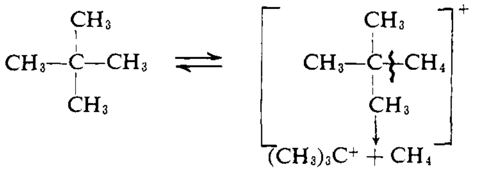
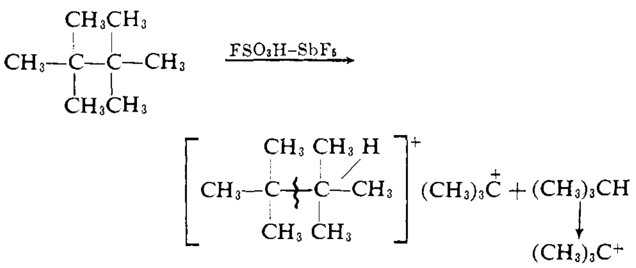
at room temperature, whereas the latter necessitates more forcing conditions. The complete exclusion of atmospheric oxygen during the experiments argues against the possibility of an oxidative process. No trace of fluorinated hydrocarbon was found, indicating the absence of radical-type fluorinating degradation.

Ethane and higher alkanes show similar reactivity in "magic acid" relating to both hydrogen exchange and "polycondensation" reactions. The intermediacy of protonated alkane-type ions is well substantiated by studies involving deuterated neopentane ($(CD_3)_4C$) and neopentane with deuterated acid (FSO_3D-SbF_5). In both cases, the methane and *t*-butyl cation formed in the reaction, as well as recovered neopentane, showed extensive hydrogen exchange. Thus neopentane is first protonated and then cleaved.



When the reaction is carried out in FSO_3H-SbF_5 diluted with SO_2ClF at lower temperatures (−30°), no protolytic cleavage reaction is observed. Instead, protonated neopentane liberates hydrogen and forms the *t*-amyl cation, obviously through fast rearrangement of the intermediate neopentyl cation. Differences in the energetics of the two cleavage reactions must be responsible for the different behavior (at different temperatures and involving different solvent systems).

The protolytic cleavage of 2,2,3,3-tetramethylbutane[2] also can be best explained by a similar mechanism.



The formation of CH_5^+ and related protonated alkanes in super acid solutions (FSO_3H-SbF_5, $HF-SbF_5$, or related acids) is remarkable. CH_5^+ is well known from mass spectroscopic studies of methane.[4] Radiation-induced polymerization of methane,[5] as well as radiolysis and photolysis of methane in the solid state,[6] was suggested to involve similar ion formation. Recently developed chemical ionization mass spectroscopy also takes advantage of the gaseous ion chemistry of methane.[7] Our observation, however, of the protonation of methane and related hydrocarbons seems to open up, for the first time, the solution chemistry of CH_5^+ and related hydrocarbon ions. The structure and chemistry of these ions, based on chemical evidence and theoretical calculations (with Professor G. Klopman), is discussed in a forthcoming full paper.

Based on the results presented in this communication and our previous work,[2] it seems appropriate to recommend that saturated hydrocarbons should be referred to only as alkanes and not as paraffins. The high chemical reactivity demonstrated by methane and other alkanes in strong acid system is no longer compatible with a name referring to "*parum affinis.*" It is, however, with some nostalgia that we make this recommendation, as "inert gases" at least maintained their "nobility" as their chemical reactivity became apparent, but referring to "noble hydrocarbons" would seem to be inappropriate.

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Thermolysis and Photolysis of 3,3a,5a,6,6a,6b-Hexahydro-3,6-ethenocycloprop[*g*]indazole[1]

Sir:

Speculating on several intermediates which may be involved in valence tautomerization of $(CH)_{10}$ hydrocarbons,[2] one most often encounters the never-isolated tetracyclo[4.4.0.0^{2,10}.0^{5,7}]deca-3,8-diene (**1**).[2] In view of the recent accumulated knowledge[3] concerning the chemistry of pyrazolines, we have chosen the title compound (**2**) and its isomer (**3**) to investigate some aspects of the $(CH)_{10}$ hydrocarbon isomerization. We have synthesized **2** and wish to present a preliminary account of its chemistry.

