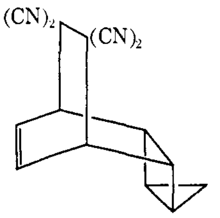
2 H, H_E), 8.14 (m, 2 H, H_D), 8.78 (m, 2 H, H_C), 9.20 (m, 2 H, H_A, H_B)].

When **1** reacts with tetracyanoethylene (TCNE) the nature of the adduct depends on the experimental conditions. Addition of a solution of TCNE in toluene to an equimolar solution of **1**, followed by subsequent heating at reflux, gave a 1:1 adduct (70%, mp 262–263° dec), assigned the structure of **8** from its physical properties. Addition of **1** in THF to an excess of TCNE in THF, followed by heating to reflux for 48 hr, gave, after purification, the adduct **9** (75%, mp 141–141.5°), identical with that previously reported.[14] The mass spectrum (*m/e* 246) confirmed that **9** was a 1:1 adduct, and the fragmentation pattern differed from those found for the adducts **4** and **8**. These latter adducts had the base peak at *m/e* 66, ($C_5H_6^+$) whereas the base peak in the mass spectrum of **9** is at *m/e* 117 ($C_9H_9^+$). The nmr spectrum (100 MHz, acetone-d_6) shows resonance signals at τ 3.63 (dd, 1 H), 3.9–4.4 (m, 5 H), 5.61 (m, 1 H, H_A or H_B), 6.27 (m, 1 H, H_A or H_B), and 7.30 (dd, 2 H, H_C), indicating that **9** is bicyclic. Irradiation at the frequency of the τ 5.61 signal removes the major coupling (J = 10 Hz) of the τ 6.27 signal (and *vice versa*). Irradiation at the frequency of the signal at *ca.* τ 4.0 causes the high-field double doublet at τ 7.30 to collapse to a broad singlet. The olefinic region is significantly further resolved at 220 MHz, the band at τ 3.9–4.4 now appearing as two multiplets at τ 3.88–4.11 (3 H) and τ 4.16–4.34 (2 H), and the observation was made that the spectrum is temperature dependent.[15] The nmr spectrum of the corresponding adduct from 9,9-dideuteriobicyclo[6.1.0]nonatriene shows the absence of the τ 7.30 signals, and a modified olefinic region.

The structure **9** is in accord with the nmr spectral evidence, although the large chemical shift difference of the bridgehead protons was unexpected.[16] The uv spectrum of **9** shows only end absorption and a shoulder at 230 nm,[14] and is also consistent with the diene structure. The temperature dependence of the spectrum reflects the conformational mobility of the nine-membered ring. Attempted catalytic hydrogenation of **9** (Pt$_2$O, HOAc) led to the slow uptake of more than the theoretical amount of hydrogen, and gave a complex mixture of products.[17] The compound **9** appears to be thermally stable but is extremely labile to photoirradiation.[18]



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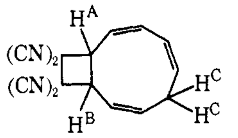

9

The main pathway for dienophile addition to *cis*-bicyclo[6.1.0]nonatriene is *via* the tricyclic tautomer **2**, the preference of the dienophile for the more reactive diene overcoming the strain energy engendered by formation of the cyclopropane ring.[19] The formation of **9** appears likely to arise from the nonconcerted reaction of TCNE with **1**,[21] but further experimental data, including a knowledge of the stereochemistry of the ring junction of **9**, are required for a mechanism to be established. Attempts to prepare **9** from *cis*-cyclononatetraene[22] have so far been unsuccessful.

Acknowledgment. We thank the Badische-Anilin und Sodafabrik, A.G., for a generous gift of cyclooctatetraene, and the Science Research Council for a studentship (C. S. B.). We thank Dr. J. E. Anderson for valuable discussions.

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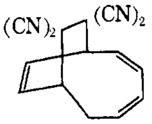
[14] T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 5194 (1964).

[15] We thank Mr. M. C. McIvor, Imperial Chemical Industries, Ltd., for the 220-MHz spectrum and for the observation that the spectrum is temperature dependent.

[16] A number of alternative bicyclic structures can be considered, and for some time we favored the structure i. However the large



i

coupling constant between the bridgehead protons, together with the temperature dependence of the spectrum, appears to rule out this formulation.

[17] Hydrogenation under milder conditions with a variety of catalysts resulted in no hydrogen uptake.

[18] Further chemical support for structure **9** is being sought and the chemistry of the photoproduct is under investigation.

[19] The behavior of **1** resembled that of cycloheptatriene[1] and cyclooctatetraene epoxide.[20]

[20] A. C. Cope, P. T. Moore, and W. R. Moore, *J. Amer. Chem. Soc.*, **80**, 5505 (1958).

