the strongest peak and the expected fragmentation peaks. Thin layer chromatographic analysis of the methyl ester of **2** using silica gel plates freshly treated with ethereal ammonia revealed a single spot of R_f 0.51 (ether–acetone 3:1). Full spectral details on **2** and intermediates are available from the authors. An unambiguous synthesis of the biologically less active 5,6-(*E*)-isomer of **2** (methyl ester of which shows pmr peak for H-5 at δ 4.77) will be described elsewhere.

(7) Excess pyridine and *O*-benzylhydroxylamine hydrochloride were added directly to the hydrolysis mixture and after 3 h at 60 °C the O-benzyl oxime of 6-keto-$PGF_{1\alpha}$ was isolated. Silylation was accomplished by treatment with *N*-trimethylsilylimidazole in THF at 23 °C for 1 h. The mass spectrum showed in addition to the molecular ion at *m/e* 705 all the expected fragments (see ref 3d).

(8) These tests were kindly carried out by Dr. Babette Weksler, Cornell University Medical College, and Dr. Peter Ramwell and associates, Georgetown University School of Medicine (see *Clin. Res.*, in press; *Prostaglandins*, in press).

(9) This research was assisted financially by a grant from the National Science Foundation and also the award of an IREX Fellowship to Istvan Székely.

(10) Note Added in Proof: Subsequent to the submission of this manuscript for publication a report has appeared (*Chem. Eng. News*, Dec 20, 1976) indicating that Vane and co-workers also assign structure **2** to PGX.

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Mixed Charge Exchange–Chemical Ionization Mass Spectrometry of Polycyclic Aromatic Hydrocarbons

Sir:

The exact structural identification of polycyclic aromatic hydrocarbons (PAH) and their alkylated derivatives is a difficult problem, particularly when they are encountered as complex mixtures. The analytical power of mass spectrometry, which has had wide application in this field,[1-4] has been limited because electron impact mass spectra of isomeric PAH are almost identical. The purpose of this note is to report that charge exchange–chemical ionization mass spectrometry, using an argon–methane reagent gas,[5] easily differentiates PAH isomers.

The mass spectra of a series of PAH were measured with a Hewlett-Packard 5982A gas chromatographic–mass spectrometer system by injecting approximately 200 ng of each compound (dissolved in methylene chloride) on a 180 × 0.32 cm o.d. stainless steel column packed with 3% Dexsil 300 on 80/100 mesh Chromosorb W. The reagent gas mixture (10% methane in argon) served as the carrier gas for the gas chromatographic column which was held isothermally at a temperature appropriate to each sample being analyzed. The mass spectrometer was continuously scanned from 50 to 350 amu at 81.2 amu/s. The ion source pressure was 0.8 Torr and its temperature was 170 °C. Data were collected and processed by a HP 5933A data system. Precautions were taken to assure the absence of water vapor in the ion source, since water is an excellent proton donor and can greatly increase the abundance of the protonated molecular ion. In these experiments, there were no observable traces of water vapor (*m/e* 18 or 19).

The resulting mass spectra showed considerable differences in the relative abundances of the molecular (M^+) and protonated molecular ($M + 1^+$) ions when different PAH isomers were analyzed. Table I lists the compounds analyzed in this study, the resulting ratio of the abundance of the protonated molecular to molecular ion ((M + 1)/M), and the first ionization potential of each compound. It is obvious from this table that the (M + 1)/M ratio has a high positive correlation with ionization potential ($r = 0.877$, $P \ll 0.01$). This trend is consistent with the expectation that as the ionization potential increases, charge transfer processes will be less effective for electron extraction while at the same time protonation becomes more favorable.

This technique should be quite useful for the elucidation of specific isomeric structures of PAH. By using a mixed charge exchange–chemical ionization reagent gas, such as described here, different mass spectra can be obtained for most PAH isomers while conventional mass spectral techniques provide little differentiation. This fact is demonstrated by the series of tetracyclic compounds shown in Figure 1. The (M + 1)/M ratio of each compound is plotted as a function of its first ionization potential. It is interesting to note that this abundance ratio increases from 0.45 to 1.73 as the isomer becomes more nonlinear, making differentiation quite easy. If a standard PAH compound were not available, it seems probable that the mass spectrum of that compound could be predicted from its ionization potential. The ability to calculate ionization potentials from molecular orbital theory[7,8] offers considerable promise for the future identification of presently unknown PAH.

