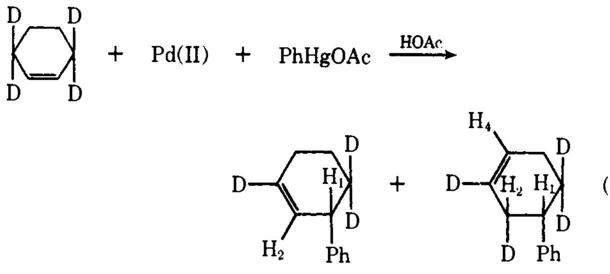
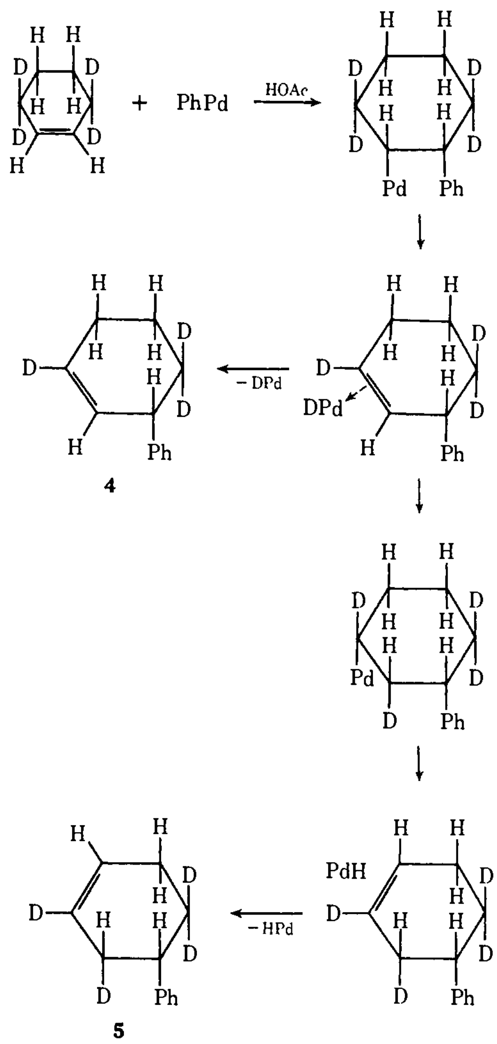


4 5

and H_2 appear at approximately 3.4 and 5.7 ppm, respectively.[8] H_1 in **5** appears at δ ~2.8 ppm and H_4 at δ ~5.8 ppm.[9] At 25°, the temperature at which most of the spectra were run, deuterium coupling broadened the H_1 signal in compound **5** to such an extent that $J_{1,2}$ could not be determined. However, upon cooling to − 60°, the H–D coupling was reduced due to quadrupolar effects,[10] and the signal became a doublet with $J_{1,2} = 3.0 \pm 0.5$ Hz. This value is clearly in the range of a cis coupling constant,[11] indicating H_1 and H_2 have cis stereochemistry.

The structure of **5** is consistent with Scheme I if phenylpalladation has cis stereochemistry. It is inconsistent with trans palladium(II) hydride elimination–readdition or concerted 1,2 shifts unless the rather unreasonable postulate is made that acetoxypalladation is cis and phenylpalladation is trans. The formation of **4** and **5** would thus proceed as shown in Scheme II.

Scheme II



The fact that the allylic product consists entirely of **4** rather then containing some of its allylic isomer[8] indicates that symmetrical intermediates such as π-allylic complexes are not intermediates. In the $Pd(OAc)_2$ oxidation the allylic acetates consisted of a 1:1 mixture of the two possible allylic isomers indicating the intermediacy of symmetrical intermediates.[3] However, the two systems would be expected to have considerable differences since phenylpalladium contains Pd(II)–carbon bonds while the acetate system does not.

In conclusion, no matter what the absolute stereochemistry, the addition of the elements of Pd(II) and acetate across double bonds must have different stereochemistry from that of the addition of phenylpalladium across double bonds. This result supports the earlier contention[2] that addition of nucleophiles and palladium(II) across double bonds can have either cis or trans stereochemistry depending on the nature of the nucleophile. The most important factor is probably the ability of the nucleophile to coordinate to palladium(II) prior to addition.

