The Rearrangement of 2-Methylcyclohexylidene[1,2]

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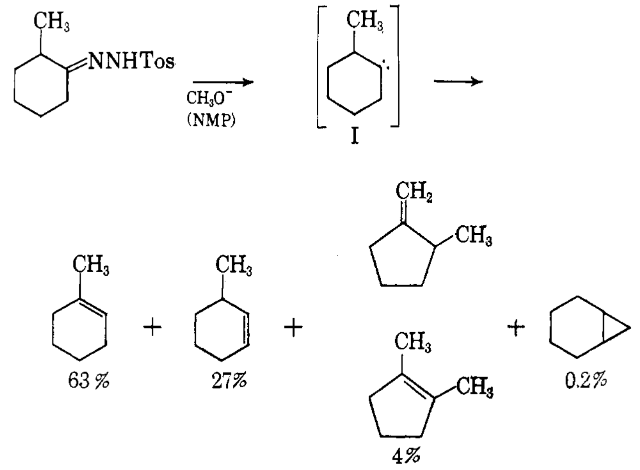
Received January 14, 1963

The intramolecular reactions of tosylhydrazone-engendered carbenes in aprotic media include hydrogen migration, alkyl or aryl migration, and insertion.[3] The recent report[4] of *exclusive* hydrogen migration in cyclohexylidene prompted our describing the results of our investigations of both this carbene and 2-methylcyclohexylidene (I).

Decomposition of 2-methylcyclohexanone tosylhydrazone in the usual way with sodium methoxide in N-methylpyrrolidone (NMP) led to a complex mixture of hydrocarbon products in 54–64% yield, having eight closely grouped, but discernible, components *via* gas chromatography on a Carbowax 20M column. The hydrocarbon products identified are shown below.



The methylcyclohexenes represent products of hydrogen migration,[5] the 2-methylmethylenecyclopentane together with its thermally produced isomer result from an alkyl migration, and the norcarane is an insertion product. With the exception of the 1,2-dimethylcyclopentene, the individual products were shown not to be derived from the others under the reaction conditions. So *all* the recognized carbene processes are recognizable in this case, if not in the parent ring compound itself. An interesting side reaction, apparently one involving dehydrogenation of the methylcyclohexenes, produced variable amounts of toluene in the above reaction. When cyclohexanone tosylhydrazone was similarly decomposed, a small yield of benzene in addition to the reported product,[4] cyclohexene, was observed. One might rationalize these aromatic products as being formed *via* a dehydrogenation promoted by some sulfur compound at the relatively high reaction temperature (180°) employed.[6]

The relative proportion of the methylcyclohexenes obtained in the tosylhydrazone reaction is very similar to the proportion obtained in the acid-catalyzed dehydration of mixed *cis*- and *trans*-2-methylcyclohexanol, *viz.*, $\Delta^3/\Delta^1 = 0.29$ (tosylhydrazone) and 0.32 (dehydration). Apparently the product-determining processes from the carbene are similar to those from the carbonium ion. Others have commented on the electrophilic similarity of the two reactive species.[7]

The observed yields indicate a reaction preference in this carbene of hydrogen migration $\gg$ alkyl migration $\sim$ insertion. The preference for hydrogen migration compared to insertion has been observed in other alicycles,[4] as well as commonly in acyclic substances.[8] The relation between the alkyl migration and insertion is, however, less clear and the present work does not give definitive results.[9] Some 6% of the products in this work were not identified and could, conceivably, be further insertion products. If this were so, then the observed alkyl migration–insertion ratio (4:0.2) would not be valid. In any case, the alkyl migration and insertion processes are comparable and both are much less facile than hydrogen migration, substantiating the earlier work mentioned.[4] Nonetheless, the rearrangement of 2-methylcyclohexylidene (I) is somewhat more complex than the previous data on cyclohexylidene itself[4] would have indicated.

