demonstrates a stereospecific complex or verifies the postulated stereochemistry. That the observed solvent-dependent chemical shifts may reflect time-averaged environments for the groups involved or that the relative insensitivity of some calculated chemical shifts to variations in stereochemistry of the complex are possibilities which may not be ignored.

Experimental

1,1,1-Trideuterio-4-methyl-3-penten-2-one.—Methyl-d_3 bromide (Merck Sharp and Dohme of Canada, 909 mg., 9.27 mmoles) was transferred in a dry vacuum line to a magnetically stirred mixture of freshly cut lithium (158 mg., 22.8 mg.-atoms) in 40 ml. of ether. When the methyl-d_3 bromide had reacted, an atmosphere of dry, oxygen-free nitrogen was established. The ethereal methyllithium solution was frozen with a liquid nitrogen bath, 2.16 g. (1.82 mmoles) of β,β-dimethylacrylyl chloride was injected into the reaction mixture through a rubber serum-bottle stopper, and the reaction mixture was allowed to warm to room temperature with stirring in 15 min. The reaction mixture was filtered through glass wool into 10 ml. of aqueous ammonium chloride, and the ethereal layer was passed through a column of acid-washed alumina, wet-packed with ether. The fractions containing the labeled mesityl oxide were found by t.l.c. on alumina, concentrated, and analyzed by v.p.c. on a 20M Carbowax column. The product mixture contained approximately 33% of labeled 2,4-dimethyl-1,3-pentadiene and 37% of labeled mesityl oxide.

The n.m.r. spectrum of 1,1,1-trideuterio-4-methyl-3-penten-2-one isolated by preparative v.p.c. showed absorptions at τ 7.9 and 8.13 in a ratio of 1.46:1.0.

2,4-Dimethyl-1,3-pentadiene from trial preparations of mesityl oxide with unlabeled methyl bromide was collected by preparative v.p.c. and identified through its physical properties: b.p. 90° (Emich tube), $n^{22}\text{D}$ 1.4400 (lit.[16] b.p. 93°, $n^{20}\text{D}$ 1.4408), $\nu_{\max}^{\text{CCl}_4}$ 890 cm.$^{-1}$ (terminal methylene).

trans-**3-Penten-2-one (IV)** was isolated by v.p.c. on a 4-methyl-4-nitropimelonitrile column[17] from a commercial sample (Aceto Chemical Co., Inc.) of ethylideneacetone. Irradiation of the commercial ethylideneacetone as a solution in cyclohexane with ultraviolet light (Hanovia 450-w. high-pressure mercury lamp) for 22 hr. followed by repeated v.p.c. gave *cis*-**3-penten-2-one (III).**

Chemical shifts for the protons in these two isomers are reported in Table I. In addition to the reported absorptions, the *cis* isomer showed a weak signal at τ 7.97, presumably due to a trace impurity.

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[16] G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1939, p. 315.

[17] Compare H. O. House, D. D. Traficante, and R. A. Evans, *J. Org. Chem.*, **28**, 348 (1963).

Decomposition of the Anion of the Tosylhydrazones of Several Cycloalkene Aldehydes[1]

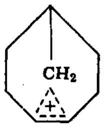
Meyer Schwarz,[2] Albert Besold, and Edward R. Nelson

Harry Diamond Laboratories, Washington, D. C.

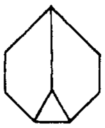
Received January 14, 1965

The products of the thermal decomposition of the title compounds were investigated. In the case of the cycloheptenecarboxaldehyde and the cyclopentenylacetaldehyde derivatives intramolecular carbene addition to the double bond took place to a minor extent, with formation of tricyclo[5.1.0.0^{4,8}]octane (II) and nortricyclene (VII), respectively. No intramolecular carbene-addition product could be detected in the decomposition product of the cyclohexenylacetaldehyde tosylhydrazone anion. The major product of the decomposition reaction of the cycloheptenecarboxaldehyde derivative was found to be 2,3-diazatricyclo[3.3.2.0^{2,6}]dec-2-ene (III) formed by intramolecular 1,3-addition. The decomposition of the cycloheptenecarboxaldehyde and the cyclohexenylacetaldehyde derivatives took place at low temperatures indicating double-bond participation.

