Concerning the Nature of Dimethylvinylidenecarbene

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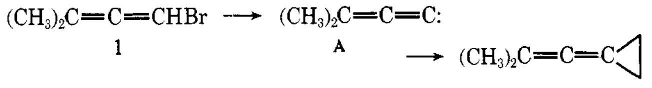
Dimethylvinylidenecarbene has been generated as the free species by use of the crown ether, 18-crown-6, and its relative olefin selectivity has been studied. These studies give evidence which indicates that the reactive species is the potassium ion associated carbenoid when the usual *t*-BuOK-induced reaction is used in the absence of 18-crown-6. Relative olefin selectivities of the species when generated from either phase-transfer catalysis or *t*-BuOH-complexed *t*-BuOK are also discussed.

Dimethylvinylidenecarbene (A) exhibits singlet and electrophilic characteristics in its reactions with olefins. This species is considered as a free carbene rather than a carbenoid because of its nearly identical olefin selectivity when generated from different precursors.[2] However, a carbene–anion pair has been suggested as the possible reactive species.[3]

Phase-transfer catalysts[4] and crown ethers[5] have proven advantageous for generating A in high yields as discerned from the yields of adducts with olefins. Since olefin selectivity studies have proven invaluable for describing the nature of carbenic species,[6] we have expanded our earlier studies on phase-transfer catalyzed and potassium *tert*-butoxide induced generation of A,[4a] and have included an investigation on the olefin selectivity of A generated in the presence of the crown ether, 18-crown-6.[5] The results of these studies are reported for the purpose of providing a better understanding of the nature of the dimethylvinylidenecarbene species.

Results and Discussion

Dimethylvinylidenecarbene (A) was generated from 1-bromo-3-methyl-1,2-butadiene (1)[7] under basic conditions



in the presence of a large excess of cyclohexene and a second olefin. Analysis of the reaction mixtures by use of GLC and authentic samples for product identification furnished the product ratios from which relative reactivities were calculated. Identical runs were performed until at least three results within ±1% were obtained. Cross-checks were performed to ensure internal consistency; these results were within ±5% of the cyclohexene standard results. The results are reported in Table I.

Potassium ion is particularly well complexed by 18-crown-6 ether, thereby effecting ready solubility of *t*-BuOK in nonpolar solvents.[9,10,11] Moss and Pilkiewicz[12] elegantly showed that this extreme complexing ability allows the generation of free phenylhalocarbenes from benzal halides and *t*-BuOK in the presence of 1 equiv of 18-crown-6 ether; the carbenoid was formed in the absence of 18-crown-6 ether. Stang and Mangum[13] used this approach to show that isopropylidenecarbene ($(CH_3)_2C{=}C{:}$) generated from *t*-BuOK and 2-methylpropenyl triflate in the presence and absence of 18-crown-6 was the free carbene. The data in Table I show that large differences are observed in the *t*-BuOK-induced formation of A in the presence and absence of 18-crown-6 ether. Since previous studies have revealed independence of A from the leaving group,[2] we conclude that a potassium ion associated vinylidene carbene complex is the reactive species when elimination is effected from free *t*-BuOK alone.

The results obtained for both the phase-transfer catalyzed and *t*-BuOH/*t*-BuOK induced reactions seem surprisingly close to the results obtained for the 18-crown-6 ether data and suggest unexpected freeness for A in these systems. Phase-transfer catalytic generation of carbenes may involve complexed species;[14] alcohol mediated carbene reactions may involve carbene–ylide intermediates.[15] However, since these are comparisons between reactions conducted in protic media and reactions conducted under aprotic conditions, an accurate description of A for the protic systems may not obtain.

The yields of dimethylvinylidene adducts are reported in Table II. Previous reports from these laboratories and others[4] have shown that phase-transfer-catalyzed reactions generally give better product yields than does the use of *t*-BuOK. Recently, crown-ether-catalyzed reactions have been reported to give even better results than phase-transfer-catalyzed methods, and sensitive olefinic substrates could be used.[5] Our results show that 18-crown-6, when used in stoichiometric amounts, is not as effective as either the phase-transfer method or the catalytic crown ether method. Furthermore, this stoichiometric crown ether method is not economical and the reaction workup is difficult.

