COMMUNICATIONS TO THE EDITOR

CHEMICAL EVIDENCE FOR THE GROUND STATE OF METHYLENE

Sir:

The stereospecific addition to olefins of methylene produced photochemically suggests that it is in the singlet state.[1,2,3] Under these conditions, however, methylene has a very short lifetime and this may not be the ground state.[4,5] To obtain evidence about the ground state of methylene, experiments were undertaken on its addition to *cis*-butene-2 in the presence of very large excesses of inert gases. As a result of work on this system it has been claimed recently that methylene has a triplet ground state. While we believe this conclusion is correct, we feel it cannot be unambiguously adduced from the experimental data presented, for reasons which will be referred to later.[6] Spectroscopic evidence indicates that methylene may be produced in the triplet state by the photolysis of diazomethane and a large excess of inert gas[7,7a]; this information was not available at the time these experiments were performed.

The methylene–*cis*-butene-2 system has been studied previously.[1,2,8,9] At pressures above 500 mm. the products are *cis*-1,2-dimethylcyclopropane, *cis*-pentene-2 and 2-methylbutene-2; below 500 mm. some of the excited *cis*-1,2-dimethylcyclopropane undergoes isomerization before it is collisionally stabilized, yielding *trans*-1,2-dimethylcyclopropane, *cis*- and *trans*-pentene-2, 2-methylbutene-1 and 2-methylbutene-2. (This is exactly analogous to its thermal isomerization, the geometrical being faster than the structural isomerization.[10])

Triplet methylene would not give stereospecific products by addition. To observe its possible presence it was necessary to work at high pressures to avoid the isomerizations just mentioned. Since the inert gases used, nitrogen, argon and carbon tetrafluoride, were all much less efficient than butene-2 in stabilizing the excited dimethylcyclopropane[9] pressures above 2100 mm. were used in all experiments. (Even at 2100 mm. a little geometrical isomerization occurs.) Since methylene reacts more rapidly with diazomethane than with butene-2, the olefin was always present in large excess. (Diazomethane photolyzed in the presence of inert gas alone yielded ethylene 63.5%, ethane 2.7%, propylene 7.0%, cyclopropane 1.4%, propane 2.0%, *n*-butane 2.5%, acetylene 2.6%, butene-1 9.0%, *trans*-butene-2 1.0%, *cis*-butene-2 0.9%, pentene-1 3.8%, *trans*-pentene-2 1.1%, *cis*-pentene-2 0.8%).

The yields of C_5 hydrocarbons (the major products) for experiments with argon as inert gas are shown in Table I. The results with nitrogen are almost identical. (In a few experiments using carbon tetrafluoride the results indicate that it is more efficient than argon at producing triplet methylene.) From the results it is clear that at high ratios of argon to butene-2 much of the methylene must undergo a singlet to triplet transition before reacting. Triplet methylene appears only able to add to the carbon double bond in butene-2 (unlike singlet methylene). The resulting addition product gives rise to either *cis*- or *trans*- 1,2-dimethylcyclopropane, *cis*- or *trans*-pentene-2, or 3-methylbutene-1. These products may be formed by two mechanisms; addition product may first undergo a triplet to singlet transition, and then the singlet cyclises to *cis*- or *trans*-1,2-dimethylcyclopropane. Alternatively, it may undergo isomerization to the triplet state of one of the olefins mentioned and then undergo the electronic transition. *In contrast* to the isomerization of vibrationally excited 1,2-dimethylcyclopropane, 3-methylbutene-1 is a product of the triplet addition compound and 2-methylbutene-2 and 2-methylbutene-1 are not.

The effect of the addition of a small quantity of oxygen is remarkable. The formation of *trans*-1,2-dimethylcyclopropane, 3-methylbutene-1 and *trans*-pentene-2 is inhibited almost completely. Clearly oxygen reacts either with the triplet methylene or with its triplet addition product. Such a reaction between two reactive triplet species would be expected to be fast.

The results presented in Table I indicate that methylene initially produced in the singlet state undergoes a transition to a triplet state after many collisions with an inert gas. This implies that the triplet state is the ground state.