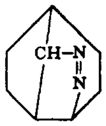
The chemistry of carbenes and their reactions with olefins has attracted considerable attention during the past 15 years.[3] There are, however, very few reports in the literature of intramolecular addition of methylenes to double bonds. The majority of the cases reported deal with the intramolecular reaction of unsaturated α-ketocarbenes, obtained from the corresponding α-diazo ketone either by copper powder catalyzed thermal decomposition or by photolysis.[4] One other instance was reported by Skattebøl,[5] who obtained tricyclo[4.1.0.0^{4,6}]heptane from 1,1-dibromo-2-(but-3-enyl)-cyclopropane and methyllithium *via* the cyclopropylidene intermediate. It occurred to us that unsaturated carbenes amenable to intramolecular addition might be derived from systems analogous to those which have been reported to undergo facile ring closure, yielding bridged compounds by the so-called "π-route." The first such system was disclosed by Le Ny,[6] and involved the acetolysis of 4-cycloheptenylmethyl *p*-bromobenzenesulfonate, which led to *cis*-2-bicyclo[3.2.1]octyl acetate *via* the nonclassical carbonium ion I. Subsequently, Lawton,[7a] Bartlett and Bank,[7b] and Winstein and Carter[7c] reported other model compounds, such as 3-cyclopentenylethyl and 3-cyclohexenylethyl arenesulfonates, from which bicyclo[2.2.1]heptane, bicyclo[2.2.2]octane, and bicyclo[3.2.1]octane derivatives may be obtained by the "π-route." Most recently Hanack and Kaiser[8] showed that the solvolysis of 4-



I



II



III

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[1] Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964; Abstracts, p. 34C.

[2] To whom inquiries should be sent: Entomology Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Md. 20705.

[3] J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964.

[4] G. Stork and J. Ficini, *J. Am. Chem. Soc.*, **83**, 4678 (1961); W. von E. Doering and B. Ferrier, cited by W. von E. Doering and W. R. Roth, *Angew. Chem., Intern. Ed. Engl.*, **2**, 115 (1963); W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, **No. 17**, 961 (1964); S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964).

[5] L. Skattebøl, *Chem. Ind.* (London), 2146 (1962).

[6] G. Le Ny, *Compt. rend.*, **251**, 1526 (1960).

[7] (a) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961); (b) P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); (c) S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961).

[8] M. Hanack and W. Kaiser, *Angew. Chem., Intern. Ed. Engl.*, **3**, 583 (1964).

cyclooctenylmethyl *p*-toluenesulfonate leads to a mixture of bicyclo[3.3.1]nonane and bicyclo[4.2.1]nonane derivatives.

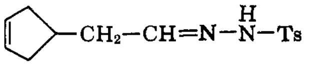
As our first model we chose 4-cycloheptenylmethylcarbene which, if intramolecular addition takes place, should yield tricyclo[5.1.0.0^{4,8}]octane (II). For the synthesis of this carbene 4-cycloheptenecarbonyl chloride, prepared from the corresponding acid,[9] was reduced to 4-cycloheptenecarboxaldehyde with lithium aluminum hydride *via* the aziridine derivative.[10] The aldehyde was then converted to the corresponding tosylhydrazone. Heating of the latter compound at 150° in the presence of a slight excess of sodium methoxide in diglyme or in N,N-dimethylformamide, *i.e.*, aprotic solvents favoring carbenoid decomposition,[11] resulted in the evolution of nitrogen, but in amounts far below the theoretical expectation. Processing of the reaction mixture revealed a nitrogen-containing compound of m.p. 206–208°, which analyzed for $C_8H_{14}N_2$ (III). This compound was formed in 35% yield, together with a mixture of hydrocarbons which could not be completely resolved but was shown to contain compound II (*vide infra*) in 2% yield and olefinic hydrocarbons in 15% yield. When the decomposition was subsequently carried out in N,N-dimethylformamide at 100°, the same products were obtained in the ratio of five parts of compound III to one part of the same hydrocarbon mixture as above, in 37% over-all yield.

