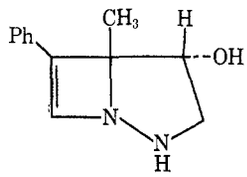


1a, R = H
b, R = *p*-$CH_3C_6H_4SO_2$

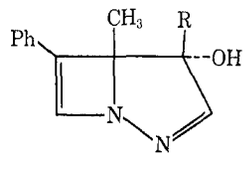


2

Contrary to expectation, **2** proved to be relatively inert; the dienone was recovered largely unchanged after refluxing for 16 hr with methanolic sodium methoxide or with methanolic hydrochloric acid. Treatment of **2** with sodium borohydride at room temperature leads to the saturated alcohol **3**.[5] At −40°, reduction with borohydride gave a small amount of **3** and, as the major product, the secondary alcohol **4a**, which was not further reduced to **3** at higher temperature, suggesting that **3** may arise from **2** by 1,4 addition. Methyllithium at −70° also added selectively to the carbonyl group to give **4b**. The *endo*-hydroxyl configuration in **4a,b** is assumed on the basis of exo attack of hydride; this has been established in the reduction of **1a** to **3**. Reactions with acetic anhydride, Grignard reagents, a phosphorus ylide, or organolithium compounds at higher temperature gave mixtures of starting material and several products which were not resolved. From this survey of the reactivity of **2**, the only clearly defined pathway observed is nucleophilic addition at the C-4 carbonyl group; the azetine and –N=C–C=O systems are surprisingly resistant to solvolytic attack.



3



4a, R = H
b, R = CH_3

One of the main points of interest in the chemistry of **2** was the possibility of thermal conversion to a diazatropone by ring opening analogous to the isomerization of bicyclo[3.2.0]-2,6-heptadienone to tropone.[6] The dienone **2** decomposed slowly in refluxing toluene to give a mixture containing apparently polymeric material. Heating **2** in higher boiling solvents or in sealed ampoules, or sublimation through a glass coil at temperatures up to 320° similarly caused incomplete conversion to material showing broad featureless nmr absorption. However, mixtures from pyrolysis at higher temperature showed evidence of two products, and these were isolated from a preparative scale pyrolysis in which a benzene solution of **2** was vaporized into a helix-packed column heated to 475°. After

* To whom correspondence should be addressed.

(1) Supported by Grant No. GP-9322 from the National Science Foundation.

(2) M. G. Pleiss and J. A. Moore, *J. Amer. Chem. Soc.*, **90**, 1369 (1968).

(3) 3-Oxo-2-phenylindolenine, R. J. Richman and A. Hassner, *J. Org. Chem.*, **33**, 2548 (1968); 1-alkyl-1,2-diazepin-4-one, J. A. Moore and W. J. Theuer, *ibid.*, **30**, 1887 (1965); imidazolinedione, E. Goldstein and D. Ben-Ishai, *Tetrahedron Lett.*, 2631 (1969).

(4) E. D. Hannah, W. C. Peaston, and G. R. Proctor, *J. Chem. Soc. C*, 1280 (1968), and earlier papers.

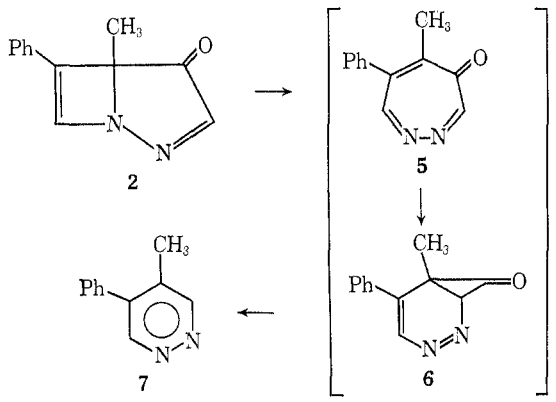
(5) J.-L. Derocque, W. J. Theuer, and J. A. Moore, *J. Org. Chem.*, **33**, 4381 (1968).

