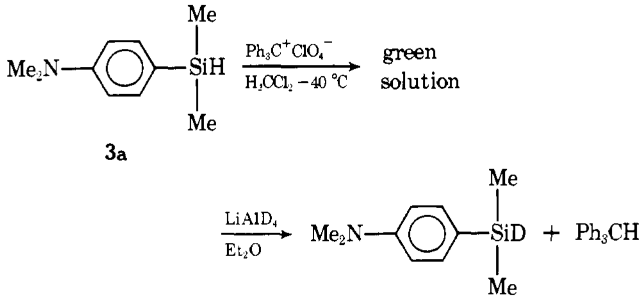

3a

3b

In summary, while it is still possible that silanes **1a** and **2a** do form the silylenium ions, all of the evidence thus far presented can be reproduced with systems for which there is no particular reason to presume silylenium ion involvement.

Note Added in Proof. Well after this work was submitted for publication, we learned that Professors J. Lambert and K. Mislow had each independently arrived at similar conclusions.

Acknowledgment. Financial support was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) Although the cation R_3Si^+ is referred to as a silicenium ion in ref 3 and 4, if a protonated carbene is to be called a carbenium ion a protonated silylene (R_2Si:) should be named a silylenium ion.
(2) See R. J. P. Corriu and M. Henner, *J. Organomet. Chem.*, **74**, 1 (1974), for a review of previous attempts.
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(9) V. Wannagat and W. Liehr, *Angew. Chem.*, **69**, 783 (1957).
(10) The synthesis and chemistry of this compound will be reported separately.
(11) C. G. Swain and Y. Okamoto, *J. Am. Chem. Soc.*, **92**, 3409 (1970), and references therein.
(12) The failure to observe the amine radical $Et_3N^{\cdot +}$ could be due to band-broadening due to rapid electron exchange with other molecules of Et_3N.[13]
(13) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, New York, N.Y., 1969, p 312.
(14) M. Rosenblum, "Chemistry of Iron Group Metallocenes", Wiley, New York, N.Y., 1965.
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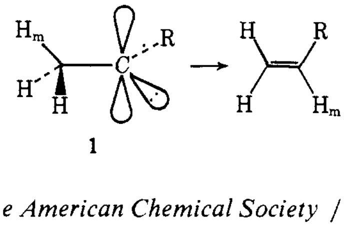
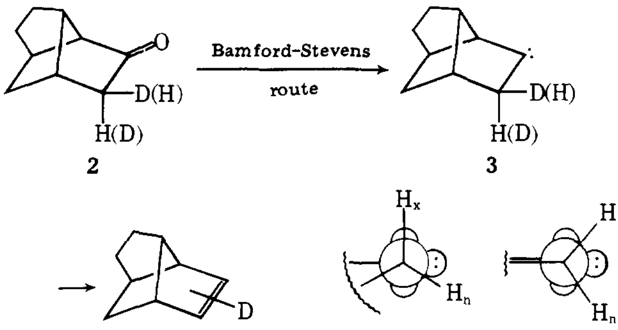
1,2-Hydrogen Shifts in Carbenes. The Question of Stereoelectronic Control of Migration

Sir:

In recent years there have been a number of theoretical investigations concerning stereoelectronic control in the 1,2-hydrogen shift to a carbene center to give the corresponding olefin.[1] The prediction arising from these calculations is that the group which migrates is that which is aligned with the empty orbital as in **1** (H_m migrates). Until recently, this prediction had not been tested experimentally with a relatively rigid, stereochemically well-defined system.[2] The carbene **3** derived from the Bamford-Stevens reactions on the *exo*(x)- and *endo*(n)-4-deuteriobrexan-5-one (**2**) recently described by Nickon and his co-workers[3] appeared to be such a system. It was stated on the basis of examination of models, that the ethylene bridging unit twists the molecules **2** and **3** such that the exo-hydrogen (H_x) tends to align with the empty p-type orbital of the carbene as in **5**, instead of being symmetrically disposed, which is the case in normal [2.2.1] systems (e.g., **6**).

