scattering reaching the photomultiplier used for monitoring the transmitted light. Using photon counting, ratios of emissions over references (*E/R*) were electronically recorded and analyzed on a PDP-11 minicomputer. All reported spectra are excitation corrected.

(7) In FDCD, the optically active sample is irradiated by right and left CPL using, typically, a photoelastic modulator (instead of the quarterwave plate). Information is obtained by monitoring the difference in fluorescence intensities for left and right circularly polarized excitation by scanning, usually, the excitation spectrum.[8] In contrast to FDCD, the sample in the present work is excited only at one wavelength (by CPL), and the emission is scanned. We note in passing that none reportedly looked at FDCD for both enantiomers of a given optically active molecule.[9]

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(10) Although optical rotations of D-Trp and L-Trp were found to be identical in methanol and glycerol, fluorescence efficiencies in the latter solvent was 0.6 (compared to 0.2 in methanol). The enhanced fluorescence efficiency in glycerol is the consequence, of course, of the greater viscosity of the solvent and hence the reduction in the overall quenching processes which depopulate the excited state.

(11) R. H. Conrad and L. Brand, *Biochemistry*, **7,** 777 (1968).

(12) T. Förster in "Modern Quantum Chemistry, Part III", O. Sinanoglu, Ed., Academic Press, New York, 1965.

(13) The overlap integrals calculated in the present work agree well with that given in ref 11.

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(15) This effect is related to photoselectivity and the procedure used to calculate *T* values (see footnote *a* in Table II) is unlikely to correct for it. Concentrations of given conformers are, of course, the same for dansyl-D-Trp and dansyl-L-Trp.

(16) Transfer efficiencies are extremely sensitive to intrachromophoric distances (see eq 1 and ref 11). *R* values in given conformers are, of course, the same for dansyl-D-Trp and dansyl-L-Trp.

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Regiochemistry of the Addition of DCl to *trans*-1,3-Pentadiene

Sir:

We report here the first clear evidence on the regiochemistry of addition of a Brønsted acid to a 1,3-diene proceeding through a symmetrically substituted intermediate allylic carbenium ion. The data show a characteristic preference for 1,2 over 1,4 addition and thus reveal the operation of association effects in the mechanism. The results provide a needed basis for the interpretation of related observations involving unsymmetrical ions. They have significance as well to the question of carbocation structure in the addition of acids to norbornene.

Competitive 1,2 and 1,4 additions of electrophilic agents to conjugated dienes have received considerable attention.[1] The fundamental case of reaction of a Brønsted acid with a diene whose protonation should afford a symmetric allylic cation, however, has been addressed previously only once. Hammond and Warkentin[2] in 1961 examined the course of polar addition of DBr to 1,3-cyclohexadiene in pentane. Their results, however, admitted the possibility of dominant interconversions of first-formed products.

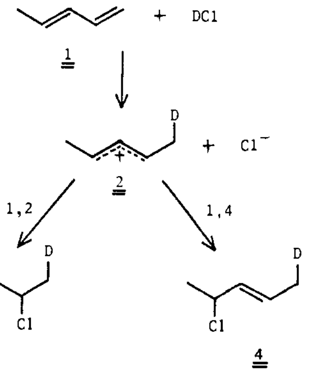
trans-1,3-Pentadiene (**1**) is the prototype of addition substrates parent to allylic ions free per se from electronic and steric bias, as shown in Scheme I. Diene **1** adds DCl in no solvent, pentane, acetic acid-*O-d*, or nitromethane over a range of temperatures to produce mixtures of *trans*-4-chloro-2-pentene-*5-d* (**3**) and -*1-d* (**4**); <4% cis isomers are formed. The reactions were carried out using ~0.75 equiv of DCl (from D_2O and benzoyl[3] or acetyl chloride) and were monitored by ^1H NMR. When addition was determined to be almost complete residual DCl was removed in a stream of dry nitrogen to stabilize the products. The final solutions were colorless, or nearly so, and their NMR spectra indicated yields of **3** + **4** of 90% or better.

