Table I. Chemical Shifts for Nitrogen Atoms in ATP and in Equimolar Metal Ion–ATP Solutions[a]

Sample	Nitrogen atom N-1	N-3	N-7	N-9	NH_2-6
ATP	144.7	135.6	129.5	191.6	282.8
Mg–ATP	144.9	135.0	129.5	191.6	282.3
Zn–ATP	144.4	135.0[b]	132.5[b]	190.1	279.7

[a] Chemical shifts are in parts per million relative to an external $H^{15}NO_3$ reference ($\delta_{^{15}NH_4^+}$ = +340.3 ppm relative to this reference). Except where noted, the uncertainty in chemical shifts was ±0.3 ppm as measured by the scatter of three or more separate measurements. [b] The uncertainty in these values is estimated to be ±0.6 ppm because of a broadening and partial overlap of the peaks.

moiety, either the diamagnetic shielding about that nitrogen or the paramagnetic contribution to its chemical shift should have changed. Since no shifts occurred, it may be concluded that Mg^{2+} does not bind to the adenine ring in the Mg–ATP complex. The chemical shift data in Table I for the Zn–ATP complex indicate that a Mg^{2+}–adenine ring interaction could have been detected if it were present.

The nmr spectrum of the Zn–ATP complex shows that Zn^{2+} ions cause small low-field shifts in the N-9 and 6-amino nitrogen resonances. The shifts are well outside of the experimental uncertainty, which is ±0.3 ppm, and indicate a reduced diamagnetic shielding of these nitrogens in the complex. The N-7 resonance of ATP is shifted to higher field in the Zn–ATP complex.

These shifts are consistent with a model in which Zn^{2+} interacts at both the 6-amino nitrogen and N-7 positions. The high-field shift for N-7 indicates a reduced paramagnetic contribution to its shift due to chelation. The low-field 6-amino nitrogen shift in the presence of Zn^{2+} is the same as that observed when Mg^{2+} ions are added to glycine to form the Mg–glycine complex.[7] In the latter complex, chelation is known to involve the amino group and causes a 3.2 ppm low-field shift in the amino nitrogen nmr.

Acknowledgment. We wish to thank Dr. Paul Srere for consultations during the course of this work. We also thank the Bio-Medical Division, Lawrence Radiation Laboratory, for providing the labeled ATP. This work was performed in part under the auspices of the U. S. Atomic Energy Commission.

(7) J. Happe, unpublished reslts.
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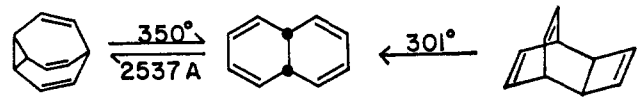
9,10-Dihydronaphthalene. Formation from Bullvalene and Nenitzescu's Hydrocarbon, Thermal Reorganization, and Photorearrangement to Bullvalene

Sir:

In the final step of a rational synthesis of tricyclo[3.3.2.0^{4,6}]deca-2,7,9-triene (I),[1] acetic acid is eliminated pyrolytically from 9-acetoxytricyclo[3.3.2.0^{4,6}]deca-2,7-diene under conditions similar to those reported by Schröder[3] to convert bullvalene (I) to naphthalene. In an effort to maximize the yield in this elimination, the behavior of bullvalene (I) on heating has been reinvestigated. Surprisingly, the first isolable product of the thermal reorganization of bullvalene is 9,10-dihydronaphthalene (II),[4] identified by comparison of nuclear magnetic resonance and ultraviolet spectra with those reported by van Tamelen and Pappas.[5] When I is partially decomposed at 350° in a flow system, II is the only product, while on heating at 400° or at 359° for a longer contact time, three additional major products are produced, at the expense of II. These products, which are themselves stable at 400° and are formed in the approximate ratios 4:2:1, are 1,4-dihydronaphthalene, 1,2-dihydronaphthalene, and naphthalene (each identified by comparison of nuclear magnetic resonance and infrared spectra with those of authentic samples[6,7]). These same products are formed in approximately the same ratios when II itself is heated[8] at 396° and are thus products of the thermal reorganization of 9,10-dihydronaphthalene, not bullvalene.

Although we shall not speculate on the mechanism, the formation of 1,4-dihydronaphthalene cannot be rationalized by any sequence of 1,5-hydrogen shifts and may present a novel mechanistic problem, as indeed may the formation of naphthalene.