(6) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **87**, 1623 (1965).

removal of hydrocarbons derived from the solvent, a crystalline solid A was isolated in 3% yield and, as the main product, 4-methyl-5-phenylpyridazine (7) was obtained in 30% yield. These two products accounted for all of the clearly resolved peaks in the nmr spectrum of the total reaction mixture. The structure of the minor product A, $C_{24}H_{20}O_2$, is not known (see Part B).

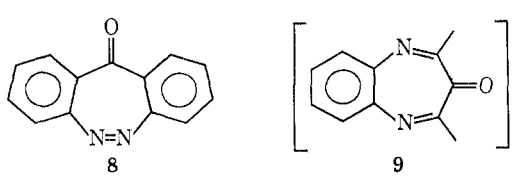
In an attempt to effect valence isomerization at a lower temperature, the dienone **2** was refluxed with excess silver tetrafluoroborate in dioxane and with methanolic cuprous chloride. These transition metal salts have been found to catalyze the thermal ring opening of fused cyclobutene systems when a concerted disrotatory process is sterically inaccessible.[7] No significant reaction was observed with **2** under these conditions, however.

Although no intermediates or other direct evidence are available, we presume that the pyridazine **7** is formed by ring opening of **2** at 350–400° (discussed in Part B) followed by valence isomerization of the diazatropone **5** and extrusion of CO. These steps have been observed with carbocyclic compounds. Bicyclo-[3.2.0]-2,6-heptadien-4-one rearranges quantitatively to tropone at 300°,[6] and the conversion of tropones to benzenes, presumably *via* bicyclo[4.1.0] intermediates, occurs at 600–700°.[8] The possibility that **2** undergoes thermal rearrangement directly to **6** is not excluded.



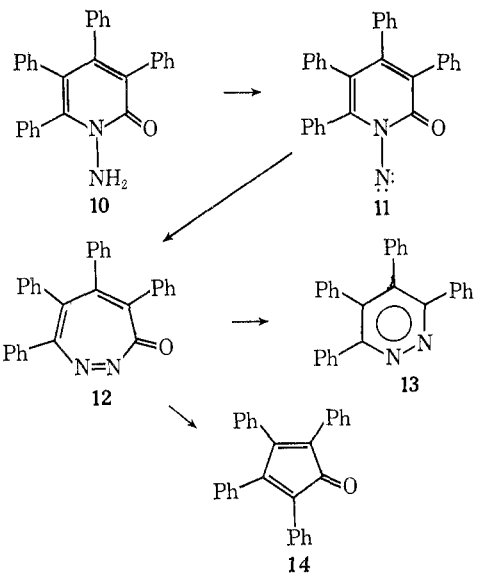
Part B

The Stability of Azatropones.—If the diazatropone **5** is the precursor of **7**, it must be considerably less stable than carbocyclic tropones. This inference is consistent with the limited data that have been reported on aza- or diazatropones comparable to **5**, containing only sp^2 nitrogen atoms. The dibenzo[*c*,*f*]-1,2-diazepinone **8**



has been characterized,[9] but a compound to which a dibenzo[*b*,*d*]azepinone structure was assigned has recently been found to be a dimer,[4,10] and attempts to obtain the benzodiazatropone **9**[11] or a monocyclic azatropone[12] were unsuccessful.

Rees and Yelland recently observed the formation of tetraphenylpyridazine (60%) and tetraphenylcyclopentadienone (1%) in the oxidation of 1-aminotetraphenyl-2-pyridinone at room temperature, and consider it likely that these products arise by thermal elimination of CO and N_2, in respectively concerted and nonconcerted processes, from the 2,3-diazatropone **12**.[13] The nature and relative amounts of products suggest a similarity in mechanism between this reaction and the thermolysis of **2**. If these reactions proceed *via* diazatropones, it seems quite remote, from the formation of **13** at 25°, that a diazatropone could be isolated from any reaction requiring elevated temperatures.



