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).

[2] (a) K. Mislow and A. J. Gordon, *J. Amer. Chem. Soc.*, **85**, 3521 (1963); (b) T. Miwa, M. Kato, and T. Tamano, *Tetrahedron Lett.*, 1761 (1969); (c) T. Mukai and K. Kurabayashi, *J. Amer. Chem. Soc.*, **92**, 4493 (1970).

[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).

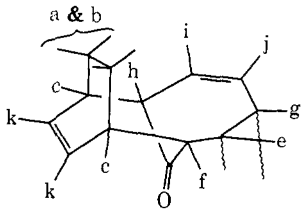
[8] (a) R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Commun.*, 15 (1966); (b) S. Ito, Y. Fujise, T. Okuda, and Y. Inoue, *Bull. Chem. Soc. Jap.*, **39**, 1351 (1966); (c) T. Nozoe, T. Mukai, K. Takase, and T. Nagase, *Proc. Jap. Acad.*, **28**, 477 (1952).

[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).

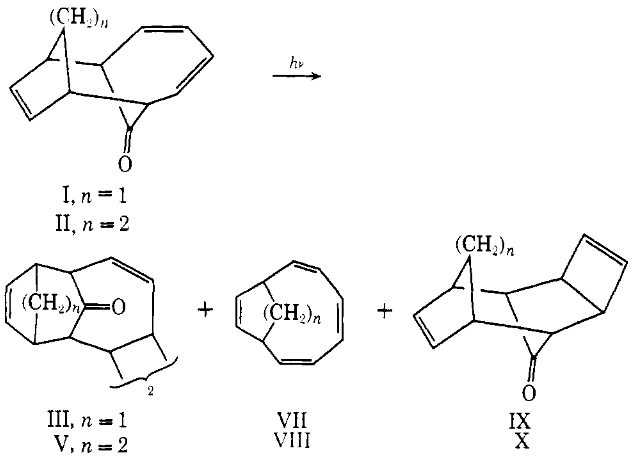
[10] These cyclic polyenes, upon heating or irradiation, exhibit interesting behavior. Y. Akasaki and T. Mukai will soon report the results elsewhere.

[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_{e-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



I, $n = 1$
II, $n = 2$

III, $n = 1$
V, $n = 2$

VII
VIII

IX
X

25 and 15% yields accompanied by 11% of dimer III.[13] The spectral properties of VII and IX are as follows: ir, VII, no carbonyl; IX, 1740 cm^{-1}; uv max (cyclohexane) (log ϵ) VII, 242 nm (3.20); IX, 239 (sh 2.88), 259 (sh 2.56), and 270 nm (2.45); *m/e*, VII, 144; IX, 172; nmr (τ, CDCl$_3$) VII, 4.35 (8 H, multiplet, olefinic protons), 6.82 (2 H, multiplet, methine protons), and 7.78 (2 H, AB protons of ABX$_2$ system); IX, 3.62 and 3.67 (4 H, singlet and doublet, olefinic protons), 6.80–7.80 (6 H, doublet and two double doublets, methine protons), and 5.87 and 8.91 (2 H, doublet and double triplet, methylene protons).[14]

A similar irradiation of II afforded $C_{12}H_{14}$ hydrocarbon VIII, an oil, and ketone X, mp 143–144°, in 10 and 32% yields, respectively. The spectral data of these photoproducts are analogous to those of VII and IX.

When a benzene solution of I was irradiated with light of 350 nm (Rayonet) in the presence of benzophenone or fluorenone, the yield of the dimer III was increased, whereas no hydrocarbon VII was formed. In addition, on irradiation of I (with 300-nm light), the formation of VII and IX was not affected by the presence of piperylene.[15] These results, coupled with the phenanthrene sensitization, indicate that the dimerization of I arises from the triplet state and the decarbonylation and a valence isomerization leading to VII and IX proceed *via* the singlet state.[16]

