

2-METHYL-7-NORBORNENYLIDENE--THE METHYL PROBE

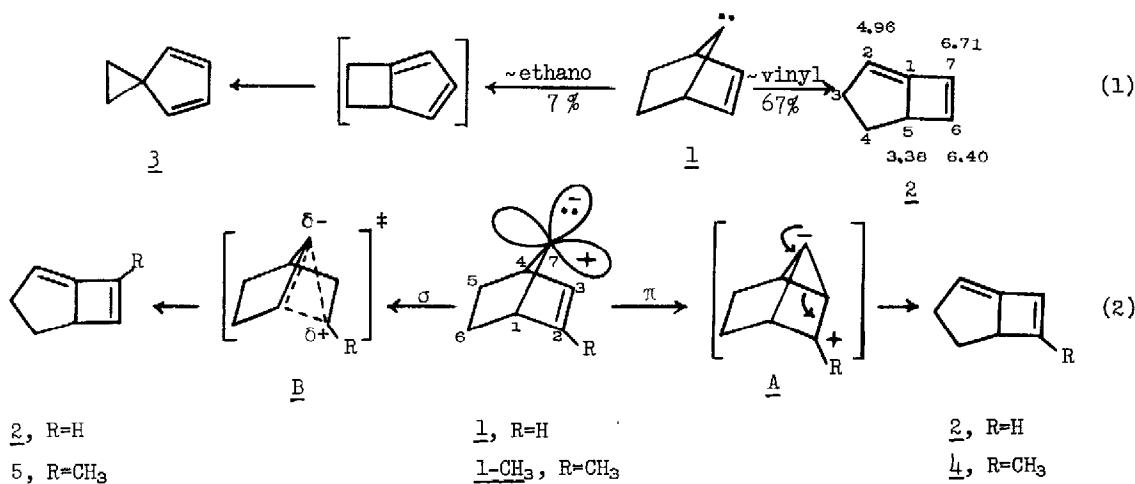
FOR HOMOALLYLIC DELOCALIZATION

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The prediction of homoallylic stabilization in 7-norbornenylidene, 1,¹ has stimulated interest in its chemistry and in that of other "foiled methylenes."² The intramolecular chemistry of 1 is characterized by competing rearrangements, with that of the carbene's vinyl group dominant, eq. (1).^{3c,d} To rationalize this, and parallel results obtained for related carbenes, a "π" mechanism has been offered,^{3c,d,g,h} which follows from the prediction¹ that the carbenic bridge of 1 should incline ~20° toward the double bond. The π-type rearrangement is initiated by interaction between the vacant carbenic p orbital and the olefinic π electrons. Inclusion of a zwitterionic intermediate, e.g., A in eq. (2), appears to have gained currency^{2b,c,g,h} for heuristic reasons, if not because of mechanistic necessity.³

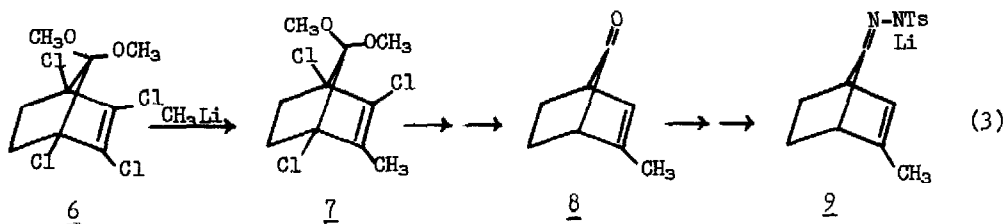


In an alternative formulation, the carbenic p orbital interacts with the C₁-C₂ σ electrons, affording a direct vinyl migration from C₁ to C₇ via transition state B, eq. (2). This mechanism demands serious consideration because 1,2-vinyl shifts are surprisingly successful competitors in carbenic rearrangements.^{4,5}

A new probe of the carbene-π interaction in 1, and of the importance of species A, can be obtained by studying 2-methyl-7-norbornenylidene, 1-CH₃, eq. (2). If the p-π interaction were dominant and best formulated as in eq. (2), then C₇ would add mainly at C₃, placing positive

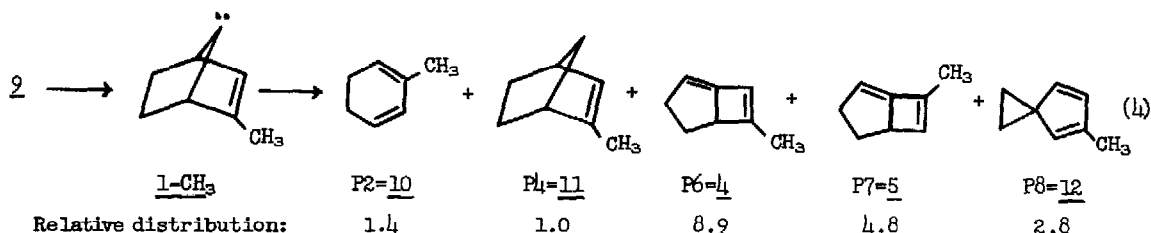
charge in A at C₂, where it would be stabilized by CH₃; completion of the rearrangement would give 4.⁶ However, if the rearrangement followed a σ mechanism, positive charge build-up on the migrating vinyl carbon would favor transition state B, eq. (2), in which this atom carries the donating methyl group; diene 5 would be preferentially formed.⁷ We now describe the rearrangement of 1-CH₃ to 4, 5, and other products, and comment on the significance of the results.