We have assigned to the nitrogen compound structure III, believed to be formed by the intramolecular 1,3-addition to the diazomethane part of the molecule to the double bond. It is interesting to note that the double bond has considerable activating influence on the decomposition of the tosylhydrazone anion, manifested by the low temperature at which it decomposed. Similarly, accelerations of solvolysis rates by double-bond participation have been observed in "π-route" ring closures.[6-8] The tosylhydrazone of camphor could be recovered unchanged when heated at 100° with sodium methoxide in N,N-dimethylformamide. The anions of tosylhydrazones of aromatic aldehydes and ketones,[12] the monotosylhydrazones of 1,2-diketones,[13] and tosylhydrazones of α,β-unsaturated carbonyl compounds[14] are, however, known to decompose under comparably mild conditions.

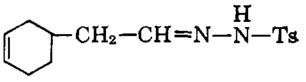
The assignment of the 3,4-diazatricyclo[3.3.2.0^{2,6}]dec-3-ene structure to compound III is supported by: (1) its ultraviolet spectrum, which is similar to those reported for 2,3-diazabicyclo[2.2.1]hept-2-ene and 2,3-diazabicyclo[2.2.2]oct-2-ene by Cohen and co-workers,[15] and (2) the formation of a cuprous chloride complex.[16] The n.m.r. spectrum shows a multiplet at δ 4.78 (tetramethylsilane, 60 Mc. in CCl_4), which may be assigned to methine hydrogen next to a double-bonded nitrogen.[17] Absorption in the same region was also found by Cohen and Zand[15b] for the bridgehead protons in the bicyclic diazo compounds and by Moriarty[18] for the bridgehead protons adjacent to the azo group in 6,7-diazaquadricyclo[3.2.1.1^{3,8}.0^{2,9}]non-6-ene. Integration of the spectrum gives the required ratio of one-seventh of the total number of protons for those next to the azo group. The infrared spectrum (tetrachloroethylene) shows a strong absorption band at 6.61 μ, attributable to —N=N— stretching vibration.[15b]

Pyrolysis or photolysis of III led to a liquid hydrocarbon, which was also present in the original reaction mixture and which was analyzed to be C_8H_{12}. The infrared spectrum of this hydrocarbon revealed a strong absorption band at 9.92 μ, usually associated with the cyclopropane ring.[19] The n.m.r. spectrum (tetramethylsilane, 60 Mc. in CS_2) showed no olefinic protons, but a broad multiplet at δ 2.6 equal to one proton and two overlapping multiplets at 1.8 and 1.4, equalling 11 protons. It was assigned structure II, tricyclo[5.1.0.0^{4,8}]octane.[20] Hydrogenolysis of this hydrocarbon yielded bicyclo[3.2.1]octane (identified by comparison with an independently prepared sample) as its only product, substantiating the assignment of structure III and, hence, structure II. Interestingly, no bicyclo[3.3.0]octane, the other possible hydrogenolysis product, was found. The tendency for the most strained bond to break in similar hydrogenolysis has been observed in other instances.[21] The results of our decomposition experiment of the cycloheptenemethyl tosylhydrazone anion left in doubt whether or not intramolecular carbene addition had taken place in this system. The small amount of the tricyclic hydrocarbon II which was found in the reaction mixture might have resulted either from thermolysis of the tricyclic diaza compound or from intramolecular addition of carbene formed from the primary diazo compound. Stability experiments of the tricyclic diaza compound showed that solutions of the latter in dimethylformamide were stable for 0.5 hr. at 150° as evidenced by the constancy of the absorbance in the ultraviolet region. This result would thus point toward intramolecular carbene addition, but only to a small extent in this system. However, most probably due to very favorable steric conditions, the 1,3 dipolar addition of the diazomethane moiety of the molecule to the double bond occurs at a much greater rate than the competing reaction of carbene formation. Normally pyrazoline formation with unactivated double bonds is very sluggish[22] and would only be expected to occur at low temperatures where the primary diazomethane derivative is stable.

To test the possibility of intramolecular additions in related systems we investigated the base-induced decompositions of the tosylhydrazones of 3-cyclopentenylacetaldehyde (IV) and of 3-cyclohexenylacetaldehyde



IV



V

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[9] G. Stork and H. K. Landesman, *J. Am. Chem. Soc.*, **78**, 5129 (1956).

[10] H. C. Brown and A. Tsukamoto, *ibid.*, **83**, 4549 (1961).

[11] L. Friedman and H. Shechter, *ibid.*, **81**, 5512 (1959).

[12] D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).

