Reactive Intermediates in the Bicyclo[3.1.0]hexyl and Bicyclo[3.1.0]hexylidene Systems. II.[1] The Carbenoid Decomposition of the *p*-Toluenesulfonylhydrazones of 3-Bicyclo[3.1.0]hexanone and 2-Bicyclo[3.1.0]hexanone

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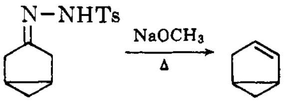
Sodium methoxide induced decomposition of the *p*-toluenesulfonylhydrazone of 3-bicyclo[3.1.0]hexanone produces bicyclo[3.1.0]hexene-2, while sodium methoxide induced decomposition of the *p*-toluenesulfonylhydrazone of 2-bicyclo[3.1.0]hexanone results in bicyclo[3.1.0]hexene-2, 1,3-cyclohexadiene, 1-hexen-5-yne, 1,2,5-hexatriene, and *trans*-1,3,5-hexatriene.

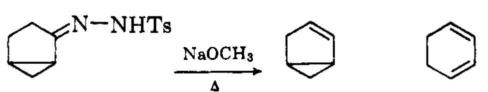
Our recent interest[1] and the interest of others[2] in the 2-bicyclo[3.1.0]hexyl and 3-bicyclo[3.1.0]hexyl carbonium ions aroused our curiosity concerning the analogous carbene intermediates (**8** and **9**). One might logically expect that, if transannular interactions occur during or subsequent to formation of a carbonium ion, an analogous carbene intermediate would exhibit similar interactions.

In order to make this comparison, the *p*-toluenesulfonylhydrazones of 3-bicyclo[3.1.0]hexanone and 2-bicyclo[3.1.0]hexanone were prepared from the corresponding ketones. Decomposition of the *p*-toluenesulfonylhydrazone of 3-bicyclo[3.1.0]hexanone (**1**) with sodium methoxide in bis(2-ethoxyethyl) ether at 160° produced a 91% yield of bicyclo[3.1.0]hexene-2 (**2**), which was identical with an authentic sample.[1] No other C_6H_8 hydrocarbons were present.



1 **2**

A sharp contrast to this reaction was provided when a carbenoid center was generated at C-2, rather than C-3. Decomposition of the *p*-toluenesulfonylhydrazone of 2-bicyclo[3.1.0]hexanone (**3**) with sodium methoxide in bis(2-ethoxyethyl) ether at 160° produced a 49.0% yield of C_6H_8 hydrocarbons: 18.6% **2**, 14.2% 1,3-cyclohexadiene (**4**), 13.1% 1-hexen-5-yne (**5**), 12.3% 1,2,5-hexatriene (**6**), and 41.8% *trans*-1,3,5-hexatriene (**7**).



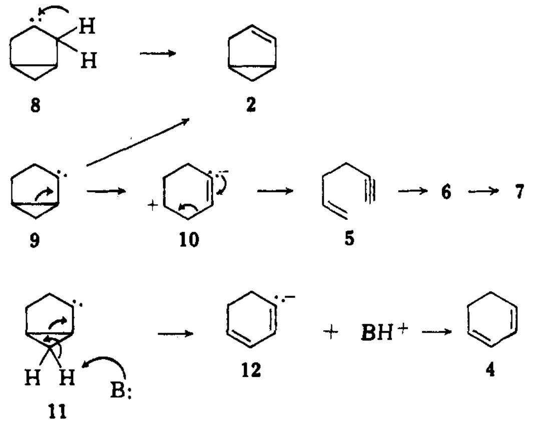
3 **2** **4**

$CH_2{=}CH{-}CH_2CH_2{-}C{\equiv}CH$
5

$CH_2{=}CH{-}CH_2{-}CH{=}C{=}CH_2$
6

$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$
7

Carbenoid decomposition of *p*-toluenesulfonylhydrazone **1** should generate bivalent intermediate **8**, which by 1,2-hydrogen migration produces bicyclo[3.1.0]hexene-2. This is not an unexpected route for a cyclic bivalent carbon intermediate, occurring as one of the major reaction pathways for cyclic bivalent carbon intermediates with ring sizes from C_4 to C_{10}.[3a,b] On the other hand the products generated by decomposition of **3**, *via* bivalent intermediate **9**, appear to be best explained as the result of three different mechanistic routes. Migration of hydrogen from C-3 to C-2 apparently occurs producing bicyclo[3.1.0]hexene-2. Secondly, the generation of the open-chain isomers may possibly involve the electronic shifts pictured in **9** and **10**. This type of ring-cleavage mechanism for cyclic carbene intermediates has been suggested recently.[3a,4]



Furthermore, it appears likely that allene **6** and triene **7** are formed by base-catalyzed isomerization of **5**. This possibility is supported by an additional experiment in which it was found that the base used in the *p*-toluenesulfonylhydrazone decompositions, sodium methoxide, is sufficiently strong enough to catalyze isomerization of **5** to **6** and **7** (Table I).