[21] For an example of a 1,2-dienophile addition, see P. G. Gassman, H. P. Benecke, and T. J. Murphy, *Tetrahedron Lett.*, 1649 (1969).

[22] E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965); V. G. Boche, H. Böhme, and D. Martens, *Angew. Chem. Intern. Ed. Engl.*, **8**, 594 (1969).

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Carbonium Ion Intermediates and Neighboring Group Participation in the Decomposition of Azo Compounds

Sir:

Although diradical,[1,2] dipolar ion,[3] reverse Diels–Alder,[4] and concerted[5–7] mechanistic pathways have been reported for thermal decomposition of cyclic azo compounds, there never has been a report of a mechanism which involves carbonium ion intermediates. We wish to report that the acetolyses of azo *p*-bromobenzenesulfonates Ia-OBs and IIa-OBs provide the first examples of carbonium ion mechanisms. We also report the first evidence for neighboring group participation by the -N=N- group.

2,3-Dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]heptan-5-ol[8] was converted to *exo*-2,3-diazabicyclo[2.2.1]hept-2-en-5-ol by known procedures.[9,10] Treatment

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[1] R. J. Crawford and A. Mishra, *Can. J. Chem.*, **47**, 1515 (1969); R. J. Crawford and B. H. Al-Sader, *ibid.*, **46**, 3301 (1968); R. J. Crawford and D. M. Cameron, *ibid.*, **45**, 691 (1967); R. J. Crawford and G. L. Erickson, *J. Amer. Chem. Soc.*, **89**, 3907 (1967); R. J. Crawford and L. H. Ali, *ibid.*, **89**, 3908 (1967); R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); and other papers in the series.

[2] E. L. Allred and R. L. Smith, *ibid.*, **91**, 6766 (1969).

[3] D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *Can. J. Chem.*, **43**, 1407 (1965).

[4] J. C. Hinshaw and E. L. Allred, *Chem. Commun.*, 72 (1969).

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[6] M. Martin and W. R. Roth, *Chem. Ber.*, **102**, 811 (1969).

[7] J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969).

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Table I. Acetolysis Rate Data for Ia-OBs and IIa-OBs[a]

Compd	Temp, °C	10^5k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Relative rate
Ia-OBs	50.0	0.654 ± 0.024			
	75.0	13.9 ± 0.1			
	100.0	196[b]	26.6	−0.1	18,200 (117)
IIa-OBs	75.0	0.138 ± 0.008			
	100.0	1.67 ± 0.06	25.0	−13.8	155 (1)
III	100.0	0.0108[c]			1

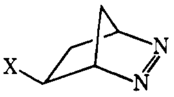
[a] Dry acetic acid with 0.015 *M* ROBs and 0.017 *M* NaOAc. [b] Calculated from data at other temperatures. [c] Gas phase decomposition data based on extrapolation from higher temperatures.[10]

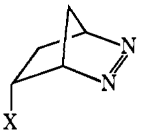
Table II. Acetolysis of Ia-OBs, IIa-OBs, IVa-OBs, and Acetic Acid Deamination of IVb-NH_2[a]

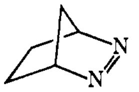
Compd	Temp, °C	Time, min	% acetolysis[b]	% yield of VI[c]	% yield of acetate[d]	% acetate composition[e,f] V	% acetate composition[e,f] VII
Ia-OBs	75	15	10		60	3	97
	100	33	96	37	51	3	97
IIa-OBs	100	55	5	38	57	17	83
IVa-OBs	75	8	10			43	57
	100	33	∼100	39		40	60
IVb-NH_2	100	6		3[g]	60	23	77

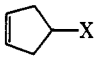
[a] *p*-Bromobenzenesulfonates and amine 0.1–0.2 *M* with a slight excess of NaOAc. For the amine excess sodium nitrite was added. [b] Based on kinetic data, Table I. [c] Vpc analysis with a 20 ft × 0.125 in. 15% tetraethylene glycol on Chromosorb P column using cyclohexane as an internal standard. [d] Vpc analysis with a 15 ft × 0.25 in. 15% FFAP on Chromosorb W column using dodecane as an internal standard. [e] These values were reproduced several times; reproducibility better than ±2%. [f] Control experiments showed the acetate products to be stable under the experimental conditions. [g] This result only demonstrates that cyclopentadiene is a product of deamination. A control experiment showed that cyclopentadiene is largely consumed under the deamination conditions.

of the latter alcohol with *p*-bromobenzenesulfonyl chloride in pyridine produced Ia-OBs, mp 84.4–84.8°.[11] 2,3-Dicarbomethoxy-*endo*-2,3-diazabicyclo[2.2.1]hept-2-en-5-ol[8] was converted in an analogous manner to IIa-OBs, mp 146–147°.[11]