[13] M. P. Cava, R. L. Little, and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2257 (1958).

[14] G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963).

[15] (a) S. G. Cohen, R. Zand, and C. Steel, *ibid.*, **83**, 2895 (1961); (b) S. G. Cohen and R. Zand, *ibid.*, **84**, 586 (1962).

[16] O. Diels, J. H. Blum, and W. Koll, *Ann.*, **443**, 242 (1925).

[17] E. C. Taylor and R. O. Kan, *J. Am. Chem. Soc.*, **85**, 776 (1963).

[18] R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963).

[19] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 29.

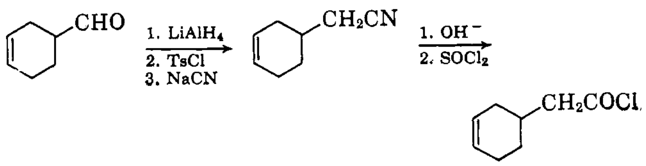
[20] The same structure has also been assigned to the hydrogenation product of one of the components of the reaction mixture resulting from the photoisomerization of 1,3,5-cyclooctatriene by J. Zirner and S. Winstein [*Proc. Chem. Soc.*, 235 (1964)]. The n.m.r. spectrum reported by these authors appears to be identical with ours.

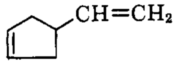
[21] J. Newham, *Chem. Rev.*, **63**, 123 (1963).

[22] R. Huisgen, *Angew. Chem.*; *Intern. Ed. Engl.*, **2**, 633 (1963), and references cited therein.

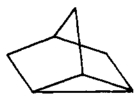
(V). The 3-cyclopentenylacetaldehyde was prepared by reduction of 3-cyclopentenylacetic acid, which was previously synthesized by Lawton,[7a] according to the method of Brown and Tsukamoto.[10] The cyclohexenylacetaldehyde was also prepared from the corresponding acid, which in turn was prepared in the reaction sequence shown in Scheme I. Decomposition of the 3-cyclopentenylacetaldehyde tosylhydrazone yielded two products. The major product was an unsaturated hydrocarbon (in 30% yield), which was identified as 4-vinylcyclopentene (VI). This assignment is based on the infrared spectrum, which showed absorption at 6.1 (vinyl double bond) and at 6.2 μ (cyclopentene double bond).[23] The n.m.r. spectrum (tetramethylsilane, 60 Mc. in $CDCl_3$) showed the presence of an equal number of olefinic protons and nonolefinic protons, and appeared to be identical with the spectrum of the compound reported by Freeman, George, and Rao.[24] The minor reaction product was identified as nortricyclene (VII), which is the anticipated reaction product of intramolecular carbene addition and was formed in 3% yield. Thus, in this case as in the case of 3-cycloheptenylacetaldehyde tosylhydrazone, intramolecular addition took place only to a minor extent. In this case, however, *no* volatile nitrogen-containing compound could be detected, nor was any significant decomposition of the anion noticeable below 140°.

SCHEME I

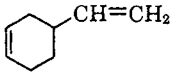




VI



VII



VIII

With the 4-cyclohexenylacetaldehyde tosylhydrazone anion we did again observe decomposition to occur slightly above 100°. In this case, however, 4-vinylcyclohexene (VIII) was found to be the only volatile product, and was obtained only in trace amount. The main products from this reaction were very high-boiling materials which were not further investigated.

In conclusion it would thus appear that these systems, which are very prone to react intramolecularly in solvolytic displacement and other reactions[25] involving double-bond participation, show this tendency to a much smaller extent in carbene reactions. Interestingly we have found double-bond participation, as evidenced by the lowering of the temperature at which the tosylhydrazone anions decompose, in two of our cases. Also in the cyclopentenyl and in the cyclohexenyl cases we have found no evidence for carbene insertion reactions.[11] In the cycloheptene case it is of course possible that the insertion reaction took place, with its product part of the as yet unidentified hydrocarbon mixture.

Experimental[26]

4-Cycloheptenecarboxylic Acid.—This compound was prepared by the method described by Stork and Landesman[9] from the methiodide of the reaction product of acrolein and the pyrrolidine enamine of cyclopentanone. This method was modified by the use of diethyl ether in place of dioxane as the solvent in the reaction of acrolein and the pyrrolidine enamine which allowed the removal of the solvent at lower temperatures without affecting the yield. The methiodide was prepared in methyl ethyl ketone, which gave the best yield of all the solvents tried. The 4-cycloheptenecarboxylic acid had m.p. 71–72°, lit.[9] m.p. 65–67°, and was obtained in 22% over-all yield.