This result suggested that decomposition of *p*-toluenesulfonylhydrazone **3** in the absence of excess sodium methoxide would not result in isomerization of 1-hexen-5-yne to 1,2,5-hexatriene and 1,3,5-hexatriene. However, while decomposition of the sodium salt of **3**, in the absence of excess sodium methoxide, resulted in a significantly greater per cent of **5** and no triene **7**, allene **6**

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[1] Part I: P. K. Freeman, M. F. Grostic, and F. A. Raymond, *J. Org. Chem.*, **30**, 771 (1965).

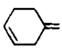
[2] (a) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961); **83**, 3244 (1961); (b) E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963); (c) T. Norin *Tetrahedron Letters*, **No. 1**, 37 (1964).

[3] (a) L. Friedman and H. Schechter, *J. Am. Chem. Soc.*, **82**, 1002 (1960); (b) *ibid.*, **83**, 3159 (1961); (c) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964).

[4] S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963).

TABLE I

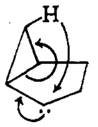
DECOMPOSITION OF *p*-TOLUENESULFONYLHYDRAZONES 1 AND 3 AND ISOMERIZATION OF 1-HEXEN-5-YNE

Reaction	% yield of C_6H_8 hydrocarbons	% compositions of C_6H_8 hydrocarbon **2**	**4**	**5**	**6**	**7**
1, $NaOCH_3$, 160°	91	100				
3, $NaOCH_3$, 160°	49.0	18.6	14.2	13.1	12.3	41.8
=N–NTs⁻Na⁺, 160°	36.0	16.7	1.2	62.8	19.3	0.0
5, $NaOCH_3$, 160°		0.0	0.0	84.9	6.9	8.2
5, =NNTs⁻Na⁺, 160°		0.0	0.0	94.2	5.8	0.0

was still formed (Table I). In addition, very little 1,3-cyclohexadiene was found. This suggests that the sodium salt of **3** is a sufficiently strong enough base to cause isomerization of **5** to **6**, but not **6** to **7**. This was borne out in an isomerization experiment in which **5** was treated with the sodium salt of the *p*-toluenesulfonylhydrazone of cyclohexanone in order to simulate the basic effect of the sodium salt of the *p*-toluenesulfonylhydrazone **3** (Table I).

The third mechanistic route which is suggested by these results is a base-promoted isomerization of the carbene intermediate from **3**, which is pictured in **11**. Such an isomerization might very well produce a 1,3-cyclohexadienyl carbanion as the anion portion of ion pair **12**. Proton transfer would then result in 1,3-cyclohexadiene.

Two factors may contribute to a decreased electrophilicity at the carbenoid carbon C-2, thus encouraging attack upon C-6 hydrogen. Some electron drain from the cyclopropane ring to C-2 would be anticipated by analogy to the enhanced stability of the 2-bicyclo[3.1.0]hexyl carbonium ion.[1,2b] Secondly, although represented as a two-step process, the formation of **12** may have some concerted character (carbon–nitrogen bond breaking at C-2 occurring in conjunction with C-6 hydrogen abstraction). The dependence of 1,3-cyclohexadiene formation upon sodium methoxide argues against an intramolecular *endo*-C-6 hydride shift as pictured in **13**. An argument can also be made against



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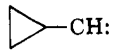
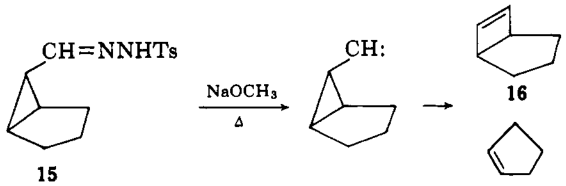
a random proton elimination from **9** (or a resonance hybrid of **9** and **10**) involving either protons at C-4 or C-6, since the product expected from loss of a proton at C-4, 1,4-cyclohexadiene, was found to be stable to the reaction conditions. Finally, the possibility that 1,3-cyclohexadiene is the result of base-catalyzed isomerization of bicyclo[3.1.0]hexene-2 may be ruled out, since the decomposition of *p*-toluenesulfonylhydrazone **1** in excess sodium methoxide results in bicyclo[3.1.0]hexene-2 as the sole C_6H_8 hydrocarbon.



