scale of observation, even though they are generally considered to be labile. Tetrahedral complexes are known to undergo ligand replacement in the first coordination sphere more readily than octahedral complexes, presumably because of the ease with which the classical five-coordinate intermediate is formed. The lability of the tetrahedral $[MnBr_4]^{2-}$ complex toward ligand replacement demonstrated in this work is thus consistent with these trends.

(8) (a) NASA Predoctoral Fellow, 1966–1967; (b) Alfred P. Sloan Research Fellow.

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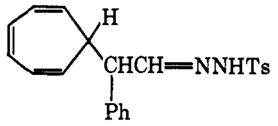
Isolation of a Potential Intermediate Leading to 9-Phenylbicyclo[4.2.1]nona-2,4,7-triene in the Thermal Decomposition of α-Phenyl-α-tropylacetoaldehyde Tosylhydrazone[1]

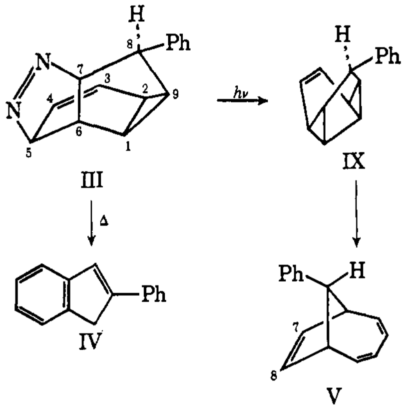
Sir:

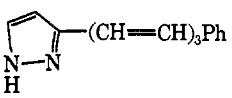
In connection with recent progress in the chemistry of C_9H_{10} hydrocarbons,[2,3] the unexpected formation of bicyclo[4.2.1]nona-2,4,7-triene in the thermal decomposition of tropylacetoaldehyde tosylhydrazone[4] directed us to carry out more detailed studies in this field. We chose the thermal decomposition of α-phenyl-α-tropylacetoaldehyde tosylhydrazone (I), from which we could isolate an interesting rearranged product (II) and a potential intermediate (III) leading to bicyclo[4.2.1]nona-2,4,7-triene and indene derivatives.

Heating of the sodium salt of I in dioxane at 80–83° afforded two products, II, mp 134° (25%), and III, mp 94° (7%), both having formula[5] $C_{15}H_{14}N_2$ (*m/e* 222), and 2-phenylindene (IV; 2%) in addition to the reported products[4] 9-phenylbicyclo[4.2.1]nona-2,4,7-triene[6] (V; 30%) and 9-phenyltricyclo[3.3.1.0^{4,6}]nona-2,7-diene (VI; 3%).[7] Product II was confirmed to be 1-phenyl-6-(3-pyrazolyl)-1,3,5-hexatriene from the following chemical and spectral evidence: ir (KBr) 3175, 2883 (hydrogen bonding and NH band of pyrazole), 987 (*trans* CH═CH), 746 cm^{-1} (*cis* CH═CH); uv (MeOH) 340 mμ (ε 46,710); nmr (60 Mc) ($CDCl_3$) τ 2.4–3.9 (very complex), including an AB pattern at τ 2.46 and 3.59 (J = 2.0 Hz) ascribed to pyrazole ring protons. The decisive evidence for the presence of the pyrazole ring was oxidation of II with potassium permanganate, from which pyrazole-3-carboxylic acid[8] and benzoic acid were obtained. Catalytic reduction of II resulted in the absorption of 3 mol of hydrogen, giving a hexahydro compound (VII), bp 175–178° (3 mm).[9] When II was heated in benzene containing iodine, an isomer (VIII), mp 202°, was obtained, and its uv spectrum (325, 344, and 360 mμ in MeOH) is very similar to that of all-*trans*-1,6-diphenyl-1,3,5-hexatriene.[10] These facts could establish the structure of II, except for the geometry of the triene system, which contains at least one *cis* ene.

