

Table I. Sensitized Photolyses of 1-Menthene in Alcohol Solvents

Entry	ROH	Sensitizer	k , sec ⁻¹ , at 25–30° ^a	Composition after 6 hr, %			
				1	2	3	4
1	CH ₃ OH	None	1.3×10^{-6}	75	9.5	6.0	9.5
2	CH ₃ OH	Toluene	6×10^{-6}	26	29	18	27
3	CH ₃ OH	Xylene ^b	13×10^{-6}	6.0	34	24	37
4	CH ₃ OH	Xylene ^{b,c}	5×10^{-6}
5	CH ₃ CH ₂ OH	Xylene ^b	11×10^{-6} ^d	10	40	21	28
6	(CH ₃) ₂ CHOH	Xylene ^b	9×10^{-6}	12	61	10	17
7	(CH ₃) ₃ COH	Xylene ^b	0.7×10^{-6}	84 ^e	16 ^e
8	H ₂ O ^f	Xylene ^b	8×10^{-6}	17	23	26	33

^a Reactions were carried out on 5 g of **1** in 400 ml of ROH containing 4 ml of the sensitizer. The rate constants were calculated from the disappearance of **1** as measured by gas chromatography using ca. 5% of a 1:1 mixture of *cis*- and *trans*-menthene as an internal standard. Owing to inherent design limitations of the reactor, constant temperature could not be maintained. ^b A mixture of isomers. ^c Oxygen was bubbled through the reaction mixture. ^d Average of two runs. ^e Interpolated from 4- and 8-hr points. ^f A 50% solution of aqueous *t*-butyl alcohol was used.

We also found that ethanol (entry 5) and 2-propanol (entry 6) likewise added to 1-menthene (**1**) under the same conditions affording the ethers **3b**, **4b**, **3c**, and **4c**. In *t*-butyl alcohol (entry 7) the isomerization reaction greatly outweighed ether formation and no more than trace amounts of the *t*-butyl ethers **3d** and **4d** could be detected by gas chromatography, even after 18-hr reaction times. Interestingly, the isomerization was substantially slower in this solvent. In aqueous *t*-butyl alcohol hydration of 1-menthene (**1**) took place readily, giving alcohols **3e** and **4e** (entry 8).

The stereochemical assignments for ethers **3** and **4** were made on the basis of the data presented in Table II. Supporting chemical evidence for the methyl and ethyl ethers comes from our isolation of **3a** and **3b** as the predominant products (**3**:**4** \approx 3.5:1) of acid-catalyzed alcohol additions to 1-menthene under equilibrating conditions (8–9-day reaction times).

Table II. Properties of Isomeric Ethers **3** and **4**

Ether	$H-C-O-$ $\delta_{TMS}^{CCl_4}$, ppm	Quaternary CH ₃ ^a		Relative retention time ^b
		$\delta_{TMS}^{CCl_4}$, ppm	$\Delta W_{1/2}$, Hz	
3a	3.08	1.03	0.30	1
4a	3.13	1.10	0.60	1.4
3b	3.27 ^c	1.03	...	1
4b	3.37 ^c	1.09	...	1.6
3c	3.67 ^e	1.08	0.38	1
4c	3.80 ^e	1.10	...	1.4

^a Cf. K. L. Williamson, T. Howell, and T. A. Spencer, *J. Am. Chem. Soc.*, **88**, 325 (1966). ^b Expressed as the retention time of **4** divided by the retention time of **3** on a 10% DC-550 silicone oil on 60–80 Chromosorb W Column. ^c A quartet, $J = 7.0$ Hz. ^d Not measured because of overlapping with the CH₂CH₃ triplet. ^e A septet, $J = 6.0$ Hz. ^f Not measured because of overlapping with the isopropyl doublets.

The facts which emerge from these and related findings⁸ suggest a reaction pathway involving the olefin's triplet state which, perhaps because of excessive steric strain, gives way to an intermediate possessing

(7) Authentic material (a 3:2 mixture of **3e** and **4e**) was prepared from 4-isopropylcyclohexanone and methylolithium.

