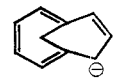
(double doublet) and H_9 at τ 7.65 (pentuplet), and integration of the spectrum indicated that the band at τ 7.65 represented 1.0 proton. The change in H_8 from a double triplet in I to a double doublet in III plus the appearance of only one proton at C_9 in III and the absence of any signal at τ 7.35 in III is uniquely consistent with stereospecific deuterium incorporation at C_9 as depicted at III.

In addition, when III was treated with sodium dimethyl-d_5-sulfinyl anion in dimethyl-d_6 sulfoxide the anion II which resulted had an nmr spectrum identical with that of the anion produced from I and no bands were observed for dimethyl-d_5 sulfoxide, monoprotiodimethyl sulfoxide. Therefore, the deuterium atom at C_9 in III must have been removed stereospecifically by the base when II was generated.

The results prompted an investigation of the base-catalyzed exchange of I. The hydrocarbon was allowed to react with a saturated solution of NaOD in dimethyl-d_6 sulfoxide at 30° and the reaction was followed by nmr. By this technique a value of *ca.* 240 sec was calculated for the half-life of exchange of one proton. The reaction was followed for the equivalent of 20,000 half-lives and no exchange of H_9 for deuterium could be detected. Upon quenching the reaction mixture after 20,000 half-lives and isolating the product, it was found that it was identical with III, obtained from the quenching of the anion II with D_2O. These results indicate that there is a difference of at least 10^4 in kinetic acidity between H_9 and H_{10} in I.[4]

We have also prepared 9-methyltricyclo[4.3.1.0]deca-2,4,7-triene (IV)[6] by allowing II in dimethyl sulfoxide to react with methyl iodide and subjected it to an exchange experiment. When treated with NaOD in dimethyl-d_6 sulfoxide even after 3 months at 30°, IV was not observed to undergo any proton exchange for deuterium. Furthermore, it was found that allowing IV to react with sodium dimethylsulfinyl anion did not give rise to an aromatic ten-π-electron anion.

It seemed unlikely that a steric effect accounted for the difference in kinetic acidity of the two protons at C_9 in I since this hydrocarbon had been so readily generated by the elimination of HCl from V with potassium hydroxide in methanol.[1] Since this elimination was probably *trans* in nature, the proton *cis* to the cyclopropane ring was removed and could therefore not be hindered from attack by hydroxide ion. We have confirmed that a steric effect is not responsible for the stereospecificity of the exchange reaction with I by conducting the same exchange experiment on VII. This ketone (VII) was prepared by chromic acid oxidation of the alcohol[1] VI and was subjected to an exchange experiment using NaOD in dimethyl-d_6 sulfoxide. The exchange was followed by nmr, and the band at τ 7.78, which had all eight of the methylene protons which are on the five- and six-membered rings, was observed to rapidly and smoothly decrease in area until it contained only the four methylene protons adjacent to the double bond in the six-membered ring, after which no more deuterium atoms were incorporated.[7] This result demonstrates that the protons *cis* to the cyclopropane ring in I are not sterically prevented from undergoing base-catalyzed exchange with NaOD in dimethyl-d_6 sulfoxide.



IX

We contend that the stereospecificity of the exchange of hydrogen for deuterium in I is due to the rigid stereoelectronic requirement that the cyclopropane ring places upon the molecule. H_{10} is more readily abstracted by the base than H_9 because the electron pair in the orbital between C_9 and H_{10} can overlap much more effectively in the transition state with the electron pair in the zero-bridge bond (C_1–C_6) of the cyclopropane ring than can the electron pair between C_9 and H_9. Furthermore, in the anion II we suggest that the orbitals at C_1 and C_6 are not of the p–π type, as valence bond resonance structures for II, *e.g.*, IX, imply, but are directed anisotropically so that the face of the molecule opposite the methylene bridge has a higher electron density. This effect renders the face opposite to the methylene bridge to be the preferential one for attack of an electrophile, *e.g.*, proton or deuteron.

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equivalent it is the proton which is *cis* to the cyclopropane ring which appears at higher field.[3]

(3) Unpublished work: S. Winstein, P. Radlick, R. Boikess, and J. Brauman.

(4) Exchange experiments conducted on indene under identical conditions resulted in complete exchange of all three protons on carbons 1 and 3. For an excellent discussion of the exchange of indene see ref 5.

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(6) The stereochemistry of the methyl group could not be rigorously determined. However, we believe that, in analogy to the attack of II by D_2O, attack by methyl iodide must occur from the side opposite the methylene bridge.

(7) The protons adjacent to the carbonyl group stood out clearly from the others and despite our efforts it was not possible to determine any kinetic acidity difference between the *cis* and *trans* protons.