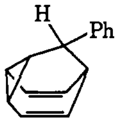


I





II



VI

The structure of III could be deduced on the basis of the following spectral data and chemical evidence: ir (KBr) 1642, 725 (*cis* CH═CH), and 1534 cm^{-1} (N═N);[11] uv (MeOH) 260 sh (ε 1080), 269 sh (660), and 340 mμ (240) (N═N). The mass spectrum of III is very similar to that of V except for the molecular ion (*m/e* 222). Nmr spectra (100 Mc, $CDCl_3$) and decoupling experiments permitted the following assignment of the signals of III (chemical shifts in τ values in parentheses) and provided the following coupling constants: H-1 (triplet of doublet, 7.90), H-2 (octet, 8.42), H-3 (split quartet, 3.84), H-4 (quartet, 4.01), H-5 (split doublet, 4.97), H-6 (octet, 7.37), H-7 (triplet, 4.29), H-8 (split doublet, 7.48), and H-9 (split quartet, 8.13); $J_{1,2}$ = 7.5, $J_{1,6}$ = 7.0, $J_{1,9}$ = 7.0, $J_{2,3}$ = 4.5, $J_{2,9}$ = 8.0, $J_{3,4}$ = 10.5, $J_{3,5}$ = 2.0, $J_{4,5}$ = 2.8, $J_{5,6}$ = 8.0, $J_{6,7}$ = $J_{7,8}$ = 8.7, and $J_{8,9}$ = 2.0 Hz. These nmr data are consistent with the formulation of structure III and are also similar to those of the pyrazoline obtained from the tosylhydrazone of bicyclo[6.1.0]nona-2,4,6-triene-9-al.[12] In addition, the fact that irradiation of

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[1] Organic Thermal Reaction. VIII. Preceding paper: T. Nakazawa, K. Okayama, T. Mukai, and A. Amano, to be published.

[2] T. S. Cantrell and H. Shechter, *J. Am. Chem. Soc.*, **89**, 5868 (1967).

[3] (a) L. G. Cannell, *Tetrahedron Letters*, 5967 (1966); (b) W. Grimm, *Ber.*, 100, 113 (1967); (c) U. Biethan, H. Klusacek, and H. Musso, *Angew. Chem.*, **79**, 152 (1967); (d) M. Jones, Jr., and S. D. Reich, *J. Am. Chem. Soc.*, **89**, 3935 (1967); (e) A. S. Kende and T. L. Bogard, *Tetrahedron Letters*, 3383 (1967); (f) W. Eberbach and H. Prinzbach, *Helv. Chim. Acta*, 50, 2490 (1967); (g) J. Daub and P. von R. Schleyer, *Angew. Chem. Intern. Ed. Engl.*, 7, 468 (1968).

[4] H. Tsuruta, K. Kurabayashi, and T. Mukai, *Tetrahedron Letters*, 3775 (1967).

[5] Satisfactory elemental analyses were obtained for all new compounds.

[6] The melting point reported in ref 4 should be revised to 39–41°.

[7] Although inspection of the nmr spectrum (τ 2.90 (m, 5 H), 4.34 (m, 2 H), 6.00 (m, 4 H), 7.58 (m, 3 H)) proved the structure of VI, the similar retention times on vpc of VI and V made it impossible to separate a pure sample.

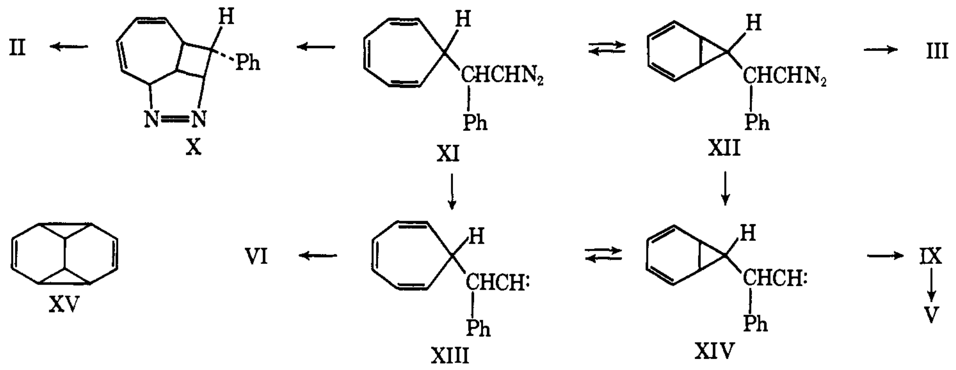
[8] L. Knorr and J. Macdonald, *Ann.*, **279**, 231 (1894).

[9] The nmr spectrum (60 Mc, CCl_4) of VII shows signals at τ 2.63 and 4.07 (doublet, J = 2.0 Hz, 2 H, pyrazole ring), 2.88 (5 H, phenyl ring), 7.42 (broad quartet, 4 H, α protons of the aromatic rings), and 8.61 (multiplet, 8 H, methylene protons).

[10] K. Lunde and L. Zechmeister, *J. Am. Chem. Soc.*, **76**, 2308 (1954).

[11] W. Kirmse and H. Dietlich, *Ber.*, 100, 2710 (1967).

[12] S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Am. Chem. Soc.*, **90**, 2727 (1968).