The products were identified through comparison with authentic samples. The methylcyclohexenes were prepared by dehydration as mentioned. Dichlorocarbene addition to cyclohexene followed by reduction afforded norcarane. The Wittig reaction of methylidenetriphenylphosphorane on 2-methylcyclopentanone gave, in very poor yield, however, 2-methylmethylenecyclopentane (and the 1,2-dimethylcyclopentene isomer). In attempts to identify the remaining products, other substances were prepared, *e.g.*, ethylidenecyclopentane. Unfortunately, none of the materials synthesized proved to be the unknown reaction products. Infrared and nuclear magnetic resonance data were employed, together with gas chromatography, in the structural assignments.

Experimental

All melting points are uncorrected for stem exposure and were taken on a Fisher-Johns block. An unpacked distillation

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[1] Taken from the M. S. Thesis of W. J. Wagner, Loyola University, June, 1963.

[2] The term "cyclohexylidene" was suggested by the Editor in place of other nomenclature we proposed. Carbene nomenclature, like that of carbonium ions and carbanions, is not very precise. The basis for most names for these intermediates is usually (notwithstanding "cyclohexylidene") the carbinol system of alcohols, thus, Ph_2C: is diphenylcarbene, like Ph_2CHOH, diphenylcarbinol. However, such nomenclature does not lend itself well to many structures (such as in this work) or to polycarbenes. We are, therefore, suggesting other nomenclature to Chemical Abstracts Services.

[3] For a recent review, *cf.* E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963).

[4] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **83**, 3159 (1961).

[5] 1-Methylcyclohexene might also represent a methyl-shifted product to some unknown extent.

[6] *p*-Thiocresol was present (odor) in some of the reaction mixtures. This suggests a dehydrogenation (oxidation) path involving some higher oxidation state sulfur compound, since the thiol represents the ultimately reduced product.

[7] *Inter alia*, H. Philip and J. Keating, *Tetrahedron Letters*, 523 (1961).

[8] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

[9] Not many studies of this aspect exist, but the few that do[8,10] indicate that alkyl migration (in the form of ring expansion) is preferred in small rings and insertion is preferred in acyclics. NOTE ADDED IN PROOF.—*Cf.*, however, H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964), where insertion, rather than the reported[10] ring expansion, occurs as the major process with cyclopropanecarboxaldehyde tosylhydrazone.

[10] L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960).

apparatus was used for all distillations and for boiling point determinations, which are also uncorrected for stem exposure. Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer, equipped with sodium chloride optics. All gas chromatography was performed on a Wilkens A-90-P instrument. Helium was the carrier gas and the column (5 ft. × 0.25 in.) was Carbowax 20 M (20%) on firebrick, thermostated at 70 ± 5°. Microanalyses were performed by the Microtech Laboratories, Skokie, Ill.

2-Methylcyclohexanone Tosylhydrazone.—A mixture of 2-methylcyclohexanone (K and K Laboratories, 10.1 g., 0.09 mole), *p*-toluenesulfonylhydrazine (16.76 g., 0.09 mole), glacial acetic acid (15 drops), and ethanol (80 ml.) was refluxed for 30 min. Water (5 ml.) was then added to the cooled mixture and the precipitated tosylhydrazone was collected and recrystallized once from a 60:40 mixture of water and ethanol (white solid, m.p. 121–122°, 15.9 g., 63.5%).

Anal. Calcd. for $C_{14}H_{20}N_2O_2S$: C, 59.97; H, 7.19. Found: C, 60.15; H, 7.38.

1-Methyl- and 3-Methylcyclohexene.—These olefins were prepared by the dehydration of 2-methylcyclohexanol (mixed *cis* and *trans* isomers)[11] using sulfuric acid, as described for the preparation of cyclohexene[12] (64%, b.p. 110–112°). Gas chromatographic analysis indicated a composition of $\Delta^3/\Delta^1 = 0.32:1$.

Norcarane.—Reduction by a literature method[13] of 7,7-dichloronorcarane[14] gave this hydrocarbon (19%, b.p. 116°, n^{25}_D 1.4567; lit.[13] b.p. 116°, n^{25}_D 1.4550).

