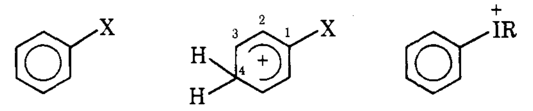
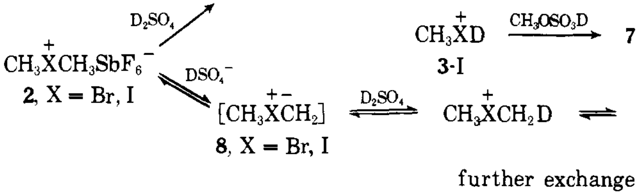
(6-CH_3, Table I). The I-protonated structure 6-H is therefore assigned to this ion; the shielding of C_{ipso} and the deshielding of C_{ortho} in 6-H compared to 6-CH_3 is consistent with the removal of a β- and γ-CH_3 group, respectively.[5] As in the case of 3-I, the proton in 6-H is evidently exchanging rapidly (on the NMR scale) with the excess acid. 6-H does not, however, rearrange to 5-I even when the temperature is raised to −20°.



4, X = Cl, Br, I **5**, X = Cl, Br, I **6**, R = H, CH_3

When the dimethylhalonium ions 2-I, 2-Br, are added (as the stable hexafluorantimonate salt) to sulfuric acid (H_2SO_4), no reaction occurs below 0°, but at 30° dimethyl sulfate (7)[8] is slowly formed. 1-I also reacts with H_2SO_4, and, after 2 hr, spectra of the H_2SO_4 solution indicate the presence of 7[8] and a second species resonating at δ 4.00 (^1H NMR) and δ 1.2 (^{13}C NMR) (cf. 3-I, Table I) and proves the intermediacy of 3-I in the second methylation step from 2-I as shown in the reaction scheme. However, when 2-Br and 2-I are dissolved in D_2SO_4 at 30°, the ^1H NMR spectrum shows that H–D exchange occurs during the course of the reaction.[9] The H–D exchange is considered to have occurred *via* the intermediacy of methylenemethyliodonium (bromium) ylide (8-I, 8-Br). Aryliodonium ylides have previously been studied and even isolated in a number of cases.[10] Attempts to trap 8-I formed under basic conditions have, however, so far proved unsuccessful.[11]



Our results show that alkyl bromides and iodides, indeed can be protonated on the *n*-donor halogen atom to form stable hydridohalonium ions. This observation has direct bearing on the mechanism of Bronsted acid-catalyzed electrophilic alkylation with alkyl halides. The exclusive formation of 6-H from 4-I indicates that iodine is also at least as basic toward protonation as the π-donor benzene ring.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

References and Notes

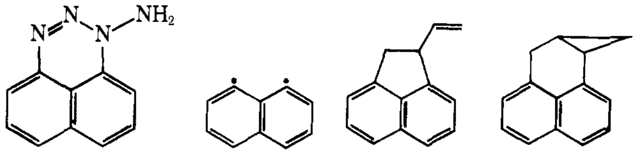
(1) Part XIV. G. A. Olah and Y. Yamada, *J. Org. Chem.*, in press.
(2) G. A. Olah, "Organic Halonium Ions," Wiley-Interscience, New York, N.Y., in press.
(3) G. A. Olah, J. R. DeMember, Y. K. Mo, J. J. Svoboda, P. Schilling, and J. A. Olah, *J. Am. Chem. Soc*, **96**, 884 (1974); G. A. Olah and J. J. Svoboda, *Synthesis*, 203 (1973).
(4) Spectra as reported previously: G. A. Olah, P. W. Westerman, E. G. Melby, and Y. K. Mo, *J. Am. Chem. Soc.*, **96**, 3565 (1974), and ref 3.
(5) J. B. Stothers, "Carbon-13 Nmr Spectroscopy," Academic Press, New York, N.Y., 1972, Chapter 3.
(6) The inability to observe $^3J_{HH}$ and $^2J_{CH}$ splittings in 3-I is probably due to rapid proton exchange with the HSO_3F–SbF_5, which resonates as an unusually broad ($W_{1/2}$ = 0.25 ppm) absorption at δ 11–11.5. This exchange is not slowed even at −105°.
(7) Fluorobenzene has previously been reported to yield the *p*-fluorobenzenium ion (5-F) under similar conditions: G. A. Olah and T. E. Klovsky, *J. Am. Chem. Soc.*, **89**, 5692 (1967).
(8) ^1H NMR δ 4.67; ^{13}C NMR δ 62.0: confirmed by comparison with an authentic sample of 7 in H_2SO_4.
(9) Indicated by the appearance and continued increase of the $HDSO_4$ resonance, δ 11.0, during the reaction. Attempts to detect H–D exchange in 2-Br by quenching the reactions have not been successful.
(10) D. Prikale and O. Neilands, *Zh. Org. Khim*, **6**, 2509 (1970), cf. *Chem. Abstr.* **76** 58766 (1971), and earlier references cited therein; Y. Hayashi, T. Okada, and M. Kawanisi, *Bull Soc. Chem. Jpn.*, **43**, 2506 (1970); W. A. Sheppard and O. W. Webster, *J. Am. Chem. Soc.*, **95**, 2695 (1973); see also ref 2.
(11) 4-*tert*-Butylcyclohexanone gave no products corresponding to oxirane formation and was recovered unchanged under a variety of conditons. cf. E. J. Corey, and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1355 (1965).
(12) Postdoctoral Research Associates.

