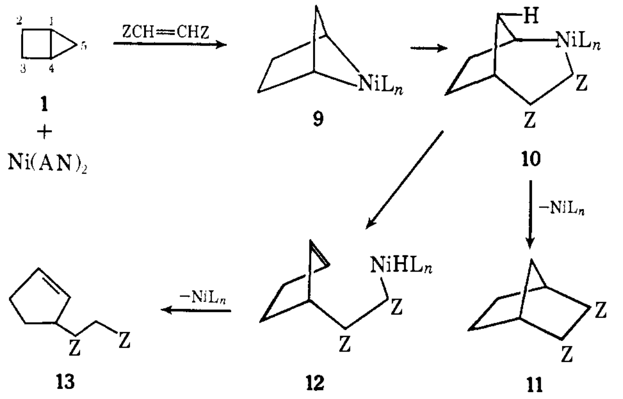
results. When **1** (1.2 mmol) was allowed to react with dimethyl fumarate (3.7 mmol) in benzene (3 ml) containing Ni(AN)$_2$ (0.2 mmol) at 60° for 45 hr, a single cycloadduct **5** was obtained in 30% yield. A small amount of the monocyclic adduct **6** was also produced. Similarly, the reaction of **1** and dimethyl maleate afforded a mixture of coupling products, **5**, **6**, **7**, and **8** (46% total yield). The stereospecificity of the cycloaddition was at least 91%,[12] as determined by the ratio **7** + **8**/**5** + **7** + **8**. The identity of the adducts **5**, **7**, and **8** was established by comparison with respective authentic samples.[13,14]

Although the situation is oversimplified, the overall reaction producing bicyclo[2.2.1]heptanes and cyclopentene derivatives may be reasonably illustrated by Scheme II: (1) the initial oxidative addition of the strained C-1–C-4 bond of **1** onto the nickel(0) atom (formally d^{10} → d^{8} conversion) forming the organonickel intermediates **9** (L = AN or ZCH=CHZ),[15,16] (2) the insertion of the coordinated olefin into the Ni–C σ bond[17] to produce the new organonickels **10**, and (3) the reductive elimination to give the bicyclic products **11**, and the regeneration of the nickel(0) catalyst (d^{8} → d^{10}). Formation of the cyclopentene derivatives would tentatively be accounted for by assuming the nickel-hydride elimination at the stage of **10** followed by the ejection of the nickel(0) catalyst (**10** → **12** → **13**). Rigorously, however, the mechanistic possibility that the formation of the cycloadducts of type **11** is a transition-metal catalyzed concerted reaction[18] could not be excluded.

Scheme II



Attempted reaction of bicyclo[3.1.0]hexane or bicyclo[4.1.0]heptane with methyl acrylate in the presence of Ni(AN)$_2$ resulted in recovery of the starting materials. The lack of reactivity in these higher homologs could reasonably be attributed to the reduced strain energy of the *central* σ bonds.[19]

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[12] Unsaturated esters recovered from the reaction of **1** and dimethyl maleate consisted of maleate and fumarate (97:3). Dimethyl fumarate was not isomerized during the reaction.

[13] H. Bode, *Ber. Deut. Chem. Ges. B*, 70, 1167 (1937).

[14] The spectral data of **6** are identical with those reported: P. de Mayo, S. T. Reid, and R. W. Yip, *Can. J. Chem.*, **42**, 2828 (1964). Compound **6** produced by the reaction of **1** and dimethyl fumarate is indistinguishable from that derived from **1** and dimethyl maleate (ir, nmr, glpc, and tlc), though the detailed stereochemistry is unknown.

[15] J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

[16] For the oxidative addition of strained C–C single bonds, see: L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 3515 (1970); L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970); P. E. Eaton and S. A. Cerefice, *ibid.*, 1494 (1970); T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 2405, 6519 (1969); *Tetrahedron Lett.*, 2561 (1969).

[17] *Cf.* W. H. Baddley and M. S. Fraser, *J. Amer. Chem. Soc.*, **91**, 3661 (1969).

[18] R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, **47**, 71 (1969); J. Wristers, L. Brener, and R. Pettit, *J. Amer. Chem. Soc.*, **92**, 7499 (1970), and references cited therein.

[19] In the absence of the olefins, no isomerization of **1** was observed under identical reaction conditions.

