

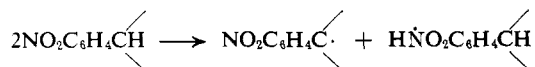
Table I. Free-Radical Formation in the Pyrolysis of Nitroaromatic Compounds

Nitroaromatic	Free-radical formation Temp., °C. ^a	Max. amt. ^b
<i>o</i> -Nitroaniline ^c	250	+++
<i>m</i> -Nitroaniline ^c	160	+++++
<i>p</i> -Nitroaniline	260	+++
<i>N,N</i> -Dimethyl- <i>m</i> -nitroaniline ^c	160	+++++
<i>N,N</i> -Dimethyl- <i>p</i> -nitroaniline	250	+++
2,4-Dinitroaniline ^c	260	+++++
2,4,6-Trinitroaniline ^c	160	++
2,4-Dinitrodiphenylamine	150	+
<i>o</i> -Nitrotoluene	180	+
<i>m</i> -Nitrotoluene	230	+
2,4-Dinitrotoluene	260	++
2,4,6-Trinitrotoluene	240	+++
4'-Nitroacetophenone	120	++
Phenyl <i>p</i> -nitrobenzyl ether	140	+++
Methyl (<i>p</i> -nitrophenyl)acetate	80	++
<i>p</i> -Nitrophenylacetonitrile	240	+++
α -Bromo- <i>p</i> -nitrotoluene	250	+++++
<i>p</i> -Nitrobenzyl alcohol	100	+
Bis(<i>p</i> -nitrophenyl)methane ^c	240	++
<i>p</i> -Nitrophenyldiphenylmethane	120	+++
Tris(<i>p</i> -nitrophenyl)methane ^c	120	+++++
<i>o</i> -Nitrobenzaldehyde	80	+++
<i>m</i> -Nitrobenzaldehyde ^c	200	++
<i>p</i> -Nitrobenzaldehyde	160	+++
2,4,6-Trinitrobenzaldehyde	100	+
<i>m</i> -Nitrophenol	240	++
<i>p</i> -Nitrophenol	140	++
2,4,6-Trinitrophenol	130	+++
Bis(<i>o</i> -nitrophenyl) disulfide	140	+++++
Bis(<i>p</i> -nitrophenyl) disulfide	100	+++++

^a Lowest temperature for first detection of radicals or rapid increase of concentration of radicals if starting material contains free radicals. ^b Maximum concentration of radicals observed at any temperature up to 300° (highest temperature available); approximate concentrations: + = 10⁻⁶ M, ++ = 10⁻⁸ M, +++ = 10⁻⁴ M, etc. ^c Readily detectable amounts of free radicals in commercially available or preparatively pure chemicals.

up to 300°, 2,4-dinitrotoluene and 2,4,6-trinitrotoluene produced radicals readily. Nitrobenzyl derivatives (e.g., methyl *p*-nitrophenylacetate, *p*-nitrobenzyl alcohol, phenyl *p*-nitrobenzyl ether, *p*-nitrophenyldiphenylmethane, and tris(*p*-nitrophenyl)methane) gave free radicals at relatively low temperatures. In the case of *p*-nitrophenyldiphenylmethane a triplet was first seen at lower temperatures (120°) which was dominated at higher temperatures by a single peak with hyperfine structure resembling the trityl radical. The intensity of this peak was reversibly dependent on temperature, as should be expected for a trityl-hexaarylethane equilibrium.

A hydrogen atom transfer mechanism seems most feasible for the free-radical formation for these nitroaromatic compounds where unpaired electrons are not available.^{5,6}



In the case of *p*-nitrophenyldiphenylmethane at 120° both products of the disproportionation can be seen, but in most other cases the radicals observed probably

(5) Evidence for this mechanism will be presented in a following paper; e.g., the hydrocarbon related to Koelsch's radical (C. F. Koelsch, *J. Am. Chem. Soc.*, **79**, 4439 (1957)), 2-phenylbis(biphenylene)propene, gives the e.s.r. spectrum of Koelsch's radical in nitrobenzene at 80–190° under nitrogen.