It has been reported that, in the photoreaction of cyclohepta-3,5-dienone (XI), the decarbonylation arose from the $n-\pi^*$ singlet state, and the formation of bicyclo[3.2.0]hept-6-en-3-one (XII) from the $\pi-\pi^*$ triplet state.[6] On the other hand, 2,2,7,7-tetramethylcyclohepta-3,5-dienone (XIII), on irradiation, afforded only 3-methyl-4-caren-2-one probably *via* the triplet state.[7] No occurrence of the photodecarbonylation in XIII was ascribed to a secondary steric effect of the four methyl groups which prevents the formation of a planar transition state for extrusion of carbon monooxide. The occurrence of the photodecarbonylation in rigid systems such as I and II seems to be compatible with the explanation, which is based on the steric effect of the substituents, because such a transition state is brought less sterically in I or II than in XIII. The formation of XII from XI was suggested to be the photochemical conversion to *cis,-trans*-cyclohepta-3,5-dienone followed by conrotatory thermal cyclization.[17] The kind of isomerization of the carbon–carbon double bond seems to be difficult in a rigid system such as I and II. This steric demand may be related to the reason why the formation of the valence isomer IX arises from the singlet state, this being similar to the case of simple cisoid butadiene[18] but different from that of the formation of XII from the triplet state of XI. In addition, it should be noted that, in the case of XI, each reaction ascribed to the singlet or triplet state took place *separately* and led to different products,[6] whereas the compounds I and II, under direct irradiation, exhibited both reactions due to the singlet and triplet states *simultaneously*. This difference seems to originate from the different behaviors of the lowest singlet states between flexible dienone XI and the rigid dienones I and II. Schuster, *et al.*,[6] pointed out that the lowest singlet of XI may have a great deal of the characteristics of a diene singlet state, as a result of the interaction of π systems between carbonyl and diene, which would account for the low efficiency of intersystem crossing.[19] On the other hand, such mixing may decrease in the rigid molecules of I and II because the transition moment of the carbonyl group is deviated from that of the diene system. Therefore, ketones I and II exhibit the photobehavior of usual carbonyl compounds in which the intersystem crossing was not so retarded as in XI that triplet state energy of the carbonyl group transfers to the diene system. Consequently the photoreaction of the triplet state of I, that is, the formation of III, would take place competitively with the formation of VII and IX arising from the $n-\pi^*$ and $\pi-\pi^*$ singlet state of I.[21]

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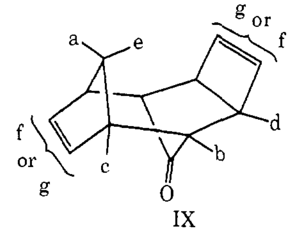
(13) When the irradiation of I was carried out in a more concentrated solution (4.7×10^{-2} *M*) under the same condition, the yield of III was increased (77%) and the yields of VII and IX were decreased (1 and 3%, respectively).

(14) Chemical shifts and coupling constants of protons of the ketone IX could be determined as follows by application of the decoupling technique (τ, CDCl$_3$): H_a, 8.91; H_b, 7.80; H_c, 7.09; H_d, 6.80; H_e, 5.87; H_f and/or H_g, 3.67 and 3.62; *J* in hertz: $H_{a-c} = 4.0$; $H_{a-e} = 11.0$; $H_{b-c} = 5.5$; $H_{b-d} = 7.5$; and $H_{e-c} = 0$.



IX

Although four stereoisomers are possible for the ketone IX, the structure shown here can be selected as most preferable because its observed coupling constants better fit to the dihedral angles between H_a-H_c (50°), H_b-H_c (40°), H_b-H_d (20°), and H_c-H_e (90°) which can be measured from the Dreiding model. In addition, appearance of the H_e signal at very low field should be noticed. This is to be ascribed to the unique compression effect of a double bond located very near, which will be discussed in detail elsewhere by T. Uehara (Ph.D. Thesis of Tohoku University, 1970, under Professor Kitahara's supervision).

(15) Because of no satisfactory method for analysis of a mixture of I, III, VII, and IX, especially in the presence of sensitizer or quencher, an accurate estimation of the ratio of the photoproducts has not been made.

(16) The fact that the formation of IX arises from the singlet state of I was added when revisions were requested by a referee.

(17) R. S. H. Liu, *J. Amer. Chem. Sc*[illegible], [illegible], 112 (1967).

(18) R. Srinivasan and F. I. Sonnta *ibid.*, **87**, 3778 (1965).

(19) There are the following differences of uv maxima between I and XI: I in methanol, (ϵ) 238 (2840), 248 (3307), 257 (4520), 266 (4630), and 300 nm (480);[8] XI in ether, 213 (log ϵ 3.77), 352.5 (ϵ 5.90), 372.5 nm (ϵ 4.57).[20]

(20) D. I. Schuster, B. R. Sckolnick, and F.-T. H. Lee, *J. Amer. Chem. Soc.*, **90**, 3299 (1968).

(21) A referee has suggested that a low rate for decarbonylation from the singlet state of I may be ascribed to disadvantageous requirement for axisymmetric fragmentation in I compared with XI. The authors cannot agree on this suggestion.

Acknowledgment. We are indebted to Mr. K. Kurabayashi for his help in some experiments. Financial support from Sankyo Co. is also acknowledged.