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The Transition Metal Complex Induced Rearrangement of 1-Methyl-2,2-diphenylbicyclo[1.1.0]butane. A New Route to Azulenes[1]

Sir:

The intriguing nature of the transition metal induced rearrangement of derivatives of bicyclo[1.1.0]butane has been amply demonstrated by the plethora of publications in this area.[2] Although the role of the transition metal catalysts and the detailed mechanistic aspects of the rearrangements are of theoretical interest, it seems apparent that the published transformations of exotic derivatives of bicyclo[1.1.0]butane into simple dienes must be described as something less than an advance in organic synthesis. We now wish to report what we believe to be a synthetically useful new route to the azulene nucleus which has as the critical reaction the transition metal induced rearrangement of a phenyl-substituted bicyclo[1.1.0]butane.

When 1-methyl-2,2-diphenylbicyclo[1.1.0]butane[3] (**1**) was treated with 4 mol % of rhodium dicarbonyl chloride dimer in chloroform for 2 hr at room temperature, a mixture was formed which consisted of the three primary products, **2**, **3**, and **4**, and the two secondary products, **5** and **6**. The identity of **2** was established on the basis of its spectroscopic properties. The nmr absorptions occurred at τ 2.86 (10 H, broad singlet, aromatic protons), 3.40 (1 H, quartet, H$_X$), 4.76 (1 H, doublet of doublets, H$_B$), 5.00 (1 H, doublet of doublets, H$_A$), and 8.10 (3 H, singlet, methyl group). The coupling constants were J_{AB} = 1.5 Hz, J_{AX} = 10 Hz, and J_{BX} = 17 Hz, in good agreement with the constants previously reported for 3,4-dimethylpenta-1,3-diene.[4] The uv spectrum of **2** showed $\lambda_{max}^{pentane}$ 237 (ε 15,000) and 277 nm (ε 21,000). The ir spectrum of **2** was consistent with the proposed structure and the high-resolution mass spectrum showed a parent peak at *m/e* 220.1248 (calcd 220.1252).

The structures of **3** and **4** could not be unequivocally established due to spontaneous air oxidation[5] and our

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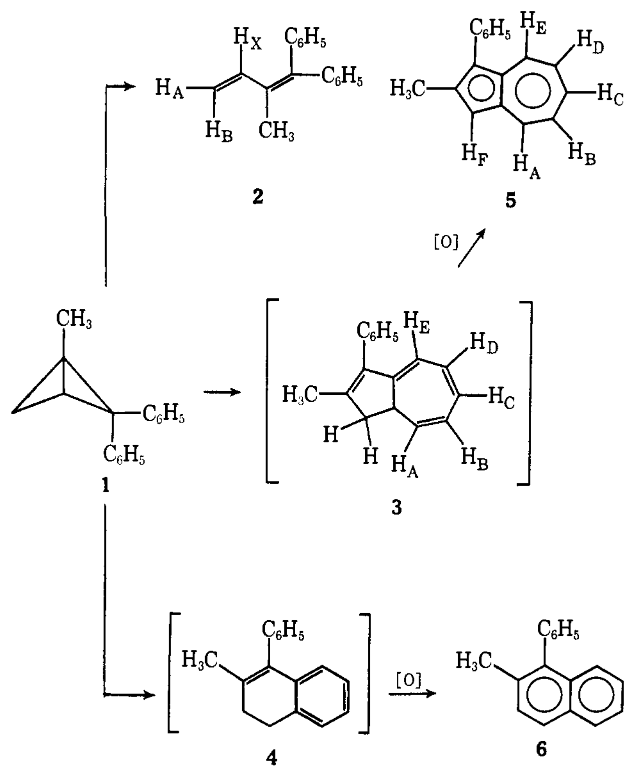
[1] Paper XXVI on the "Chemistry of Bent Bonds." For the previous paper in this series see P. G. Gassman, E. P. Williams, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 5199 (1971).

[2] For leading references see (a) P. G. Gassman, T. J. Atkins, and F. J. Williams, *ibid.*, **93**, 1812 (1971); (b) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, **93**, 1043 (1971); (c) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **93**, 1288 (1971).

[3] The bicyclo[1.1.0]butane (**1**) can be prepared in greater than 70% yield from the dibromocarbene adduct of 1,1-diphenyl-2-methylpropene according to the excellent method of W. R. Moore and J. B. Hill, *Tetrahedron Lett.*, 4553 (1970).

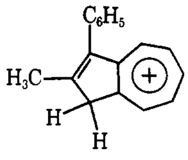
[4] P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **92**, 7631 (1970). See also L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p 85.