Tetrachloroketal 6⁸ was converted (90%) to the monomethyl substitution product 7^{9,10} with CH₃Li (2.0 equiv, 3 hrs. at 0-5°, 42 hrs. at 25°). Dechlorination of 7, followed by deketalization^{8,11} gave 2-methylnorbornene-7-one, 8,¹² in 46% overall yield from 7, eq. (3). Ketone 8



was converted to its *p*-toluenesulfonylhydrazone (1 equiv of TsNHNH₂ in refluxing CH₃OH, 2 hrs) and thence, without purification,¹³ to Li salt 9 (1.16 equiv. of C₄H₉Li in hexane).

Kugelrohr pyrolysis (177-180°, 0.5 mm-Hg) of dried 9 gave ~40% of crude product, which was trapped at 77°K and stored over Dry-Ice. Gc analysis (100' SF-96 Golay column, -15°) revealed 8 products, P1-P8, cf., eq. (4), which could be separated (15' x 0.25" 15% SF-96 on 60/70 Anakrom ABS, 48°) into 4 components: P1, P2+P3, P4+P5, and P6-P8.¹⁴ P2 appeared to be 2-methyl-



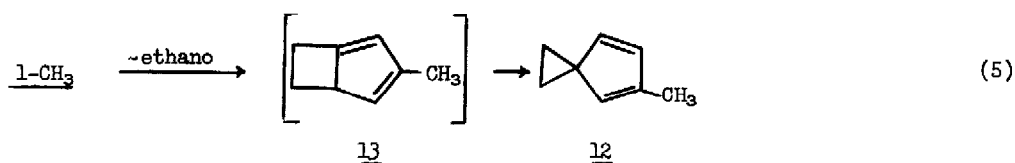
1,3-cyclohexadiene, 10, on the basis of its nmr spectrum [δ (CCl₄) 5.80, m, 2H; 5.48, m, 1H; 2.10, m, 4H; 1.73, m, 3H; fine splittings observable in all but the 5.48 (broad) multiplets], although correspondence to the reported spectrum was not exact.¹⁵ P₄ was identified as 2-methyl-2-norbornene, 11, by nmr and gc comparisons with an authentic sample.¹⁶

Ternary mixture P6-P8 consisted of C₈H₁₀ dienes. Anal. Calcd: C, 90.50; H, 9.50%; M⁺, 106.0782. Found: C, 90.30; H, 9.31%; M⁺, 106.0745. Catalytic reduction over 10% Pd/C gave saturated products with the uptake of 104% of the theoretical quantity of H₂. P8 was identified as 5-methylspiro[2.4]hepta-4,6-diene, 12, by gc and nmr comparisons with an authentic sample.¹⁷ Particularly revealing was the sharp singlet,¹⁷ δ (CS₂) 1.37, for the cyclopropyl protons of 12, readily discernable in the nmr spectrum of the P6-P8 mixture.

Identification of P6 and P7 as 6-methyl (4) and 7-methylbicyclo[3.2.0]hepta-1,6-diene (5) followed from the analytical data and from comparison of the P6-P8 nmr spectrum to that of 9 (see structure for δ values). Thus, narrow multiplets due to H₇ of 4 and H₆ of 5 appeared at δ (CS₂)

6.33 and 6.07, respectively,¹⁸ whereas multiplets due to H₂ of 4 and 5 absorbed at 4.93 and 4.75. The H_c protons were visible as broad overlapping multiplets peaking at 3.30, 3.16, and 3.07. Two finely split methyl resonances appeared at 1.94 and 1.77, superimposed on the residual absorptions of 4 and 5. Nmr integration showed diene 4 (H₇ at δ6.33) to exceed diene 5 (H₆ at δ6.07, corrected for concomitant vinyl absorption by 12) by ~1.4 times. More accurate 4/5 ratios were obtained by gc, and ranged from ~1.7-2.0 over several pyrolyses.¹⁹ These ratios were not significantly altered by repyrolysis of the product mixture from Li p-toluenesulfinate at 200°.

Products 10-12 are analogous to those formed from carbene 1.²⁰ Diene 10 presumably stems from cycloreversion with carbon loss²⁰ of 1-CH₃, whereas 11 could be an abstraction product. Spirodiene 12 is most reasonably formulated as the sigmatropic rearrangement product of 13,²¹ the proximate product of 1,7-ethano migration of 1-CH₃, eq. (5).