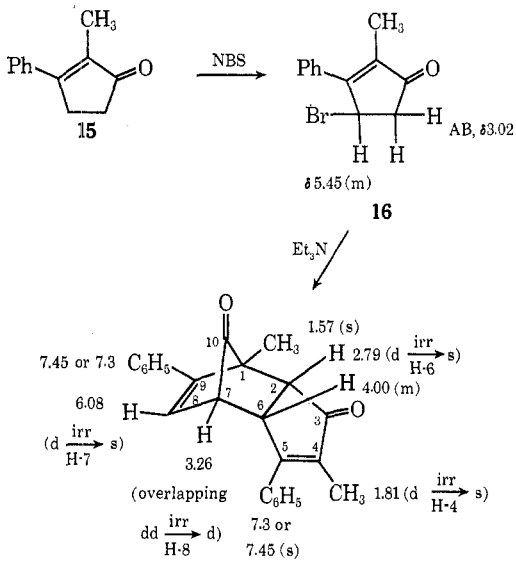
Minor Pyrolysis Product (A).—The characterization of this compound was limited by the small quantity available. Analysis and nmr data indicated a composition $C_{24}H_{20}O_2$, corresponding to loss of both nitrogen atoms from **2** and dimerization. The spectra of A [ir ν_{CO}^{KBr} 1770, 1680 cm^{-1}; nmr δ 1.61 (s, 3), 1.78 (s, 3), 2.78 (d, J = 4.9 Hz, 1), 3.37 (d, J = 1.8 Hz, 1), 3.73 (dd, J = 1.8, 4.9 Hz, 1), 6.56 (s, 1), 7.33 (s, 5), 7.4–7.8 (m, 5) ppm] were in part similar to those expected for a methylphenylcyclopentadienone dimer. These limited data, and the possible parallel with the dienone **14** isolated from the presumed diazatropone **12**,[13] prompted comparison with an authentic sample of the dimer of 2-methyl-3-phenylcyclopentadienone, which would arise by extrusion of N_2 from the diazatropone **5**.

2-Methyl-3-phenylcyclopentenone[14] (**15**) was brominated with NBS; the nmr data establish the 4-bromo structure **16**. Treatment of **16** with boiling triethylamine gave the dimer **17**. The spectral data, including all of the coupling constants, can be compared with those reported recently for several cyclopentadi-

(7) W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 4788 (1967).
(8) T. Miyashi, M. Nitta, and T. Mukai, *Tetrahedron Lett.*, 3433 (1967); T. Mukai, T. Nakazawa, and K. Okayama, *ibid.*, 1695 (1968).
(9) R. B. Johns and K. R. Markham, *J. Chem. Soc.*, 3712 (1962).
(10) R. G. Cooke and I. M. Russell, *Tetrahedron Lett.*, 4587 (1968).
(11) J. A. Barltrop, C. G. Richard, D. M. Russell, and G. Ryback, *J. Chem. Soc.*, 1132 (1959).
(12) N. A. Evans, R. B. Johns, and K. R. Markham, *Aust. J. Chem.*, **20**, 713 (1967).
(13) C. W. Rees and M. Yelland, *Chem. Commun.*, 377 (1969).
(14) H. O. House and R. L. Wasson, *J. Org. Chem.*, **22**, 1157 (1957).

enone dimers,[15] and uniquely define the *endo*-3,10-dione structure **17**.

The synthetic dimer **17** was distinctly different from the thermolysis product A. Although the ir stretching frequencies and the nmr proton groupings are very similar for the two substances, the single low field signal and the rather simple proton couplings in the nmr spectrum of A rule out a homodimer of any of the six isomeric methylphenylcyclopentadienones. The unlikely possibility that compound A arose from a subsequent thermal rearrangement of **17** was ruled out by pyrolysis of **17** at 350°. The product was not fully characterized, but the ir suggested decarbonylation, as expected;[15] compound A was not detected.

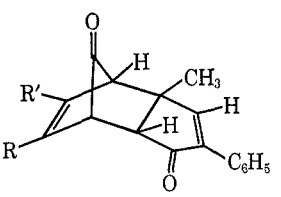


$J_{2,6} = 6.3$ Hz, $J_{6,7} = 4.5$ Hz, $J_{7,8} = 3.9$ Hz, $J_{4\,CH_3,6} = 1.6$ Hz

ir: C-3, ν_{CO} 1680 cm^{-1}, C-10, ν_{CO} 1770 cm^{-1}

$\frac{\text{irr}}{\text{H-6}}$ = spin decoupling by irradiation of H-6

The spectrum of A would be best accommodated by structure **18**, but the structure cannot be specified from the evidence available, nor can it be stated whether this product arises from the diazatropone **7** or by some other decomposition process of the dienone **2**.