2-Methylmethylenecyclopentane (and 1,2-Dimethylcyclopentene).—Treatment of excess 2-methylcyclopentanone (Columbia) with the Wittig reagent from methyltriphenylphosphonium bromide (48 g., 0.13 mole) in the usual manner[15] led to a crude mixture of these hydrocarbons (3.8 g., b.p. 110–130°). Gas chromatographic analysis indicated two major olefinic components. These were collected (0.97 g., 7.5%) and the structures were confirmed spectrally; infrared (cm.$^{-1}$, *inter alia*): 3077 ($=CH_2$), 1653 ($C=C$), 1377 ($C—CH_3$), and 887 ($=CH_2$); n.m.r.[16] (A-60, $CDCl_3$ solvent, TMS internal standard, in δ, p.p.m.): 4.7 multiplet ($=CH_2$), complex absorption (0.7–2.5) with a sharp singlet at 1.28 ($=C\text{-}CH_3$), and a doublet centered at 0.93 ($>CH\text{-}CH_3$). Calculations based on the integration of the terminal methylene group at δ 4.7 indicated a composition of *ca.* 60% 2-methylmethylenecyclopentane and 40% 1,2-dimethylcyclopentene.

Ethylidenecyclopentane.—Although this compound was not definitely shown to be present, its easy preparation *via* the Wittig reaction is reported. This olefin was prepared similarly to those above from acetaldehyde and the Wittig reagent from cyclopentyltriphenylphosphonium bromide (m.p. 268–270°, lit.[17] m.p. 261–263°, 17.35 g., 0.042 mole). After the customary isolation[15] of the crude product (b.p. 105–120°), pure olefin was collected gas chromatographically (1.34 g., 33%, n^{10}_D 1.4534, lit.[18] n^{20}_D 1.4490); infrared (cm.$^{-1}$, *inter alia*): 3058 ($>C=CH$), 1686 ($>C=CH-$), 1379 ($C—CH_3$), 838, 803 ($>C=CH$); n.m.r.[16] (A-60, $CDCl_3$ solvent, TMS internal standard, in δ, p.p.m.): multiplet centered at 5.3 (1H, $>C=CH-$), broad peak centered at 2.2 (4H, allylic methylene hydrogens), and a complex multiplet (1.9–1.4, 7H).

Decomposition of 2-Methylcyclohexanone Tosylhydrazone.—Four decompositions were performed. The following is the general procedure followed. The tosylhydrazone was dissolved in N-methylpyrrolidone (10 ml./g. of tosylhydrazone) and freshly prepared sodium methoxide (1.12 moles/mole of tosylhydrazone) was added. The mixture was held at 180° until the evolution of nitrogen (collected over water) had ceased (85–95% of the theoretical nitrogen was obtained). Two runs, however, were held at 180° overnight even though the nitrogen evolution was always complete in less than 30 min. Water (10 ml.) was then added and the olefin products (54–64% yield) were collected by codistillation or by decantation with a micropipet. The products were then immediately gas chromatographed. The scale of the decompositions was 0.02 to 0.036 mole of tosylhydrazone.

Identification of Products.—Comparisons with the above hydrocarbons in gas chromatographic retention time and infrared spectra were made. No attempt to separate the product olefins was made because the peak separations were too small, but the infrared spectrum of the product contained all of the peaks found in the spectra of the individual olefins shown to be present by gas chromatography. *Toluene* was present in two of the four decomposition mixtures (g.c. and infrared) and the odor of *p*-thiocresol was evident in these toluene-containing mixtures as well. The olefins thus shown to be present were (with indicated per cent of the total product and g.c. retention time, t_r, in min.) 3-methylcyclohexene (27.2%, t_r 6), 1-methylcyclohexene (62.6%, t_r 7), 2-methylmethylenecyclopentane and 1,2-dimethylcyclopentene[19] (3.8%, t_r 4 and 5, respectively), norcarane (*ca.* 0.2%, t_r 8.5), and toluene (variable, t_r *ca.* 16). Ethylidenecyclopentane under these g.c. conditions had the retention time of 1-methylcyclohexene and its presence was not confirmable.