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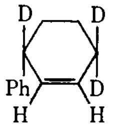
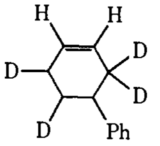
(8) All CH_2 and CDH protons in both **4** and **5** have δ 1.3 to 2.4 ppm. Area measurements indicate that less than 10% of the allylic isomer of **4**, i, is present.



i

(9) The areas of H_1 and H_4 in **5** were the same to within 10% so large amounts of the other possible homoallylic isomer, ii, cannot be present.



ii

(10) C. Brevard, J. P. Kintzinger, and J. M. Lehn, *Chem. Commun.*, 1193 (1969).

(11) H. Booth, *Progr. Nucl. Magn. Resonance Spectrosc.*, **5**, 149 (1969).

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On the Structure of Protonated Ethylene

Sir:

In the light of the considerable interest in recent literature in the structure of the ethyl cation, $C_2H_5^+$,[1]

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(1) R. Sustman, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969); J. E. Williams, V. Buss, L. C. Allen, P. von R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **92**, 2141 (1970); G. V. Pfeiffer and J. G. Jewett, *ibid.*, **92**, 2143 (1970); W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, **93**, 808 (1971).

we would like to report some findings which seem to have considerable bearing on this problem.

In recent work on the ion cyclotron resonance (icr) spectra of a series of dialkyl-*N*-nitrosamines, we have observed the formation of the corresponding alkyl fragments and the subsequent ion molecule reaction in which the alkyl ion transfers a proton to the neutral nitrosamine.[2] In particular, we have observed that the ion $C_2H_5^+$ is formed by fragmentation from diethyl-*N*-nitrosamine molecular ion. The ion in turn, as shown by double resonance, transfers a proton to the parent compound to form its conjugate acid. Since the ion $C_2H_5^+$ may be considered as the conjugate acid of ethylene, we have here a ready way of producing this conjugate acid at low energies, and may be able to obtain information about the structure.

In connection with the work on the dialkylnitrosamines, we had occasion to prepare diethyl-*N*-nitrosamine-d_6, *i.e.*, the compound in which the primary carbon atoms are fully deuterated. In the icr, this compound gives the fragment $C_2D_3H_2^+$. Again using double resonance techniques, we have found that this ion is a precursor to an ion of mass 110 which is the deuterated conjugate acid of the parent, while no 109 arises directly from the ion of mass 32. Actually in single resonance, the ion of mass 109, *i.e.*, the proton conjugate acid, is extremely weak. This finding then clearly indicates that $C_2D_3H_2^+$ transfers exclusively deuterons and no protons. This finding may be interpreted in either of two ways. Either the conjugate acid of ethylene in the gas phase exists as a localized ion CD_3-CH_2^+ without any exchange between the various hydrogens, or it exists as a bridged ion in which the bridge is formed from one of the deuterons of the originally saturated carbon, and there is no subsequent exchange of bridging hydrogens with simple σ-bonded hydrogens. Although the latter alternative cannot be excluded by the data here reported, it seems highly improbable.

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(2) S. Billets, H. H. Jaffé, and F. Kaplan, *J. Amer. Chem. Soc.*, **92**, 6964 (1970); S. Billets, Ph.D. Dissertation, University of Cincinnati, Cincinnati, Ohio, 1971; S. Billets, H. H. Jaffé, and F. Kaplan, manuscript in preparation.

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Photochemical Reaction of Bridged Cyclohepta-3,5-dienone Systems[1]

Sir:

The photodecarbonylations,[2] as well as the thermally induced decarbonylations,[3] of cyclic unsaturated ketones are intriguing problems from experimental and theoretical points of view.[4] For instance, cyclohepta-3,5-dienone, upon irradiation, gives rise to a cheletropic decarbonylation[5] in addition to a cyclization,[6] whereas its 2,2,7,7-tetramethyl derivative shows substantially different photobehavior.[7] In connection with these facts, we have studied the photoreaction of the bridged cyclohepta-3,5-dienones such as I and II,[8] and found not only the first example of photodimerization in this system,[9] but also a clue to the synthesis of the $C_{11}H_{12}$ and $C_{12}H_{14}$ hydrocarbons.[10] We wish to report preliminary results and, in addition, to outline the complexity of the reaction path observed.

