apparent position of the 0–0 peak by 1–2 nm to the red, so the true 0–0 position for the trans isomer is somewhat uncertain, and perhaps somewhat shorter than 632.5 nm.[12] The structure of the second series between 592.5 and 560.0 nm is not a reasonable looking progression for a single mode: either the apparent 1200-cm^{-1} mode seen in the photoelectron spectrum is in fact a superposition of nearly degenerate modes, or there is some other more subtle effect leading to the odd looking intensity pattern of these peaks.

Based on the normal-mode analysis of the neutral molecule,[13] the observed ion vibrational progressions are reasonable: only A_g vibrations can be excited in this transition, and since it is a II-system excitation, only carbon-framework motions are expected to be significantly excited. The ion progression at 350 cm^{-1} corresponds to one of the two framework bending modes ν_{12} (453 cm^{-1} in the neutral) and ν_{13} (347 cm^{-1}), while the progression at ~1200 cm^{-1} is associated with the framework stretching modes ν_5–ν_{10} distributed from 1187 to 1623 cm^{-1} in the neutral. A Huckel-MO analysis[14] of the II states involved in this optical transition yields additional qualitative insight: The principal bond length changes on excitation should be a lengthening of C_2–C_3 (and C_4–C_5) and a shortening of C_3–C_4. Two modes[13] closely correspond to this motion: ν_5 (1623 cm^{-1}) and ν_9 (1238 cm^{-1}). It is thus reasonable to suspect, as above, the simultaneous excitation of two framework-stretching vibrations in the ion. No similar elementary considerations seem appropriate to the bending motion, and we are unable to choose between the two likely modes.

The photodissociation rate is linear in light intensity; it appears that the heat of dissociation to $C_6H_7^+ + H$ is less than the 2.0 eV corresponding to the 0–0 excitation, and that there is no reason to suspect a two-photon process.[15]

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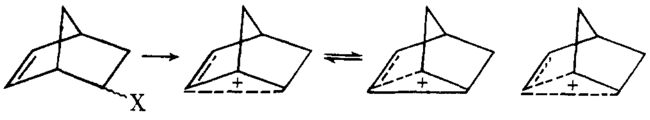
Reactions of 5-Norbornene-2-diazonium Ions and Nortricyclene-3-diazonium Ions

Sir:

The nature of the carbocations intervening in the acetolysis of 5-norbornen-2-yl brosylates (**1**-OBs) has not been established satisfactorily.[1] Both unsymmetrical (**2a**) and symmetrical delocalization (**2c**) have been postulated, based on contradicting reports on the scrambling of labels over positions 2,3 and 1,7.[2-6] Readdition of acetic acid to norbornadiene as a source of scrambling has been maintained by one group[6] but rejected by others.[5]



1 **2a** **2b** **2c**

We report here on the decomposition of 5-norbornene-2-diazonium ions (**4**) and nortricyclene-3-diazonium ions (**8**) in aqueous sodium hydroxide. Reactants and reaction conditions are such that carbocations will be generated and trapped irreversibly. The nature of the intermediates was investigated with the aid of optically active precursors as well as by deuterium labels.

Photolysis of tosylhydrazone sodium salts generates diazo compounds[7] which are protonated by ROH to give diazonium ions and products derived therefrom.[8] 5-Norbornen-2-one tosylhydrazone (**3**) and nortricyclanone tosylhydrazone (**7**) afforded product distributions depending but slightly on the concentration of base (Scheme I, Table I). Optically active **3**[9] produced **5** with 40–50% retention of configuration (50–60% racemization) (Table II). Photolysis of **3** in D_2O-DONa introduced deuterium at C-2 of **4**. Mass spectrometric analysis[5,6] of [$^2H_1$]-**5** indicated 27–28% rearrangement of D (i.e., 54–56% equilibration), in agreement with the polarimetric data.