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Ionic Organoboranes. III. The 1-Methyl-2-tropenyliumyl-1,2-dicarbaclovododecaborane(12) Cation[1,2]

Sir:

The 1,2-dicarbaclovododecaborane(12) (*o*-carborane) cage has been shown to be electron attracting.[6] In a

(1) Work supported by the National Science Foundation, Grant GP-5554, and the Petroleum Research Fund, Grant 443-A4.

(2) We have used the name "tropenylium"[3,4] for the $C_7H_6^+$– substituent obtained by hydride removal from a C_7H_7– tropenyl group. In a new system for naming cycloheptatriene derivatives,[5] the name "tropenylium" is assigned to the $C_7H_7^+$ ion, and the $C_7H_6^+$– substituent becomes "tropenyliumyl."

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recent, comprehensive study, Hawthorne, *et al.*,[7] by measurements of K_a for carboranylbenzoic acids and carboranylanilinium ions, and ^{19}F nmr chemical shifts of carboranylfluorobenzenes, have shown that the $-I$ effect of the *o*-carborane cage is similar in magnitude to that of the halogens, and that ground-state cage–ring π interaction does not occur. They found, however, that isomer ratios in nitration of 1-phenyl-1,2-dicarbaclovododecaborane(12) (*o*:*m*:*p* = 4:26:70) indicate electron donation by the cage in the nitration transition state. These observations suggest that the *o*-carboranyl group is a ($-I$, $+T$) substituent similar to the halogens.[8]

We have recently synthesized the 1-methyl-2-tropenyliumyl-1,2-dicarbaclovododecaborane(12) cation; this species offers excellent opportunity to examine the response of the π system of the cage to strong electron demand. Reaction of 1-methyl-1,2-dicarbaclovododecaborane(12)[6a] with *n*-butyllithium followed by tropenyl methyl ether[9] affords 79% 1-methyl-2-(7-cyclohepta-1,3,5-trienyl)-1,2,-dicarbaclovododecaborane(12) (I), white prisms from methanol, mp 57.5–58° *Anal.* Calcd for $C_{10}H_{20}B_{10}$: C, 48.34; H, 8.11; B, 43.55. Found:[10] C, 48.21; H, 8.27; B, 43.29. Ultraviolet spectrum (cyclohexane): λ_{max} 251.5 nm (ϵ 3230). Nmr spectrum (τ, $DCCl_3$):[11] triplet 3.21, 3.26, 3.31 (2 H); sextet 3.60–3.93 (2 H); quartet 4.55–4.80 (2 H): singlet 8.22 imposed on triplet 8.22, 8.33, 8.43 (4 H). With triphenylcarbonium ion, I gives 80% triphenylmethane but no other isolable products. Rearrangement[12] of I at 165° for 45 min gives quantitative conversion to 1-methyl-2-(3-cyclohepta-1,3,5-trienyl)-1,2-dicarbaclovododecaborane(12) (II), white needles from methanol, mp 93–94°. *Anal.* Found:[10] C, 48.64; H, 7.84; B, 43.41. Ultraviolet spectrum (cyclohexane): λ_{max} 267 nm (ϵ 6570). Nmr spectrum (τ, $DCCl_3$):[11] doublet 2.81, 2.90 (1 H); quartet 3.62–3.87 (2 H); sextet 4.18–4.87 (2 H); triplet 7.70, 7.83, 7.94 (2 H); singlet 8.28 (3 H).[13] The Dauben reaction[14] of II with triphenylcarbonium hexafluoroantimonate[15] in refluxing 1,2-dichloroethane affords 99.5% 1-methyl-2-tropenyliumyl-1,2-dicarbaclovododecaborane(12) hexafluoroantimonate (III), white prisms from acetonitrile–ether, decomposes on extended heating but no melting point below 300° [*Anal.* Calcd for $C_{10}H_{19}B_{10}SbF_6$: C, 24.86; H, 3.96; B, 22.39. Found:[10] C, 25.12; H, 4.14; B, 22.29. Ultraviolet spectrum (96% sulfuric acid): λ_{max} 224.5 nm (ϵ 33,400), 287 (sh), 294.5 (6360), and 302 (sh); (acetonitrile) λ_{max} 231 nm (ϵ 32,400), 286 (sh), and 292.5 (6420). Nmr spectrum (τ, D_3CCN):[11] multiplet 0.49 (2 H), singlet 0.65 (4 H), singlet 8.15 (3 H)], and 96.9% triphenylmethane, mp 93.5–94°. III is nonhygroscopic and stable to the atmosphere.

