

- Tetrahedron Lett.*, 407 (1976); for *o*-tolylid-*tert*-butylcarbinols, -4.2 (J. S. Lomas, P. K. Luong, and J. E. Dubois, unpublished results).
- (16) H. C. Brown, H. Bartolomay, and M. D. Taylor, *J. Am. Chem. Soc.*, **66**, 431 (1944).
- (17) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **96**, 263 (1974); **97**, 2892 (1975).
- (18) From ref 2b; the lower value is based on Allinger's force field, the higher on Schleyer's. For further details on tri-*tert*-butylmethane, see L. S. Bartell and H. B. Burgi, *J. Am. Chem. Soc.*, **94**, 5239 (1972).
- (19) D. F. DeTar and C. J. Tenpas, *J. Am. Chem. Soc.*, **98**, 7903 (1976).
- (20) A referee has requested comment upon the effect of the change of solvent from acetic acid (dehydration) to aqueous acetone (solvolysis) upon the rate comparisons. Transferring the solvolysis reaction to acetic acid would only affect the relative rates to the extent that Grunwald-Winstein *m* values or solvent nucleophilicity effects vary within the series. No such variation is to be anticipated: tertiary carbonyl derivatives solvolyze uniformly via an S_N1 mechanism and adamantyl systems are particularly immune to nucleophilic solvent participation. Relative solvolysis rates of alkylid-*tert*-butylcarbonyl *p*-nitrobenzoates are slightly enhanced by solvent change from aqueous dioxane to acetic acid.⁵

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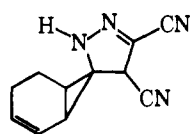
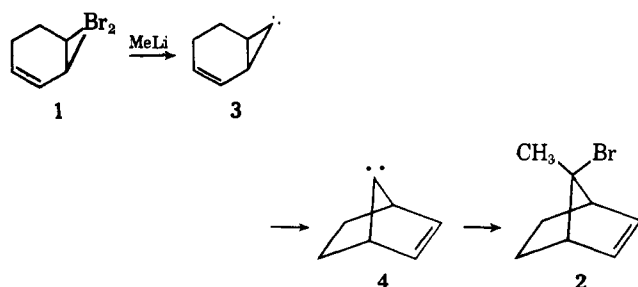
A Novel Carbene-Carbene Rearrangement

Sir:

The reaction of 7,7-dibromo-2-norcarene (**1**) with methyl-lithium gave as the main product *syn*-7-bromo-7-methylnorbornene (**2**).^{1,2} It was proposed that formation of compound **2** involved rearrangement of 7-norcar-2-enylidene (**3**) to 7-norbornenylidene (**4**)³ (Scheme I). Several cases of carbene-carbene rearrangements have been reported,⁴ particularly in aromatic systems, but the interconversion of carbenes **3** and **4** would be a novel example. It was therefore of interest to attempt the generation of carbene **3** unambiguously and record its behavior. One way to accomplish this would be to treat the appropriate *N*-nitrosoarea with base,⁵ a reaction that has successfully generated cyclopropylidenes.⁶ A diazotate is an intermediate in this reaction and it can be isolated as a salt under special conditions.⁵

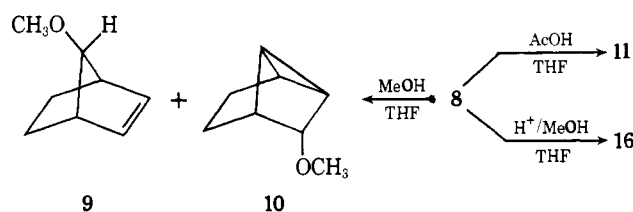
From *anti*-7-carboxy-2-norcarene (**5**)⁷ the corresponding urea **6**⁸ was prepared in the usual way via the isocyanate in 65% overall yield. Oxidation of **6** at -78 °C with N_2O_4 in THF afforded a 79% yield of the *N*-nitrosoarea **7**.⁹ Treatment of **7** with $KOC(CH_3)_3$ in THF at -40 °C gave diazotate **8** as a

Scheme I



- 5**, X = CO₂H
6, X = NHCONH₂
7, X = N(NO)CONH₂
8, X = N=NOK
11, X = OCOCH₃
13, X = NH₂·HCl
14, X = OCH₂CH₃
16, X = OCH₃

Scheme II



light brown powder.¹⁰ The salt reacted with excess methanol with evolution of nitrogen, giving *anti*-7-methoxynorbornene (**9**) and *endo*-2-methoxytricyclo[4.1.0.0^{3,7}]heptane (**10**) in a ratio of 2:1, identified by comparison with authentic samples.¹¹ The same products in a ratio of 3:1 were formed in a reaction of **8** with 2 equiv of methanol in pentane. On the other hand, decomposition of the salt **8** with excess acetic acid afforded *anti*-7-acetoxy-2-norcarene (**11**)¹² as the sole volatile product (Scheme II).