Ia, X = OBs
b, X = OCH_3


IIa, X = OBs
b, X = OCH_3


III


IVa, X = OBs
b, X = NH_2

The azo *p*-bromobenzenesulfonates Ia-OBs and IIa-OBs were solvolyzed in dry acetic acid buffered with sodium acetate. Rate measurements were made by following the development of *p*-bromobenzenesulfonic acid by the usual titrimetric technique.[12] The rate constants were nicely first order. The kinetic data are summarized in Table I. A reactivity comparison of Ia-OBs and IIa-OBs acetolyses and the gas-phase thermolysis of 2,3-diazabicyclo[2.2.1]hept-2-ene (III) also is included. Azo compound III is stable in acetic acid–sodium acetate at 100° for >100 acetolysis half-lives of Ia-OBs. Both *p*-bromobenzenesulfonates produce quantitative yields of nitrogen. The other products are cyclopentadiene and mixtures of Δ^2- and Δ^3-cyclopentenyl acetates.[13] The product yields and ratios are summarized in Table II. Acetolysis product data for Δ^3-cyclopentenyl derivatives IVa-OBs[16] and IVb-NH_2[17] are included for comparison.

The gas-phase thermal decomposition of azo compounds such as Ib-OCH_3, IIb-OCH_3, and III is known to occur by a mechanism which involves diradical-like intermediates.[1,2] Several observations make it clear that Ia-OBs and IIa-OBs lose nitrogen in acetic acid–sodium acetate by a fundamentally different kind of reaction pathway. If the acetolysis reactions involved a diradical mechanism, decomposition of III under similar conditions would be expected. Further, it would be anticipated that the reactivity ratio of Ib-OCH_3, IIb-OCH_3, and III in the gas phase should be comparable to the ratio for Ia-OBs, IIa-OBs, and III in acetic acid. However, the ratios are 4.9:0.7:1 for Ib-OCH_3:IIb-OCH_3:III[2] and 18,200:155:1 for Ia-OBs:IIa-OBs:III. If diradical intermediates were involved in the acetolysis reactions, *cis*- and *trans*-2-substituted bicyclo[2.1.0]pentanes[2] and/or Δ^3-cyclopentenyl derivatives should be the products. In the latter regard, Δ^3-cyclopentenyl derivatives are reported as the only products from solvolysis of *cis*- and *trans*-bicyclo[2.1.0]-2-pentyl 3,5-dinitrobenzoates.[18] Such expectations are not realized. Both Ia-OBs and IIa-OBs yield cyclopentadiene and Δ^2-cyclopentenyl acetate as the major products and only a small amount of Δ^3-cyclopentenyl acetate. On the other hand, Ia-OBs and IIa-OBs yield the same products as observed for the acetolysis of IVa-OBs and deamination of IVb-NH_2 in acetic acid.

These considerations clearly indicate that acetolysis of Ia-OBs and IIa-OBs involves formation of cationic

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(9) O. J. Diels, J. H. Blum, and W. Koll, *Ann.*, **443**, 242 (1925).

(10) S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, **83**, 2895 (1961).

(11) Satisfactory elemental analyses were obtained for Ia-OBs, IIa-OBs, and IVa-OBs. The nmr, ir, and uv spectral data were in complete agreement with the structural assignments.

(12) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, 70, 821 (1948).

(13) The products were identified by vpc retention time. The acetates were isolated by preparative vpc and their identity was confirmed by nmr spectral comparison with authentic samples of Δ^2- and Δ^3-cyclopentenyl acetates.[14,15]

(14) K. Alder and F. H. Flock, *Chem. Ber.*, **89**, 1732 (1956).

(15) H. M. Hess and H. C. Brown, *J. Org. Chem.*, 32, 4138 (1967).

(16) IVa-OBs was prepared from Δ^3-cyclopentenol[15] by the usual pyridine method, mp 61.3–62.0°.[11]

(17) Prepared according to K. C. Murdock and R. B. Angier, *J. Org. Chem.*, **27**, 2395 (1962).

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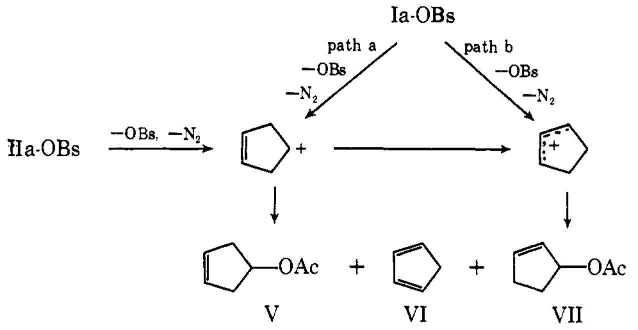
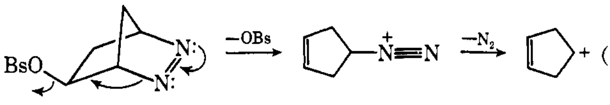
Scheme I



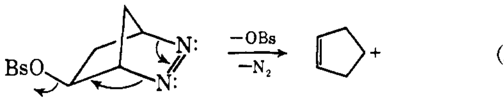
intermediates. A mechanistic scheme which accounts for the results is formulated in Scheme I.