The carboranyl cage in this cation shows a strong $-I$ effect, but little if any $+T$ donation to the ring. These conclusions result from the following observations: (1) the ring protons are deshielded relative to tropenylium ion ((D_3CCN)[11] singlet τ 0.70 (7 H)), while the ring protons of bromotropenylium ion,[14,17] where $+T$ effect can operate, are significantly shielded ((CH_3CN)[11] doublet τ 0.63, 0.74 (2 H); singlet 1.00 (4 H)); (2) the cage methyl is shielded relative to that of 1-methyl-1,2-dicarbaclovododecaborane(12) ((D_3CCN)[11] singlet τ 8.05 (3 H)); and (3) the ultraviolet spectrum of the cation closely resembles that of methyltropenylium ion (λ_{max} 226 nm (ϵ 40,200), 289 (3600), 298 sh[18])[14] or carboxytropenylium ion (λ_{max} 226 nm (ϵ 37,900), 286 (4300)[18])[17] but is completely unlike that of bromotropenylium ion (λ_{max} 210 nm (ϵ 15,000), 247 (22,800), 323 (8800)[18])[14,17] or other substituted tropenylium ions[3,4,14,17,19] where $+T$ effects are operative; the absorption at 294.5 nm is best ascribed to slight perturbation of the $^1E_{3u}$ band[20] of tropenylium ion rather than to cage–ring excitation. The failure of the *o*-carboranyl cage to respond to the strong electron demand of the ring in either the ground or excited state is in marked contrast to the case of tropenyliumyl-substituted borane anions where the ($+I$, $+T$)[21] cage shows extensive donation to the ring in both ground and excited state.[3,4]

Reaction of III with sodium methoxide and treatment of the resulting ether with anhydrous hydrogen bromide affords a quantitative yield of 1-methyl-2-tropenyliumyl-1,2-dicarbaclovododecaborane(12) bromide (IV), pale yellow prisms, mp 103–105° with prior sintering. *Anal.* Calcd for $C_{10}H_{19}B_{10}Br$: C, 36.68; H, 5.85; B, 33.05; Br, 24.41. Found:[10] C, 36.58; H, 6.12; B, 33.21; Br, 24.18. The bromide gives an instantaneous precipitate with alcoholic silver nitrate, and in sulfuric acid shows the ultraviolet spectrum of the cation, λ_{max} 224 nm (ϵ 32,200), 287 (sh), 294 (6350), 302 (sh). It dissolves readily, however, in hydrocarbons, ether, or methylene chloride to give colorless solutions with the spectrum (smooth peak at 286 nm) of a covalent triene; the spectrum in acetonitrile indicates an equilibrium mixture of ion and triene. Such borderline covalency is unique for a monosubstituted tropenylium ion; the destabilization of the ring by the $-I$ effect of the cage would appear to be similar in magnitude to that ob-

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Cleavage of Sulfonamides with Sodium Naphthalene[1]

Sir:

We wish to report that regeneration of amines from many types of sulfonamides can be achieved in excellent yield by treatment with sodium naphthalene anion radical in 1,2-dimethoxyethane solution. The procedure consists simply of mixing either the solid sulfonamide or its solution (in dimethoxyethane) with 3–6 equiv of sodium naphthalene in dimethoxyethane under nitrogen or argon and stirring the resulting solution for ~1 hr at room temperature. Addition of a small amount of water quenches the reaction, and the amine may be isolated by usual procedures. Some typical results are presented in Table I.

The technique is quite similar to that reported earlier for cleavage of toluenesulfonates,[2] but the sulfonamide cleavage appears to proceed slightly better in dimethoxyethane than in tetrahydrofuran solution.[3] Dimethoxyethane does react slowly with sodium naphthalene[4] but the process is slow enough at room temperature that it does not interfere with the cleavage reaction.

From Table I it can be seen that benzene- and *p*-toluenesulfonamides of most simple amines are cleaved in yields of over 90%, but methanesulfonyl derivatives exhibit variable behavior. In particular, it appears that methanesulfonamides of primary or aliphatic amines are inert to the cleavage conditions. Toluenesulfonamides of some simple dipeptides have been cleaved in good yield by this technique (see Table I), and the method may be of use in peptide synthesis. The well-known ease of N-alkylation of sulfonamides of primary amines[5] also makes possible a relatively simple synthesis of a wide variety of pure secondary amines.