(8) P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4091 (1966).

carbonium ion character in its subsequent reactions. The strain factor appears essential to the reaction since the exocyclic olefin **2** shows no tendency to give ethers **3** and **4**. The slight preponderance of ether **4** fits well with the expectation of a kinetically controlled addition to the double bond of 1-menthene or the related carbonium ion.

We are using these mechanistic concepts as guide lines in exploring new synthetic applications of photochemically initiated addition reactions to olefins. We have thus far found that 1-methylcyclohexene and 1-methylcycloheptene undergo both the isomerization and the addition reaction and that the former readily affords 1-methylcyclohexyl acetate upon irradiation in acetic acid with xylene as the photosensitizer.

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Ionic Organoboranes. II.¹ Cesium Tropenylum Undecahydroclovodecaborate. Cage-Ring Interactions in C₇H₈B₁₀H₉⁻ and C₇H₈B₁₂H₁₁⁻ Ions²

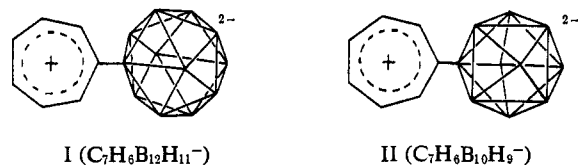
Sir:

The purpose of this paper is threefold: (1) to report the synthesis of the tropenylum³ undecahydroclovodecaborate anion (I), (2) to confirm our proposed¹ structure for the tropenylum nonhydroclovodecaborate anion (II), and (3) to demonstrate the direction and extent of electronic interaction between the cage and ring in such compounds.

(1) Paper I: K. M. Harmon, A. B. Harmon, and A. A. Macdonald, *J. Am. Chem. Soc.*, **86**, 5036 (1964).

(2) Work supported by the National Science Foundation and the Petroleum Research Fund.

(3) The tropenylum substituent nomenclature has been discussed.¹



Slow addition of excess tropenium bromide⁴ to an aqueous solution of hydronium dodecahydroclododecaborate⁵ produces a pale yellow solution containing an 86% yield of the hydronium salt of I;⁶ concentration of this solution followed by addition of cesium bromide affords a precipitate of 88% cesium tropenylum undeca-hydroclododecaborate as yellow needles, no melting point or decomposition below 300°, ultraviolet spectrum (water): λ_{max} 215 m μ (ϵ 33,800), 261.5 (13,000), and 349 (10,300). The salt can be recrystallized from acetonitrile by slow addition of methylene chloride.

Anal. Calcd for $C_7H_{17}B_{12}Cs$: C, 23.10; H, 4.71; B, 35.66. Found:⁷ C, 23.23; H, 4.66; B, 35.68.

In our initial paper¹ we tentatively assigned the structure shown for II on the basis of infrared, visible, and ultraviolet spectra; this assignment is now supported by nmr spectra. The ¹¹B nmr spectrum⁸ of $B_{10}H_{10}^{2-}$ shows two symmetrical doublets, area ratio 4:1, for the equatorial and apical borons, respectively. The ¹¹B nmr spectrum of II⁹ shows a symmetrical doublet for the apical borons and a complex multiplet for the equatorial borons; the equatorial:apical ratio is 4.01:1.00. Thus the boron cage bears a substituent in an equatorial position. The ¹H nmr spectrum of tropenium ion shows a single spike for the seven equivalent protons; the six ring protons of II are divided into a doublet (2 H) and a septuplet (4 H) in a manner characteristic of monosubstituted tropenium ions.¹⁰ The existence of a carbon-boron bond on an equatorial position on the boron cage is consistent with this data.

Examination of a variety of physical properties shows significant electronic interaction between the boron cage and the carbocyclic ring in these ions; this interaction is more extensive in II than in I. Among these properties are: (1) ¹¹B Nmr. In $B_{10}H_{10}^{2-}$ the apical borons appear at 1.4 ppm¹¹ and the equatorial borons at 28.5 ppm; in II the apical borons are at -13.5 ppm and the equatorial boron multiplet is centered at 18 ppm with the furthest downfield peak at 5 ppm. This strong downfield shift of all boron resonances indicates extensive ground-state deshielding of the cage by electron donation to the ring, with the greatest effect felt by the boron to which the ring is attached. The $B_{12}H_{12}^{2-}$ ion¹² shows a symmetrical doublet at 16.9

(4) H. J. Dauben, Jr., *et al.*, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

(5) Prepared from a sample of the triethylammonium salt generously furnished by J. L. Boone.