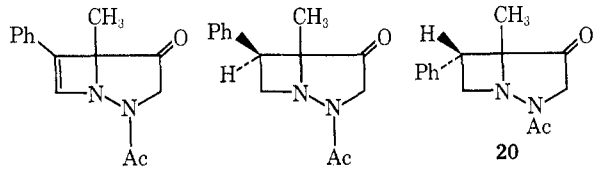


18, R, R′ = CH_3 and C_6H_5

The Mechanism of Ring Opening of Dienone 2 and Related Diazabicyclo[3.2.0]heptanones.—The results of the thermolysis of **2** indicate a significant activation barrier for ring opening of this [3.2.0] system, and invite comparison of the thermal stability of **2** with that of some related compounds. Of particular interest are the diazabicyclo[3.2.0]heptenones **1**, R = H, or CH_3, which rapidly isomerize to the diazepinones **22** at room temperature.[5]

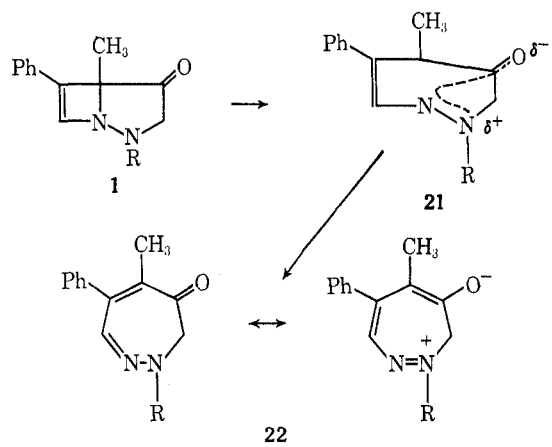
(15) E. W. Garbisch, Jr., and R. F. Sprecher, *J. Amer. Chem. Soc.*, **91**, 6785 (1969).

To extend this series, the diazabicycloheptanones **19** and **20** were prepared by hydrogenation of **1**, R = Ac, with a palladium catalyst. Approximately equal amounts of the stereoisomeric ketones, **19** and **20**, were obtained and were readily separated by crystallization. Configurational assignments were based on the large upfield nmr shift of the CH_3 in **19** due to the eclipsing 5-*exo*-phenyl group.[5] Hydrogenation of the unstable ketones **1**, R = H and CH_3, led to air-sensitive mixtures which could not be separated.



The stabilities of the unsaturated ketone **1** (R = Ac), dienone **2**, and the saturated ketone **19** were compared at 80° in chloroform solution. Isomerization of **1** (R = Ac) to the diazepinone **22** (R = Ac) was 30% complete after 48 hr and over 90% after 310 hr. The diazadienone **2** decomposed, probably by polymerization, to the extent of 40–50% in 300 hr; **19** was unchanged.

It has been suggested[16] that the facile isomerization of the enones **1** to **22** may occur by orbital symmetry allowed conrotatory thermal ring opening, permitted by inversion of the bridgehead nitrogen atom. We have viewed the lability of **1** (R = H or Me) as a consequence of interaction of the unshared electron pair at N-2 with the carbonyl group in a dipolar transition state (**21**).[5] The rates of isomerization are dependent on solvent and on the electron-releasing ability of the R group; the rate of isomerization of **1**, R = Ac, is many times slower than that of **1**, R = CH_3. Furthermore, debridging does not occur with the corresponding alcohols. In this mechanism, the Δ^6 double bond is required for dissipation of charge as the product develops.

