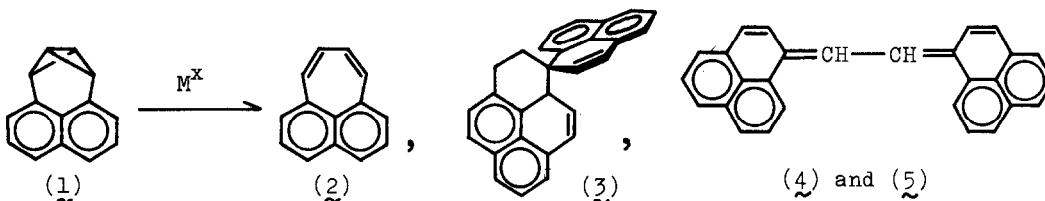


THE CHEMISTRY OF PHENALENIUM SYSTEM XVI ¹⁾
 EVIDENCE FOR INTERMEDIATES IN TRANSITION METAL PROMOTED REACTION OF
 NAPHTHO[1,8]TRICYCLO[4.1.0.0^{2,7}]HEPTENE

Ichiro Murata, Kazuhiro Nakasuji and Hirokazu Kume
 Department of Chemistry, Faculty of Science, Osaka University,
 Toyonaka, Osaka 560, Japan

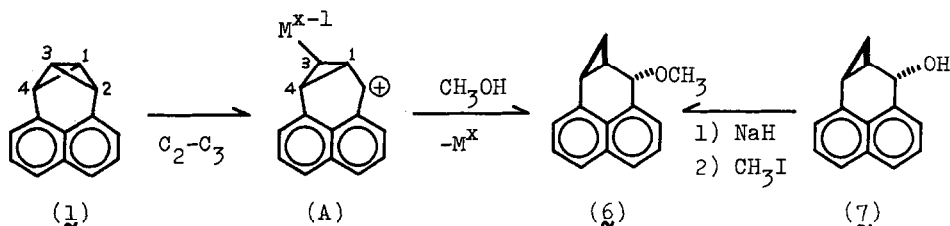
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In the preceding communication¹⁾ we have demonstrated that the Ag(I) promoted reaction of naphtho[1,8]tricyclo[4.1.0.0^{2,7}]heptene (1) provides pleiadene (2) as a sole product whereas Pd(II) and Rh(I) complex catalyzed reaction of 1 gives a wide range of products involving spiro-dimer (3) and 10,10'-biphenylfulvenyls (4) and (5) along with 2. The nature and the ratio of the products formed were dependent on the metal and on the ligands attached to the metal. We have proposed the intermediacy of the one bond cleavage intermediate (A), metal complexed carbene (B) metal bonded carbonium ion (C) hybrid and phenylfulvene (D) for this reaction. We now wish to present evidence in support of the intermediacy of (A) and the transient existence of (D).

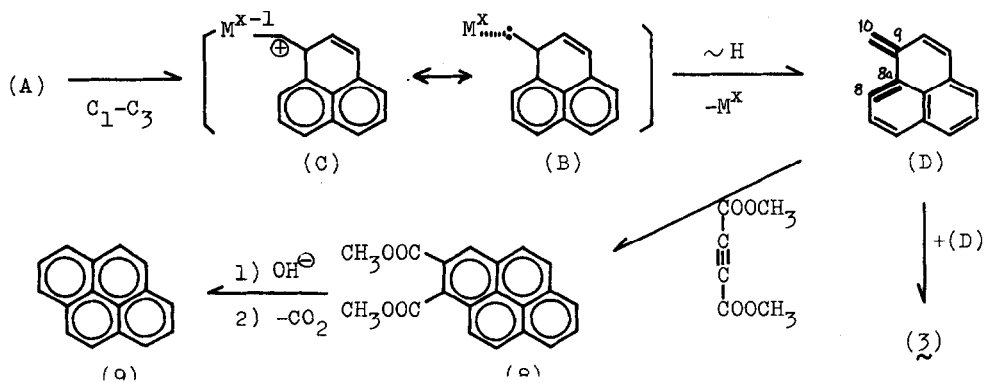


For the purpose of detection of (A) we attempted to trap (A) by carrying out the reaction in a methanol solution. Treatment of 1 with 2.2 mole % of rhodium dicarbonyl chloride dimer in methanol afforded in 71% isolated yield of naphtho[1,8]trans-methoxybicyclo[4.1.0]heptene (6) accompanied by a mixture of minute amount of 2 and 3. The structure of 6 was proven by nmr spectrum which showed three

complex multiplets centered at δ 0.25(1H), 1.00(1H) and 2.05(2H) due to the cyclopropyl protons, a sharp singlet at δ 3.00(3H) due to the methoxyl protons, a broad singlet at δ 4.90(1H) resulting from the proton attached to carbon bearing methoxyl group and an aromatic proton multiplet at δ 7.1-7.7. The broad singlet signal at δ 4.90 suggests the trans-configuration of the methoxyl group respect to the cyclopropane ring.²⁾ This conclusion was further confirmed by spectral comparison with an authentic sample. Thus, methylation of known trans-alcohol (7)³⁾ with sodium hydride-methyl iodide gave 6.