I II III

In a second approach to the synthesis of bullvalene, we had conceived a series of thermal reorganizations in which Nenitzescu's hydrocarbon, tricyclo[4.2.2.0^{2,5}]-deca-3,7,9-triene (III),[9] might rearrange by way of bicyclo[4.2.2]deca-2,4,7,9-tetraene (IV; by cleavage in III of the cyclobutene ring) and tetracyclo[4.4.0.0^{3,7}.-0^{2,10}]deca-3,8-diene (V; by intramolecular Diels–Alder reaction in IV) to bullvalene (by homolytic cleavage in V of carbon–carbon bonds 1,2 and 6,7 and formation of carbon–carbon bond 4,7). Although the pyrogenic products at 315° were naphthalene and 1,2-dihydronaphthalene, bullvalene was not formed and the project was abandoned.[10,11]

Reinvestigation in a flow system has given more interesting results. At 301° partial decomposition leads to the formation of 1,2-dihydronaphthalene (ten parts), 9,10-dihydronaphthalene (three parts), and *cis*-1-phenyl-

(1) W. von E. Doering, B. Ferrier, and G. Klumpp, briefly announced in a recent review.[2]
(2) G. Schröder, J. F. M. Oth, and R. Merényi, *Angew. Chem.*, 77, 774 (1965).
(3) G. Schröder, *Chem. Ber.*, **97**, 3140 (1964).
(4) W. von E. Doering and G. Klumpp, unpublished results.
(5) E. E. van Tamelen and B. Pappas, *J. Am. Chem. Soc.*, **85**, 3296 (1963).
(6) E. S. Cook and A. J. Hill, *ibid.*, **62**, 1995 (1940).
(7) F. Straus and L. Lemmel, *Ber.*, **54**, 25 (1921).
(8) van Tamelen and Pappas report only naphthalene as the product of heating 9,10-dihydronaphthalene in carbon tetrachloride at 150–200°.[5]
(9) M. Avram, E. Sliam, and C. D. Nenitzescu, *Ann.*, **636**, 184 (1960).
(10) W. von E. Doering and M. Jones, Jr., unpublished results.
(11) In a parallel investigation, Nenitzescu and co-workers[12] heated tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene at 300° for 2 hr and obtained naphthalene (48%), 1,2-dihydronaphthalene (27%), and tetrahydronaphthalene (25%). His hypothetical explanation involves tricyclo-[4.4.0.0^{2,5}]deca-3,7,9-triene as an intermediate.
(12) C. D. Nenitzescu, M. Avram, I. I. Pogany, Gh. D. Mateescu, and M. Fărcasiu, *Acad. Rep. Populare Romine Studii Ceretari Chim. (Filiala Bucaresti)*, **11** (1), 7 (1963).

butadiene (two parts).[13] At 354° and higher conversion, the same products are formed in the ratios 7:4:2, while at 404° phenylbutadiene is no longer observed and naphthalene and 1,4-dihydronaphthalene appear at the expense of 9,10-dihydronaphthalene.

Since both molecules give rise to II, I and III may be placed on interconnected energy surfaces. Whether they are also interrelated through the attractive hypothetical common precursor, V, which can hypothetically lead to II by cleavage of carbon–carbon bonds 5,7 and 2,10, is not known.[14] Specifically, the thermal reorganization of I to II may involve VI (tricyclo-[5.3.0.0^{4,8}]deca-2,5,9-triene) as an intermediate. VI could suffer cleavage of carbon–carbon bonds 4,8 and 1,7 and thence proceed to II by way of cyclodecapentaene. VI might arise from I by a vinylcyclopropane type of rearrangement in analogy to

IV V VI

the thermal reorganization at 305° of homotropilidene to bicyclo[3.3.0]octa-2,6-diene.[15]

Ultraviolet irradiation of 9,10-dihydronaphthalene, reported by van Tamelen and Pappas[5] to lead "in ether to a distillable product mixture possessing only end absorption in the ultraviolet spectrum," leads under somewhat different conditions (irradiation in degassed pentane for 15 hr at 0° with a 2.5-w low-pressure mercury lamp) to a mixture of four products which were separated by glpc (2 m, 2.5% 20M Carbowax on 50/60 Anakrom column at 80°). The most striking product was identified by infrared spectrum as bullvalene. A second product is naphthalene. The other two are under investigation, but are not identical with the photoisomer of bullvalene isolated by Jones.[16] Coupled with the thermal rearrangement of Nenitzescu's hydrocarbon, III, this phototransformation of II represents the successful synthesis of bullvalene from III and a second path for the conversion of cyclooctatetraene to bullvalene.[3]