4-Cycloheptenecarboxaldehyde.—4-Cycloheptenecarbonyl chloride, b.p. 77–80° (10 mm.), prepared from 4-cycloheptenecarboxylic acid and thionyl chloride at low temperature, was reduced according to Brown and Tsukamoto.[10] To a cooled solution of 27.6 g. (0.64 mole) of ethylenimine and 65.4 g. (0.46 mole) of triethylamine in 300 ml. of anhydrous ether was added dropwise a solution of 104.5 g. (0.64 mole) of the acid chloride in 100 ml. of anhydrous ether over a period of 1 hr. After an additional 0.5 hr. of stirring, the reaction mixture was filtered. To the cooled filtrate was added with stirring a solution of 7.5 g. (0.2 mole) of lithium aluminum hydride in 200 ml. of ether over a 0.5-hr. period. After an additional 0.5 hr. the reaction mixture was decomposed with excess 5 *N* sulfuric acid and extracted with ether. The ether layer, after washing with a solution of sodium bicarbonate and drying, yielded 44.2 g. (56% yield) of 4-cycloheptenecarboxaldehyde, b.p. 63–70° (14–16 mm.). This material was 97% pure by v.p.c. analysis.

The 2,4-dinitrophenylhydrazone, after recrystallization from aqueous alcohol, had m.p. 138–139°.

Anal. Calcd. for $C_{14}H_{16}N_2O_4$: C, 55.2; H, 5.3. Found: C, 55.2; H, 5.5.

4-Cycloheptenecarboxaldehyde Tosylhydrazone.—To a warm solution of 67.8 g. (0.37 mole) of tosylhydrazide in 250 ml. of methanol was added 44 g. (0.35 mole) of 4-cycloheptenecarboxaldehyde. After 0.5 hr. water was added, and the product was allowed to crystallize, yielding 82 g. (82% yield) of material of m.p. 89–90° dec. A sample for analysis, recrystallized from methanol–water, melted at 90–91° dec.

Anal. Calcd. for $C_{15}H_2N_2O_2S$: C, 61.6; H, 6.9. Found: C, 61.4; H, 6.9.

Decomposition of 4-Cycloheptenecarboxaldehyde Tosylhydrazone. A. In Diglyme.—To a suspension of 8.2 g. (0.15 mole) of sodium methoxide in 300 ml. of diglyme was added 40 g. (0.14 mole) of the tosylhydrazone. The mixture was heated rapidly to 150° with stirring, and kept at this temperature for about 5 min., at which time nitrogen evolution had ceased. The reaction mixture was allowed to cool, poured into 2 l. of ice–water, and extracted with ether. The extract was dried and the ether was evaporated leaving a yellow residue of 7.4 g. (*ca.* 50% yield). Vapor phase chromatography, using silicone gum rubber on firebrick revealed the presence of four major reaction products, two of which could be cleanly separated. These were tricyclo[5.1.0.0^{4,8}]octane (II), found in 2% yield, and 3,4-diazatricyclo[3.3.2.0^{4,6}]dec-3-ene (III), formed in 34% yield. The two other hydrocarbons were found to be formed in 15% yield but could not be completely separated. The reaction product was taken up in pentane and III crystallized on cooling. Sublimation (120° at 30 mm.) afforded a pure sample: m.p. 207–209° (closed capillary); $\lambda_{max}^{isooctane}$ 349 mμ (ε 332), 345 mμ (ε 265); λ_{max}^{DMF} 351 mμ (ε 300).

Anal. Calcd. for $C_8H_{12}N_2$: C, 70.5; H, 8.9; N, 20.6. Found: C, 70.5; H, 8.9; N, 20.3.

The compound (III) was soluble in concentrated hydrochloric acid and gave a complex with cuprous chloride.

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[23] R. N. Jones and C. Sandorfy, "Technique of Organic Chemistry," Vol. IX, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 369, 370.

[24] P. K. Freeman, D. E. George, and V. N. M. Rao, *J. Org. Chem.*, **28**, 3234 (1963).