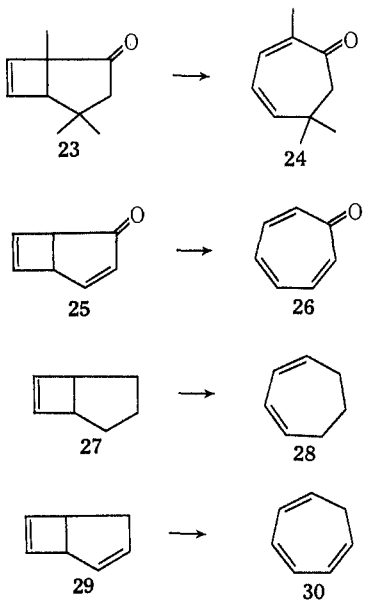


The thermal isomerization of eucarvone (**23**)[17] and the dienone **25**[6] have been carried out at 320 and 300°, respectively; these qualitative data suggest no major effect in the activation barrier for ring opening of these ketones due to the second double bond in **25**.

(16) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 51.

(17) G. Buchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960).

Kinetic measurements of the isomerization of **27** and **29** have shown that the second double bond lowers the activation energy for the disrotatory ring opening by 6 kcal, the difference being attributed to allylic stabilization of a diradical intermediate.[18] Ring opening of bicyclo[*n*.2.0]alkenes such as **27** has more recently been suggested to occur by initial concerted conrotatory electrocyclic reaction followed by 1,5-hydride shift.[19]



In contrast to the ring opening of these carbocyclic-[3.2.0]heptenes and heptadienes, the Δ^2 double bond in **2** has a profound stabilizing effect in the 1,2-diazaheptenone series, indicating an entirely different mechanism for the thermolysis of **1** and **2**. Neither nitrogen inversion nor participation of N-2 is available in the diazadienone **2**; ring opening to **5** must occur by a pathway with an activation energy comparable to that of the dienone **25**.

Experimental Section

5-Methyl-6-phenyl-2-*p*-toluenesulfonyl-1,2-diazabicyclo[3.2.0]-6-hepten-4-one (1b).—A solution of 0.50 g of dihydrodiazepinone **22** in 250 ml of MeOH was irradiated in sunlight[5] for 30 min and evaporated *in vacuo* to a homogeneous (tlc) pale yellow oil. Treatment of this oil with 4.5 ml of pyridine and 520 mg of *p*-toluenesulfonyl chloride for 2 hr followed by addition of water and the usual isolation gave 707 mg (80%) of **1b** in two crops. Recrystallization from methanol gave white needles: mp 151–152° dec; λ_{max}^{MeOH} 224 mμ (ε 21,000), 266 (19,000); ν^{KBr} 1750, 1340, and 1165 (SO_2); δ^{CDCl_3} 1.12 (s, 3), 2.45 (s, 3), 4.60 (d, J = 4 Hz, 2), 6.72 (s, 1), 7.2–8.0 ppm (m, 9).

Anal. Calcd for $C_{19}H_{18}N_2O_3S$: C, 64.40; H, 5.12; N, 7.91. Found: C, 64.25; H, 5.05; N, 7.69.

5-Methyl-6-phenyl-1,2-diazabicyclo[3.2.0]-2,6-heptadien-4-one (2).—To a suspension of 2.13 g (0.04 mol) of sodium methoxide in 150 ml of toluene (Na dried) was added a solution of 2.05 g of **1b** (0.0055 mol) in 100 ml of toluene. The mixture was stirred for 24 hr under nitrogen at 25° and water was added. The toluene layer was washed, dried, and evaporated to a yellow oil. Crystallization from hexane gave pale yellow prisms of **2**: 0.99 g (85%); mp 70°; λ_{max}^{MeOH} 265 mμ (ε 17,000), 342 (370); ν^{KBr} 1730 cm^{-1}; δ^{CDCl_3} 1.73 (s, 3), 7.20 (s, 1), 7.37 (s, 5), 7.83 ppm (s, 1); mass spectrum (70 eV) *m/e* (rel intensity) 198 (57), 170 (9), 143 (10), 129 (4), 116 (19), 115 (32), 102 (100).

Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.09; N, 14.13. Found: C, 72.86; H, 5.02; N, 13.82.

The experiment described was the best run. In other runs, longer reaction times (up to 48 hr) were required for complete reaction of **1b** (by ir). Poor yields were sometimes obtained, perhaps due to inferior methoxide. A lower boiling solvent would probably be suitable.

