substantiate our assignments of the 365- and 314-cm^{-1} bands as the antisymmetric and symmetric stretching modes, respectively, of the Fe–S$_4$ tetrahedron. In this regard, one notes that Heath and Martin[11] have recently assigned the infrared-active Fe–S stretch to a band at 348 cm^{-1} in the spectrum of tris(dithioacetylacetonato)iron(III), a compound in which the ferric ion is surrounded by an octahedron of sulfurs. It is interesting that the intensity enhancement of the vibrational lines of the iron–sulfur polyhedron of rubredoxin occurs upon irradiation in either the 632- or the 502-nm band of the chromophore. A resonance or preresonance Raman effect has similarly been invoked to account for the appearance of only the Fe–Fe stretching mode in the laser-excited Raman spectrum of $[(C_5H_5)Fe(CO)]_4$.[12]

(11) G. A. Heath and R. L. Martin, *Aust. J. Chem.*, **23**, 1721 (1970).
(12) A. Terzis and T. G. Spiro, *Chem. Commun.*, 1160 (1970).

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Ion Radicals. XX. Aromatic Nitration. A New Preparation of 3-Nitroperylene and 1-Nitropyrene[1,2]

Sir:

3-Nitroperylene is ordinarily prepared by the nitration of perylene. The procedure is tedious, requires caution against polynitration, and entails the use of large volumes of solvent. For example, the best procedure in the literature for the mononitration of perylene uses approximately 1 g of perylene in over 1.5 l. of a dilute solution of nitric acid in acetic anhydride. The nitration takes 24 hr at 15°, and involves extensive work-up after hydrolyzing the acetic anhydride.[3]

In contrast with this, we have found that perylene can be mononitrated within a matter of minutes by treating the perylene cation radical with nitrite ion.

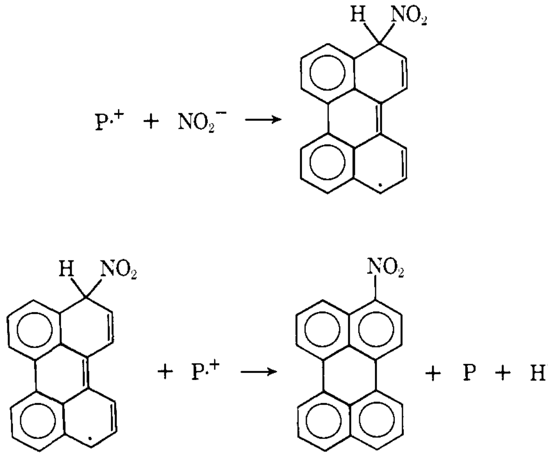
Perylene cation radical is readily obtained as a solid by two methods: anodic oxidation[4] and oxidation with iodine in the presence of silver perchlorate.[5] According to Williams,[4] the former gives a crystalline 1:1 complex of perylene and perylene cation radical perchlorate. In our hands, the method gave solid mixtures of perylene and the cation radical perchlorate of variable composition but containing approximately 30% of perylene. The solid is, nevertheless, suitable for studying reactions of the cation radical.[6] The iodine–silver perchlorate method precipitates a mixture of silver iodide and perylene cation radical perchlorate. This mixture is also suitable for studying certain of the cation radical reactions[6] and, in particular, the reaction with nitrite ion.

A sample of perylene cation radical–silver iodide ($P\cdot^+$/AgI) mixture was prepared and found by iodimetry[6] to contain 99% of the stoichiometrically required cation radical. Of this, 3.7 g (6.3 mmol) was suspended in 450 ml of dry acetonitrile, and an excess of dry sodium nitrite was added. The color of the stirred mixture changed rapidly from purple to orange-red. The mixture was stirred for 10 min and filtered. The filtrate was evaporated to dryness on a rotary evaporator and chromatographed on alumina (Woelm, neutral; 5.5 cm × 50 cm column). The blue fluorescent perylene band was eluted with 50:50 benzene–cyclohexane. The orange fluorescent 3-nitroperylene band was eluted with benzene, giving 642 mg (69% of theory) of brick-red 3-nitroperylene, mp 208–209°. Chromatographing a second time and crystallizing from benzene gave mp 209–209.5° (lit.[3] mp 210–211°).