Experimental Section

General. Temperature readings are uncorrected. IR spectra were determined as neat samples on a Perkin-Elmer Model 337 spectrometer. NMR spectra were determined in deuteriochloroform solution with tetramethylsilane internal standard (δ 0.0) on a Varian T-60 spectrophotometer. Analytical GLC was performed on a Varian 1440 flame ionization gas chromatograph equipped with a 5 ft × 1/8 in. stainless steel column of 3% SE-30 on Chrom W (80/100 mesh).

Materials. Aldrich potassium *tert*-butoxide was sublimed immediately before use. Potassium *tert*-butoxide/*tert*-butyl alcohol complex was prepared according to Johnson[16] and the complex stoichiometry was determined by titration. Aliquat-336 (tricaprylylmethylammonium chloride) was obtained from General Mills, Kankakee, Ill.

1-Bromo-3-methyl-1,2-butadiene[7] and 18-crown-6[17] were prepared according to published procedures. All olefins were obtained from commercial sources and purified by distillation before use.

Relative Reactivity Procedures. Stock solutions containing cyclohexene (30 mmol), competing olefin (30 mmol), and 1-bromo-3-methyl-1,2-butadiene (3.0 mmol) were mixed and allowed to react under the following conditions: (a) 0–5 °C, 1 h, 18-crown-6 (3.0 mmol), sublimed *t*-BuOK (3.0 mmol); (b) same as (a) but without 18-crown-6; (c) same as (a) except *t*-BuOK/*t*-BuOH (3.0 mmol) was used; and (d) room temperature, 1 h, 1.5 mL of 50% NaOH (or KOH) solution, and 0.1 g of aliquat-336. The magnetically stirred solutions were analyzed directly by GLC. Peak areas were standardizd with authentic samples and relative olefin reactivities were determined by the Doering–Skell equation.[6]

Preparation of Authentic Adducts. (a) Sublimed *t*-BuOK. A 125-mL Erlenmeyer flask was charged with 20–30 mL of pure olefin and sublimed *t*-BuOK (3.3 g, 0.03 mol). The stirred mixture was cooled to 0–5 °, and 1-bromo-3-methyl-1,2-butadiene (1) (3.0 g, 0.02 mol) was added. After 1 h, water was added and the mixture was thoroughly extracted with ether. The residue from the dried and concentrated ether extract furnished the pure adduct on short-path distillation.

(b) *t*-BuOK/*t*-BuOH. The procedure used was the same as in (a) except that *t*-BuOK containing 1 equiv of *t*-BuOH (0.03 mol) was

Table I. Relative Reactivity of Dimethylvinylidenecarbene with Olefins under Various Conditions of Generation

		Relative reactivity[a]				
Substrate	Registry no.	*t*-BuOK/ 18-crown-6	NaOH(KOH)[b] Aliquat-336	*t*-BuOK/ *t*-BuOH	*t*-BuOK	*t*-BuOK[c]
2,3-Dimethyl-2-butene	563-79-1	16.9	19.3	14.7	7.4	15.8
2-Methyl-2-butene	513-35-9	7.6	6.6	5.5	4.3	4.9
Dihydropyran	110-87-2	1.1	2.1	1.5	2.7	
2-Methyl-1-buten-3-yne	78-80-8	3.1	1.9		2.0	
Cyclohexene	110-83-8	1.0	1.0	1.0	1.0	1.0
1-Hexene	592-41-6	0.1	0.2	0.2	0.3	0.2

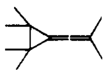
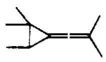
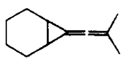
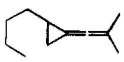
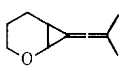
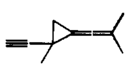
[a] Cyclohexene internal standard, 0–5 °C. [b] Room temperature. [c] A was generated at −10 °C from 1-chloro-3-methyl-1-butyne and *t*-BuOK, ref 8a.