Phenafulvene (methylenephthalene) (D), one of the fundamental cross-conjugated system involving the phenalene skeleton, was suggested as a possible precursor of 3. In spite of many efforts, the syntheses of the simple phenafulvene derivatives have so far not been successful due to their pronounced thermal and air labilities.⁴⁾ In order to gain a clear picture about the transient existence of the as yet elusive phenafulvene (D), we are pursuing a trapping of this hydrocarbon during the transition metal promoted reaction of 1. The phenafulvene (D) contains formally a diene segment, namely the double bonds of $C_8=C_{8a}-C_9=C_{10}$, the



terminal carbon atoms of which are held in a site that provides suitable regional conditions (fixed in a cisoid-butadiene) for the occurrence of a symmetry allowed [4+2]cycloaddition with dienophiles. It was previously observed that 1 underwent trans-chlorocarbonylbis(triphenylphosphine)rhodium catalyzed reaction to provide spiro-dimer (3) exclusively while the reaction of 1 with rhodium dicarbonyl acetylacetonate affords mainly 2 (75%) along with 3 (15%) and traces of 4 and 5.¹⁾ In a typical trapping experiment, treatment of 1 with 3.1 mole % of $\text{Rh}(\text{Ph}_3\text{P})_2(\text{CO})\text{Cl}$ in chloroform in the presence of dimethyl acetylenedicarboxylate at 55°C for 2 hr afforded dimethyl pyrene-1,2-dicarboxylate (8) in 33% yield instead of 3 together with a trace of pleiadiene (2). Also when a chloroform solution of 1 was treated with 2.9 mole % of $\text{Rh}(\text{CO})_2\text{acac}$, a rapid reaction occurred to give 2 and 8 in 75% and 15% yield, respectively. The latter experiment denotes that the precursor leading to the spiro-dimer (3) was trapped completely by dimethyl acetylenedicarboxylate. Although dimethyl pyrene-1,2-dicarboxylate (8) is not a known derivative, the uv spectrum, λ_{max} (ethanol) 395 nm(log ϵ 3.34), 374(3.24), 339(4.51), 325(4.30), 311(3.92), 280(s, 4.45) and 263(4.76), is quite similar to that reported for pyrene-2-carboxylic acid.^{5,6)} The structure proof of 8 was based on its characteristic nmr data, δ (60 MHz, CDCl_3), 4.05(s, 3H), 4.15(s, 3H), 8.05-8.25(m, 7H) and 8.73(s, 1H). In addition, 8 was hydrolyzed to give pyrene-1,2-dicarboxylic acid which on decarboxylation with copper-powder in quinoline afforded pyrene (9). The uv spectrum of 9 is identical in detail with that reported for the authentic pyrene.⁷⁾ The formation of 8 as the addition product in these reactions closely parallels the trapping experiments of the reactive heptafulvene with dimethyl acetylenedicarboxylate,⁸⁾ and constitutes further support for the structural assignment to the phenafulvene.

The facile Diels-Alder reaction between phenafulvene (D) as a 4 π -component and dimethyl acetylenedicarboxylate as a reactive dienophile serves to provide a major reason for the formation of the spiro-dimer (3) in the Pd(II) and Rh(I) catalyzed reaction of 1.

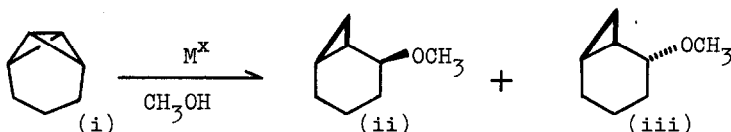
On the other hand, upon treatment of 1 with silver perchlorate in benzene in the presence of dimethyl acetylenedicarboxylate, pleiadiene (2) was obtained as the only characterizable product in 85% yield. This example demonstrates that the

course of the Ag(I) catalyzed isomerization of 1 is highly selective and is entirely different from those of Pd(II) and Rh(I) catalyzed reaction.

The synthetic utility of the reactive phenylfulvene for the many polycyclic compounds containing the phenalene skeleton is now under examination.

REFERENCES AND FOOTNOTES

- 1) For part XV of this series, see : I. Murata, K. Nakasuji and H. Kume, Preceding communication.
- 2) The Ag(I) catalyzed conversion of tricyclo[4.1.0.0^{2,7}]heptane (i) in methanol in the presence of a trace of sodium methoxide was reported to afford a 94:6 mixture of cis- and trans-methoxybicyclo[4.1.0]heptanes, (ii) and (iii) : M. Sakai, H. H. Westberg, H. Yamaguchi and S. Masamune, J. Amer. Chem. Soc., 93, 4611 (1971).



Gassman et. al. have also observed similar results with rhodium dicarbonyl chloride dimer in methanol: P. G. Gassman and T. J. Atkins, ibid., 94, 7748 (1972). It is interesting to note that we have observed that the Rh(I) reacts with our compound (1) in methanol to give mainly a trans-methoxy derivative (6) corresponding to (iii). The difference in the stereochemistry of product is not fully understood.

- 3) I. Murata and K. Nakasuji, Tetrahedron Letters, 1591 (1973).
- 4) I. Murata, T. Nakazawa and S. Tada, unpublished observations. cf. S. Tada, MS Thesis, Osaka University (1971).
- 5) H. Vollmann, H. Becker, M. Correll and H. Struck, Justus Liebig's Ann. Chem., 531, 1 (1937).
- 6) R. A. Friedel and M. Orchin, Ultraviolet Spectra of Aromatic Compounds, No. 492, John Wiley and Sons, Inc., New York (1951).
- 7) DMS UV Atlas of Organic Compounds, Vol. II, E6/5, Verlag Chemie, Weinheim (1966).
- 8) W. von E. Doering and D. W. Wiley, Tetrahedron, 11, 183 (1960); B. M. Trost, R. C. Atkins and L. Hoffman, J. Amer. Chem. Soc., 95, 1285 (1973).