14

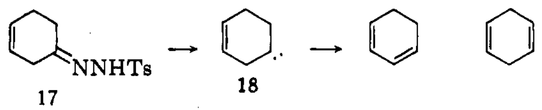
It is interesting to note that generation of bivalent intermediate **9** does not result in formation of a cyclobutene derivative as might be expected by strict analogy to the cyclobutene formed from cyclopropylcarbene (**14**).[3a] However, this appears to be the result of incorporation of the carbene site in a second ring, since decomposition of the *p*-toluenesulfonylhydrazone of bicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde (**15**) produces a 52% yield of hydrocarbons composed of *cis*-bicyclo-[3.2.0]heptene-6 (**16**) and cyclopentene. Presumably



15 **16**

acetylene is also formed in this reaction. The composition of the gases given off during the reaction was not investigated. Thus, if the carbenoid carbon of the cyclopropylcarbene system is outside the second ring, then the usual ring expansion and fragmentation reactions occur.[3a,c] The difference in behavior of the two intermediates may be simply that a bicyclo[2.2.0]hexene system would represent a considerably more strained reaction product than bicyclo[3.2.0]heptene-6.

Assuming that the transannular interaction pictured in **9** and **10** is correct for the bivalent intermediate derived from *p*-toluenesulfonylhydrazone **3**, it was of interest to compare a complementary system such as **18** (homoallylic) with **9** (cyclopropylcarbinyl), in order to see if transannular interactions would occur in the reverse direction. Sodium methoxide induced decomposition of the *p*-toluenesulfonylhydrazone of Δ^3-cyclohexenone (**17**) resulted in 1,3-cyclohexadiene and 1,4-



17 **18**

cyclohexadiene in a ratio of 3.6:1. Thus, no transannular interaction is obvious, the products apparently arising as a result of a 1,2-hydrogen migration. Recently Hanack and Keberle have been able to effect a transannular interaction with the analogous carbonium ion even though previous attempts had not been successful.[5]

Experimental[6]

2-Bicyclo[3.1.0]hexanone.—2-Bicyclo[3.1.0]hexanone was obtained by oxidation of *cis*-2-bicyclo[3.1.0]hexanol.[7] Of a variety of methods tried, the most suitable was that reported by Corey and Dawson for the oxidation of *cis*-3-bicyclo[3.1.0]-hexanol.[2b] An ether extraction of the bicarbonate and salt wash solution is necessary to obtain good recovery of product. 2-Bicyclo[3.1.0]hexanone was obtained in 80% yield, b.p. 76° (25 mm.).

Anal. Calcd. for C_6H_8O: C, 74.97; H, 8.35. Found: C, 75.02; H, 8.39.

2-Bicyclo[3.1.0]hexanone *p*-Toluenesulfonylhydrazone.—*p*-Toluenesulfonylhydrazine (1.86 g., 0.010 mole) was dissolved in 10 ml. of 60% aqueous methanol by warming to about 60°. To this warm solution was added 2-bicyclo[3.1.0]hexanone (0.96 g., 0.010 mole) while stirring. Agitation was continued for about 10 min., after which the mixture was cooled in the refrigerator for about 3 hr. to complete the product separation. The product

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[5] M. Hanack and W. Keberle, *Chem. Ber.*, **96**, 2937 (1963).

[6] Elemental analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Max-Planck Institute, Mülheim, Germany.

[7] W. G. Dauben and G. H. Berizin, *J. Am. Chem. Soc.*, **85**, 470 (1963).

was recrystallized from methanol (2.2 g., 83% yield), m.p. 176.8–178.0°.

Anal. Calcd. for $C_{13}H_{16}N_2O_2S$: C, 59.08; H, 6.06. Found: C, 59.00; H, 6.09.

Bicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde.—Raney nickel (prepared from 8 g. of Ni–Al alloy) was shaken at room temperature with a solution of bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxaldehyde[8] (6.5 g.) in 100 ml. of methanol under hydrogen in a low-pressure hydrogen apparatus. The hydrogenation was stopped at the first break in the rate of hydrogen uptake. The catalyst was removed by filtration and the methanol by distillation. The product fraction (6.1 g.) was collected at 63° (30 mm.). Further purification by v.p.c. provided material which was used to prepare the *p*-toluenesulfonylhydrazone of bicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde.