When an ethereal solution of I (5.7×10^{-3} *M*) was irradiated using a Rayonet photoreactor (350 nm) in the presence of phenanthrene (1.7×10^{-2} *M*) as a sensitizer, a photodimer, III, mp 201–202°,[11] was obtained in quantitative yield. The spectral data of III are as follows: ir (KBr) 1706 cm^{-1}; uv (MeOH), only end absorption; *m/e*, 172; nmr (τ, $CDCl_3$) 4.18 and 4.60 (8 H, broad singlet and broad doublet, olefinic protons), 7.02–7.63 (12 H, multiplets, methine protons), and 8.22 and 8.69 (4 H, doublet and multiplet, methylene protons). On catalytic hydrogenation over 10% Pd/C, III took up 4 mol equiv of hydrogen to give an octahydro compound IV, mp 177–178°; *m/e* 352.

The irradiation of II, in the same manner, afforded a photodimer V, mp 253°, which, on catalytic hydrogenation, gave an octahydro compound VI, mp 184–185°. The spectral data of V and VI are analogous to those of III and IV. The structure of the dimers III and V could be elucidated by application of the decoupling technique in 100-MHz nmr spectroscopy.[12] In addition, the fact that these dimers are considerably stable to heat may support the $_\pi2 + _\pi2$ type dimer.

When the irradiation of I was carried out in *n*-hexane (5.7×10^{-3} *M*) without the sensitizer using a Rayonet photoreactor (300 nm), a $C_{11}H_{12}$ hydrocarbon (VII) and a ketone (IX) isomeric to I, both oils, were obtained in

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(1) Organic Photochemistry. XX. Part XIX: M. Kimura and T. Mukai, *Sci. Rep. Tohoku Univ., Ser. 1*, **53**, 91 (1970).

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(3) (a) M. A. Battiste, *Chem. Ind. (London)*, 550 (1961); (b) J. M. Landesberg and J. Sieczkowski, *J. Amer. Chem. Soc.*, **91**, 2120 (1969); (c) J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966); (d) T. Mukai, T. Nakazawa, and T. Shishido, *Tetrahedron Lett.*, 2465 (1967); (e) R. McCulloch, A. R. Rye, and D. Wege, *ibid.*, 5231 (1969).

(4) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(5) (a) O. L. Chapmann and G. W. Borden, *J. Org. Chem.*, **26**, 4185 (1961); (b) O. L. Chapmann, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962).

(6) D. I. Schuster, B. R. Sckolnick, and F.-T. H. Lee, *ibid.*, **90**, 1300 (1968).

(7) L. A. Paquette, R. F. Eizember, and O. Cox, *ibid.*, 90, 5153 (1968).

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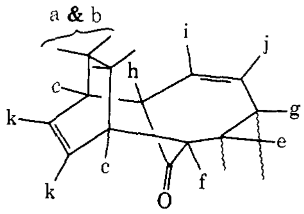
(9) Some derivatives in the bicyclo[4.2.1]nona-2,4-diene and 2,4,6-triene system, upon irradiation, afforded dimers resulting from $_\pi2 + _\pi2$ type cycloaddition: *cf.* D. Bellus, G. Helferich, and C. D. Weis, *Helv. Chim. Acta*, **54**, 463 (1971); A. G. Anastassiou and R. M. Lazarus, *Chem. Commun.*, 373 (1970).

(10) These cyclic polyenes, upon heating or irradiation, exhibit interesting behavior. Y. Akasaki and T. Mukai will soon report the results elsewhere.

(11) Satisfactory elemental analyses were obtained for all new compounds.

(12) As a typical example, chemical shifts and coupling constants of protons of V are presented here (τ, $CDCl_3$): H_a and/or H_b, 8.60 and 7.09; H_c, 7.42; H_e, 7.74; H_f, 7.26; H_g, 6.95; H_h 6.56, H_i, 4.56; H_j, 4.23 and H_k, 3.75; *J*, in hertz: $H_{e-f} = 6.8$; $H_{c-h} = 7.0$; $H_{e-g} = 7.0$; $H_{g-j} = 3.0$; $H_{h-i} = 8.0$; $H_{i-j} = 12.0$. However, its stereochemistry is still in ambiguity.



V