Since only two products are obtained, perylene and 3-nitroperylene, the stoichiometry of the reaction is undoubtedly as in eq 1, where P refers to perylene

$$2P\cdot^+ + NO_2^- \longrightarrow P + P\text{-}NO_2 + H^+ \qquad (1)$$

and P-NO$_2$ to 3-nitroperylene. The simplest interpretation of the reaction (since, in the absence of kinetic data, distinction between mono- and dication reaction cannot be made[7]) is given in eq 2. This stoichiometry, and the easy oxidation of perylene by iodine in the presence of silver ion, suggests that oxidation of perylene by an excess of iodine–silver nitrite should convert all of the perylene into 3-nitroperylene. This has been achieved with a fair degree of success, as follows.



(2)

Perylene (57 mg, 0.23 mmol) and iodine (114 mg, 0.45 mmol) were placed in 50 ml of dry acetonitrile and 138 mg (0.9 mmol) of dry silver nitrite was added. The reaction mixture turned orange-red almost immediately. After 15 min of stirring, perylene was found to be absent by tlc. Working up as described above gave 45 mg (66% of theory) of 3-nitroperylene. The stoichiometry of reaction in this case is presumed

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(1) Supported by the National Science Foundation, Grant No. GP-25989X.
(2) Part XIX: H. J. Shine, L. Hughes, and P. Gesting, *J. Organometal. Chem.*, **24**, 53 (1970).
(3) M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1441 (1956).
(4) D. F. Williams, Abstracts, Fourth Molecular Crystal Symposium, Enschede, Holland, July 1968, and private communication.
(5) Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, *Bull. Chem. Soc. Jap.*, **42**, 3051 (1969).
(6) Manuscript in preparation.
(7) Y. Murata and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969).

to be as in eq 3. This reaction represents the most

$$P + I_2 + 2AgNO_2 \longrightarrow P\text{-}NO_2 + 2AgI + HNO_2 \qquad (3)$$

convenient way of mononitrating perylene at the present time.

In principle, nitration *via* the cation radical should be applicable to other aromatic hydrocarbons. We have prepared 1-nitropyrene in 80% yield as follows.

A solution of 100 mg of pyrene (0.5 mmol) in 50 ml of dry acetonitrile was cooled to 0° and to it were added 200 mg (2.9 mmol) of dry sodium nitrite, 500 mg (2 mmol) of iodine, and 825 mg (4 mmol) of silver perchlorate. Tlc showed that no pyrene remained after stirring the mixture at 0° for 30 min. Work-up as with the perylene reactions gave 98 mg of 1-nitropyrene (80% of theory), mp (crude) 147–149°, mp (glacial acetic acid) 151–151.5° (lit. mp 153–154°,[8] 155°[9]).

It is apparent that the position of "nitration" in each case is that at which positive charge density is highest, as calculated by simple HMO.[10]

Adaptation of this method to some other hydrocarbons (phenanthrene, chrysene, triphenylene, and anthracene) has not as yet proved successful. The causes are probably related to the oxidation potentials of the hydrocarbons and electrophilicity of the cation radicals, and are being investigated further.

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[8] H. V. Vollman, H. Becker, and H. Streeck, *Justus Liebigs Ann. Chem.*, **531**, 1 (1957).

[9] M. J. S. Dewar and P. M. G. Bavin, *J. Chem. Soc.*, 4486 (1955).

[10] C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press, Elmsford, N. Y., 1965.