These observations require an asymmetric precursor from which 40–50% of **5** is derived. If the asymmetric precursor was the homoallylic ion **2a**, it should produce **6** with predominant

Scheme I

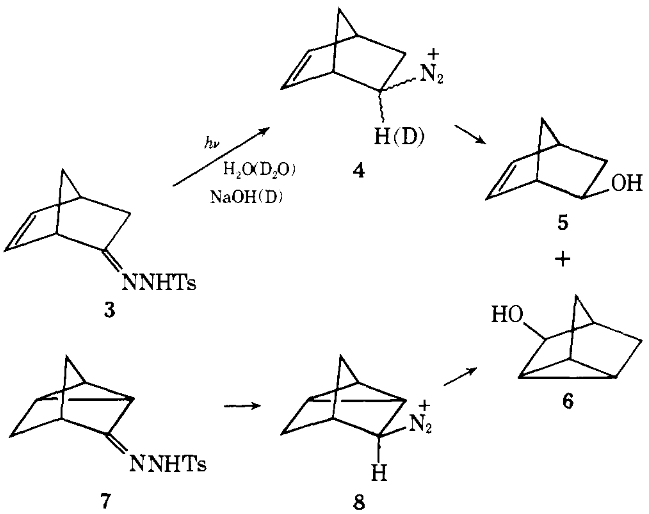


Table I. Product Distributions **5**/**6** Obtained from **4** and **8**

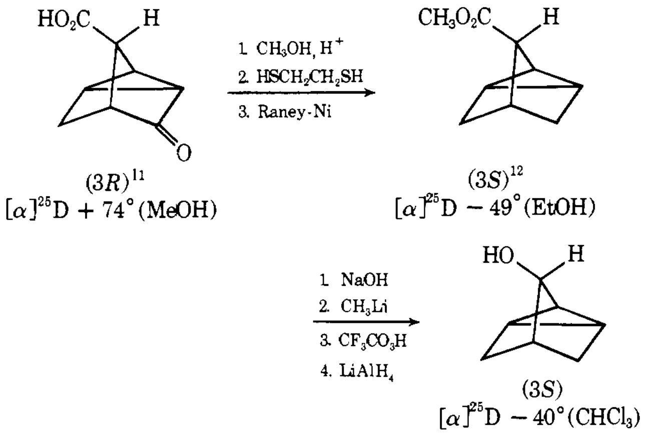
Precursor	3	7	Scheme III
0.1 N NaOH	9.9/90.1	3.9/96.1	4.0/96.0
0.2 N NaOH	10.3/89.7	3.9/96.1	3.6/96.4
0.5 N NaOH	10.8/89.2	4.4/95.6	
1.0 N NaOH	11.4/88.6	4.5/95.5	

Table II. Stereochemistry of the (1*S*)-**3** $\rightarrow$ **5** + **6** Transformation

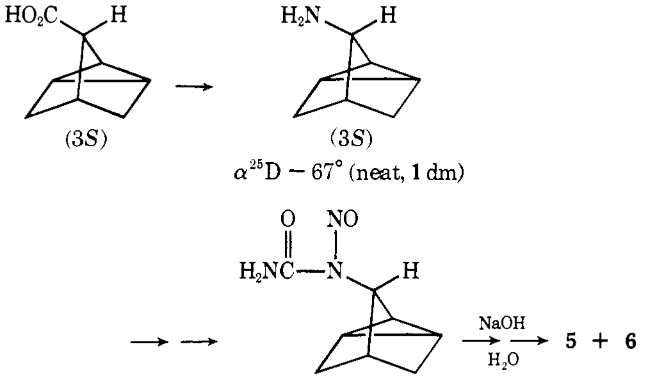
	5		**6**	
Solvent	% o.p.	% D at C-1[a]	Config	% o.p.
1 N NaOH H_2O-DME (3:2)	41.4	27.6	*S*	2.1
0.4 N NaOH H_2O-CH_3OH (3:2)	49.6	27.0	*R*	3.2
0.3 N NaOH	46.2		*R*	1.8

[a] Photolysis of **3** in D_2O-DONa; estimated by mass spectrometry (*m/e* 66, 67) of the fragment containing C-1,4,5,6,7.