Table I. Abundance Ratios for Selected PAH Obtained by CH_4–Ar Chemical Ionization Mass Spectrometry

Compound	Formula	First ionization potential (eV)[a]	Abundance ratio, (M + 1)/M[b]
Pentacene	$C_{22}H_{14}$	6.42	0.32
Tetracene	$C_{18}H_{12}$	6.88	0.45
Anthanthrene	$C_{22}H_{12}$	7.02	0.38
Perylene	$C_{20}H_{12}$	7.03	0.32
Benzo[*a*]pyrene	$C_{20}H_{12}$	7.17	0.73
Anthracene	$C_{14}H_{10}$	7.42	0.82
Benz[*a*]anthracene	$C_{18}H_{12}$	7.47	0.83
Dibenz[*a.h*]anthracene	$C_{22}H_{14}$	7.55	0.95
Pyrene	$C_{16}H_{10}$	7.56	0.73
Coronene	$C_{24}H_{12}$	7.58	0.66
Benzo[*e*]pyrene	$C_{20}H_{12}$	7.58	0.82
Acenaphthene	$C_{12}H_{10}$	7.70	1.00
Chrysene	$C_{18}H_{12}$	7.74	1.26
Fluoranthene	$C_{16}H_{10}$	7.76	1.57
Fluorene	$C_{13}H_{10}$	7.86	1.66
Acenaphthylene	$C_{12}H_8$	8.02	1.34
Phenanthrene	$C_{14}H_{10}$	8.02	1.59
Triphenylene	$C_{18}H_{12}$	8.11	1.73
Naphthalene	$C_{10}H_8$	8.14	1.68
Benzene	C_6H_6	9.29	5.79

[a] Values were averaged from experimental data found in ref 6–8; their variability was usually less than ±0.1 eV. [b] The reproducibility of these measurements was ±4% over a 3-month period. The ratios have been corrected for the natural abundance of ^{13}C.

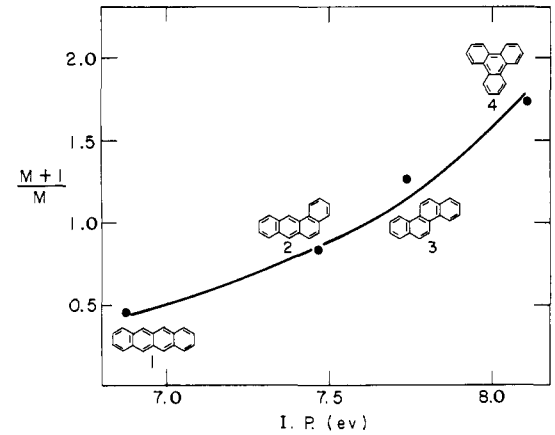

Figure 1. Plot of the abundance ratio ((M + 1)/M) obtained by CH_4–Ar chemical ionization mass spectrometry as a function of ionization potential (IP) for a series of four tetracyclic polycyclic aromatic hydrocarbons: 1, tetracene; 2, benz[*a*]anthracene; 3, chrysene; 4, triphenylene.

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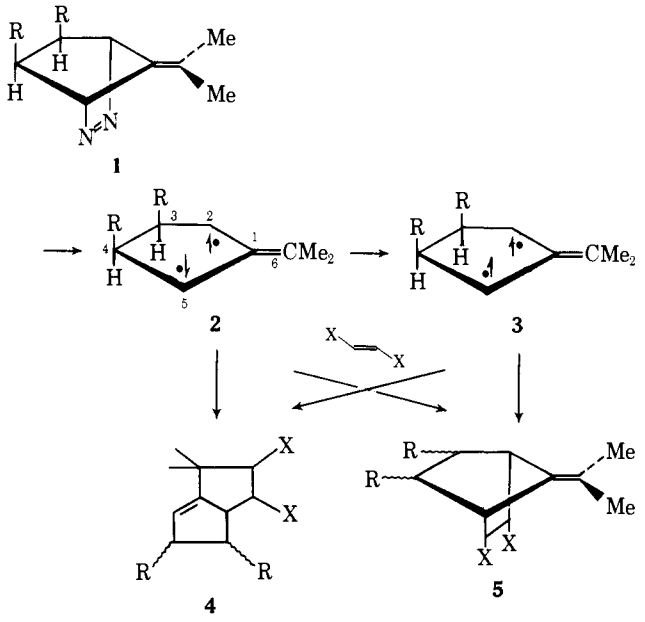
On the Nature of the Capturable Singlet Trimethylenemethane Intermediate in the Decomposition of 7-Isopropylidene-2,3-diazanorbornene[1]