[5] Column chromatography of the crude reaction mixture gave a series of almost colorless fractions which were shown by vpc analysis to contain a mixture of **3**, **4**, and **6**. Exposure of these fractions to air resulted in the immediate formation of a dark blue-black solution due to the oxidation of **3** to **5**.



inability to obtain pure samples of these two materials. The structure of **3** was tentatively assigned on the basis of the nmr spectrum of an 85% purity sample which showed a five-proton multiplet at τ 2.50–3.00 (phenyl protons), a four-proton multiplet at τ 3.60–4.30 (H_B, H_C, H_D, and H_E), a doublet of doublets (1 H, τ 4.70, H_A), a three-proton multiplet (τ 6.60–7.75, allylic protons), and a three-proton singlet (τ 8.25, methyl group).[6] J_{AB} was found to be 9.0 Hz.[6] The tentative assignment of the structure of **4** was based on a comparison of an nmr spectrum of impure material with that of an authentic sample of 2-methyl-1-phenyl-3,4-dihydronaphthalene[7] and the identity of its vpc retention times with those of an authentic sample.

In order to avoid the complications inherent in handling **3** and **4**, the crude reaction mixture was oxidized with chloranil in benzene for 2 hr at 25° Under these conditions we obtained 19% of **2**, 35% of **5**, and 7% of **6**, as a readily separable mixture. The structure of **6** was established by comparison with an authentic sample.[7] The structure of **5** was determined through its spectroscopic properties. Pure **5** was a blue-black liquid with *m/e* 218.1092 (calcd 218.1095). The nmr spectrum of **5** had peaks at τ 7.39 (3 H, singlet, methyl group), 2.20–3.10 (9 H, complex multiplet, H_B, H_C, H_D, H_F, and phenyl protons), and 1.80 and 1.94 (1 H each, doublets, H_A and H_E).[8] When **5** was added to trifluoroacetic acid, the blue color disappeared and a deep yellow solution resulted due to the formation of **7**. The nmr spectrum of **7** had peaks at τ 7.50



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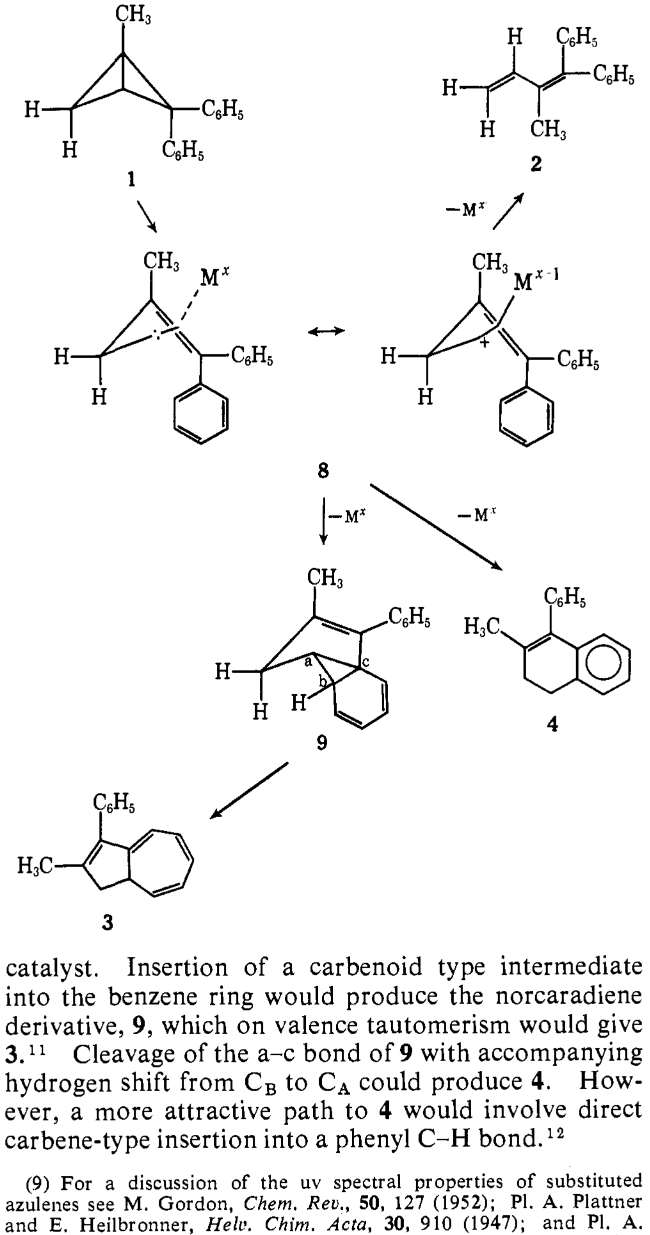
(3 H, singlet, methyl group), 5.65 (2 H, singlet, CH_2), 2.20–2.80 (5 H, multiplet, phenyl protons), and 0.9–1.6 (5 H, multiplet, tropylium ring protons).[8] The uv spectrum of **5** showed $\lambda_{max}^{pentane}$ 238 (ϵ 24,000), 290 (ϵ 11,000), 353 (ϵ 5500), 372 (ϵ 2800), 580 (ϵ 240), 625 (ϵ 220), and 690 nm (ϵ 100). These spectral data are best correlated with the 2-methyl-1-phenylazulene structure.[9]

