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TRANSITION METAL PROMOTED REACTION OF NAPHTHO[1,8]TRICYCLO[4.1.0.0<sup>2,7</sup>]HEPTENE

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The transition metal promoted isomerization of derivatives of bicyclo[1.1.0]-butane has extensively been investigated by many workers and the mechanism of this intriguing skeletal reorganization has been argued in detail.<sup>2)</sup> It has been pointed out that the behaviour of Pd(II) towards some bicyclobutanes is significantly different from that of Ag(I). For instance, Pd(II) gives rise to quantitative isomerization of tricyclo[4.1.0.0<sup>2,7</sup>]heptane into 3-methylenecyclohexene while Ag(I) catalysis produces exclusively cyclohepta-1,3-diene.<sup>3)</sup>

On the other hand, the synthesis of a novel bicyclobutane derivative, naphtho[1,8]tricyclo[4.1.0.0<sup>2,7</sup>]heptene (1), has recently been achieved by us<sup>4)</sup> and by Pagni et. al.,<sup>5)</sup> and prompted us to investigate the transition metal promoted reaction of 1. We now wish to present this investigation in a preliminary form.

We have already found that the compound 1 can be isomerized to give pleiadene (2) at room temperature by treatment with Ag(I).<sup>4)</sup> When a benzene solution of 1 was treated with 4.8 mole % of silver perchlorate, a rapid reaction occurred to give 2 as a sole product in 85% yield after 1 hr. In contrast to the behavior described above a dramatic difference exists between Ag(I) and other transition metal complexes such as palladium or rhodium. As shown in Table 1, when 1 was treated with  $\pi$ -allylpalladium(II) chloride dimer a mixture of the new compounds, designated as 3 and 4 for convenience, in yield of 82% and trace respectively along with 12% yield of 2 were obtained. When bis(benzonitrile)dichloropalladium(II) was used to promote the reaction, 1 afforded 53% of 2, ~1% of 3 and a trace of 4. In the presence of palladium(II) acetate, the major (68%) and minor (28%) products were

Table 1. Product Distribution of Metal Promoted Reaction of 1

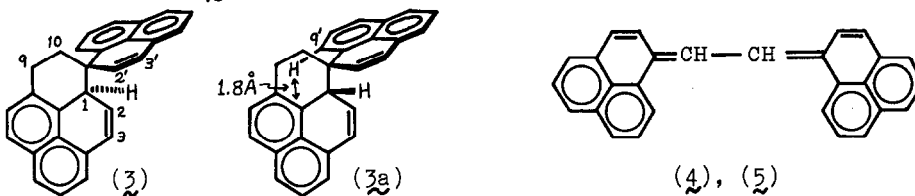
Catalyst	Conditions		Solvent	% yield of Products <sup>b)</sup>			
	Temp(°C)	Time <sup>a)</sup>		<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
AgClO <sub>4</sub>	50	1 hr	C <sub>6</sub> H <sub>6</sub>	85			
Pd(PhCN) <sub>2</sub> Cl <sub>2</sub>	30	20 min	CHCl <sub>3</sub>	53	~1	t	
[Pd( $\pi$ -C <sub>3</sub> H <sub>5</sub> )Cl] <sub>2</sub>	50	20 min	CHCl <sub>3</sub>	12	82	t	
Pd(OAc) <sub>2</sub>	50	2 hr <sup>c)</sup>	CHCl <sub>3</sub>	68	28	t	
[Rh(CO) <sub>2</sub> Cl] <sub>2</sub>	20	15 min	CHCl <sub>3</sub>	48	33	t	t
Rh(Ph <sub>3</sub> P) <sub>2</sub> (CO)Cl	60	1.5 hr <sup>d)</sup>	CHCl <sub>3</sub>	t	90	t	
Rh(CO) <sub>2</sub> acac	22	25 min	CHCl <sub>3</sub>	74	15	t	t
[Rh( $\pi$ -C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> Cl] <sub>2</sub>	50	2.5 hr <sup>e)</sup>	CHCl <sub>3</sub>	t	76	t	t
Rh(Ph <sub>3</sub> P) <sub>3</sub> Cl	50	3 hr <sup>f)</sup>	CHCl <sub>3</sub>	t	59	t	

a) Reaction times reflect the times when the presence of 1 could not be detected by tlc. b) Isolated yield. t denotes a trace. Formation of 4 and 5 are easily detected by tlc due to their blue color even in a trace amount. c) Heterogeneous reaction d) 5% of 1 was recovered after this reaction time. e) 14% of 1 was recovered. f) 21% of 1 was recovered.

again 2 and 3 respectively along with a trace of 4. The controlling effect on the mode of reaction by the ligand attached to the metal was also observed in the rhodium catalyzed reactions as shown in Table 1 in which formation of a new blue-colored product (5) was observed by tlc together with 2, 3 and 4.