Scheme II



Scheme III



"exo" attack, i.e., (*S*)-**6** from (1*S*)-**3**. We established the absolute configuration and maximum rotation of **6** as shown in Scheme II. The optical purity of **6** obtained from (1*S*)-**3** was low[13] (Table II). Moreover, the configuration of **6** varied with the solvent; e.g., in H_2O-DME or in H_2O-CH_3OH it was opposite to that observed in water.[15] Consequently, we feel that the formation of **6** is *not* controlled by stereoelectronic factors such as homoallylic delocalization. We attribute the residual optical activity of **6** to asymmetric solvation, and we take the stereochemical results as evidence against **2a**. The optically active **5** may originate directly from the diazonium ion, particularly from *endo*-**4**. Support for this view comes from the reactions of **8** and **13** (see below).

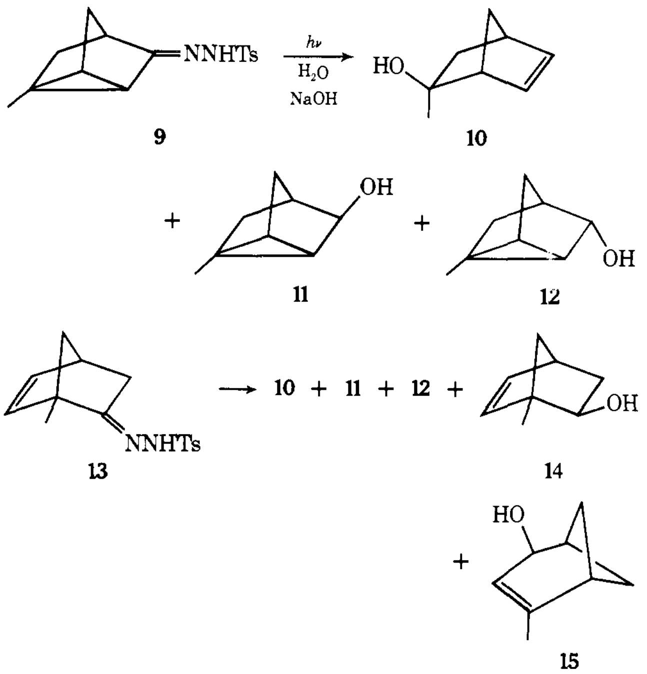
It is seen from Tables I and II that the amounts of racemic (equilibrated) **5** obtained from **3** (6–6.5%) and **7** (4–4.5%) differ slightly. In order to estimate the fraction of nortricyclene-3-diazonium ions (**8**) which avoid formation of a "free" nortricyclyl cation, we generated (3*S*)-**8** from a nitrosoamide precursor[16,17] (Scheme III). **6** was obtained with 24% inversion of configuration. We may safely assume that the fraction of **8** reacting with inversion does not produce **5** (the sequence **8** $\rightarrow$ **2a** $\rightarrow$ **5** + **6** would afford **6** with retention). A single intermediate, the 3-nortricyclyl cation, then suffices to account for the formation of **6** and of racemic (equilibrated) **5** from the diazonium ions **4** and **8**. By NMR spectroscopy in superacids the 3-nortricyclyl cation has been characterized as an essentially classical carbenium ion with slight charge delocalization into the cyclopropane ring.[18] The ratio of nucleophilic attack at C-3 and C-1 (95:5) conforms to this model.

Table III. Product Distributions (%) from the Photolysis of **9** and **13** in 0.2 N NaOH

	10	**11**	**12**	**14**	**15**
9	73.8	24.5	1.7	—	—
13[a]	64.6	17.9	1.0	7.6	7.7
	(77.4)	(21.4)	(1.2)		

[a] 1.2% of an unidentified product. Values in parentheses refer to **10** + **11** + **12** = 100, for comparison with **9**.