Elemental analysis was not possible since the aldehyde was subject to rapid autoxidation. The absorption at 6.21 μ in the infrared spectrum of the unsaturated aldehyde was no longer present in the spectrum of the product aldehyde.

Bicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde *p*-Toluenesulfonylhydrazone.—The *p*-toluenesulfonylhydrazone derivative of the aldehyde was prepared by the same method described for 2-bicyclo[3.1.0]hexanone *p*-toluenesulfonylhydrazone in 84% yield, m.p. 139.5–140.5°.

Anal. Calcd. for $C_{14}H_{18}N_2O_2S$: C, 60.43; H, 6.52. Found: C, 60.87; H, 6.57.

3-Bicyclo[3.1.0]hexanone *p*-Toluenesulfonylhydrazone.—The *p*-toluenesulfonylhydrazone derivative was prepared by the same method as that described for the 2-bicyclo[3.1.0]hexanone *p*-toluenesulfonyl hydrazone in 80% yield, m.p. 173.5–175.0°.

Anal. Calcd. for $C_{13}H_{16}N_2O_2S$: C, 59.08; H, 6.06. Found: C, 59.20; H, 6.15.

Δ^3-Cyclohexenone.—Δ^3-Cyclohexenone was prepared by a Birch reduction of anisole following the general procedure of Braude and Webb.[9] The product which was obtained was a mixture of cyclohexanone (6%), Δ^3-cyclohexenone (85%), and Δ^2-cyclohexenone (9%). Variation of the hydrolysis step failed to eliminate the conjugated isomer; v.p.c. was employed for further purification. Use of a 5-ft. 20% Carbowax 1000 on Chromosorb W column at 125° permitted separation of product which consisted of Δ^3-cyclohexenone (95%), cyclohexanone (4%), and Δ^2-cyclohexenone (1%). The respective retention volumes were 340, 290, and 540 ml. Further purification was not possible owing to thermal rearrangement on the column.

Δ^3-Cyclohexenone *p*-Toluenesulfonylhydrazone.—The *p*-toluenesulfonylhydrazone was prepared from Δ^3-cyclohexenone (95% pure, see above) using the same procedure as that described for the *p*-toluenesulfonylhydrazone of 2-bicyclo[3.1.0]hexanone. An analytical sample had m.p. 136–141°.

Anal. Calcd. for $C_{13}H_{16}N_2O_2S$: C, 59.06; H, 6.12. Found: C, 59.16; H, 6.14.

Decomposition of 2-Bicyclo[3.1.0]hexanone *p*-Toluenesulfonylhydrazone with Excess Sodium Methoxide.—The procedure was based on that reported by Friedman and Schechter.[3b] A three-necked flask was fitted with a nitrogen inlet, stirrer, and a 12-cm. Vigreux column heated to 70° with heating tape. The Vigreux column was connected to two receiving traps arranged in series and cooled with Dry Ice–isopropyl alcohol baths. Dry reagent grade sodium methoxide (4.4 g., 0.081 mole) was added to the nitrogen-purged flask along with 250 ml. of bis(2-ethoxyethyl) ether which previously had been distilled from lithium aluminum hydride. The stirred suspension was raised to a temperature of 100° by means of an oil bath. The *p*-toluenesulfonylhydrazone (6.5 g., 0.025 mole) was added in one portion and the temperature then was raised to 160°. The system was maintained at this temperature for about 3 hr., under nitrogen but with no nitrogen flow. The system was then swept briefly with nitrogen to remove all of the product. The material in the cold trap was washed twice with water. The C_6 hydrocarbon product (0.96 g., 49.0%) was recovered by decantation and was made up of 18.6% bicyclo[3.1.0]hexene-2, 14.2% 1,3-cyclohexadiene, 13.1% 1-hexen-5-yne, 12.3% 1,2,5-hexatriene, and 41.8% *trans*-1,3,5-hexatriene. Bicyclo[3.1.0]hexene-2 and 1,2,5-hexatriene were isolated by v.p.c. using a 25-ft. 20% Carbowax 1500 on Chromosorb W column at 75°. The respective retention volumes were 990 and 930 ml. The remaining isomers eluted together (retention volume, 1240 ml.) and were separated as a mixture. This mixture was resolved using a 20-ft. 20% DC-200 on Chromosorb W column at 75°. 1-Hexen-5-yne, *trans*-1,3,5-hexatriene, and 1,3-cyclohexadiene had retention volumes of 560, 750, and 925 ml., respectively. The isomers were characterized by their infrared and n.m.r. spectra. Each structure was ultimately confirmed by direct comparison of its infrared spectra with that of an authentic sample.