The semicarbazone of **2** was prepared with semicarbazide acetate in the usual way: yellow crystals from methanol; mp 222–225° dec.

Anal. Calcd for $C_{13}H_{13}N_5O$: C, 61.28; H, 5.18; N, 27.15. Found: C, 61.06; H, 5.13; N, 27.44.

Reduction of 2 with Sodium Borohydride. A. Room temperature.—Solutions of 100 mg (0.5 mmol) of **2** in 4 ml of ethanol and 35 mg of $NaBH_4$ in 0.6 ml of 2:1 EtOH–H_2O were mixed and allowed to stand at 25°. After 8 hr, excess hydride was decomposed with HCl and the mixture was neutralized with bicarbonate. The white solid was then collected, giving 74 mg (72%) of the carbinol **3**, mp 208–210° dec; ir matched with sample prepared by reduction of **1** (R = H).[5]

B. At −40°.—A solution of 500 mg of dienone **2** in 40 ml of methanol was cooled to −40° and a solution of 97 mg of $NaBH_4$ in methanol was added, with stirring, during 30 min. After stirring at −40–50° for 30 min, acetic acid was added and the solution was warmed to room temperature and concentrated. Water and CH_2Cl_2 were added and an insoluble solid was removed; this was 34 mg (7%) of the saturated alcohol **3**. The organic phase was washed, dried, and evaporated. Dilution of the oil with pentane gave 164 mg (32%) of **4a**, mp 161–163°. Recrystallization from methylene chloride gave white crystals: mp 163–164°; ν^{KBr} 3300 cm^{-1}; δ^{CDCl_3} 1.76 (s, 3), 2.42 (broad, 1), 4.72 (broad, 1), 7.09 (s, 1), 7.29 (m, 1), 7.35 ppm (s, 5).

Anal. Calcd for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 71.65; H, 6.28; N, 13.82.

4-*exo*-5-Dimethyl-6-phenyl-1,2-diazabicyclo[3.2.0]-2,6-heptadien-4-ol (4b).—To a solution of 600 mg of **2** in 30 ml of ether at −80° was added 3.4 mmol of methyllithium in ether. After stirring for 7 hr at −80°, the solution was warmed and treated with aqueous ammonium chloride. After washing and drying, the organic layer was evaporated to give 400 mg (62%) of colorless crystals of **4b**, mp 153–155°. This material was recrystallized from methylene chloride–ether: mp 154–155°; δ^{CDCl_3} 1.52 (s, 3), 1.66 (s, 3), 7.01 (s, 1), 7.14 (s, 1), 7.34 ppm (s, 5).

Anal. Calcd for $C_{13}H_{14}N_2O$: C, 72.87; H, 6.59; N, 13.08. Found: C, 72.75; H, 6.66; N, 12.96.

Thermolysis of Dienone 2.—The apparatus consisted of a helix-packed 1 × 15 cm Pyrex tube with a heating coil and outer jacket filled with sand. The tube was heated to 450–475° (thermometer in sand). A solution of 3 g of the dienone in 3 l. of benzene was dropped into the heated tube during a period of about 20 hr; the effluent was condensed in ice. After filtration to remove particles of dark solid, the solution was evaporated and the residual dark oil, in benzene–ether solution was poured through a short column of 16 g of silicic acid.

The initial fractions from this chromatogram, containing 1.7 g of material, were chromatographed on a column of 120 g of alumina. Evaporation of the initial hexane eluate gave 0.9 g of biphenyl, mp 65°, and 0.3 g of yellow oil. This oil was chromatographed again on 22 g of silicic acid to give 160 mg of crystals, mp 88–89°, corresponding to 3% of compound "A". Recrystallization from methylene chloride–pentane gave crystals with mp 88–95°; from ether–pentane, the mp was 127–130°; for spectral properties, see discussion.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.57; H, 6.69.

The residue from the later fractions from the first silicic acid column, 1.7 g, was rechromatographed in benzene solution on 36 g of silicic acid. The main fractions were evaporated to give 900 mg (33%) of colorless solid, mp 81–84°. Recrystallization from ether–pentane followed by sublimation, gave colorless crystals of **4-methyl-5-phenylpyridazine**: mp 81–82°; δ^{CDCl_3} 2.36 (s, 3), 7.35–7.55 (m, 5), 9.00 (s, 1), 9.07 ppm (s, 1) (the two low field singlets were somewhat broadened, $W_{1/2}$ = 2 Hz).

Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.35; H, 6.02; N, 16.45.

The **picrate** was crystallized from alcohol, mp 136–137°. The ir spectrum was identical with that of a previously prepared sample.[20]

(18) M. R. Willcott and E. Goerland, *Tetrahedron Lett.*, 6341 (1966).

(19) J. J. Bloomfield, J. S. McConaghy, Jr., and A. G. Hartmann, *ibid.*, 3723 (1969).

(20) R. K. Bly, E. C. Zoll, and J. A. Moore, *J. Org. Chem.*, **29**, 2128 (1964).

4-Bromo-2-methyl-3-phenyl-2-cyclopentenone (16).—A solution of 100 mg of 2-methyl-3-phenyl-2-cyclopentenone in 3 ml of carbon tetrachloride was treated with 103 mg of *N*-bromosuccinimide. After 1 hr refluxing, a rapid reaction was observed; the succinimide which separated was collected and the filtrate was evaporated to an oil which crystallized to give 140 mg (96%) of off-white solid, mp 68–75°. Recrystallization from ether–pentane and sublimation gave **16** as white crystals: mp 89–91°; ν^{KBr} 1705 cm^{-1}; δ^{CCl_4} 1.88 (d, 3, J = 1.5 Hz), 3.01 (m, 2), 5.45 (m, 1), 7.45 ppm (s, 5).

Anal. Calcd for $C_{12}H_{11}BrO$: C, 57.61; H, 4.27. Found: C, 57.39; H, 4.41.

2-Methyl-3-phenylcyclopentadienone Dimer (17).—A solution of 46 mg of bromo ketone **16** in 2 ml of triethylamine was refluxed for 1 hr. The mixture was diluted with benzene and 32 mg of triethylammonium bromide was collected by filtration. Removal of solvent gave a colorless oil which crystallized from ether–pentane to give 12 mg (38%) of colorless crystals, mp 161–163°. Recrystallization from methylene chloride–ether gave the dimer **17**, mp 163–164°; for spectral data, see structure.

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.86; H, 5.90.

Hydrogenation of 2-Acetyl-5-methyl-6-phenyl-1,2-diazabicyclo[3.2.0]-6-hepten-4-one.—A solution of 900 mg of ketone **1** (R = Ac) in 90 ml of ethyl acetate and 90 mg of 10% Pd–C catalyst was shaken with hydrogen at atmospheric pressure until the uptake of 1 mol of H_2 (1 hr). After filtering off the catalyst, the solution was evaporated to a colorless oil. The nmr spectrum of this oil showed that the starting ketone was absent; the C-5 methyl peaks of the two isomeric dihydro ketones were of essentially equal size. The oil was seeded with a crystal of product from a previous hydrogenation (the initial crystallization required several weeks). A first crop of 380 mg, mp 103–105°, was collected. Recrystallization twice from ether and then sublimation at 105° (1 mm) gave colorless crystals of 2-acetyl-5-methyl-6-*exo*-phenyl-1,2-diazabicyclo[3.2.0]heptanone (**19**): mp 114–115°; ν^{KBr} 1750, 1670 cm^{-1}; δ^{CDCl_3} 0.89 (s, 3), 2.30 (s, 3), 3.5–4.7 (m, 5), 7.42 ppm (s, 5).

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.97; H, 6.56; N, 11.52.

The mother liquor from **19** was concentrated, and 290 mg of crystals, mp 94–96°, was obtained after standing at 0°. Recrystallization of this material and final sublimation gave 2-acetyl 5-methyl-6-*endo*-phenyl-1,2-diazabicyclo[3.2.0]-4-heptanone (**20**) as white crystals: mp 94–96°; ν^{KBr} 1760 cm^{-1}; δ^{CDCl_3} 1.47 (s, 3), 2.21 (s, 3), 3.6–4.6 (9 lines, combination of C-3 CH_2, H-6 and C-7 CH_2), 6.9–7.4 ppm (m, 5).