[25] We have, for instance, found that oxidation of the tosylate of 4-cycloheptenemethanol using dimethyl sulfoxide [N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Am. Chem. Soc.*, **81**, 4113 (1959)] yields an approximately equimolar mixture of the expected 4-cycloheptenecarboxaldehyde and bicyclo[3.2.1]octanone-2. Also, while the reaction of 4-cycloheptenecarboxylic acid and thionyl chloride yields the acid chloride at room temperature or below, we have found that at about 60° the same reaction mixture yields a saturated, chlorinated bicyclic ketone (unpublished results).

[26] Melting points and boiling points are uncorrected. Elemental analyses were performed by Mr. R. J. Hall, National Bureau of Standards.

B. **In Dimethylformamide.**—To a suspension of 29.2 g. (0.54 mole) of sodium methoxide in 500 ml. of dimethylformamide was added 142 g. (0.48 mole) of the tosylhydrazone. The homogenous mixture was heated to 100° and kept at that temperature for approximately 10 min. (exothermic reaction). At the end of this period nitrogen evolution had ceased. The reaction mixture was cooled and poured into 2 l. of ice–water and extracted with ether. Work-up as above yielded a residue which contained the same components as in A, but the hydrocarbon: azo compound ratio was 1:5, with crude over-all yield of 37%. Crystallization from pentane and sublimation yielded 8 g. (10%) of pure compound III.

Tricyclo[5.1.0.0^{4,8}]octane. A. **Thermolysis of III.**—3,4-Diazatricyclo[3.3.2.0^{4,6}]dec-3-ene (III, 0.5 g., 0.037 mole) was heated in an evacuated, sealed, Pyrex tube at 300° overnight (III was found to be quite stable below this temperature). A liquid reaction product was formed in nearly quantitative yield (plus traces of charred material) and proved to be identical with one of the reaction products, tricyclo[5.1.0.0^{4,8}]octane (II), obtained in the decomposition of the 4-cycloheptenecarboxaldehyde tosylhydrazone. They had identical infrared spectra and also had the same retention time on the gas chromatograph. An analytical sample was obtained by vapor phase chromatography. It had a molecular weight of 108 by mass spectrograph.

Anal. Calcd. for C_8H_{12}: C, 88.8; H, 11.2. Found: C, 89.0; H, 11.2.

B. **Photolysis of III.**—A solution of 8 g. (0.059 mole) of 3,4-diazatricyclo[3.3.2.0^{4,6}]dec-3-ene in 300 ml. of cyclohexane was irradiated by a 550-w. immersion-type high-pressure mercury source for 2 hr. A small amount of solid was filtered off and discarded. The solvent was removed and the residue yielded 4.65 g. (73% yield) of tricyclo[5.1.0.0^{4,8}]octane, b.p. 68–72° (45 mm.), $n^{24}D$ 1.4780, shown to be identical with the product formed by the thermolysis experiment, by comparison of infrared spectra and v.p.c. retention times.

Hydrogenolysis of II.—A solution of 3.0 g. (0.028 mole) of tricyclo[5.1.0.0^{4,8}]octane in 30 ml. of glacial acetic acid was shaken in the presence of 0.1 g. of PtO_2 at 50 p.s.i. hydrogen pressure at 50° for 4 hr. The reaction mixture was diluted with water, yielding a crystalline solid in quantitative yield. It was identified as bicyclo[3.2.1]octane by comparison of the v.p.c. retention times and infrared spectrum with those of an authentic sample.[27]

3-Cyclopentenylacetaldehyde.—3-Cyclopentenylacetic acid, which was prepared according to Lawton,[7a] was converted to the acid chloride by thionyl chloride in quantitative yield. The acid chloride was reduced to the corresponding aldehyde in 80% yield, by the method of Brown and Tsukamoto[10] as outlined for the preparation of 4-cycloheptenecarboxaldehyde. For characterization purposes a 2,4-dinitrophenylhydrazone, m.p. 125–126° from ethanol, was prepared.

Anal. Calcd. for $C_{13}H_{14}N_4O_4$: C, 53.8; H, 4.95. Found: C, 53.8; H, 4.9.