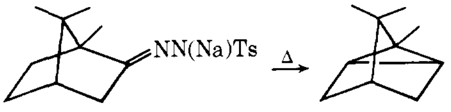


1



2 **3** **4** **5** **6**

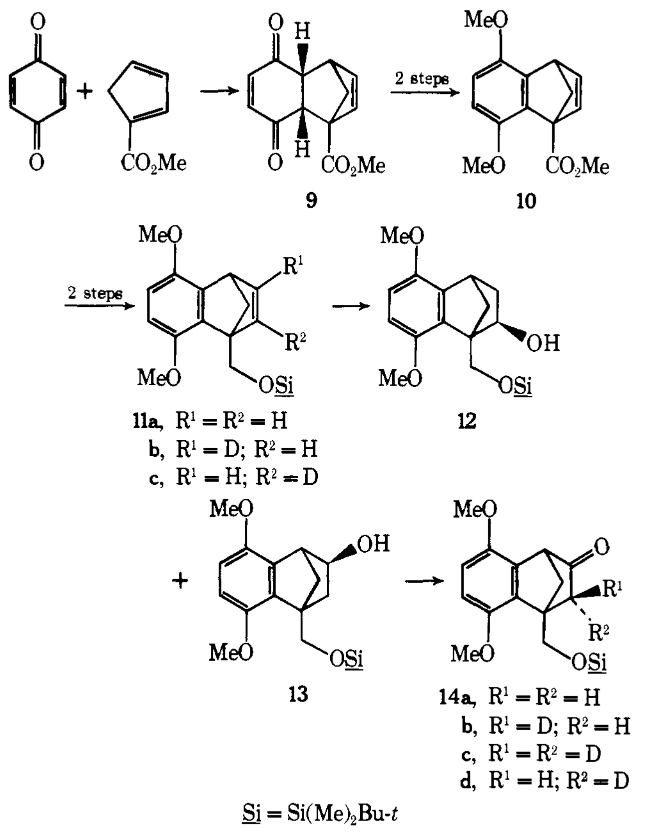
Nickon found the migratory ratio H_x/H_n in **3** to be 138, on the basis of ^{1}H NMR analysis of the position of the deuterium in **4**. This ratio presumably reflected stereoelectronic migration control in accord with theoretical predictions.[1] In order to conclude this, it is necessary to assume that H_x does not have some "natural" propensity to migrate relative to H_n, which is peculiar to the [2.2.1] system, as is well-known in carbonium ion analogues.[4] There is, to our knowledge, no information concerning carbenic migratory ratios H_x/H_n in unbiased [2.2.1] systems (e.g., **6**), the problem being that intramolecular cyclization (e.g., **7** → **8**[5]) is apparently more facile than H migration to give the olefin. Thus it was necessary to synthesize a [2.2.1] carbene precursor in which the intramolecular cyclization was precluded in order to study the H_x/H_n migratory aptitudes.



7 **8**

The synthesis of appropriately labeled carbene precursors **14** is outlined below. The Diels-Alder adduct **9**[6] obtained from benzoquinone and carbomethoxycyclopentadiene was aromatized (acid-catalyzed) and alkylated (base, dimethyl sulfate) to give the substituted benzonorbornadiene **10**. This was reduced (LAH) and protected with the *tert*-butyldimethylsilyl group[7] to give **11a**, which under hydroboration conditions (disiamylborane, −77°) gave a mixture of regioisomers **13** and **12** in a ratio of 10:1.[8] The alcohols **12** and **13** were readily separated by chromatography, and **13** was oxidized to ketone **14a** (Oppenauer, benzoquinone, $Al(OBu\text{-}t)_3$[9]). Treatment of **14a** with KOBu-*t* (1 equiv) in dioxane-D_2O at 60° for 1.25 h gave **14b**.[10a,11] Similarly, treatment of **14a** under the above reaction conditions for 60 h gave **14c**,[10b] which gave **14d**[10c] upon treatment with KOBu-*t* (1 equiv) in dioxane-H_2O at 60° for 3 h.

The tosylhydrazones of the ketones **14b** and **14d** were obtained under neutral conditions ($TsNHNH_2$ in MeOH at 60° for 1.3 h) and these were converted to the lithium salts (*n*-BuLi in THF at −77°), which were obtained free of solvent by *evaporation and pumping on the residue at 60° (2 μ)*. These salts were then decomposed in cyclohexane at 190° (0.7 h).[12] The regioisomeric mixture of olefins **11b** and **11c** was isolated by chromatography in about 30% yields.[13] ^{1}H NMR analysis[14]



9 10

11a, $R^1 = R^2 = H$
b, $R^1 = D; R^2 = H$
c, $R^1 = H; R^2 = D$

12

13

14a, $R^1 = R^2 = H$
b, $R^1 = D; R^2 = H$
c, $R^1 = R^2 = D$
d, $R^1 = H; R^2 = D$

$\underline{Si} = Si(Me)_2Bu\text{-}t$

of these olefins derived from **14b** and **14d** gave the following migratory ratios: $D_x/H_n = 7.7$; $H_x/D_n = 23$. These results lead to a deuterium isotope effect of 1.7 and thus to the migratory ratio $H_x/H_n = 13$. At 190°, this ratio corresponds to a substantial activation energy difference, $E_a{}^n - E_a{}^x \simeq 2.4$ kcal/mol, assuming similar preexponential factors for exo and endo migration.