Table II. Yields of Dimethylvinylidenecarbene–Olefin Adducts

	% yield[a]				
Substrate	*t*-BuOK/ 18-crown-6	NaOH/ Aliquat-336	*t*-BuOH/ *t*-BuOK	*t*-BuOK	*t*-BuOK[d]
2,3-Dimethyl-2-butene	47	68 (16)[c]	22	48	47
2-Methyl-2-butene	12 (37)[b]	82 (25)	15	46	36
Dihydropyran	29 (38)[b]	51 (5)	19	37	
2-Methyl-1-buten-3-yne	35	48 (24)	0	31	
Cyclohexene	25	60 (48)	14	18	26
1-Hexene	3.4	26 (25)	2	4	12

[a] Isolated yields. [b] Crown-ether-catalyzed method with KOH, ref 5. [c] Time (h) required for maximum yield. [d] Reference 8b.

Table III. Properties of Dimethylvinylidenecarbene–Olefin Adducts

Registry no.	Product	Bp, °C (torr)	IR, cm^{-1} (neat)	NMR, δ (CCl_3D)	Rel retention GLC
13303-30-5	 **2**	35–45 (0.30) mp 42	2965, 2880, 2000 (allene), 2700, 1040 (cyclopropyl), 820 (cyclopropyl)	1.75 (s, 6 H, CH_3) 1.20 (s, 12 H, CH_3)	0.43
14803-30-6	 **3**	35–45 (0.40)	2965, 2880, 2700, 2010 (allene), 1015 (cyclopropyl, 840 (cyclopropyl)	1.75 (m, 6 H, CH_3) 1.20 (m, 10 H, CH_3, CH)	0.35
4544-26-7	 **6**	55–60 (0.20)	2965, 2920, 2850, 2700, 2020 (allene), 1020 (cyclopropyl), 860 (cyclopropyl)	1.80 (d, 8 H, CH_3, CH) 1.30 (m, 8 H, CH_2)	1.0
53376-36-6	 **7**	45–55 (0.5)	2965, 2920, 2850, 2030 (allene), 1050 (cyclopropyl)	1.80 (d, 7 H, CH_3, CH) 1.45 (m, 8 H, CH_2) 1.00 (m, 3 H, CH_3)	0.94
59055-17-3	 **4**	55–65 (0.15)	2965, 2920, 2850, 2700, 2000 (allene), 1050 (cyclopropyl), 860 (cyclopropyl), 830, 810	4.10 (m, 1 H, CH) 3.60 (m, 2 H, CH_2) 2.00 (m, 3 H, CH_2, CH) 1.80 (d, 6 H, CH_3) 1.50 (m, 2 H, CH_2)	1.11
58668-76-1	 **5**	25–27 (0.15)	3280 (acetylene), 2965, 2920, 2850, 2700, 2100 (acetylene), 2010 (allene), 1060 (cyclopropyl), 880 (cyclopropyl)	2.00 (s, 1 H, CH) 1.80 (s, 6 H, CH_3) 1.40 (d, 2 H, CH_2) 1.30 (s, 3 H, CH_3)	0.40

used. This procedure was unsuccessful with the enyne, 2-methyl-1-buten-3-yne.

(c) **18-Crown-6, *t*-BuOK.** The same procedure as that described in (a) was used except that 18-crown-6 (8.0 g, 0.03 mol) was mixed with the sublimed *t*-BuOK before 1 was added.

(d) **Aliquat-336.** A 125-mL Erlenmeyer flask was charged with olefin (20–30 mL), aliquat-336 (1 g), and 50% sodium hydroxide solution (7 mL). The reaction mixture was stirred (23–27 °C) and analyzed periodically by GLC (tetralin internal standard) for maximum yield. The reaction was worked up according to (a).

All reactions except (d) were performed under a dry nitrogen atmosphere. Adduct yields are reported in Table II. Physical and spectral data are reported in Table III. The adducts 1,1,2,2-tetramethylisobutylidenecyclopropane (**2**),[8] 1,1,2-trimethylisobutylidenecyclopropane (**3**),[8] 2-oxa-7-isobutylidenebicyclo[4.1.0]heptane (**4**),[5] 2-ethynyl-2-methylisobutylidenecyclopropane (**5**),[18] 7-isobutylidenebicyclo[4.1.0]heptane (**6**),[8] and 2-*n*-butylisobutylidenecyclopropane (**7**)[8] are all known.