The formation of **2**, **3**, and **4** from **1** is readily interpreted on mechanistic grounds if **1** is initially converted to the metal-complexed carbene–metal-bonded carbonium ion hybrid, **8**,[10] by the transition metal



catalyst. Insertion of a carbenoid type intermediate into the benzene ring would produce the norcaradiene derivative, **9**, which on valence tautomerism would give **3**.[11] Cleavage of the a–c bond of **9** with accompanying hydrogen shift from C_B to C_A could produce **4**. However, a more attractive path to **4** would involve direct carbene-type insertion into a phenyl C–H bond.[12]

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(6) This spectrum compares well with those of known cycloheptatrienes. See J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3896 (1965), and H. Günther, M. Görlitz, and H.-H. Hinrichs, *Tetrahedron*, **24**, 5665 (1968).

(7) A. Ohta, Y. Ogihara, K. Nei, and S. Shibata, *Chem. Pharm. Bull.*, **11**, 754 (1963).

(8) The nmr spectral properties of methylazulenes and protonated methylazulenes are in excellent accord with our observations. For a detailed discussion see D. Meuche, B. B. Molloy, D. H. Reid, and E. Heilbronner, *Helv. Chim. Acta*, **46**, 2483 (1963).

(9) For a discussion of the uv spectral properties of substituted azulenes see M. Gordon, *Chem. Rev.*, **50**, 127 (1952); Pl. A. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **30**, 910 (1947); and Pl. A. Plattner, A. Fürst, M. Gordon, and K. Zimmermann, *ibid.*, **33**, 1910 (1950).

(10) For the initial postulate of this type of intermediate see ref 2a.

(11) For leading references to norcaradiene–cycloheptatriene interconversion, see G. E. Hall and J. D. Roberts, *J. Amer. Chem. Soc.*, **93**, 2203 (1971), and E. Ciganek, *ibid.*, **93**, 2207 (1971).

In summary, the transition metal catalyzed rearrangement of a phenyl-substituted bicyclo[1.1.0]butane leads to an azulene in a process which has potential synthetic utility. The initial formation of a dihydroazulene from a phenyl-substituted bicyclo[1.1.0]butane tends to add support to the proposed intermediacy of a metal-complexed carbene–metal-bonded carbonium ion hybrid in the transition metal promoted rearrangement of bicyclo[1.1.0]butanes. We are continuing to explore the scope and mechanistic detail of this new route to azulenes.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work.

(12) An alternate path to **3** and **4**, which cannot be ruled out on the basis of presently available data, would involve Friedel–Crafts type alkylation of one of the phenyl groups by the initially generated intermediate.

(13) The Ohio State University Postdoctoral Fellow, 1970–1971.

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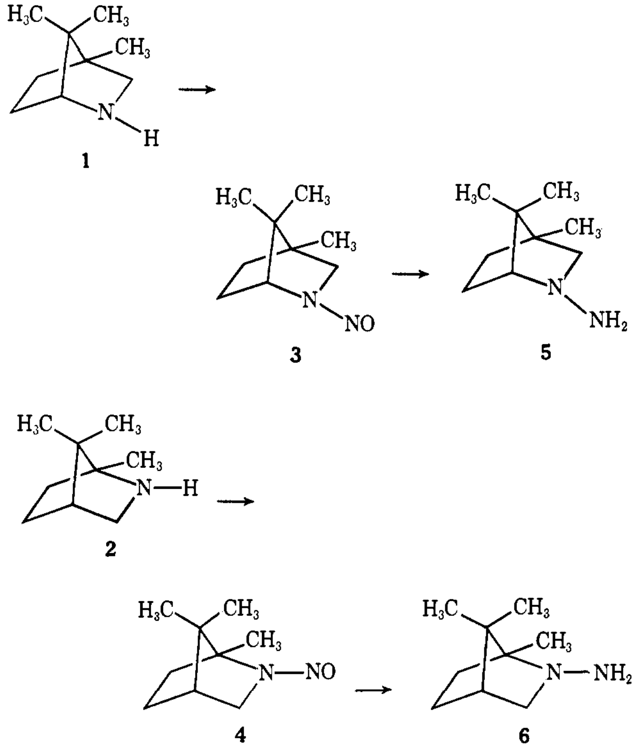
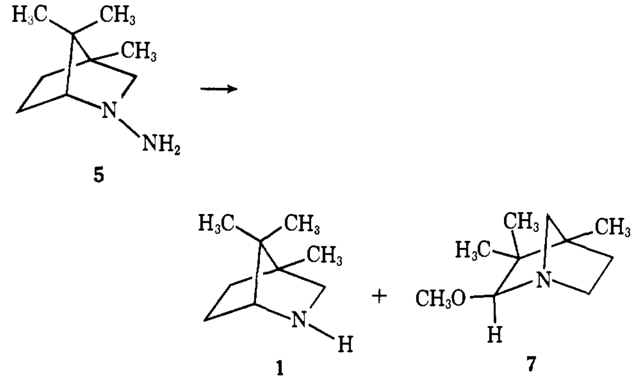
The Formation of Nitrenium Ion Intermediates in the Nitrous Acid Deamination of Dialkylhydrazines[1]