3-Cyclopentenylacetaldehyde Tosylhydrazone.—3-Cyclopentenylacetaldehyde (55 g., 0.5 mole) was added to a solution of 100 g. (0.56 mole) of tosylhydrazide in 250 ml. of methanol. The temperature of the reaction mixture was not allowed to exceed 45°. The solution was cooled and the tosylhydrazone was precipitated by the addition of water. The product was filtered, dried, and recrystallized from ether–pentane. It weighed 95 g. (70% yield) and melted at 79–81° dec. A sample for analysis, recrystallized from ether–pentane, melted at 80–81° dec.

Anal. Calcd. for $C_{14}H_{18}N_2O_2S$: C, 60.4; H, 6.5. Found: C, 60.3; H, 6.5.

This tosylhydrazone was found to be unstable at room temperature (with the formation of unidentified, ether-insoluble material) and therefore was stored at −20°, at which temperature no decomposition was observed over a 2-month period.

Decomposition of 3-Cyclopentenylacetaldehyde Tosylhydrazone.—To a solution of 21 g. (0.075 mole) of tosylhydrazone in 200 ml. of diglyme was added 4.5 g. (0.085 mole) of sodium methoxide. The mixture was heated with stirring to 140° at which temperature nitrogen evolution started. The reaction mixture was kept between 140 and 150°, and volatile products were collected as they distilled. A total of 6 g. of material was collected. V.p.c. analysis indicated the presence of 2.1 g. (30% yield) of 4-vinylcyclopentene, identified by infrared and n.m.r. spectra, and 0.2 g. (3% yield) of nortricyclene, identified by comparison with a sample prepared according to Freeman, *et al.*[28] The infrared spectrum was identical with that reported by Lippincott.[29] Comparable results were obtained when this reaction was carried out in DMF.

3-Cyclohexenylacetaldehyde.—The aldehyde was prepared by lithium aluminum hydride reduction of the acid chloride as described for the 4-cycloheptenecarboxaldehyde. The 4-cyclohexenylacetyl chloride was prepared as outlined in the text, starting with 3-tetrahydrobenzaldehyde[30] which was reduced to the alcohol by the use of lithium aluminum hydride. The alcohol was converted to the tosylate which in turn was converted to the nitrile by the use of an excess of sodium cyanide in DMF–water mixture. The cyanide was hydrolyzed and converted to the acid chloride. The over-all yield of 4-cyclohexenylacetaldehyde based on tetrahydrobenzaldehyde was 50%.

3-Cyclohexenylacetaldehyde was characterized as its 2,4-dinitrophenylhydrazone, m.p. 125–126° from ethanol.

Anal. Calcd. for $C_{14}H_{16}N_4O_4$: C, 55.3; H, 5.3. Found: C, 55.4; H, 5.2.

3-Cyclohexenylacetaldehyde Tosylhydrazone.—To a warm solution of 62 g. (0.3 mole) of tosylhydrazide in 250 ml. of methanol was added 34 g. (0.28 mole) of the aldehyde. The temperature of the reaction mixture was kept below 50°. After cooling, the reaction product crystallized upon addition of a small quantity of water. The yield was 67 g. (70%) of material melting at 90–91° dec. A sample for analysis melted at 92–93° dec. after recrystallization from methanol–water.

Anal. Calcd. for $C_{15}H_{20}N_2O_2S$: C, 61.6; H, 6.9. Found: C, 61.4; H, 6.9.

Decomposition of 3-Cyclohexenylacetaldehyde Tosylhydrazone.—A solution of 58.4 g. (0.2 mole) of the tosylhydrazone and 11.9 g. (0.22 mole) of sodium methoxide in 250 ml. of N,N-dimethylformamide was heated rapidly to 100°, at which temperature nitrogen evolution became vigorous. The reaction mixture was kept between 100 and 110° (exothermic reaction) for 10 min., at the end of which period nitrogen evolution had ceased. The reaction mixture was cooled, poured into 1 l. of ice–water, and extracted with ether. V.p.c. analysis revealed only very small amounts of low molecular weight material. Distillation yielded 0.4 g. of a liquid, b.p. 50° at 40 mm. (pot temperature 100°). There was a considerable residue (27 g.) which did not distil (pot temperature 100° and 2 mm.) and which was not further investigated. The liquid had the same retention time and infrared spectrum as a commercial sample of 4-vinylcyclohexene.

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