The compound 3 is an air-sensitive pale yellow crystals, mp 140-141°C (d.). Both elemental analysis, Found: C, 93.99; H, 5.67. calcd. for C<sub>28</sub>H<sub>20</sub>: C, 94.34; H, 5.66%, and mass spectrum of 3, m/e 356(M<sup>+</sup>, 27%), 178(M<sup>+</sup>/2, 100%), clearly indicated it to be a dimer of 1. The uv spectrum of 3 showed absorption bands at  $\lambda_{\max}$  (cyclohexane) 235 nm(log  $\epsilon$  4.84), 327(4.36), 343(4.33), 396(2.40), 420(2.21). The structure of 3 was confidently established primarily on the basis of its nmr spectrum (60 MHz, CDCl<sub>3</sub>) which showed peaks at  $\delta$  6.9-7.8(1H, m, aromatic), 6.57(1H, d, J=10 Hz), 6.38(1H, d.d, J=10 and 3 Hz), 5.88(1H, d, J=10 Hz), 5.41(1H, d.d, J=10 and 3 Hz), 4.1-4.4(1H, m), 2.9-3.3(2H, m) and 1.9-2.4(2H, m). The AB-quartet at  $\delta$  5.88 and 6.57 was due to one of the vicinal olefinic hydrogens isolated from the remaining spin systems, H-2' and H-3' respectively. An alternative AB-quartet with further doublet splitting at  $\delta$  5.41 and 6.38 was due to the H-2 and H-3. The assignment of peak at  $\delta$  4.1-4.4 to H-1 was confirmed by double resonance experiment, thus the irradiation at the site of the multiplet at  $\delta$  4.1-4.4 assigned to H-1 now

changed the H-2 and H-3 pattern to a clean AB-quartet of  $J=10$  Hz. The two 2H multiplets centered at  $\delta$  3.1 and 2.2 are reasonably assigned to the strongly coupled benzylic and non-benzylic methylene protons at C-9 and C-10, respectively. Inspection of Dreiding models reveals that, if the molecule existed in a configuration illustrated as 3a, the hydrogen attached to C-9' would have a substantial non-bonding interaction due to the close proximity (ca. 1.8 Å) to the tetrahydro-pyrene moiety whereas that of the configuration 3 may not. Therefore structure 3 seems more likely than 3a in terms of the steric considerations.