Decomposition of the Sodium Salt of 2-Bicyclo[3.1.0]hexanone *p*-Toluenesulfonylhydrazone in the Absence of Sodium Methoxide.—The sodium salt was prepared using the same general technique reported by Cristol and Harrington.[4] The dried sodium salt (3.7 g., 0.013 mole) was added to 50 ml. of dry bis(2-ethoxyethyl) ether in a three-necked flask which was equipped in the same manner as described for the excess sodium methoxide decomposition procedure. After heating for 4 hr. at 160° the hydrocarbon material (0.38 g., 36%) was recovered and found to consist of 16.7% bicyclo[3.1.0]hexene-2, 1.2% 1,3-cyclohexadiene, 62.8% 1-hexen-5-yne, and 19.3% 1,2,5-hexatriene.

Isomerization of 1-Hexene-5-yne. A. Sodium Methoxide Catalyst.—Sodium methoxide (30 mg., 5.5 mmoles) was added to 300 μl. of dry bis(2-ethoxyethyl) ether along with 15 μl. of 1-hexen-5-yne. The total was sealed in a glass ampoule and heated to 160° for 10 min. After cooling, the mixture was analyzed by v.p.c. Elution times showed the hydrocarbon product consisted of 84.9% 1-hexen-5-yne, 6.9% 1,2,5-hexatriene, and 8.2% *trans*-1,3,5-hexatriene.

B. Cyclohexanone *p*-Toluenesulfonylhydrazone Sodium Salt Catalyst.—Part A was repeated using the sodium salt of the *p*-toluenesulfonylhydrazone of cyclohexanone (100 mg., 4 mmoles) in place of sodium methoxide. The product consisted of 94.2% 1-hexen-5-yne and 5.8% 1,2,5-hexatriene.

Isomerization of 1,4-Cyclohexadiene.—Sodium methoxide (100 mg.) was added to 500 μl. of dry bis(2-ethoxyethyl) ether along with 50 μl. of 1,4-cyclohexadiene. The mixture was sealed in a glass ampoule and heated at 160° for 5 min. while gently shaking. After cooling, the mixture was analyzed by v.p.c. The results showed that only 3.2% of the 1,4-cyclohexadiene isomerized to 1,3-cyclohexadiene.

Decomposition of Bicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde *p*-Toluenesulfonylhydrazone with Excess Sodium Methoxide.—The method was the same as that described for the 2-bicyclo[3.1.0]hexanone *p*-toluenesulfonylhydrazone carbenoid decomposition. Decomposition of the *p*-toluenesulfonylhydrazone (8.0 g., 0.029 mole) resulted in the recovery of hydrocarbon product (1.27 g., 52%) which was made up of cyclopentene (28.5%) and *cis*-6-bicyclo[3.2.0]heptene (71.5%). The infrared and n.m.r. spectra of the bicycloheptene isomer were identical with those of an authentic sample of *cis*-6-bicyclo[3.2.0]heptene prepared according to the method of Dauben and Cargill.[10]

Decomposition of 3-Bicyclo[3.1.0]hexanone *p*-Toluenesulfonylhydrazone with Excess Sodium Methoxide.—The method was the same that described for the 2-isomer described above. The decomposition of the *p*-toluenesulfonylhydrazone (5.8 g., 0.022 mole) permitted recovery of hydrocarbon product (1.6 g., 91%) which consisted only of bicyclo[3.1.0]hexene-2.

Decomposition of Δ^3-Cyclohexenone *p*-Toluenesulfonylhydrazone.—The *p*-toluenesulfonylhydrazone of Δ^3-cyclohexenone (3.50 g., 0.013 mole, prepared from ketone contaminated with 4% cyclohexanone and 1% Δ^2-cyclohexenone) was decomposed by adding it as a slurry in 70 ml. of bis(2-ethoxyethyl) ether over a period of 45 min. to a stirred suspension of sodium methoxide (2.50 g., 0.046 mole) in 100 ml. of bis(2-ethoxyethyl) ether at 160°. The water-washed hydrocarbon product (0.19 g., 18%) consisted of 1,3-cyclohexadiene (65%), 1,4-cyclohexadiene (17.5%), and cyclohexene (17.5%). The cyclohexene is derived from the cyclohexanone impurity present in the original ketone.

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[8] J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Am. Chem. Soc.*, **85**, 582 (1963).

[9] E. A. Braude and A. A. Webb, *J. Chem. Soc.*, 3382 (1958).

[10] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).