A comparison of the acetolysis rates shows that Ia-OBs reacts 117 times faster than IIa-OBs. The significantly higher reactivity of Ia-OBs can be attributed plausibly to anchimeric assistance to ionization at C_5 by the -N=N- group. In the case of IIa-OBs geometry is unfavorable for such assistance. Further support for assistance is found in the observation that $\Delta S^{\ddagger}$ for Ia-OBs is 13.7 eu more positive than $\Delta S^{\ddagger}$ for IIa-OBs. Such a difference is indicative of different modes of ionization for the two *p*-bromobenzenesulfonates. Others have reported solvolysis studies where $\Delta S^{\ddagger}$ was found to be 10–14 eu more positive for systems showing neighboring group participation.[19]

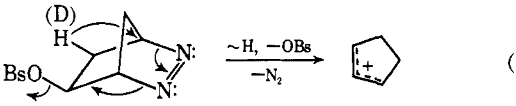
The question of the nature of the ionization–nitrogen elimination step(s) for Ia-OBs is extremely interesting. Three attractive possibilities are illustrated by eq 1-3.



(1)



(2)



(3)

We have found that k_H/k_D is 1.1 ± 0.1 at 75° for Ia-OBs and Ia-OBs-*exo*-6-*d*.[20] This precludes the completely concerted process 3 and thus one of the possibilities for path b proposed in the above mechanistic scheme. At present there is not sufficient information to allow for a distinction to be made between processes 1 and 2, and perhaps other possibilities. In the case of IIa-OBs we presume that ionization precedes nitrogen elimination. These questions are currently under investigation. Results with other azo systems will be reported later.

Acknowledgment. We express appreciation to the National Science Foundation for support of this work with Grant GP-9478.

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[20] E. L. Allred and R. L. Smith, *J. Org. Chem.*, **31**, 3498 (1966).

[21] National Institutes of Health Predoctoral Fellow, 1968–1970.

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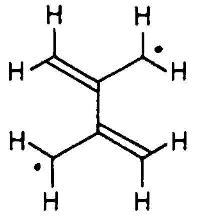
Received December 13, 1969

Tetramethyleneethane

Sir:

Tetramethyleneethane (I) is predicted by simple theory to be a ground-state triplet.[1] This molecule has long been assumed to be the central reactive intermediate in the dimerization of allene leading to the major product 1,2-dimethylenecyclobutane. Indeed, reaction of allene with $Fe_3(CO)_{12}$[2a] and $Fe_2(CO)_9$[2b] has resulted in the isolation of a compound which has been suggested to be a bis(iron carbonyl) complex of I. X-Ray structure determinations of organonickel and -palladium complexes of tetramethyleneethane have also been reported recently.[3] The stable, highly substituted diradical bisgalvinoxyl[4] is a derivative of tetramethyleneethane. Tetramethyleneethane (possibly in its singlet state) has been shown to be an intermediate in the thermal, degenerate rearrangement of 1,2-dimethylenecyclobutane.[5] The anion radical of tetramethyleneethane has been observed recently.[6]



I

As a consequence of the above results and the theoretical interest in this molecule and also in order to learn more about the mechanism of allene dimerization, it became attractive to attempt the direct observation of the diradical I using electron spin resonance spectroscopy.[7] That is, it was hoped that the knowledge gained in attempting to generate I at low temperatures might be used in the development of trapping reactions. These might then be applied to an investigation of the possible intermediates present in the allene dimerization reaction.

The necessary precursor to tetramethyleneethane (I) was prepared as follows: the known[8] *trans*-3,4-cyclopentanonedicarboxylic acid (II) was allowed to react with phosphorus pentachloride in ether at 0°.[9] The resulting bis(acid chloride) III was not isolated but was allowed to react directly with dimethylamine yielding the N,N,N′,N′-tetramethyl-3,4-cyclopentanonedicarboxamide (IV); ir ($CHCl_3$) carbonyl bands at 5.7 and 6.1 μ; nmr ($CDCl_3$) two-proton multiplet at τ 6.2, two three-proton methyl singlets at 6.8 and 7.0, and a

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[1] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

[2] (a) A. Nakamura, *Bull. Chem. Soc. Japan*, **39**, 543 (1966); (b) R. Ben-Shoshan and R. Pettit, *Chem. Commun.*, 247 (1968).

[3] W. Keim, *Angew. Chem.*, **80**, 968 (1968).

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