(6) Photoinduced hydrogen atom transfer to nitrobenzene from THF has been reported: R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963).

are derived from the reduced nitrobenzene function. A hydrogen transfer mechanism can also explain the free-radical formation in the case of the nitrobenzaldehydes



and nitrophenols



It is apparent from our experiments that nitrotoluenes, nitroanilines, nitrobenzaldehydes, and to some extent nitrophenols spontaneously react to produce free-radicals more readily (i.e., higher concentrations at lower temperatures) as the number of nitro groups increases: *p*-nitrotoluene < 2,4-dinitrotoluene < 2,4,6-trinitrotoluene; *p*-nitroaniline < 2,4-dinitroaniline < 2,4,6-trinitroaniline; *p*-nitrobenzaldehyde < 2,4,6-trinitrobenzaldehyde; *p*-nitrophenol < 2,4,6-trinitrophenol. This is consistent with the expected increased affinity of the polynitro aromatic nucleus for electron or hydrogen abstraction. Such reactions must be important in the initiation of the thermal decomposition of explosives.

In a number of cases spontaneous free-radical formation occurred in the solid state (e.g., *p*-nitrophenyldiphenylmethane, tris(*p*-nitrophenyl)methane, and the nitrophenyl disulfides), although the rate of radical formation was much more rapid at temperatures above the melting points. As indicated in the table many solid nitroaromatic compounds contain free radicals as impurities.

Except for polynitroaromatic derivatives, little change in ease of radical formation or character of signal was found whether the sample was heated in an open tube or sealed under nitrogen. In a number of cases good resolution of the signal was obtained: 2,4-dinitrotoluene, 2,4,6-trinitrotoluene, *p*-nitroacetophenone, *o*- and *p*-nitrobenzaldehyde, and the nitrophenyl disulfides gave complex spectra sometimes indicating more than one radical species present; 2,4,6-trinitrobenzaldehyde, *p*-nitrophenol, and 2,4,6-trinitrophenol gave triplets. The interpretation of some of these spectra is not straightforward and will be described at a later date.

Acknowledgment. Some of the chemicals not commercially available originated in Professor G. A. Russell's group at Iowa State University. This work was supported in part by funds provided through the Director of General Research of the University of Georgia. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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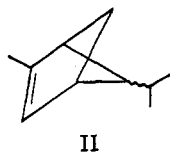
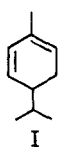
The Photoisomerization of α -Phellandrene. A Structural Reassignment¹

Sir:

In a recent publication, Crowley has reported that irradiation of an ethereal solution of α -phellandrene (I)

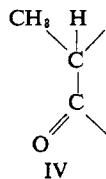
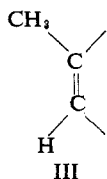
(1) The partial support of this research by National Science Foundation Grant No. G-22541 is acknowledged with pleasure.

leads to the formation of a 5-isopropyl-2-methylbicyclo[2.1.1]hexene-2 (II) of unspecified stereochemistry.² Despite extensive investigations of the chem-

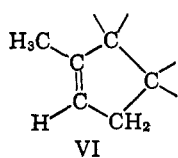
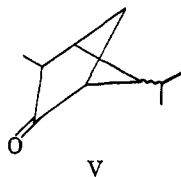


istry of bicyclo[2.1.1]hexanes,^{3,4} no other examples of bicyclo[2.1.1]hexenes are known, and this report is of significance both because of the relatively novel cycloaddition and because it would represent the first synthesis of this type of olefin. Since the possibility of studying the reactions of bicyclo[2.1.1]hexenes and of the bicyclo[2.1.1]hexenyl esters is of particular interest, we have re-examined this reaction in the hope that it could be confirmed, and perhaps generalized.

One cause for concern in connection with the assignment of structure II to the α -phellandrene isomerization product was the failure of this material (as well as of several of its transformation products) to show the usual six-proton doublet, characteristic of isopropyl groups, in its n.m.r. spectrum.² The n.m.r. spectrum does, nevertheless, give good support for the partial structure III.