Different intermediates are apparently involved in these reactions. The formation of compound **11** is reasonably explained by internal return of an ion pair,¹³ and the ethers **9** and **10** are those expected from the 7-norbornenyl cation (**12**) and methanol.¹⁴ However, on the basis of our experiments it seems unreasonable that **12** results from a carbonium ion rearrangement.¹⁵ Deamination of *anti*-7-amino-2-norcarene hydrochloride (**13**)¹⁶ with sodium nitrite in THF/acetic acid afforded the acetate **11** (72% yield), besides several minor unidentified compounds. Furthermore, treatment of the diazotate **8** with Et₃O⁺BF₄⁻ in ether/methylene chloride produced a complex mixture with the ether **14**¹⁸ as the main component; <4% of the rearranged ether, *anti*-7-ethoxy norbornene (**15**), was found. A similar reaction of the diazotate **8** with 10 molar equiv of H₂SO₄ in excess methanol/THF afforded *anti*-7-methoxy-2-norcarene (**16**)¹⁹ as the major product (75%) and no norbornene derivatives. When the latter reaction was carried out using D₂SO₄ in methanol-*d*₁/THF, no deuterium was incorporated into the product **16**. On the other hand, the decomposition of **8** in excess methanol-*d*₁ resulted in better than 97% incorporation of deuterium at C-7 of the ether **9**, as shown by the absence of a broad singlet at δ 3.12 (CCl₄). The ethers **9**, **14**, **15**, and **16** were unaffected by the reaction conditions.

Apparently, protonation of **8** results in formation of the corresponding diazonium ion which under acid conditions does not equilibrate with the diazo compound. Hence, products derived from the 7-norcar-2-enyl cation (**17**) are observed. On the other hand, basic conditions result in the diazo compound and, subsequently, the carbene **3** which rearranges to 7-norbornenylidene (**4**).²⁰ The latter should be nucleophilic rather than electrophilic, owing to interaction of the double bond with the electron-deficient carbon,²¹ a conclusion that has recently been borne out by experiment.²² Hence, protonation of **4** by methanol affords the carbonium ion **12**, from which the observed products **9** and **10** can be derived.

As expected the reaction of the *N*-nitrosoarea **7** with LiOCH₃ in pentane⁶ produced mainly a liquid (75%) which consisted of the ethers **9** and **10** in a ratio of 4:1 besides a small amount of *anti*-7-hydroxynorbornene.²³ The same products were isolated when pentane was replaced by *cis*-2-butene;²⁴ no addition to the double bond of the alkene was observed. Neither did the presence of diethyl fumarate result in formation of spiro compounds. Furthermore, we were not able to observe the expected color changes owing to formation of an intermediate diazo compound during any of the decomposition reactions; however, the base-induced decomposition of **7** in the presence of fumaronitrile gave the pyrazoline **18**²⁵ which is clear evidence for the presence of such an intermediate.

Our results contrast with those reported²⁶ for the decom-

position of the homologue *N*-nitroso-*N*-anti-bicyclo-[3.1.0]hex-2-en-6-ylurea which rearranged via carbonium ions.