Table I. Regiochemistry of DCl Addition to *trans*-1,3-Pentadiene[a]

solvent	temp, °C	% trans products[b]	% 1,2 product (**3**)[c]	% 1,4 product (**4**)[c]
none	−78[d]		75.5	24.5
	0	97.6	72.4	27.6
	25		61.5	38.5
pentene	−78	97.7	77.7	22.3
	0	96.3	68.1	31.9
	25		63.8	36.2
CH_3CO_2D[e]	25[d]	96.8	65.0	35.0
CH_3NO_2	0		71.5	28.5
	25		67.7	32.3

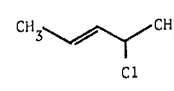
[a] Reactant (ChemSampCo) was 99% trans, 1% cis. [b] By gas chromatographic analysis after reduction of the products to 2-pentenes; remainder was cis. [c] As percentages of the *trans*-chloropentenes, **3** + **4.** [d] Recovered excess diene was found by ^2H NMR to have incorporated no deuterium (<2%). [e] Containing 2% (weight) of acetic anhydride.

Scheme I



Label analysis of the products was conducted initially by complementary 15.4-MHz proton-decoupled ^2H NMR measurements.[4] Following solvent removal at subambient temperature (pentane by distillation at 60 mmHg, acetic acid by neutralization in cold $NaHCO_3$ solution, pentane extraction, and distillation), the spectrum of the chloropentenes was recorded and the partially overlapping deuterium signals were integrated with the aid of a curve resolver.[5] The upfield absorption was assigned to the *5-d* isomer, **3**, from the comparative methyl-group chemical shifts in the ^1H spectra[6] (CCl_4, 60 MHz) of *trans*-4-chloro-2-pentene (**5**) and its dechlorination product, *trans*-2-pentene (**6**). Corroborative data were obtained by prompt reduction of the **3** + **4** mixture with lithium triethylborohydride[7] to *trans*-2-pentene-*5-d* (**7**) and -*1-d* (**8**), respectively, and integration of these isomers' fully separated ^2H NMR signals. Upon the observation of close agreement (±3%) between the analyses of **3** + **4** and **7** + **8** for three reactions, subsequent measurements were made on the olefins, **7** + **8**, alone.[8]

δ:	1.66 (d)	1.52 (d)	1.62 (m)	0.94 (t)
^3J, Hz:	4.7	6.4		7.4



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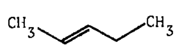

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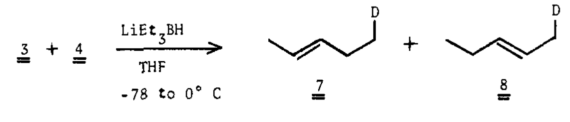
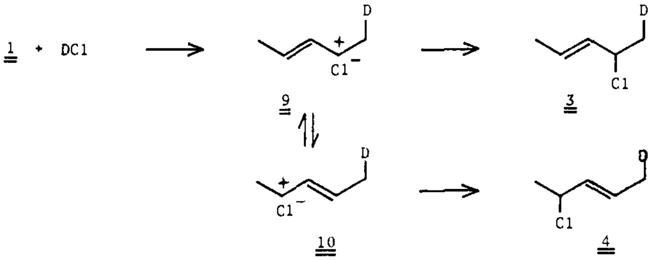


Scheme II

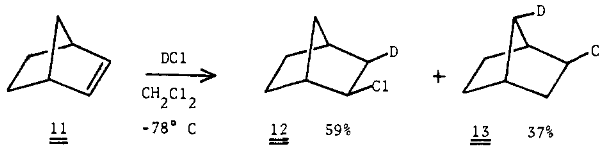


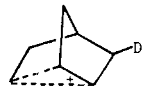
The results of the additions to **1** are presented in Table I. In two reactions, as noted, recovered excess diene was found to have incorporated no deuterium, showing carbenium-ion formation to be irreversible. While the products have been shown to be stable through the analytical procedure, minor incursions of allylic isomerization concurrent with addition cannot be excluded at this point. The significance of the results, however, is clear.