Synthesis of 2. Bicyclo[6.1.0]nona-2,4,6-triene-*cis*-9-carboxylic acid (**4**)[4] was converted into the corresponding aldehyde which provided the tosylhydrazone **5**, mp 136–138°. The dry sodium salt of **5** underwent thermal decomposition at 90–110°, and fractional distillation of the product mixture at low temperature readily separated a pure pyrazoline (**2**) free of $C_{10}H_{10}$ hydrocarbons. Compound **2** [calculated molecular weight for $C_{10}H_{10}N_2$, 158; found (probe temperature, 75°), *m/e* 158 (intensity, *ca.* 0.5% of base peak), M − 28 (55%), M − 29 (base peak)] showed a maximum at $\lambda_{max}^{95\% EtOH}$ 335 mμ (ϵ 115), $\lambda_{max}^{CHCl_3}$ 1540 cm^{-1}. Nmr spectra of model pyrazolines and decoupling experiments permitted the following assignment of nmr signals of **2** (chemical shift in parentheses): H-6 (τ 8.05–8.35), H-5a (7.75–8.0), H-6a (7.55–7.75), H-3a (7.35–7.65), H-3 and H-6b (4.80–5.10), H-7 (located above the azo group) (4.25–4.50), H-4, H-5, and H-8 (3.85–4.25). All these spectral data including coupling constants determined are consistent with the formulation of structure **2**.[5]

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(4) For example, F. H. Field and M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 3289 (1965), and references therein.

(5) D. R. Davis and W. F. Libby, *Science*, **144**, 991 (1964).

(6) P. Ansloos, R. E. Rebbart, and S. G. Lias, *J. Chem. Phys.*, **42**, 540 (1965).

(7) For a summary, see F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

(1) We are grateful to Dr. K. L. Loening, Chemical Abstracts Service, for suggesting this nomenclature.

(2) For a list of recent publications concerning $(CH)_{10}$ hydrocarbons, see M. Jones, Jr., *J. Am. Chem. Soc.*, **89**, 4236 (1967), ref 3 and 4.

(3) R. J. Crawford and G. L. Erickson, *ibid.*, **89**, 3907 (1967), and references cited therein; W. R. Roth and M. Martin, *Tetrahedron Letters*, 4695 (1967).

(4) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4804 (1967). Dr. Loening kindly informed us that presently there are no official rules in existence to describe properly the stereochemistry of **4**. *cis* is used for simplicity. **4** was converted to cyclopropane-*cis*-1,2,3-tricarboxylic acid.

(5) All the high-field (τ 7–9) protons except *one* (H-6a) were strongly

Thermolysis of 2. Thermal decomposition of **2** in a condensed phase at 110° provided bicyclo[4.2.2]deca-2,4,7,9-tetraene (**6**) (53% yield), bulivalene (**7**) (46%), and others (1%). The decomposition of **2** in deuteriochloroform provided the following kinetic data: $k_{83.6°} = (2.34 \pm 0.01) \times 10^{-5}$ sec^{-1}, $k_{99.6°} = (1.39 \pm 0.04) \times 10^{-4}$ sec^{-1}, $\Delta H^{\ddagger} = 29$ kcal/mole, and $\Delta S^{\ddagger} = 0$ eu.

Photolysis of 2. A *ca.* 0.16 *M* solution of **2** in tetrahydrofuran-d_8 was irradiated with a 200-W high-pressure mercury lamp (Osram GmbH), using a Pyrex filter. The result (the percentage yield of each product based on the initial concentration of **2**) is shown in Table I.

Table I

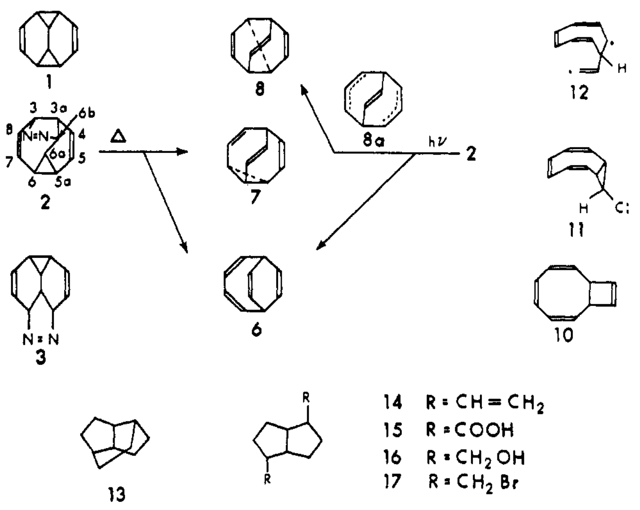
Irradiation, min	6/2 (%)	7/2 (%)	8/2 (%)
10	22.8	4.0	2.3
18	34.6	8.0	5.2
35	37.8	10.0	6.1
50	37.0	11.9	6.4
114	24.8	20.8	8.8
180	18.0	25.8	8.9

Compound **8** is tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene, and a definite structural proof is given below. It can be easily seen that pyrazoline **2** rapidly decomposed to provide **8** and **6** in a ratio of *ca.* 1:10 as the major products,[6] and the latter compound **6** underwent further photochemical conversion into **8** and **7** in a *ca.* 1:5 ratio. In fact, irradiation of **6** under identical conditions provided a very similar product distribution of **7** and **8** with approximately the same rate of formation, supporting the inference that nearly all of **7** was formed through **6** (ground state) and not directly from **2**. Compounds **7** and **8** were stable under the same conditions.