III by a high-pressure mercury lamp in dioxane in a Pyrex vessel afforded V (40%) supports structure III. The formation of V can be explained by the retro-Diels–Alder process of the severely strained intermediate IX, which is derived from III by photoelimination of the diazo group. Adoption of IX as the intermediate satisfies the stereochemistry of V in which the phenyl group is located *syn* to the C_7–C_8 double bond.

In contrast to the photolysis, thermolysis of III by refluxing in diglyme resulted in the formation of 2-phenylindene (IV; 48%) accompanied by a small amount of V.[13] In this decomposition of III, elimination of nitrogen may occur with cleavage of the cyclopropane ring and a hydrogen shift to afford 2-phenyldihydroindene, which, by air oxidation,[14] then leads to IV. On the other hand, heating V around 200° gave neither indene (IV) nor tricyclic diene (VI). It should also be noted that an attempted decomposition of III under the same conditions employed for the sodium salt of I resulted only in recovery of III. Therefore, III cannot be a general intermediate for the formation of II, IV, and V but is a potential intermediate, by which it is possible to clarify the reaction behavior of IX giving IV or V. For the formation of II, another hypothetical intermediate (X) may be proposed, arising from the 1,3-dipolar addition of the diazomethane group of XI to the C_1–C_2 double bond of the tropilidene.[15] Relief of strain by cleavage of the four-membered ring and the stabilization of the extended conjugated system including the pyrazole ring contribute the driving force for the rearrangement of X to II. On the other hand, the formation of III could be explained by the similar addition of the diazomethane group of XII, the valence isomer of XI, to the C_2–C_3 double bond of the norcaradiene. The predominant formation of V suggests that carbene XIV is formed prior to the formation of II (*i.e.*, X) and III, and XIV undergoes intramolecular addition to the double bond to give IX, which can easily isomerize to V.

Since intermediate IX has a close relationship with an intermediate (XV)[16] in bullvalene chemistry,[17,18] the present study on the isolation of the potential intermediate III should give information concerning the chemistry of C_9H_{10} and $C_{10}H_{10}$ hydrocarbons.

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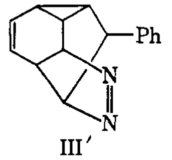
[13] This fact also ruled out another possible structure, III′, for the



III′

product III in addition to the above nmr evidence, because IV could not be derived from III′ without going through IX.

[14] The yield of IV is dropped to 5% in a nitrogen stream.

[15] W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

[16] S. Masamune reported the existence of XV at low temperatures and thermal isomerization of XV to bicyclo[4.2.2]deca-2,4,7,9-tetraene (IUPAC Symposium on Valence Isomerization, Karlsruhe, Sept 10, 1968).

[17] W. von E. Doering and J. W. Rosenthal, *J. Am. Chem. Soc.*, **88**, 2078 (1966).

[18] E. Babad, D. Ginsburg, and M. B. Rubin, *Tetrahedron Letters*, 2361 (1968).

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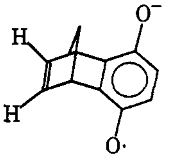
Long-Range Electron Paramagnetic Resonance Coupling in Bridged Anthracenes[1,2]

Sir:

Several interactions require consideration in the discussion of the mechanism of long-range coupling in epr spectroscopy. Recently we pointed out that the coupling constants for the vinyl hydrogen atoms of I and II were much greater than the coupling constants for the methyl hydrogen atoms of II.[3,4] The inference of



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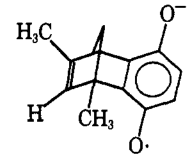

II

this observation is that the coupling of the vinyl hydrogen atoms in compounds such as I and II does not involve the transfer of spin density from the aromatic π orbitals to the isolated double bond and thence to the vinyl proton. Rather, the data suggest that long-range coupling results from an interaction of the kind implicit in the extended Hückel theory[5] or from an interaction similar to the direct (through space) or indirect (through σ bond) spin polarization mechanism advanced to account for long-range nuclear couplings.[6]

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[1] Electron Paramagnetic Resonance Spectra of Semiquinones. VII.

[2] This research was supported in part by the Petroleum Research Fund administered by the American Chemical Society and in part by the National Science Foundation.

[3] D. Kosman and L. M. Stock, *Chem. Commun.*, 551 (1968).

[4] D. Kosman and L. M. Stock, *J. Am. Chem. Soc.*, in press.

[5] The theory has been applied to some related bicyclic molecules: G. R. Underwood and R. S. Given, *ibid.*, **90**, 3713 (1968).