1,2 is seen to predominate over 1,4 addition in all cases, by factors of from 1.6 to 3.5. These reactions thus proceed by a mechanism more complex than that of Scheme I, where a free dimethylallyl cation has equivalent electrophilic centers.

Ion-paired intermediates are indicated.[9] The simplest rationalization of the present findings is that deuteronation of the diene at C-1 occurs from a molecule of undissociated DCl (possibly precomplexed) to give initially a carbenium chloride ion pair, **9**, with the anion (doubtless complexed with another molecule of DCl in nonpolar media[1c]) associated at C-2, as shown in Scheme II. Interconversion with the isomeric ion pair having the chloride opposite C-4, **10**, at a rate not greatly faster than that of covalent collapse would produce **3** in excess of **4**. Partial molecular addition, as suggested for several Brønsted acid additions to olefins,[10,11] could also contribute. A transition state with pronounced carbenium-ion character would be necessary, however, to explain exclusive addition to the less substituted double bond. Studies with *cis*-1,3-pentadiene and 1,3-cyclohexadiene are in progress to provide further information.

The present results furnish a new perspective toward earlier findings on the addition of acids to norbornene (**11**). Stille[11] and Brown[12] and co-workers have found through isotopic labeling that a variety of acids react with norbornene to produce unequal quantities of degenerate Wagner–Meerwein isomers. DCl in CH_2Cl_2 at −78 °C, for example,[12b] gives 59 ± 2% **12** and 37 ± 5% **13** (along with products arising from 6,2-hydride shift). Both authors have taken their data to disqualify a single symmetrically delocalized carbonium ion, **14**, in these reactions, in favor of a pair of interconverting classical ions, **15**, trapped prior to equilibration. We consider this conclusion compromised by the present observation that pentadiene **1** characteristically favors 1,2 addition by way of a cation which by itself is plainly symmetrically delocalized. Deuteronation (protonation) of norbornene to produce a bridged ion unsymmetrically associated with its gegenion, **16**, is as reasonable a pathway for these additions as the corresponding mechanism for **1** through **9**.





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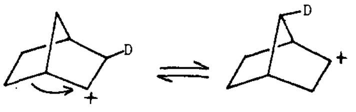

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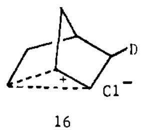

16

Acknowledgment. Support of this work by National Science Foundation Grant CHE75-04284-A02 is gratefully acknowledged.

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(4) Varian XL-100-15 Fourier-transform spectrometer.

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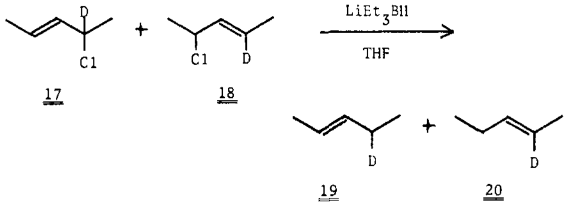
(8) In a further control experiment *trans*-3-penten-2-one was converted via *trans*-3-penten-2-ol-*2-d* to a mixture of 57% *trans*-4-chloro-2-pentene-*4-d* (**17**) and 43% *2-d* isomer (**18**), whose well-separated ^2H NMR signals permitted direct integration. Lithium triethylborohydride reduction gave a mixture of 56% *trans*-2-pentene-*4-d* (**19**) and 44% *trans*-2-pentene-*2-d* (**20**), again by uncomplicated ^2H NMR analysis, confirming clean S_N2 displacement.



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^{13}C NMR Assignment of the Side-Chain Methyls of C_{27} Steroids

Sir:

The ^{13}C NMR spectrum[1] of cholesterol (**1a**) has been analyzed in detail and all signals were assigned unambiguously with the exception of C-26 and C-27. The recent work of Popják[2] who studied samples of ^{13}C-enriched cholesterol obtained biosynthetically from labeled mevalonate completed the interpretation of the spectrum. Their assignments of the terminal methyls are based on the knowledge of the hydroge-

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