While the formation of **6** from **2** is normally expected, that the direct photoproducts of **2** are **8** and **6** deserves some comments. It is tempting to rationalize this result in terms of a diradical intermediate **8a**.[7] However, we would like to defer further discussions until deuterium-labeling experiments have been completed.

We have previously reported that photolysis of the sodium salt of bicyclo[6.1.0]nona-2,4,6-triene-*trans*-9-carboxaldehyde tosylhydrazone (**9**) afforded **6**, **8** (*vide infra*), and the major product bicyclo[6.2.0]deca-2,4,6,9-tetraene (**10**).[4] It now appears very reasonable that the carbene (**11**) generated from **9** undergoes bond cleavage to afford a diradical species **12** which leads to **8** and **6**. The absence of bullvalene (**7**) (less than 1%, if any) in the photolysate of **9** is quite consistent with this view.

Structure of 8. Catalytic hydrogenation of compound **8** provided, after uptake of 3 moles of hydrogen, a crystalline saturated compound (**13**): calculated molecular weight for $C_{10}H_{16}$, 136.1252; found, *m/e* 136.1254 (base peak).



Treatment of a divinyl compound (**14**)[8] with permanganate–periodate in aqueous *t*-butyl alcohol provided quantitatively a dicarboxylic acid (**15**), mp 237–238°, which was converted to a diol (**16**). The corresponding dibromide (**17**), mp *ca.* 25°, was treated with 0.5% lithium amalgam to provide a $C_{10}H_{16}$ hydrocarbon, which was identical with **13** in every respect. Therefore, compound **8** must be tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene.[9]

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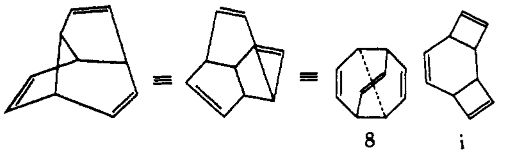
affected by the irradiation of olefinic protons and *vice versa.* This result eliminates structures isomeric to **2**, providing there is no sizeable long-range coupling between these aliphatic and olefinic protons.

[6] If the exact kinetic treatment is meaningful, then the data indicate the formation of a small amount of **7** at the initial stage of the photolysis.

[7] The thermal process of **2** leading to **7** would involve an intermediate (or possibly transition state) superficially similar to **8a** but only vibrationally excited.

[8] J. K. Crandall and C. F. Mayer, *J. Am. Chem. Soc.*, **89**, 4374 (1967).

[9] In ref 2 Jones assigned structure **8** to one of the photoproducts of **7**. On the basis of its nmr spectrum, two $(CH)_{10}$ structures, **8** and **i**, were considered, but the spectrum itself could not differentiate one from the other. Chemical information of **8** was limited and contributed very little to structural elucidation of this compound. Presumably the strongest argument in favor of structure **8** would be its infrared spectrum which is based on the assumption that the double-bond stretching band of the unknown compound **i** should appear above 1600 cm^{-1}. Therefore, the evidence was compatible with structure **8**, but further evidence was desired. Indeed, the author mentioned the progress of an X-ray crystallographic analysis of **8**.



Photolysis of the sodium salt of **9** provided, in addition to **10**, a $C_{10}H_{10}$ hydrocarbon,[5] which proved to be identical with Jones' compound by the spectral comparison. (We thank Professor M. Jones for kindly sending us an infrared spectrum.) Utilizing evidence similar to that described above, we proposed structure **8** or **i** for this compound, although some weight was given to the latter because of the structure of the major product **10** and the reaction conditions under which **8** was formed. Since then **8** has also been obtained from **2** and **6** (*vide supra*). Because of the importance of this compound in the mechanistic study of the $(CH)_{10}$ hydrocarbon isomerization, we felt it necessary to establish the structure of **9**.

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Organic Synthesis by Electrolysis. I. Electrolytic Formation of Phosphonium Ylides

Sir:

Although many methods for the preparation of phosphonium ylides have been studied, the elimination of hydrogen halide from a phosphonium halide by a strong base is the usual method of preparation. Strong bases, however, might sometimes impose a serious limi-