TABLE I

Total pressures in range 2100 to 3200 mm. *cis*-butene-2 present in at least fourfold excess.

Ratio Argon *cis*-butene-2	Percentage yield					
	trans-1,2-Dimethyl cyclopropane	*cis*-1,2-Dimethyl cyclopropane	*trans*-Pentene-2	*cis*-Pentene-2	3-Methylbutene-1	2-Methyl butene-2
1600	27.1	28.1	16.5	17.0	10.5	4.0
850	24.0	28.4	12.7	19.1	9.2	6.6
356[a]	3.6	50.9	0.9	27.7	1.8	15.0
314	22.1	30.7	10.7	21.8	8.2	6.3
300	20.8	31.1	11.1	22.4	7.5	6.9
134	18.0	33.3	8.8	24.9	6.6	8.4
69	16.3	35.4	7.8	26.4	5.8	8.4
15.3	10.6	41.4	3.6	29.9	2.9	11.4
7.6	9.5	44.3	2.4	30.4	1.9	12.9

[a] Indicates presence of 4 mm. of oxygen. For experimental details see ref. 9.

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(1) W. E. Doering and P. LaFlamme, THIS JOURNAL, **78**, 5447 (1956).

(2) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

(3) B. S. Rabinovitch, E. Tschuikow-Roux and E. W. Schlag, *ibid.*, **81**, 1081 (1956).

(4) H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957).

(5) G. B. Kistiakowsky and P. Kydd, *ibid.*, **79**, 4825 (1957).

(6) F. A. L. Anet, R. F. W. Bader and Anne-Marie Van der Auwera, *ibid.*, **82**, 3217 (1960).

(7) G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959).

(7a) G. Herzberg, personal communication.

(8) H. M. Frey, THIS JOURNAL, **80**, 5005 (1958).

(9) H. M. Frey, *Proc. Roy. Soc.* (*London*), **A251**, 575 (1959).

(10) M. C. Flowers and H. M. Frey, *ibid.*, **A257**, 122 (1960).

This same conclusion is reached in the recent publication mentioned earlier.[6] However, the authors did not work at pressures sufficiently high to eliminate the isomerization of the initially formed dimethylcyclopropane. Of the five experimental results presented, four yielded data in which the ratios of *cis-* to *trans*-1,2 dimethylcyclopropane are almost exactly those expected for simple isomerization of the excited molecule (bearing in mind the low efficiency of nitrogen in stabilizing the excited molecule). That nitrogen (and argon) are not as efficient as butene in stabilizing either excited 1,2-dimethylcyclopropane or 1,1-dimethylcyclopropane (from methylene + isobutene) has been indicated previously.[9,11] Unpublished experiments carried out at the time the work in references 9 and 11 was performed indicated that nitrogen was approximately 25% as efficient as butene in stabilizing the hot molecules. Precise figures were difficult to obtain owing to the twofold effect of the inert gas (*i.e.*, in also removing translational energy from the methylene) and this may be an *over*-estimate of its efficiency. That nitrogen (and argon) should be less efficient than butene in stabilizing excited dimethylcyclopropane is of course to be expected theoretically and from experimental work on unimolecular reactions. In the most closely similar system for which experimental data are available, the unimolecular isomerization of methylcyclopropane, nitrogen was found to have 20% of the efficiency of butenes in the activation–deactivation process.[12] Only in one experiment (see line 3 of table in ref. 6) does the ratio differ considerably from that expected from simple isomerization. Here, however, it seems certain that as well as the *trans*-1,2-dimethylcyclopropane formed by isomerization of the hot molecules and the *trans* compound from triplet methylene, a product from the complicated photolysis of pure diazomethane must have to some extent interfered with the analysis, since in this experiment a very large excess of diazomethane has been used.

(11) H. M. Frey, *Proc. Roy. Soc.*, **A250**, 409 (1959).

(12) J. P. Chesick, THIS JOURNAL, **82**, 3277 (1960).