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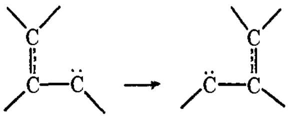
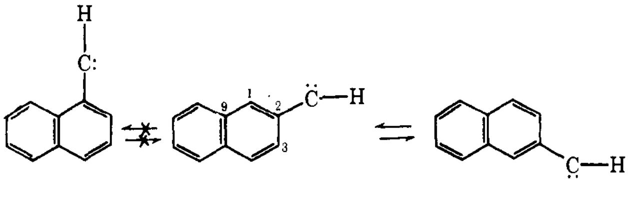
Carbene–Carbene Rearrangements. Importance of Bond Order

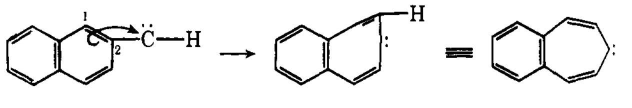
Sir:

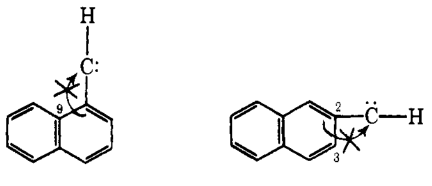
Carbene–carbene rearrangements[1] differ from carbonium ion, carbanion, and free-radical rearrangements in that the overall reaction requires cleavage of a bond with significant double bond character.[6]



In an attempt to assess the importance of bond order in this rearrangement, we have now studied the gas-phase[2] carbene–carbene rearrangement of a series of substituted naphthylcarbenes and report here our finding that scrambling of the carbene occurs *only* between positions 2 and 3 with none occurring between positions 1 and 2. These results point to facile net cleavage of the bond of highest bond order (the 1,2 bond)[9] with initial rearrangement of C-1 from C-2 to the carbene center. We found no evidence of rearrangement of either C-9 from C-1 to the carbene center or C-3 from C-2 to the carbene center.







As in a number of other studies of carbene–carbene rearrangements,[3] a methyl group was used as an internal trap for rearranged carbene (actually two rearrangements) with formation of vinylnaphthalene as proof that rearrangement had occurred.

To illustrate the method used, consider the rearrangement of 3-methyl-2-naphthylcarbene (**1**). Migration of C-1 from C-2 to the carbene center on C-2 (cleavage of a 1,2-double bond)[10] would give cycloheptatrienylidene (**2**) which, by further rearrangement would give methylnaphthylcarbene (**3**). This should undergo rapid rearrangement to 2-vinylnaphthalene. On the other

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[1] To date, carbene–carbene rearrangements have been reported in benzenoid (carbocyclic[2,3] and heterocyclic[4]), tropylium,[2] and carbonylcarbene[5] systems. Other nonaromatic multiple bond carbenes are currently under investigation.

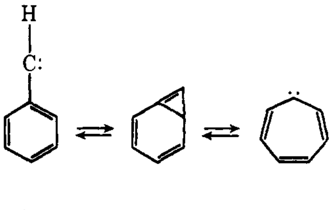
[2] R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969); J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970); and references cited therein.

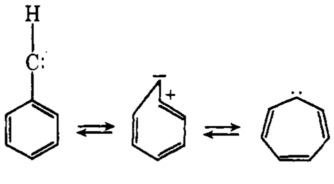
[3] G. G. Vander Stouw, *Diss. Abstr.*, **25** (12), 6974 (1965); *Chem. Abstr.*, 63, 13126b (1965), under the direction of H. Shechter; P. O. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *J. Amer. Chem. Soc.*, **92**, 2147 (1970); E. Hedaya and M. E. Kent, *ibid.*, **93**, 3283 (1971); W. J. Baron, M. Jones, Jr., and P. P. Gaspar, *ibid.*, **92**, 4739 (1970); C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970).

[4] C. Wentrup, *Tetrahedron*, **27**, 367 (1970); C. Wentrup and W. D. Crow, *ibid.*, **27**, 361 (1971); and references cited therein.

[5] G. Frater and O. P. Strausz, *J. Amer. Chem. Soc.*, **92**, 6654 (1970), and previous references; R. L. Russell and F. S. Rowland, *ibid.*, **92**, 7508 (1970).

[6] Carbene–carbene rearrangements in cyclic conjugated systems[2–4] can be visualized as occurring by at least three different mechanisms, all of which have been alluded to for nitrene–carbene rearrangements.[4] In one case, rearrangement takes the form of a simple closure of a vinylcarbene to a cyclopropene[7] followed by or concomitant with ring opening to give the new carbene. This mechanism which has been assumed by most authors[2,3] and which probably takes place from an orientation of the vinylcarbene in which the vacant orbital is conjugated with the π system[7,8] (although to date, there is no firm evidence for this) would be favored by high double bond character. Another mechanism which is intuitively less attractive for carbocyclic systems than for heterocyclic analogs[4] takes the form of a Wolff rearrangement in which the vacant orbital of the carbene is presumably[8] orthogonal to the π system and therefore properly oriented for migration of a σ bond. This mechanism, which is limited to cyclic conjugated systems, would lead to, or take place from, an intermediate zwitterion and should be favored by low double bond character. Finally, rearrangement could occur by ring opening to a diradical followed by closure to a cyclic allene which can give the carbene.





[7] G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 99 (1963), and references cited therein.

[8] R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *ibid.*, **90**, 1485 (1968).

[9] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N.Y., 1961.

[10] A Wolff type of rearrangement of C-3 of carbene **1** with cleavage of a 2,3-single bond would give a zwitterion ion which could undergo futher rearrangement to carbene **5**, while retaining the benzenoid aromaticity.