References and Notes

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- (2) The yield of **2** varied with reaction conditions; at 0 °C it was practically the sole product, while at -78 °C ~20% of three isomers C₁₄H₁₆ were also formed.
- (3) This does not imply that free carbenes are intermediates.
- (4) W. M. Jones, R. C. Joines, J. A. Meyers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis, and A. B. Turner, *J. Am. Chem. Soc.*, **95**, 826 (1973), and references therein. H. J. Hagemann and U. E. Wiersum, *Chem. Ber.*, **9**, 206 (1973); W. D. Crow and C. Wentrup, *Chem. Commun.*, 1387 (1969).
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- (6) W. M. Jones, M. H. Grasley, and W. S. Brey, *J. Am. Chem. Soc.*, **85**, 2754 (1963); W. R. Moore and R. D. Bach, *ibid.*, **94**, 3148 (1972).
- (7) I. A. D'yakov, T. V. Domareva-Mandel'shtam, and I. Z. Egenburg, *Zh. Org. Khim.*, **3**, 1441 (1967).
- (8) Mp 145 °C; IR (KBr) 3340, 2920, 1640, 1530, 770, 530 cm⁻¹; NMR (CDCl₃) δ 1.46 (2 H, m), 1.92 (4 H, m), 2.52 (1 H, m), 4.90-5.85 (3 H, m), 6.05 (1 H, m).
- (9) Mp 76 °C dec; IR (CCl₄) 3250, 2920, 1730, 1510, 1390, 670 cm⁻¹; NMR (CDCl₃) δ 1.50 (2 H, m), 1.92 (4 H, m), 2.36 (1 H, t, J = 3, 2 Hz), 5.60 (1 H, m), 5.95-6.75 (3 H, m).
- (10) IR (KBr) 2900, 2140, 1560, 1350 cm⁻¹; NMR (DMSO-*d*₆) δ 1.40 (2 H, m), 1.82 (4 H, m), 4.12 (1 H, t), 5.30 (1 H, m), 6.00 (1 H, m).
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- (12) IR (film) 3010, 2910, 1745, 1230 cm⁻¹; NMR (CCl₄) δ 1.46 (2 H, m), 1.85 (4 H, m), 1.94 (3 H, s), 3.96 (1 H, t, J = 2.2 Hz), 5.50 (1 H, m), 6.00 (1 H, m).
- (13) M. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 496 (1965); R. A. Moss and C. E. Powell, *J. Am. Chem. Soc.*, **98**, 283 (1976).
- (14) A. Diaz, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3133 (1966).
- (15) Solvolysis of *exo*-7-norcar-2-enyl triflate in CH₃COOH/CH₃COO⁻ proceeds slowly at 100 °C to a 2.28:1 mixture of **11** and *anti*-7-norbornenyl acetate; see X. Creary, *J. Am. Chem. Soc.*, **98**, 6608 (1976).
- (16) IR (KBr) 3000, 1585, 1495, 1150, 770, 680 cm⁻¹; NMR (D₂O, *t*-BuOH as standard) δ 1.80 (6 H, br m), 2.70 (1 H, t, J = 3.4 Hz), 5.04 (s), 5.66 (1 H, m), 6.08 (1 H, m).
- (17) Use of the corresponding trimethyloxonium salt was inconvenient because of low solubility.
- (18) *m/e* 138, 10459, calcd 138, 10445; IR (film) 3010, 2910, 1640, 1385, 1130, 680 cm⁻¹; NMR (CCl₄) δ 1.10 (3 H, t, J = 7, 0 Hz), 1.40 (2 H, m), 1.85 (4 H, m), 3.06 (1 H, t, J = 2.1 Hz), 3.42 (2 H, q, J = 7.0 Hz), 5.30 (1 H, m), 5.90 (1 H, m).
- (19) IR (film) 3010, 2920, 2840, 1640, 1220, 1130, 680 cm⁻¹; NMR (CCl₄) δ 1.40 (2 H, m), 1.85 (4 H, m), 3.06 (1 H, t, J = 2.1 Hz), 3.25 (3 H, s), 5.30 (1 H, m), 5.90 (1 H, m).
- (20) Under basic conditions the following alternative mechanism is not quite excluded by our results: the diazo compound formed from **8** equilibrates with the corresponding diazonium ion. Loss of nitrogen from the latter gives the cation **17** which may rearrange to **12**; however, this would require that **17** is different from any cationic intermediate formed under acid conditions. We want to acknowledge constructive suggestions from a referee.
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- (23) P. G. Gassmann and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).
- (24) Similar results have been obtained by W. M. Jones and P. H. Gebert, University of Florida; private communication from Professor Jones.
- (25) Mp 145 °C; *m/e* 198.0898, calcd 198.0905; IR (KBr) 3210, 2950, 2270, 1490 cm⁻¹; NMR (CDCl₃) δ 1.80 (2 H, m), 2.17 (4 H, m), 3.84 (1 H, m), 5.72 (1 H, m), 6.20 (1 H, m). The stereochemistry is not established.
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Detailed Potential Energy Surfaces for Carbonium Ion Rearrangements: C₃H₇O⁺