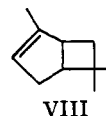
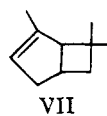
In order to learn more about the environment of this double bond, the photoisomer was prepared as previously described, carefully purified by preparative gas chromatography, and subjected to hydroboration followed by chromic acid oxidation, giving a cyclic ketone with partial structure IV.⁵ The infrared spectrum of this ketone has its carbonyl band at 5.74μ , indicative of a five-membered ring ketone⁶ but not in accord with expectations for the bicyclo[2.1.1]hexan-2-one structure V, since other bicyclo[2.1.1]hexan-2-ones absorb at



significantly shorter wave lengths (5.65 – 5.69μ).^{7,8} Direct chemical evidence excluding structure V is provided by the formation in 72% yield of a crystalline benzylidene derivative, m.p. 73 – 74° , from this ketone by treatment with benzaldehyde and sodium hydroxide. These results permit expansion of partial structure IV to VI.

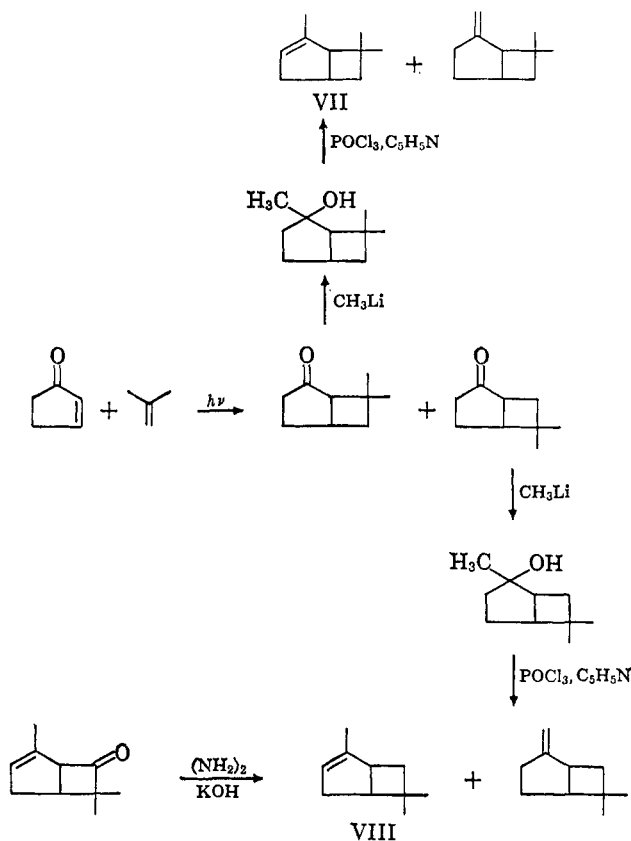
- (2) K. J. Crowley, *J. Am. Chem. Soc.*, **86**, 5692 (1964).
- (3) J. Meinwald, C. B. Jensen, A. Lewis, and C. Swithenbank, *J. Org. Chem.*, **29**, 3469 (1964), and preceding papers in this series.
- (4) See also K. B. Wiberg and R. Fenoglio, *Tetrahedron Letters*, 1273 (1963), and other papers in this series.
- (5) All new compounds described in this communication gave satisfactory elemental analytical data.
- (6) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 148.
- (7) G. Büchi and I. M. Goldman, *J. Am. Chem. Soc.*, **79**, 4741 (1957).
- (8) J. Meinwald and P. G. Gassman, *ibid.*, **82**, 2857 (1960).

At this point, we considered a number of alternative structures which could be rationally derived from I and which would accommodate the newly found data. Structures VII and VIII appeared attractive, and independent syntheses of both of these hydrocarbons were

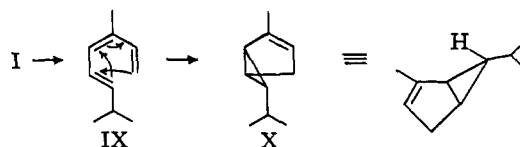


carried out as outlined in Chart I.⁹ (It may be noted that two different syntheses of VIII were completed, thus establishing the orientation of the cyclopentenone-isobutylene adducts.) The resultant hydrocarbons, however, proved to be different from the unknown.