Scheme IV



Charge delocalization in the nortricyclyl cation becomes asymmetric and more intense upon introduction of a methyl group at C-1. The product distribution obtained from 1-methyl-3-nortricyclanone tosylhydrazone (**9**)[19] (Table III) reveals increased nucleophilic attack at the substituted site, giving 2-methyl-5-norbornen-2-*exo*-ol (**10**), and a high ratio of exo:endo attack at C-3 (**11**:**12** = 14.5). No 1-methyl-5-norbornen-2-*exo*-ol (**14**) was found among the products from **9** whereas 7.6% of **14** arose from 1-methyl-5-norbornen-2-one tosylhydrazone (**13**).[21] In addition, **13** afforded 4-methylbicyclo[3.1.1]hept-3-en-2-ol (**15**) by a C(1-7) migration.[23] It is tempting to attribute the formation of **14** and **15** to synchronous substitution and rearrangement of the endo-diazonium ion. The remaining products, **10–12**, were formed in essentially the same proportions from **9** and **13**.

In summary, a rather simple mechanistic picture emerges from our studies on 5-norbornene-2-diazonium ions. A small portion (ca. 5%) of the products comes from an asymmetric, *localized* precursor which may well be the endo-diazonium ion. The majority of the products arise from the symmetrical, slightly delocalized nortricyclyl cation, in agreement with the solvolytic results of Cristol et al.[5] There is no need for invoking asymmetric, *delocalized* intermediates (**2a**, **b**) and their interconversion. The variations induced by a 1-CH_3 group are in accord with expectation.

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(13) In addition to **5** and **6**, the photolysis of **3** affords minor amounts of unsaturated isomers, e.g., bicyclo[3.1.1]hept-3-en-2-ol,[14] which are not readily separated from **6**. Therefore, **6** was purified by ozonolysis, followed by GLC and sublimation, before rotations were taken at 365 nm; maximum $[\alpha]^{25}{}_{365}$ 116.6° (*c* 21.4, $CHCl_3$).

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(15) Photolysis of (1*S*)-**3** in H_2O–CH_3OH (3:2) afforded 3-methoxynortricyclene (40%) and 2-methoxy-5-norbornene (7%) in addition to **5** (10%) and **6** (39%). The configuration of 3-methoxynortricyclene was (*S*), opposite to that of **6** obtained in the same run. (*S*)-3-Methoxynortricyclene, prepared by methylation of (*S*)-**6**, had $[\alpha]^{25}{}_{\mathrm{D}}$ 1.48° (neat, *l* = 1 dm).

(16) Some leading references concerning the basic hydrolysis of nitrosoamides are given below: (a) R. A. Moss, *J. Org. Chem.*, **31**, 1082 (1966); (b) W. Kirmse and G. Wächtershäuser, *Justus Liebigs Ann. Chem.*, **707**, 44 (1967); (c) R. A. Moss, D. W. Reger, and E. M. Emery, *J. Am. Chem. Soc.*, **92**, 1366 (1970); (d) S. M. Hecht and J. W. Kozarich, *J. Org. Chem.*, **38**, 1821 (1973).

(17) No incorporation of deuterium into **6** was observed when **8** was treated with 0.1 N NaOD in D_2O. This excludes intervention of 3-diazonortricyclene as a possible source of racemization.

(18) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **95**, 3792 (1973); **97**, 1920 (1975).

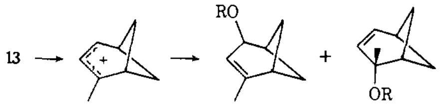
(19) Mp 134–135 °C, obtained from 1-methyl-3-nortricyclanone[20] and tosylhydrazine in methanol-HCl.

(20) J. Paasivirta, *Ann. Acad. Sci. Fenn., Ser. A2*, **116**, 8 (1962).

(21) Mp 140–141 °C, obtained from 1-methyl-5-norbornen-2-one[22] and tosylhydrazine in methanol-HCl.

(22) H. L. Goering and C. S. Chang, *J. Org. Chem.*, **40**, 2565 (1975).

(23) The C(1,7) shift sould lead to alcohols **15** and **15′** (R = H) by way of the allylic cation **16**. **15′** (R = H) was not observed and may have rearranged during GLC. However, photolysis of **13** in CH_3OH–CH_3ONa afforded both **15** and **15′** (R = CH_3) in 4–5% yield.