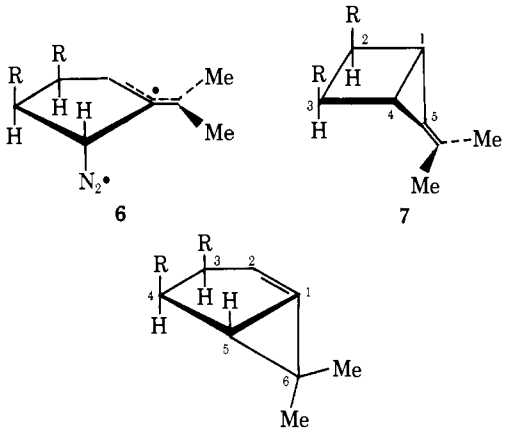
Sir:

The formation of the ground state triplet trimethylenemethane **3**[2,3] in thermal or direct photolytic decompositions of diazene **1** occurs by a sequential mechanism involving a proximate intermediate, which can be captured by olefins.[4-8] Although it has been convenient to formulate this first intermediate as the singlet state of 2-isopropylidenecyclopentane-1,3-diyl (**2**, Scheme I), the evidence so far has not excluded the possibility that the species might have quite a different structure, for example, a diazenyl biradical **6**[9] or one of the bicyclic hydrocarbons, **7** or **8**. In this paper we report both stereochemical and kinetic evidence that strongly favors the symmetrical singlet diyl **2** rather than **6**, **7**, or **8**.

Scheme I



1–5a, R = H
b, R = D



6–8a, R = H
b, R = D

Thermal decomposition at 50 °C of a CH_3CN solution of 2–2.5 M in fumaronitrile and 1 M in stereospecifically labeled **1b**[5] gives (>90% yield, >98.5% regiospecific) two fused adducts **4b** (X = CN) which are separated preparatively by gas chromatography (GC). Both have the trans dicyano configuration and result from capture of the first intermediate.[6] Although each adduct **4b** in principle could give two epoxides, *m*-chloroperbenzoic acid converts each predominantly to one member of the corresponding pair. Examination of the lanthanide shifted (LIS)[10] NMR spectrum of the epoxide prepared from the **4b** (X = CN) isomer of lower GC retention time (XE-60 column, 185 °C) shows that the deuterium configuration of the product is at least 90% randomized. Similar results are observed in epoxides from **4b** derived by thermal decomposition of **1b** in the presence of O_2 and by photolysis, both in degassed and O_2-saturated solutions.

For the sake of argument, the stereorandomization of the singlet adduct **4b** (X = CN), like that of the triplet adduct[6] **5b** (X = CO_2Me) whose stereochemistry we reported earlier,[5] may be assumed to result from static or time-averaged structural equivalence of two faces of the intermediate (rather than mere accidental equivalence of two competing cycloaddition rates). The capturable singlet intermediate then still could be either of the unsymmetrical bicyclic hydrocarbons **7** or **8**, but only if stereomutation by reversible cleavage of the weak bond, C_1–C_4 of **7**[2] or C_5–C_6 of **8**,[11] were rapid relative to capture. We are confronted, therefore, with the problem of distinguishing between a very weak bond, as in **7** or **8**, and no bond, as in the singlet diyl **2**.

We note first that the direct photolytic decompositions of **1** at 22 and 0 °C produce a species that seems to be the same as the first thermal intermediate. It adds stereospecifically to olefins,[8,13] and although direct comparison of the fused/bridged product ratio (**4/5**, Scheme I) is difficult because the photolyses must be carried out at low temperature to avoid pyrolysis of **1**, the photolytic fused/bridged (F/B) ratios fall on a smooth curve of the thermal data as a function of temperature. Even at −168 °C (105 K in Et_2O–isopentane–ethanol), photolysis of **1** in the presence of acrylonitrile gives the high F/B product ratios characteristic[8] of a large contribution of singlet-derived adduct.[7b]

Some photophysical observations confirm the chemical evidence for persistence of the cascade mechanism at low temperatures. At or near room temperature, the observed fluorescence intensities of methanol solutions of **1** monitored at 420 nm suggest a fluorescence yield of the order of 0.1%, which means that the fluorescence rate constant must be $\sim 10^9$