Chart I

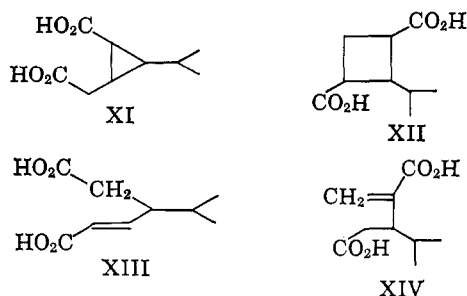


One other structure, whose formation *via* the triene IX^{2,10} has good analogy,¹¹ is the bicyclo[3.1.0]hexene X. We have now been able to obtain both chemical and physical evidence that X is the correct structure of the hydrocarbon previously described as II.



- (9) J. J. Beereboom *ibid.*, **85**, 3525 (1963). We are indebted to Dr. Beereboom for a generous gift of 2,6,6-trimethylbicyclo[3.2.0]hept-2-en-7-one.
- (10) R. J. de Kock, N. G. Minaard, and E. Havinga, *Rec. trav. chim.*, **79**, 922 (1960).
- (11) The conversion of vitamin D₂ to suprasterol-II (W. G. Dauben, I. Bell, T. W. Hutton, G. F. Laws, A. Rheiner, Jr., and H. Urscheler, *J. Am. Chem. Soc.*, **80**, 4116 (1958)) provides one example of this type of cyclization. A survey of several more recent examples was provided by Prof. W. G. Dauben at the 19th National Organic Chemical Symposium; cf. ref. 12.

Aside from the transformations already discussed, permanganate-periodate degradation¹³ of X, followed by hypobromite oxidation of the resultant methyl ketone, gave the crystalline acid XI, m.p. 131–132° (previously described as XII). Esterification followed by a base-catalyzed reverse Michael addition and hydrolysis gave XIII (rather than the reported isomeric acid, XIV). It should be noted that XIII (as well as



XIV) would be expected to give isopropylsuccinic acid upon oxidative ozonolysis, as has been observed.² However, hydrogenation of XIII gave 3-isopropyladipic acid¹⁴ (m.p. and m.m.p. 79–80°, infrared spectrum superimposable on that of an authentic sample). Infrared spectra and gas chromatographic retention times of the corresponding dimethyl esters were also identical. These results confirm the structure of XIII and exclude the original structural assignment.

Ultraviolet and n.m.r. absorption spectra lend further support to these conclusions. Thus, X shows $\lambda_{\text{max}}^{\text{cyclohexane}}$ 205 m μ (ϵ 5070), characteristic of many vinylcyclopropanes,¹⁵ and a single broad proton absorption, attributable to the cyclopropyl hydrogen at C-6, at τ 10.08.

Although it may be concluded that a synthesis of the first bicyclo[2.1.1]hexene remains to be realized,¹² it is interesting to note that the original clue to this circumstance (absence of a resolved isopropyl doublet) was, in fact, irrelevant.¹⁶

We plan to prepare the full details of both this synthetic and degradative work for publication in the near future.

(12) These results were presented in part by Prof. W. G. Dauben at the 19th National Symposium on Organic Chemistry in Tempe, Arizona, June 14–17, 1965.

(13) R. Lemieux and R. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

(14) C. G. Overberger, A. Fischman, C. W. Roberts, L. N. Arond, and J. Lal, *J. Am. Chem. Soc.*, **73**, 2540 (1951).

(15) We are indebted to Professor W. G. Dauben for measuring this ultraviolet absorption spectrum, as well as for comparison of the result with those obtained from many similar chromophores.

(16) This spectral feature is evidently not an infallible diagnostic tool. For an ominous comment on this type of error, see T. S. Eliot, "Murder in the Cathedral," Harcourt, Brace and Company, New York, 1935, p. 44.