The theoretical considerations of Hoffmann and Woodward[17] permit the concerted photochemical transformation of 9,10-dihydronaphthalene to tetracyclo[4.4.0.0^{5,7}.0^{2,10}]deca-3,8-diene (V) which thus becomes an attractive focus of mechanistic speculation. We prefer to defer further discussion of the mechanisms of both the thermal and photochemical transformations until current experiments have been completed.

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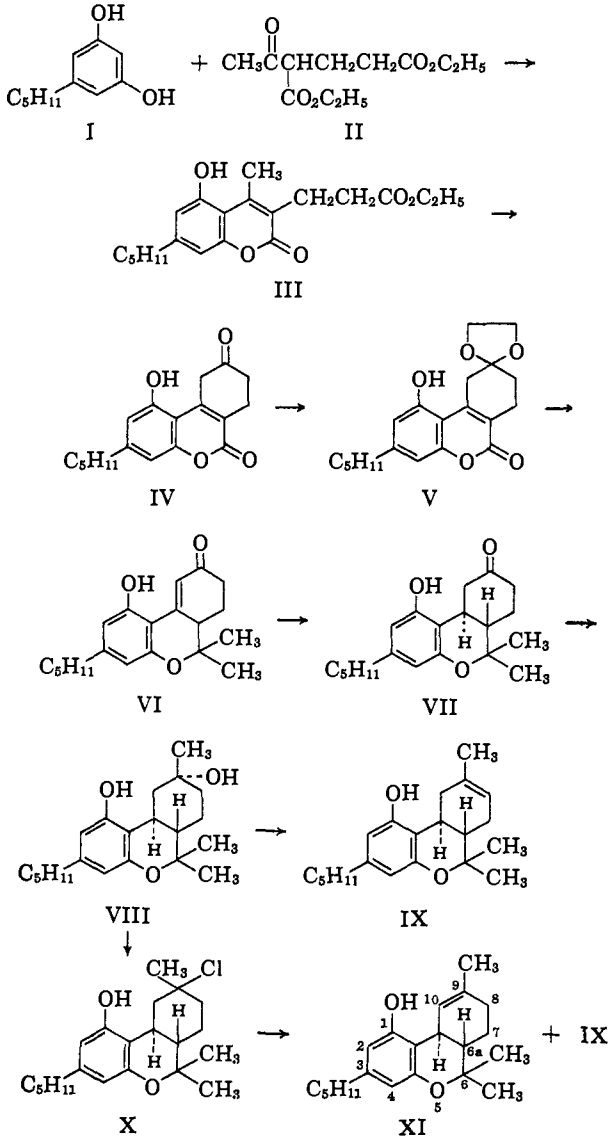
(13) I. E. Muskat and M. Herrman, *J. Am. Chem. Soc.*, **53**, 252 (1931).
(14) This scheme has been proposed by Schröder as a partial rationalization of the formation of naphthalene from bullvalene and, in related form, as a rationalization of the conversion of cyclooctatetraene to the 76° dimer.[3]
(15) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).
(16) M. Jones, Jr., private communication.
(17) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

Total Synthesis of *dl*-Δ^9-Tetrahydrocannabinol and of *dl*-Δ^8-Tetrahydrocannabinol, Racemates of Active Constituents of Marihuana

Sir:

The crude resin (marihuana, hashish) obtained from the female flowering tops of different *Cannabis sativa* L. varieties has long been known to possess psychotomimetic activity. The major active constituent of this resin has recently been shown to be *l*-Δ^9-tetrahydrocannabinol (XI),[1,2] and a total synthesis of *dl*-XI has



I II III IV V VI VII VIII IX X XI

(1) Y. Gaoni and R. Mechoulam, *J. Am. Chem. Soc.*, **86**, 1646 (1964).
(2) Compound XI has been called Δ^1-tetrahydrocannabinol by other workers. However, we feel the numbering system used here is preferable, conforming to the *Chemical Abstracts* nomenclature of dibenzo[*b*,*d*]pyran compounds.