Table I. Cleavage of Sulfonamides with Sodium Naphthalene[a]

Sulfonamide (mp, °C)	Yield of amine, %[b,c]	Sulfonamide (mp, °C)	Yield of amine, %[b,c]	Sulfonamide (mp, °C)	Yield of amine, %[b,c]
N-*p*-Tolylbenzene-	99 (86)[d]	N-*p*-Tolyl-*p*-chlorobenzene	89	N-Octylmethane- (56.3–56.6°)[e]	<2[i]
N-Methyl-N-phenylbenzene-	100	N-Methyl-N-phenyl-*p*-chlorobenzene- (95–95.4°)[e]	67	N-*p*-Tolylmethane-	9
N-Octylbenzene- (52.5–53.5°)[e]	97 (65)	N-*p*-Tolyl-*p*-bromobenzene-	89	N-Methanesulfonyl-piperidine (48.5–50°)[e]	0[i]
N-*p*-Tolyl-*p*-toluene- Sodium salt (>300°)[f]	87 (93)[d] 88	N-*p*-Tolyl-*p*-acetamidobenzene-	80	N-Methyl-N-phenylmethane-	92
N-*p*-Anisyl-*p*-toluene-	98 (94)[d]	N-*p*-Tolyl-*p*-methoxybenzene- (109.5–110°)[e]	95 (83)	N,N-Diphenylmethane- (116.5–117°)[e]	94
N-Phenyl-*p*-toluene-	(97)	N-Methyl-N-phenyl-*p*-methoxybenzene- (109–110.3)[e]	92	N-*p*-Toluenesulfonylglycylglycine	87[i]
N-Hexyl-*p*-toluene- (59–60°)[e]	(96)[d]	N-*p*-Tolyl-β-naphthalene-	89 (93)[d]	N-*p*-Toluenesulfonyl-DL-alanyl-DL-leucine[k,l]	95[i]
N-Octyl-*p*-toluene-	98 (95)	N-Methyl-N-phenyl-β-naphthalene- (102–102.6°)[e]	91	N-*p*-Toluenesulfonyl-DL-leucyl-DL-alanine[k,m]	93[i]
N-(2-Heptyl)-*p*-toluene- (oil)[g]	(91)	N-Octyl-α-toluene- (100–101°)[e]	84	N-*p*-Toluenesulfonyl-DL-alanyl-DL-valine (188–190°)[k]	89[i]
N-(1-Phenylethyl)-*p*-toluene- (82–83°)[e]	(98)	N-α-Toluenesulfonylpiperidine (137.5–138°)[e]	62	N-*p*-Toluenesulfonyl-DL-alanyl-DL-phenylalanine (167–168°)[k]	96[i]
N-(*m*-Chlorophenyl)-*p*-toluene-	(94)[h]				
N-Methyl-N-phenyl-*p*-toluene-	96 (68)[d]				
N-*p*-Toluenesulfonylpiperidine	82				

[a] Unless otherwise specified, reactions were carried out by treating sulfonamide with 3–6 equiv of sodium naphthalene in dimethoxyethane at 25° under N_2 or Ar and stirring the mixture for about 1 hr before quenching with water. [b] Determined by gas chromatographic measurement of the amine or corresponding acyl derivative unless otherwise specified. Reproducibility was at least ±5%. [c] Figures in parentheses refer to yields using tetrahydrofuran solvent. [d] Isolated and weighed. [e] New compound; carbon–hydrogen analyses agree with calculated values. [f] Titration required 99.3% of theoretical amount of standard HCl solution. [g] Identity of material based on recovery of 2-heptylamine from cleavage reaction. [h] Product was aniline. [i] Unreacted sulfonamide recovered from reaction mixture. [j] Reactions run for 0.5–1 hr using 20 equiv of sodium naphthalene. Analysis was by ninhydrin colorimetry; identity of product was checked by thin-layer chromatography. [k] Identity of material based on recovery of corresponding dipeptide from cleavage reaction. [l] Ethyl ester: mp 95–98°. [m] Ethyl ester: mp 108–110°.

The only comparable cleavage techniques are those using alkali metal–liquid ammonia (or amine) com-

(1) Supported in part by the National Science Foundation (Grant GP-5658) and by the Public Health Service (Research Grant No. 1-RO1-AM11419-01 from the National Institute of Arthritis and Metabolic Diseases).

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(3) An additional advantage of DME is the greater ease of formation of the anion radical in this solvent. For example, one can carry out the reaction by placing enough sodium, naphthalene, and DME in an erlenmeyer flask to yield a solution 0.5–1.0 *M* in anion radical, capping it with a rubber septum, and stirring it magnetically (glass-covered bar) for 1–1.5 hr. By this time the anion radical will have formed and have scavenged the O_2 from the interior of the flask, and a solution of the sulfonamide may then be injected by syringe through the septum. Quantitative yields of N-methylaniline from its toluenesulfonamide have been obtained in this fashion, and the technique should work equally well for toluenesulfonate ester cleavage.[2] The sodium–naphthalene dispersion (mole/mole, crushed solid), available from the Matheson Co., yields the anion radical even more rapidly on solution in DME, but the homogeneity of this material leaves a bit to be desired.

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