George A. Olah,* Yorinobu Yamada,[12] Robert J. Spear[12]
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106
Received November 14, 1974

1,2- and 1,3-Addition of 1,8-Dehydronaphthalene to Conjugated Acyclic Dienes

Sir:

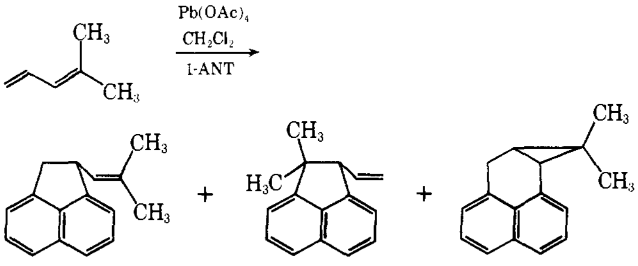
Recently we reported that the addition of "1,8-dehydronaphthalene" (2)[1] to cyclopentadiene gave a bridged 1,3-adduct as well as 1,2- and 1,4-adducts.[2] This unanticipated result led us to examine the addition of 2 to some acyclic, conjugated dienes, which would not be restricted to an s-cis conformation. In an exploratory experiment, lead tetraacetate oxidation of 1-aminonaphtho[1,8-*de*]triazene (1-ANT, 1)[1] in a methylene chloride solution of butadiene afforded two 1:1 adducts (ca. 10% yield), identified as vinylacenaphthene (3, 43%) and naphtho[1′,8′]bicyclo[4.1.0]hept-2-ene (4, 52%).[3] The structure of 4 was confirmed by independent synthesis from phenalene[4,5] using the Harrison version of the Simmons-Smith reaction.[6,7]



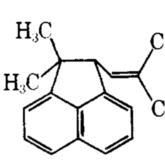
1 2 3 4

The possibility of 1,3-addition to an acyclic diene is thus established. In the remainder of this paper we would like to present the results of our studies of reactions with alkyl substituted dienes, which serve to delineate the regioselectivity of these reactions and which suggest that these two modes of addition utilize substantially different mechanisms.

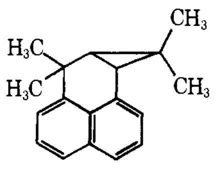
With 4-methyl-1,3-pentadiene (eq 1), 1,2-addition occurred preferentially but not exclusively at the less substituted double bond, while 1,3-addition seemed to produce only the adduct corresponding to attack by 2 (or its equivalent) at the less substituted end of the diene. (The analogous reaction of 2,5-dimethyl-2,4-hexadiene, carried out chiefly to obtain PMR chemical shift values for the methyl groups, gave 8 and 9 in the relative amounts indicated below.)



5 (23%) 6 (4%) 7 (72%) (1)

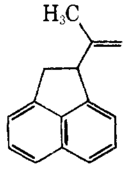


8 (74%)

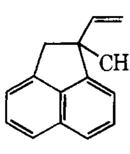


9 (19%)

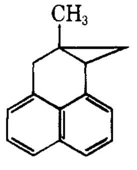
Regioselectivity similar to that shown in eq 1 was also observed with 2-methylbutadiene. 1,2-Addition was again favored at the less substituted double bond, and the only 1,3-adduct found was 6-methylnaphtho[1′,8′]bicyclo[4.1.0]hept-2-ene (**12**), whose structure was confirmed by synthesis from 2-methylphenalene.[6-8] Diene **13** was isolated as a minor product. The reaction of **2** with 2,3-dimethylbutadiene also yielded a dienic adduct (**16**) along with the expected products (**14** and **15**). The formation of dienes **13** and **16** can be considered to occur via a hydrogen atom transfer reaction in an initially formed diradical intermediate (eq 2).