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Registry No.—A, 4209-13-6; 1, 6214-32-0.

References and Notes

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Hydrogen Migration in 2-Carbena-6,6-dimethylnorbornane[1]

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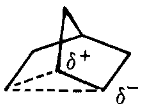
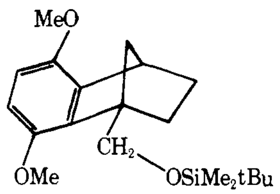
A study of the dry salt pyrolysis and the photolysis of the lithium salts of the tosylhydrazone of 6,6-dimethylnorbornan-2-one, *exo*-3-deuterio-6,6-dimethylnorbornan-2-one, and *endo*-3-deuterio-6,6-dimethylnorbornan-2-one revealed a preference for exo-C-3 → exo-C-2 over endo-C-3 → endo-C-2 hydride migration of approximately 20:1. This stereoselectivity is interpreted in terms of torsional interactions in the hydride migration transition state of a classical singlet carbene.

Although studies of the chemistry of the 2-norbornyl carbonium ion have absorbed the attention of many chemists over the past 25-year period,[3] and substantial effort has been expended in investigations of the nature of the related radical intermediate,[4] much less is known concerning the analogous carbanion[5] and carbene intermediates.[6] A consideration of this history suggests that characterization of 2-carbenanorbornane might be of considerable interest, since, in the singlet state, delocalization involving the empty p orbital at C-2 and the C-1–C-6 σ bond is possible (**1**).



1

Since most alicyclic carbene intermediates react by way of intramolecular rather than intermolecular pathways,[7] characterization of a 2-carbenanorbornane intermediate would appear to require the analysis of an insertion or hydrogen migration reaction. The nature of the 2-norbornyl carbonium ion has been revealed to some degree through studies of the stereospecificity of 3,2-hydride shifts. Investigations by Collins[8] and Berson[9] have shown that exo-C-3 to exo-C-2 hydride migration is preferred over endo-C-3 to endo-C-2 migration ($k_{\text{exo-exo}}:k_{\text{endo-endo}} > 100$). Since 1,2 hydrogen shifts are common intramolecular reaction pathways for bivalent carbon intermediates,[7] it appeared to us that a study of the stereochemistry of the C-3–C-2 hydride shift in 2-carbenanorbornane would be an excellent approach to an understanding of the chemistry of this intermediate. Unfortunately, 2-carbenanorbornane reacts predominantly via C-6 insertion with C-3–C-2 hydrogen migration as a barely detectable component of the reaction (nortricyclene–norbornene = 99.5:0.5).[6a] This difficulty was circumvented in a recent study by Kyba and Hudson,[10] who studied the benzo-2-carbenanorborene intermediate **2**, whereas Nickon and co-workers[11] have investigated 2-carbenanorbornane species **3**, which possesses a built-in bias favoring exo-C-3 hydrogen migration, since the additional bridge twists the exo-C-3 hydrogen into coplanarity with the empty p orbital of the adjacent singlet carbene center. Our approach is to consider 2-carbena-6,6-dimethylnorbornane (**12**), since much of the simplicity and symmetry of the parent system is preserved and γ C–H insertion is blocked, C–C insertion being a rarely observed process.[12]



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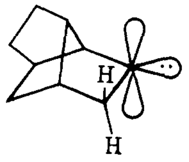

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The required *endo*- and *exo*-deuterated tosylhydrazone lithium salts (**7b** and **10**) were prepared starting with 5,5-dimethylnorbornene epoxide (**4**)[13] and 6,6-dimethylnorcamphor (**8**).[13] Epoxide **4** with lithium aluminum deuteride treatment followed by chromic acid oxidation produces *endo*-3-deuterio-**6**. Treatment of **6** with $TsNHNH_2/H^+$ yields tosylhydrazone, which is converted to lithium salt with an equivalent of methyllithium. Ketone **8** was converted to *exo*-deuteriotosylhydrazone salt by treatment with CH_3ONa/CH_3OD, conversion to tosylhydrazone and subsequently to lithium salt **10** as in the endo case.