The preferred formation of 4 over 5 is modestly supportive of a π mechanism for the "vinyl" rearrangement of 1-CH₃, but the low selectivity indicates that charge-separated species such as A are neither intermediates nor representative of the transition state of a concerted rearrangement. By way of contrast, monomethylation of anti-7-norbornenyl-p-nitrobenzoate at C₂ is worth a kinetic factor of 13.3, relative to the parent compound, in hydrolysis via the 7-norbornenyl cation at 140°.²² Though inexact, this comparison emphasizes the minimal kinetic selectivity conferred on 1 by methylation, and reinforces both the prediction that C₇-p orbital- π interaction should be weaker in 1 than in the corresponding cation,¹ and the experimental demonstration that such interaction in 1 is not strong enough to control the stereochemistry of its intermolecular addition reactions.^{2a,23} There remains important evidence in favor of the control of 7-norbornenylidene chemistry by C₇- π interaction, *i.e.*, the low efficiency of both self-insertion^{2c,h,j} and intermolecular capture^{2b} of 1, but the present results illustrate the limits of this formulation and suggest care in its application.

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- (3) The π mechanism can be formulated in an alternative, concerted fashion, which avoids the formal charge-separation connoted by A.
- (4) The σ alternative was specifically noted in reference 2c.
- (5) F. G. Gassman and F. J. Williams, J. Amer. Chem. Soc., 94, 7733 (1972).
- (6) Less desirable would be addition of C_2 at C_3 , ultimately affording isomeric diene 5 via a less stabilized zwitterion.
- (7) The less desirable σ shift of the unmethylated vinyl carbon of 1-CH₃ would give diene 4. Relative to the build-up of positive charge on migrant groups in 1,2-carbenic rearrangements, see J. A. Landgrabe and A. G. Kirk, J. Org. Chem., 32, 3499 (1967); and P. B. Sargent and H. Shechter, Tetrahedron Lett., 3957 (1964).
- (8) F. G. Gassman and L. Marshall, Org. Syn., 48, 68 (1968).
- (9) δ , 108-112°/2 mm-Hg; M^+ at m/e 270, ($M^+ - Cl$) at m/e 235 (100%); $\delta(CCl_4)$: 3.61, s, 3H; 3.53, s, 2H; 2.46-2.36, s, 4H; 2.27, s, 2H.
- (10) The CH_3 - CH_2 exchange reaction was modeled after F. G. Gassman and T. J. Atkins, Tetrahedron Lett., 3035 (1975); F. G. Gassman, J. P. Andrews, Jr., and D. S. Patton, Chem. Commun., 437 (1969).
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- (12) The nmr spectrum agreed with that described by R. L. Cargill, A. B. Sears, J. Boehm, and M. R. Willcott, J. Amer. Chem. Soc., 95, 4346 (1973); except that our vinyl and bridgehead proton resonances [$\delta(CCl_4)$ 5.15, 2.75, and 2.56] appeared at slightly lower field. The CH_3 doublet, δ 1.90, J=2 Hz., was prominent.
- (13) The crude product, mp 108-117°, was not stable to recrystallization.
- (14) Non-carbenic "products", P1, P3, and P5 were identified as n-butanol, toluene, and n-octane, respectively, by nmr and gc comparisons with authentic materials.
- (15) Cargill, et. al.,¹² report the low field signal at δ 6.68. However, actual comparison of our spectrum with that of Cargill, et. al., has established their identity, and made definite the assignment of structure 10 to P2. We thank Professor Cargill for his aid in this assignment.
- (16) Cf., H. C. Brown and K-T. Liu, J. Amer. Chem. Soc., 97, 600 (1975).
- (17) R. A. Clark, W. J. Hayles, and D. S. Youngs, ibid., 97, 1966 (1975). The 4-methyl isomer of 12 was not present in our product mixture.
- (18) In each case, shielding by the cis-CH₃ shifts the resonance -0.3-0.4 ppm upfield, relative to the analogous protons of 2.
- (19) Photolysis of dry 9 (450 W high-pressure Hanovia lamp, Pyrex filter, 25°, 10 hrs, reduced pressure) afforded a product mixture in which 4/5 was -1.9.
- (20) Cf., P. B. Shevlin and A. P. Wolf, Tetrahedron Lett., 3987 (1970).
- (21) Attempts to prepare the parent homoannular diene [bracketed in eq. (1)] have led only to 3: N. K. Hamer and M. E. Stubbs, ibid., 3531 (1972); M. Oda and R. Breslow, ibid., 2537 (1973).
- (22) P. G. Gassman and D. S. Patton, J. Amer. Chem. Soc., 91, 2160 (1969).
- (23) It is also noteworthy that methylation of 1 at C_2 does not enhance vinyl as opposed to ethano migration: for 1, 2/3 ~ 9.6,^{20,24} whereas for 1-CH₃, (4+5)/12 ~4.9. To the extent that the π mechanism for rearrangement resembles the addition of a carbene to a π bond, one might have expected methylation of the vinyl group to enhance its rearrangement relative to that of the ethano group: cf., R. A. Moss in "Carbenes," Vol. I, M. Jones, Jr., and R. A. Moss, Ed., Wiley-Interscience, New York, 1973, pp. 153ff.
- (24) Murahashi, et. al.,^{2d} give this ratio as 5.8.