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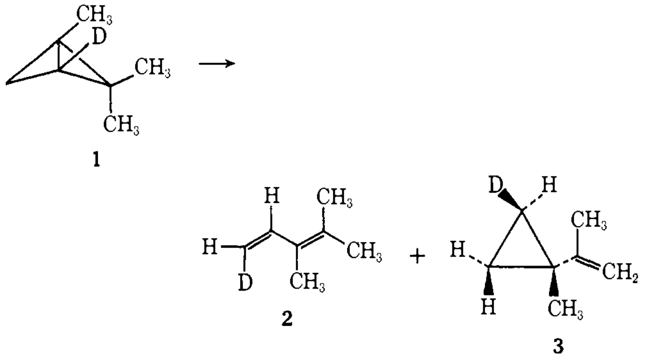
The Effect of Alkyl Substitution on the Course of the Rearrangements of Derivatives of Bicyclo[1.1.0]butane Promoted by Metal Carbonyls[1]

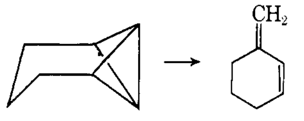
Sir:

Recently, we reported[2,3] on the metal-promoted conversion of **1** to **2** and **3**, and of **4** to **5**. Within the limits of analysis by nmr methods the isomerization of **1** to give **2** and **3** was completely stereospecific.[4] We now wish to report that the course and stereospecificity of these transition metal carbonyl-promoted rearrangements are extremely sensitive to the presence of alkyl substituents on the bicyclo[1.1.0]butane ring systems.

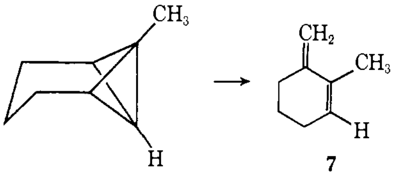
Treatment of **6**[5] with rhodium dicarbonyl chloride dimer for 15 min at 25° (room temperature), followed by vacuum transfer of the volatile materials, gave a 96% yield of **7**. Similarly, the use of iridium tricarbonyl chloride dimer allowed **6** to be converted into **7** in 93% yield. The structure of **7** was established on the basis of its characteristic spectral data: nmr τ 4.37 (one-proton multiplet), 5.17 (broad one-proton singlet), and 5.30 (broad one-proton singlet); ir 6.09, 6.22, and 11.28 μ; uv λ_{max}^{hexane} 234 nm (ε 16,200).[6] In addition, **7** was catalytically hydrogenated to give a mixture of *cis*- and *trans*-1,2-dimethylcyclohexane and dehydrogenated to give *o*-xylene. The transition metal carbonyl-promoted opening of **6** was extremely specific. No trace of any isomeric hydrocarbon could be detected by vpc.



1 **2** **3**

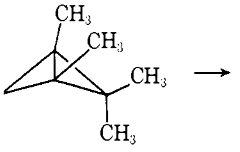


4 **5**

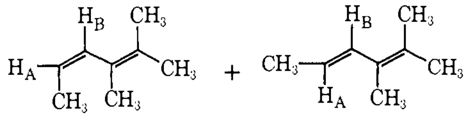


6 **7**

Whereas the rearrangement of the methylated version of **4** occurred with unusual stereospecificity, the addition of another methyl group to **1** resulted in a loss of stereospecificity. When **8**[7] was treated with 5 mol % of rhodium dicarbonyl chloride dimer in chloroform at room temperature, no trace of **8** remained after 5 min. We found that during this time **8** had rearranged to give a 46% yield of **9** and a 50% yield of **10**.[8] Both **9** and **10** were readily hydrogenated to 2,3-dimethylhexane which was identical in all respects with an authentic sample. The stereochemistry of the two isomers was established on the basis of both nmr and ultraviolet



8



9 **10**

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[1] Paper XVII on "The Chemistry of Bent Bonds." For the previous paper in this series see P. G. Gassman, J. Seter, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1673 (1971).

[2] P. G. Gassman and F. J. Williams, *ibid.*, **92**, 7631 (1970).

[3] P. G. Gassman and T. J. Atkins, *ibid.*, **93**, 1042 (1971).

[4] The stereochemistry of **3** was established by analysis of the nmr spectrum of **3** with that of its epimer. We wish to thank Professor William Moore for providing the nmr spectrum of the epimer of **3**.

[5] For the preparation of **6** see G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963).

[6] Exact mass mol wt calcd for C_8H_{12}: 108.09389. Found: 108.09379.

[7] For the preparation of **8** see W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *Tetrahedron Lett.*, 2365 (1970).

[8] Both **9** and **10** are known compounds: D. F. Schneider and C. F. Garbers, *J. Chem. Soc.*, 2465 (1964).