(17) Public Health Service Postdoctoral Fellow, 1964–1965.

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A Stable Paramagnetic Complex of Gold¹

Sir:

No paramagnetic compound of gold in the formal oxidation state II hitherto has been isolated in pure

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form and fully characterized.^{2–4} Known compounds having the appropriate stoichiometry are diamagnetic, and in two cases have been shown by X-ray diffraction studies to consist of distinguishable Au(I) and Au(III) units.^{5,6} An electron spin resonance spectrum which almost certainly corresponds to the gold(II) diethyldithiocarbamate complex in solution has been reported,⁷ but the compound could not be isolated. Rich and Taube have presented⁸ convincing kinetic evidence for the transient existence of a complex of Au(II) in aqueous solution as a result of one-electron reduction of AuCl_4^- . Very recently MacCragh and Koski have reported⁹ the e.s.r. and optical spectra of gold(II) phthalocyanine. Although the compound was not obtained completely free of unspecified organic components and no magnetic moment data were given, there is little doubt that the reported sample contained Au(II). We now report the isolation and full characterization of a monomeric, paramagnetic Au(II) complex.

The complex $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Au}(\text{mnt})_2]$ ¹⁰ shows a reversible one-electron polarographic reduction wave in DMF at -0.961 v.¹¹ The reduction of this complex with $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{BH}_4$ in carefully degassed THF solution at low temperature gives in small yield the light green, microcrystalline complex $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Au}(\text{mnt})_2]$.¹² The poor yield is presumed to be due in part to further reduction of the Au(II) complex by the boron hydride by-products of the initial reaction; the reaction was carried out under the lowest possible pressure in order to remove as much as possible of the boron hydride.

The solid is not noticeably affected by standing for short periods in contact with air. Solutions are quickly oxidized by air to regenerate the red color of the monoanionic complex. In the absence of air, solutions retain their green color indefinitely; the complex shows no tendency to disproportionate to Au(I) and Au(III).

In solution the complex shows an e.s.r. spectrum consisting of four equally spaced, equally intense lines. Four lines are expected from electron-metal-nucleus interaction since gold in natural abundance is 100% ^{197}Au with $I = 3/2$. The g value in 2:1 DMF–diglyme is 2.009, and the hyperfine constant $A_{\text{av}}(^{197}\text{Au})$ is 41.7 gauss; for the gold(II) diethyldithiocarbamate complex⁷ in benzene solution, $g = 2.040$, $A_{\text{av}}(^{197}\text{Au}) = 29.4$ gauss. The conductance of the $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Au}(\text{mnt})_2]$ com-

(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Division, John Wiley and Sons, Inc., New York, N.Y., 1962, p. 862.

(3) A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford University Press, London, 1962, p. 857.

(4) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 210 (1964).

(5) N. Elliott and L. Pauling, *J. Am. Chem. Soc.*, **60**, 1846 (1938).

(6) F. H. Brain, C. S. Gibson, J. A. J. Jarvis, R. F. Phillips, H. M. Powell, and A. Tyabji, *J. Chem. Soc.*, 3686 (1952).

(7) T. Vännngård and S. Åkerström, *Nature*, **184**, 183 (1959).

(8) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 6 (1954).

(9) A. MacCragh and W. S. Koski, *J. Am. Chem. Soc.*, **87**, 2496 (1965).

(10) The abbreviation mnt refers to the ligand maleonitriledithiolate: see H. B. Gray, *Prog. Transition Metal Chem.*, **1**, in press, and references therein.

(11) Relative to Ag/AgClO_4 electrode; we thank Mr. R. Williams for assistance.

(12) *Anal. Calcd.* for $\text{C}_{40}\text{H}_{72}\text{N}_4\text{S}_4\text{Au}$: C, 49.91; H, 7.54; N, 8.73; S, 13.33. *Found*: C, 50.57, 49.80; H, 7.77, 7.55; N, 8.43, 8.48; S, 13.62, 12.95.

(13) Alfred P. Sloan Research Fellow, 1964–1966.