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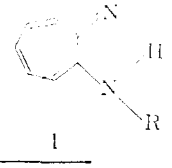
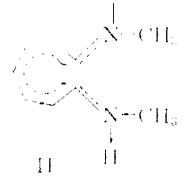
N,N-DISUBSTITUTED-1-AMINO-7-IMINO-1,3,5-CYCLOHEPTATRIENES, A NON-CLASSICAL AROMATIC SYSTEM

Sir:

A general synthesis of the 1-amino-7-imino-1,3,5-cycloheptatrienes (I) together with an indication of their aromatic character was reported recently.[1]


I


II

Although these compounds are related chemically and structurally to tropolone, evidence now has been obtained that the reasons for aromaticity in these two systems are fundamentally different.

Infrared spectral studies of I (R = CH_3) and of its N–D derivative have shown that the hydrogen is intramolecularly bonded, even in the solid state.[2] The absorption at $3.10\ \mu$ (NH) is shifted slightly to $3.08\ \mu$ in carbon tetrachloride solutions of varying concentrations. In addition, n.m.r. studies of I (R = CH_3) and its N–D derivative show only a single methyl resonance, even at −80°. These results establish the equivalency of the nitrogen atoms, and suggest either a symmetrical hydrogen-bonded structure or an extremely fast intramolecular hydrogen (or deuterium) exchange. In addition, the fine structure attributable to the ring protons in I (R = CH_3) is essentially unchanged in the cation II (although shifted downfield approximately 1.2 p.p.m. because of deshielding) and in the nickel chelate at −70°.[3] These results indicate appreciable electron delocalization in I (R = CH_3).

Dipole moment studies of I (R = CH_3) and its 4-bromo derivative have led to the surprising conclusion that although the seven-membered ring in both tropolone and azulene is electropositive in the ground state, it is electronegative in the aminoimine. The dipole moments, determined in benzene, are: tropolone, 3.71[4]; 5-bromotropolone, 2.07[5]; azulene, 1.0[6]; I (R = CH_3), 1.24; 4-bromo I (R = CH_3), 2.52. The assumption that the dipole is directed into the ring of the aminoimine, together with the reported[7] group moment of 1.55 D for bromine, leads to a calculated value of 2.79 D[8] for the 4-bromo derivative, in good agreement with the observed moment. On the other hand, if the dipole is assumed to be directed away from the ring as is the case in tropolone, the observed moment should be about 0.3 D.

Verification for the relative electronegative character of the ring compared with that of tropolone was found in n.m.r. studies. The tropolone resonance occurs at lower fields (center at 2.4 τ) compared with that of I (R = CH_3) (3.45–4.05 τ), indicating less shielding, and hence more positive character for tropolone.

Clearly, the aromaticity observed in the aminoimines cannot be attributed to contributions from

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(1) W. R. Brasen, H. E. Holmquist and R. E. Benson, THIS JOURNAL, **82**, 995 (1960).

(2) Tropolone is extensively intermolecularly hydrogen bonded in the solid state. In solution the hydrogen bonding becomes intramolecular, however. See K. Kuratani, M. Tsuboi and T. Shimanouchi, *Bull. Chem. Soc. Japan*, **25**, 250 (1952).

(3) W. D. Phillips and R. E. Benson, *J. Chem. Phys.*, **33**, 607 (1960). At temperatures above −70° chemical shifts are observed that have been attributed to a ground singlet and a thermally accessible triplet state.

(4) Y. Kurita, T. Nozoe and M. Kubo, *Bull. Chem. Soc. Japan*, **24**, 10 (1951).

(5) Y. Kurita, T. Nozoe and M. Kubo, *ibid.*, **26**, 242 (1953). The 5-position of tropolone is equivalent to the 4-position of the aminoimine.

(6) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

(7) W. Hückel, "Theoretical Principles of Organic Chemistry," Vol. II, Translated by F. H. Rathnann, Elsevier Publishing Co., N. Y., 1958, p. 127.

(8) Molecular orbital calculations (LCAO-MO method with conventional assumptions) by Dr. H. E. Simmons have given a moment of 0.3 D directed into the ring.