(6) At least 1 mole of cycloheptatriene per mole of I can be recovered from the reaction, in accord with our proposed route for the formation of such compounds.¹

(7) Analysis by Schwarzkopf Microanalytical Laboratory.

(8) W. N. Lipscomb, M. F. Hawthorne, and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5833 (1959).

(9) We are indebted to R. E. Williams for the ¹¹B nmr spectra of these ions.

(10) H. J. Dauben, Jr., and K. M. Harmon (unpublished work) have determined the ¹H nmr spectra of a number of substituted tropenium ions.

(11) All ¹¹B chemical shifts are in part per million relative to boron trifluoride etherate = 0. Spectra are in acetonitrile.

(12) E. L. Muetterties, *et al.*, *Inorg. Chem.*, **3**, 444 (1964).

ppm, while ion I shows an unsymmetrical doublet at 13.7. Deshielding of the cage by electron donation is significantly less in I than in II. (2) ¹H Nmr. Tropenium ion, $C_7H_7^+$, shows a spike at 0.60 ppm,¹³ while the ring protons of II give a doublet at 2.0 ppm (2 H) and a multiplet at 2.71 ppm (4 H). The ring in II thus shows considerable shielding, presumably by electron enrichment from the cage. Ion I shows a similar but smaller shift, with a multiplet at 1.27 ppm (4 H) and a doublet at 1.37 ppm (2 H). (3) $E_{1/2}$. Tropenium ion is reduced at the dropping mercury electrode in an irreversible, one-electron process at -0.3 v,^{14,15} and $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ anions are inert to polarographic reduction.¹² We find that ion II is reduced at the dme in 1 N KCl in a one-electron, irreversible process at -0.74 v; ion I is reduced in a similar process at -0.69 v. Although we do not know where the electron enters these ions, it is clear that either the ring is more difficult to reduce than tropenium, or the cage is easier to reduce than the free borane anions; either case argues for electron donation from cage to ring. (4) Electronic Spectra. Both ions I and II have spectra whose shape and relative ϵ values¹ are characteristic of substituted tropenium ions.⁴ Z-Value plots¹⁶ for water-acetone or water-ethanol mixtures give positive slopes for the hypsochromic shift¹ of the long-wavelength band with increasing solvent polarity, indicating internal reduction of dipole in the excitation. (5) Infrared Spectra. It is not possible to discuss the infrared spectra in detail in this space; we wish to note, however, that the B-H stretching frequencies of II are in accord with equatorial substitution, and, while the aromatic C-C region of II strongly resembles that of tropone, this region in I more nearly resembles that of chlorotropenium ion, a species with less substituent-ring interaction.¹⁷

(13) All ¹H chemical shifts are in parts per million relative to tetramethylsilane = 10 (τ). Spectra are in acetonitrile.

(14) P. Zuman, J. Chodkowsky, and F. Santavy, *Collection Czech. Chem. Commun.*, **26**, 380 (1961).

(15) Half-wave potentials are relative to the saturated calomel electrode.

(16) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

(17) Full details will be presented in a paper now in preparation for this journal.

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Facile Reduction of Alkyl Halides with Chromium(II) Complexes. Alkylchromium Species as Intermediates

Sir:

Simple chromous salts are readily accessible and have proven to be versatile reducing agents for a variety of organic compounds, including organic halides.¹ Among halides, the application of this reagent has been limited to the rather reactive allylic and benzylic halides, as well as α -halo carbonyl and cyano compounds, etc.² The inertness of chromous ion toward most alkyl halides has restricted its synthetic utility.

(1) (a) J. K. Kochi and D. D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964); (b) L. H. Slaugh and J. H. Raley, *Tetrahedron*, **20**, 1005 (1964).

(2) C. E. Castro and W. C. Krav. Jr., *J. Am. Chem. Soc.*, **85**, 2768 (1963).