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 69.08; H, 6.78; N, 11.37.

Thermal Behavior of 1 (R = Ac), 2, and 19.—Solutions of 15 mg of the three ketones in 0.3 ml of $CDCl_3$ were sealed under nitrogen in nmr tubes and then heated in an 80° bath and spectra were recorded at intervals. **1** (R = Ac): After 48 hr, conversion to the diazepinone **22** (R = Ac), was 30% complete; after 90 hr, conversion was about 50%; after 310 hr the spectrum was essentially that of **22** (R = Ac) with about 5% of **2** (R = Ac) and negligible impurity peaks. **2**: After 260 hr, the only sharp peaks in the spectrum were those of unchanged **2**; very broad signals comprising about half of the total integral were present at δ 1.8–2.2 and 7.2–7.6. **19**: The spectrum was unchanged after 270 hr at 80°.

Registry No.—**1b**, 26439-91-8; **2**, 21039-49-6; **2** semicarbezone, 26439-93-0; **3**, 17831-34-4; **4a**, 26439-95-2; **4b**, 26439-96-3; **7**, 26439-97-4; **16**, 26439-98-5; **17**, 26439-99-6; **19**, 26440-00-6; **20**, 26440-01-7.

Models for the Stepwise Solvolysis of Unsaturated Ditosylates

JOSEPH B. LAMBERT,[1a] H. GILBERT SMITH, JR.,[1b] AND ANDREW P. JOVANOVICH[1c]

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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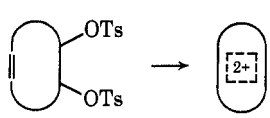
The solvolytic behavior of *cis*-4,5-cyclohexanediol ditosylate (I) has been studied as a model for the stepwise ionization of unsaturated ditosylates. Double ionization to form a bishomocyclobutenium ion is stereoelectronically prohibited in I. For comparison, the solvolyses of *trans*-4,5-cyclohexanediol ditosylate (II), *cis*-1,2-cyclohexanediol ditosylate (III), *trans*-1,2-cyclohexanediol ditosylate (IV), 4-cyclohexenyl tosylate (V), and cyclohexyl tosylate (VI) have also been studied. The rates of all the compounds are compared at 160°. Activation parameters and product analyses are reported. It is found that the double bond in I or II conveys no significant acceleration relative to III or IV, and that the unsaturated *cis*-ditosylate I reacts even more slowly than the *trans*-ditosylate II. These results are taken to be characteristic of the stepwise mechanism. Properties required of a mechanism involving double ionization to a dication are discussed.

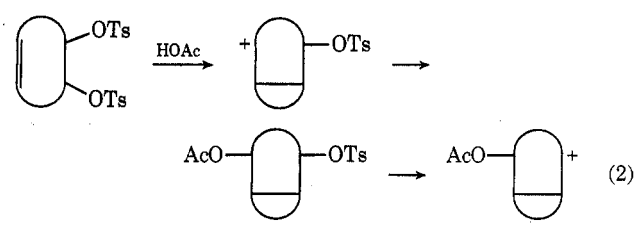
Part A

In this series of papers,[2] it has been our object to examine systems that could give rise to a doubly charged species as a transient intermediate under normal solvolytic conditions. The two positive charges are to be produced by solvolysis of adjacent tosylate groups, and the requisite stabilization is to be provided by an appositely positioned double bond (eq 1). The



(1)

novel intermediate so formed would be termed a bishomocyclobutenium ion and would receive its stabilization by possession of a planar bishomocyclic structure with $4n + 2$ electrons (n = 0). We have previously studied a system[2] that is stereochemically ideal for formation of a bishomo dication, but the kinetic data could not differentiate between the double ionization mechanism of eq 1 and pathways exemplified



(2)

by eq 2, in which ionization is stepwise and an acetoxy tosylate intermediate intervenes. In the present work, we have examined the solvolysis of *cis*-4,5-cyclo-

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(2) For the first paper, see J. B. Lambert and A. G. Holcomb, *J. Amer. Chem. Soc.*, **91**, 1572 (1969).