16 15 15′

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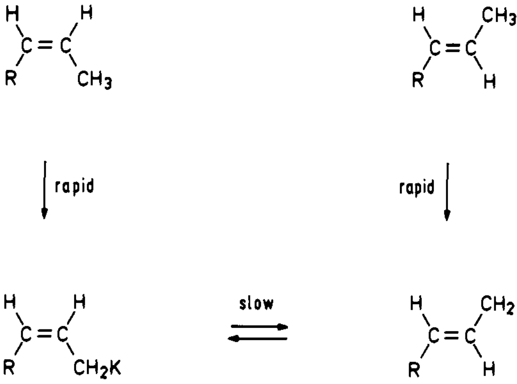
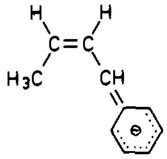
2-Alkenyl Anions and Their Surprising Endo Preference. Facile and Extreme Stereocontrol over Carbon–Carbon Linking Reactions with Organometallics of the Allyl Type

Sir:

Allyl type organometallic compounds merit special attention on account of their potential in the field of organic synthesis.[1] Of particular interest is their stereoselective and regioselective behavior. Organometallic compounds of the allyl type, previously hardly known,[2] became easily available through alkene metalation with butyllithium in the presence of potassium *tert*-butoxide[3-5] or with trimethylsilylmethylpotassium.[6,7] Spectral[8,9] and chemical[5,10] evidence are in good agreement with a "contact pair" ("contact species") structure[11] and rule out the presence of (solvent-separated) ion pairs or even free carbanions in substantial concentrations. *Z*-Isomers ((*Z*)-**1**) may be converted into the corresponding *E*-isomers ((*E*)-**1**) and vice versa, as was previously established for Grignard[12] and lithium[13] compounds. New and astonishing, however, is the observation[1,4,5,10] that allylpotassium derivatives undergo such configurational changes only very slowly,[14] half-lives of pure isomers falling in the range of hours at normal temperatures in the case of simple hydrocarbon derivatives.



Most surprising was the finding that butenyl-,[5] hexenyl-,[5] 2-methyl-butenyl-,[15] and other alkenylpotassium compounds[1,5,16] drastically favor the *Z*-configuration. Although base-catalyzed alkene isomerizations[17] have been known to be highly cis selective, this does not necessarily imply an exceptional thermodynamic stability of the intermediary endo-(cis)-alkenyl carbanion, since these isomerizations occur under kinetic control and thus may merely reflect differences in the hydrogen transfer mechanisms for cis- and trans-alkene formation.[18,19] Furthermore the *Z* preference of alkenylpotassium compounds may be, but do not have to be, related to the strong tendency of 1-phenylbutenylpotassium[20] to accommodate the terminal methyl group in an endo(cis) position. In liquid ammonia,[20] the phenylbutenylpotassium probably forms a solvent-separated ion pair and it benefits from extensive charge delocalization. Therefore, fundamental dissimilarities with alkenylmetal compounds should still be envisaged. For instance, the electron excess of the 1-phenylbutenyl anion could mainly reside in the aromatic ring and thus make the carbanion (limiting structure **2**) resemble the *Z*-crotonitrile (**3**) which is known to be more stable than the corresponding *E*-isomer.[21] In order to gain deeper insight into the stereochemical behavior of alkenylmetal compounds, we investigated the effects of the organic part, the metal, and the solvent on the equilibrium position.



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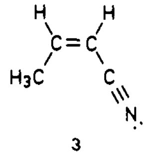

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In general, the *Z*/*E* equilibrium for each system was established by the metalation of each of the pure olefin isomers. The resulting reaction mixture was stirred until the equilibrium point was reached (at least 24 h in tetrahydrofuran[22]), oxirane was then added and the derived isomeric alcohols were analyzed by gas phase chromatography.[23] The *Z*/*E* ratios of the product mixtures should be equal to the *Z*/*E* ratios of the organometallic precursors provided that product yields are high and α/γ-ratios (oxirane attack at the vinylogous vs. the terminal position of the allylic system) observed for both confi-