Sir:

In earlier work,^{1,2} we have emphasized that reactions occurring in the field-free regions of conventional magnetic sector mass spectrometers do so with excess energies in the transition state, which are comparable to, or less than, those present in solution reactions. Important experimental evidence for this

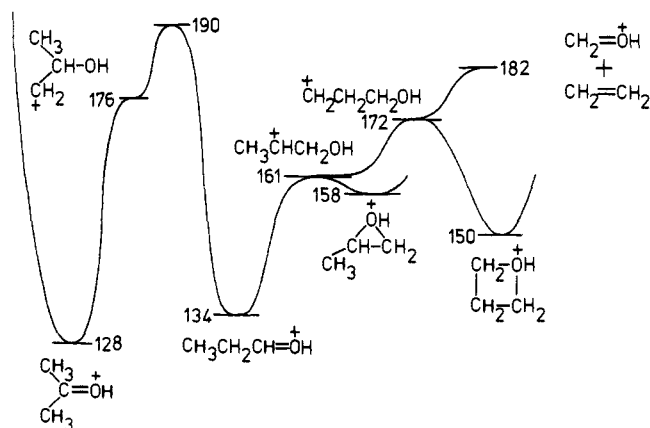
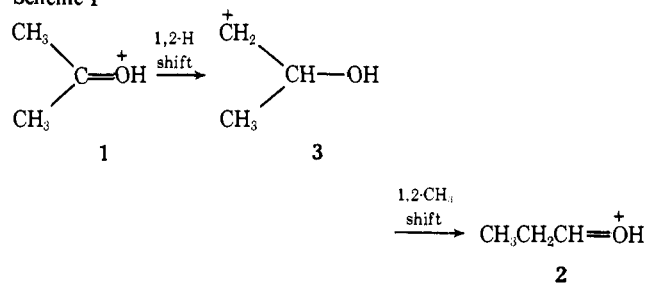


Figure 1. Potential surface for unimolecular reactions of protonated acetone and protonated propionaldehyde.

Scheme I



view is found in the occurrence of large primary deuterium isotope effects.²⁻⁴

Investigations of such unimolecular reactions (i.e., those responsible for metastable peaks) have uncovered cases where isomerization of an ion is the rate-determining step, followed by more rapid dissociation from the newly formed isomeric structure.^{5,6} A specific case is the rate-determining isomerization of protonated acetone (**1**) to protonated propionaldehyde (**2**) prior to dissociation.⁶ The most plausible mechanism for this reaction is via the primary carbonium ion **3** as, or near to, a transition state (Scheme I). The approximate heat of formation of **3** (176 kcal mol⁻¹) can be estimated;⁷ the agreement with the measured transition-state energy (190 kcal mol⁻¹)⁶ for the rate-determining step for isomerization of **1** prior to dissociation is satisfactory.

This scheme is incorporated into the potential energy surface shown Figure 1. A consequence of this potential surface is that ions initially generated as structure **2** should not be able to attain configuration **3**. This follows since the activation energy for elimination of C₂H₄ from **2** (~48 kcal mol⁻¹; measured transition-state energy⁶) is less than the energy (~56 kcal mol⁻¹) which would be needed to cause isomerization of **2** to **1** via **3**.

The most plausible mechanism whereby C₂H₄ loss can occur from **2** is via two successive 1,2-hydride shifts followed by cleavage of the central C-C bond in the primary carbonium ion **5**. 1,2-Hydride shifts of this type are symmetry allowed and are known from calculations⁸ and solution NMR experiments⁹ to proceed with negligible energy barriers, i.e., with activation energies close to the reaction endothermicities or exothermicities. Other possible isomerizations are ring closure of **4** and **5** to form the more stable protonated oxirane **7** and protonated oxetane **8**, respectively. These isomerizations, which should be rapid and reversible at energies appropriate to slow unimolecular dissociations, are incorporated into Scheme II and Figure 1.

Since we have deduced that the primary carbonium ion **3** is not accessible starting from **2**, it follows that **7**, once formed, must open exclusively to the secondary cation **4**. However,