The difference in H^x/H^n migratory ratios between our system and that of Nickon and co-workers (13 cf. 140) might be rationalized a number of ways,[4b,16] but no unambiguous explanation is possible, based on present data. We have demonstrated, however, that carbene migratory preferences in a bicyclo[2.2.1] system (albeit in a benzo analogue[17]) may be unique and subject to various interpretations, as they are in the corresponding carbonium ion analogues. We are currently investigating a system which we hope will provide an unambiguous demonstration of the theoretical predictions discussed above.

Acknowledgment. Grateful acknowledgment is made to the Robert A. Welch Foundation (F-573) and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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(8) At room temperature the ratio **13**/**12** was ca. 2/1.

(9) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960).

(10) (a) By MS analysis, **14b** had $d_0:d_1:d_2 = 0:93:7$. By ^{1}H NMR, no exo-H was evident <2%. (b) By MS analysis, **14c** had $d_0:d_1:d_2 = <1:<1:>99$. (c) By MS analysis, **14d** had $d_0:d_1:d_2 = 8:81:11$. By ^{1}H NMR no endo-H was evident in the d_1 material (<3–4%).

(11) T. T. Tidwell, *J. Am. Chem. Soc.*, **92**, 1448 (1970).

(12) Although the lithium salts of the tosylhydrazones were insoluble in cyclohexane at room temperature, at elevated temperatures (>120°) the reaction mixture was homogeneous until decomposition set in, depositing TsLi.

(13) By MS analysis, it was found that the conversion of **14b** or **14d** → **11** resulted in ≤3% H–D exchange.

(14) These analyses were corrected for the amount of d_0 (**11a**) material present. The results presented are averages of duplicate runs which gave essentially identical results.

(15) Assuming the same kinetic isotope effect (kie) for both exo and endo migration, the kie is then obtained from the equations $y/x = 7.7$ and $yx = 23$, where x = the kie and y = the migratory ratio H_x/H_n.

(16) H. Tanida, *Acc. Chem. Res.*, **1**, 239 (1968), and references contained therein.

(17) We feel that interaction of the benzo group (endo-side) with the carbene center should be minimal, since any resonance interaction must involve charge separation. In fact, it has been found that substituent effects are quite minor in rearrangements of *o*- and *p*-X-$C_6H_4(Ph)_2\ddot{C}H$ (using σ^+, $\rho = -0.28$); see P. B. Sargeant and H. Schecter, *Tetrahedron Lett.*, 3957 (1964).

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Photolysis of Carbonyl Ylides. Double-Irradiation Studies

Sir:

Photochromism is a phenomenon characteristic of vicinal diaryl and other suitably substituted oxiranes. In many cases the color associated with oxirane photolysis is apparent only in matrices at 77 K.[1] Color formation is attributed to C–C bond cleavage with formation of carbonyl ylides which may fragment to carbenes and carbonyl compounds.[1,2] In fact several such photogenerated carbonyl ylides, including that derived from 3,3-dicyanostyrene oxide (**1a**) have been intercepted at ambient temperature in solution with common dipolarophiles.[2-4]

The mechanism for the potential conversion of carbonyl ylides to carbenes has been the subject of interest in connection with the photofragmentation of oxiranes to carbenes.[1] It has been recognized that carbene formation is *not* associated with the thermal generation of carbonyl ylides from styrene and stilbene oxides including 2,3-dicyanostilbene oxide[5] as well as ethyl *trans*-2-cyano-3-phenylglycidate.[6] Furthermore, photodecarbonylation of 2,2,4,4-tetraphenyloxetanone may be accomplished in solution (25°; 350 nm)[7] to give tetraphenyloxirane presumably through an ylide intermediate without fragmentation to diphenylcarbene.[8] It is clear from these observations that thermal carbene formation from those ground state ylides studied is at best inefficient.

The possibility that carbonyl ylide fragmentation may be photoinduced remained to be tested since concerted oxirane fragmentation to carbene and/or sequential process(es) involving initial C–O bond photocleavage also provide viable mechanistic alternatives. The transformation of 3,3-dicyanostyrene oxide (**1a**) in 2,3-dimethyl-2-butene was selected for study since the [3 → 2 + 1] photocycloelimination reaction to dicyanocarbene is suppressed to the point where [3 + 2] cycloaddition becomes competitive.[3] Irradiation[7] of **1a** in the presence of 2,3-dimethyl-2-butene produces the spectrum of products **2–5** whose relative yields provide a reference for comparison of levels of cycloelimination and [3 + 2] cycloaddition.[9]

Experiments were designed using **1a** to test the validity of the assumption that products **2**, **3**, and **4a** derived from [3 →