Decomposition of Cyclohexanone Tosylhydrazone.—This substance[20] (m.p. 150–151°, lit.[4] m.p. 155–156°) was decomposed as described above. Gas chromatography indicated four components, the first three showing the proper retention time for C_6 hydrocarbons. The major product was cyclohexene (*ca.* 94%, t_r 3 min., identity confirmed with standard). Benzene (<0.5%, t_r 8 min.) was also identified and *p*-thiocresol (odor) was in the reaction residue. A volatile product eluting prior to the cyclohexene (*ca.* 6%) resisted identification, although it was neither methylenecyclopentane nor bicyclo[3.1.0]hexane (see below). A slowly eluting substance (t_r *ca.* 15 min.) was also present in small amounts and it, too, was not identified.

Methylenecyclopentane.—Preparation was effected from paraformaldehyde and cyclopentyltriphenylphosphonium bromide *via* the Wittig reaction,[21] b.p. 74°; infrared (cm.$^{-1}$, *inter alia*): 3003, 1667, and 875. Its retention time did not match that of the volatile unknown from the cyclohexanone tosylhydrazone decomposition.

Bicyclo[3.1.0]hexane.—Treatment of cyclopentene with methylene iodide in the Simmons–Smith[22] process using a modified zinc–copper couple[23] yielded this hydrocarbon (n^{13}_D 1.4434, lit.[22] n^{25}_D 1.4373), purified by gas chromatography; infrared (cm.$^{-1}$, *inter alia*): 3049 (cyclopropyl CH_2), 2941, 2874, 1449, 1020 (cyclopropyl?), 952, 816, and 750. No olefinic absorption was observed.

Anal. Calcd. for C_6H_{10}: C, 87.73; H, H, 12.27. Found: C, 87.56; H, 12.36.

Its retention time also failed to match the unknown volatile substance mentioned above.

Control Experiments.—The methylcyclohexenes and norcarane were subjected to the exact reaction conditions employed for the tosylhydrazone decomposition (omitting only the tosylhydrazone itself). Gas chromatography indicated no change occurred in these substances. Likewise, the 2-methylmethylenecyclopentane and 1,2-dimethylcyclopentene were unchanged save for the isomerization previously mentioned.

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(11) Hydrogenated *o*-cresol. We thank Dr. H. Posvic of this department for a generous supply of this material.

(12) G. H. Coleman and H. F. Johnstone, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 183.

(13) W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(14) W. E. Parham and E. E. Schweitzer, *J. Org. Chem.*, **24**, 1733 (1959).

(15) For details on Wittig preparations, see, *e.g.*, G. Wittig and U. Schöllkopf, *Ber.*, **87**, 1318 (1954); U. Schöllkopf, *Angew. Chem.*, **71**, 260 (1959); S. Trippett, "Advances in Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1960, pp. 83–102.

(16) We thank Mr. Ronald Zigman and the Analytical Department of G. D. Searle and Co., Skokie, Ill, for the determinations of the n.m.r. spectra.

(17) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 67 (1957).

(18) J. R. van der Bij and E. C. Kooyman, *Rec. trav. chim.*, **71**, 837 (1952).

(19) As in their Wittig preparation, the exocyclic olefin predominated in the reaction product. The ratio of *exo* to *endo* product was, however, a function of the reaction time and indicated a thermal conversion of the *exo* to the *endo* isomer, as would be expected from the reported properties of these olefins when formed in ester pyrolysis; *cf.* D. H. Froemsdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).

(20) We thank Mr. Ronald Orlowski for this preparation.

(21) The method used was that of C. F. Hauser, T. W. Brooks, M. L. Miles, M. A. Raymond, and G. B. Butler, *J. Org. Chem.*, **28**, 372 (1963).

(22) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(23) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).