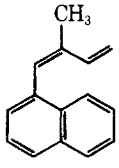
10 (18%)



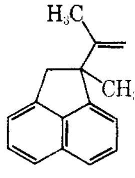
11 (10%)



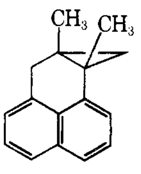
12 (68%)



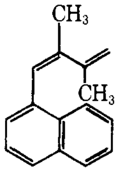
13 (4%)



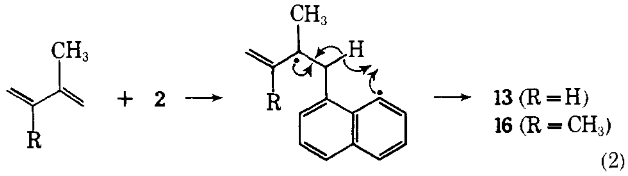
14 (46%)



15 (26%)

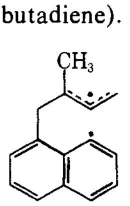


16 (28%)

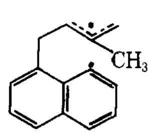


(2)

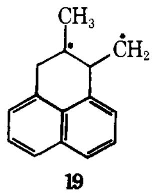
Since 1,2-additions are favored at the less substituted double bond of a diene, a concerted process which does not involve an intermediate diradical (and which does not reflect the ability of substituents to stabilize such a species) is implied. Singlet 1,8-dehydronaphthalene might well be the attacking reagent. On the other hand, the selectivity of the 1,3-additions can be rationalized best on the basis of a stepwise process, involving the formation of a single bond at one end of the diene to give the more stable of the two possible diradical intermediates (e.g., **17** rather than **18** from 2-methyl-1,3-butadiene). If a species such as **17** were produced by attack of triplet 1,8-dehydronaphthalene on 2-methyl-1,3-butadiene, it might then proceed to form a new diradical (**19**) by bonding of the aryl radical site to the central atom in the allylic system, since formation of a five- or seven-membered ring would be unlikely for triplet **17**. Finally, collapse of **19** to the corresponding cyclopropane would give the observed 1,3-adduct. The important feature of this hypothesis for 1,3-addition is that, in contrast to the 1,2-addition, it involves a stepwise process. It should be noted that instead of triplet 1,8-dehydronaphthalene, some other (nitrogen- or lead-containing) reactive intermediate which could bond selectively to one end of the diene might be involved. Further work to elucidate the many questions raised by these reactions is now in progress.



17



18



19

Acknowledgment. The partial support of this research by a grant from the National Science Foundation (GP-40351X) is acknowledged with pleasure.

References and Notes

(1) C. W. Rees and R. C. Storr, *J. Chem. Soc. C*, 765 (1969).
(2) J. Meinwald and G. W. Gruber, *J. Am. Chem. Soc.*, **93**, 3802 (1971).
(3) Each product mixture was purified by chromatography on basic alumina, followed by separation of the products using preparative GLPC. All products were shown to be stable under the separation and purification conditions. Yields of individual products throughout this paper are expressed as percentages of the total monomeric hydrocarbon fraction isolated. Structural and stereochemical assignments for new compounds are based chiefly on mass spectra, 60-MHz ^{1}H NMR spectra, and infrared spectra.
(4) R. M. Pagni and C. R. Watson, *Tetrahedron Lett.*, 59 (1973).
(5) R. M. Pagni and C. R. Watson, *Tetrahedron*, **29**, 3807 (1973).
(6) H. E. Simmons, T. L. Cairns, S. A. Vladuchick, and C. M. Hoiness, *Org. React.*, **20**, 1 (1973).
(7) I. T. Harrison and R. J. Rawson, *J. Org. Chem.*, **35**, 2057 (1970).
(8) V. Boekelheide and C. E. Larrabee, *J. Am. Chem. Soc.*, **72**, 1240 (1950).

J. Meinwald,* L. V. Dunkerton, G. W. Gruber
Spencer T. Olin Laboratory
Department of Chemistry, Cornell University
Ithaca, New York 14853
Received October 7, 1974

Concerning the Oxygen Electrodes in Nitrate Melts

Sir:

In nitrate melts, nitronium ion, NO_2^+, has often been assumed as an intermediate to explain kinetic processes[1] as well as nitration reactions of aromatic organic compounds.[2-4] It was generally thought that there should be an equilibrium of the sort, $NO_3^- = NO_2^+ + O^{2-}$, quite analogous to the dissociation of water. As a result, the first "oxide ion" electrode in nitrate melts was reported by Kust and Duke,[5] and subsequent publications[6-10] have confirmed that this electrode responds to Lux-Flood acids and bases yielding Nernst slopes which correspond to a two-electron process, $O^{2-} = \frac{1}{2}O_2 + 2e^-$.

Later, however, Zambonin and Jordan[11] reported that addition of O^{2-} to nitrate melts resulted in its oxidation by nitrate to peroxide and superoxide if the melt is free of acidic species such as silica and water. They therefore questioned the validity of the oxide ion electrode first proposed by Kust and Duke. Subsequently, Zambonin and his colleagues[12] have shown that oxide ion cannot exist in nitrate melts in any appreciable concentration, and that the "true" oxygen electrode is one which responds to the redox couple, $O_2^- = O_2 + e^-$, having a Nernst slope which corresponds to a one-electron transfer.