Sir:

The recent survey of the chemistry of nitrenium ions has amply illustrated the diversity of applications which these divalent positively charged species have in organic synthesis.[2] As part of our interest in exploring reactions which involve the generation of nitrenium ion intermediates, we have reinvestigated the nitrous acid deamination of 1,1-disubstituted hydrazines.[3] We now wish to report that the reaction of 1,1-disubstituted hydrazines with nitrous acid produced an intermediate which appears to decompose by two alternate routes. One of these reaction paths involves the formation of nitrenium ion intermediates.

In order to establish whether nitrenium ions could be generated *via* the diazotization of hydrazines, in a process analogous to the generation of carbonium ions by the diazotization of aliphatic primary amines,[4] we chose to investigate a system in which the behavior of the nitrenium ion had been well established.[5] Both **1**[5] and **2**[6] were readily converted into the corresponding *N*-nitroso derivatives, **3** and **4**, respectively, on treatment with nitrosyl chloride.[7] Reduction of these *N*-nitroso compounds with lithium aluminum hydride gave **5** and **6**, respectively, which were isolated as their hydrochlorides.[8] When the hydrochloride of **5** was treated with 1.1 equiv of isoamyl nitrite at 50° in methanol, we obtained 67% of **1** and 21% of **7** for an overall yield of 88%. Both of these products are known to arise from the nitrenium ion, **8**. The formation of the protonated form of **1** is thought to occur *via* the nitrenium ion triplet, while the singlet form of **8** has been shown to rearrange to the carbonium ion **9**.[5] Attack of the nucleophilic solvent, methanol, on **9** has been shown to yield **7**.[5,9] The formation of **7** in the deamination of **5** provides convincing evidence for the presence of **9** and hence the initial formation of the nitrenium ion **8**.





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(1) Paper XVII in the series "The Chemistry of Nitrenium Ions." For the previous paper in this series see P. G. Gassman and G. A. Campbell, *J. Amer. Chem. Soc.*, **93**, 2567 (1971).

(2) P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(3) The deamination of dialkyl- and diarylhydrazines has been investigated by a variety of workers over the last half-century. [For examples, see J. Thiele, *Justus Liebigs Ann. Chem.*, **376**, 264 (1910); J. Thiele, *Ber.*, **41**, 2806 (1908), and references contained therein]. However, we have found no previous work in the literature which would provide convincing evidence for the intermediacy of nitrenium ions.

(4) For recent reviews, see E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Wiley, New York, N. Y., 1968, pp 440–483; P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 1, W. A. Benjamin, New York, N. Y., 1965, pp 33–46; H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961; J. H. Ridd, *Quart. Rev., Chem. Soc.*, **15**, 418 (1961).

(5) P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 2047, 5176 (1969).

(6) P. G. Gassman and R. L. Cryberg, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 14–18, 1969, Abstracts, ORGN-14.

(7) Satisfactory elemental analyses were obtained on all new compounds or on derivatives thereof.

(8) The free hydrazines were readily oxidized in air to the corresponding tetrazines. For an example of the lithium aluminum hydride reduction of *N*-nitroso derivatives to unsymmetrical hydrazines see C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *J. Amer. Chem. Soc.*, **79**, 6430 (1957).

(9) P. G. Gassman, K. Shudo, and R. L. Cryberg, unpublished results. A detailed account of the nature of **9** will be provided in a forthcoming publication.