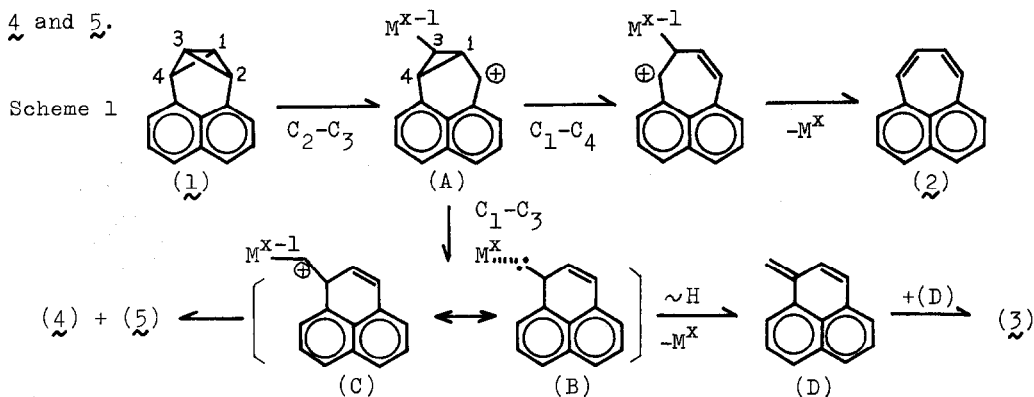


The compounds, 4 and 5, are easily characterized by their bright blue color indicating the presence of extending conjugation. The molecular formula of 4 was confirmed by high-resolution mass spectrometry to be 354.1393 (calcd. for  $C_{28}H_{18}$ , 354.1408) and it possessed the appropriate fragment at  $m/e$  177.0697 for  $C_{14}H_9^+$ . The visible spectrum of 4 showed the vibrational fine structure,  $\lambda_{max}$  (ethanol) at 494, 532 and 575 nm,<sup>6)</sup> while that of 5 had similar in shape with slight red-shift,  $\lambda_{max}$  (ethanol) at 503, 540 and 587 nm. The nmr spectrum of 4 had a complex multiplet only in an aromatic region,  $\delta$  6.9-8.2. Although the precise structural elucidation of 4 and 5 could not be performed due to their limited quantities available, the above-mentioned spectroscopic properties are suggestive of the geometrical isomers of 10,10'-biphenylfulvenyl for the structures of 4 and 5.<sup>7)</sup>

The overall product distribution of the transition metal complex promoted reaction of 1 can be interpreted in terms of the mechanism shown in Scheme 1 which was identical with that of tricyclo[4.1.0.0<sup>2,7</sup>]heptane proposed by Gassman et al.<sup>2c)</sup> Thus initial attack of the metal complex resulted in  $C_2-C_3$  bond cleavage to give the cyclopropylcarbinyl cation (A). Subsequent opening of the  $C_1-C_4$  bond followed by loss of  $M^X$  would produce 2. Formation of 3 is simply rationalized by involving the hybrid intermediate of metal complexed carbene (B) and metal bonded carbonium ion (C).<sup>8)</sup> A hydrogen shift and loss of metal from (B) would afford phenylfulvene (D), which upon dimerization by way of Diels-Alder reaction resulted

in the formation of 3. Very minor products, 4 and 5, could arise from a pathway involving the coupling reaction of (B) or (D). We found earlier that the compound 4 was also obtained in a minimum quantity during the preparation of 1 from phenalenide ion and dichloromethane in the presence of *n*-butyllithium.<sup>4)</sup>

This tends to suggest that the carbene type intermediate (B) is the precursor of 4 and 5.



In the accompanying paper,<sup>9)</sup> we report the experimental evidences for the existence of the cyclopropylcarbinyl cation (A) and the phenalenyl anion (D) in the transition metal promoted reaction of 1.

- 1) For part XIV of this series, see: I. Murata and K. Nakasuji, Tetrahedron Letters, 1591 (1973).
- 2) For a detailed listing of references to this field, see : a) P. G. Gassman and F. J. Williams, J. Amer. Chem. Soc., 94, 7733 (1972); b) P. G. Gassman, G. R. Meyer and F. J. Williams, ibid., 94, 7741 (1972); c) P. G. Gassman and T. J. Atkins, ibid., 94, 7748 (1972); d) L. A. Paquette, S. E. Wilson, R. P. Henzel and G. R. Allen, Jr., ibid., 94, 7761 (1972); e) L. A. Paquette, R. P. Henzel and S. E. Wilson, ibid., 94, 7771 (1972); f) idem., ibid., 94, 7780 (1972); g) R. Noyori, Tetrahedron Letters, 1691 (1973); h) D. J. Cardin, B. Cetinkaya, M. J. Doyle and M. F. Lappert, Chem. Soc. Revs., 2, 99 (1973).
- 3) a) M. Sakai and S. Masamune, J. Amer. Chem. Soc., 93, 4610 (1971); b) M. Sakai, H. Yamaguchi and S. Masamune, Chem. Commun., 486 (1971).
- 4) I. Murata and K. Nakasuji, Tetrahedron Letters, 47 (1973).
- 5) R. M. Pagni and C. R. Watson, ibid., 59 (1973).
- 6) Compound 4 showed  $\lambda_{max}$  (THF) 233(4.53), 280(4.40), 332(3.84), 365(3.48), 467 (3.68), 498(4.28), 536(4.78) and 581nm(5.12). The quantitative uv measurement of 5 could not be performed due to its limited quantity.
- 7) Paquette et al. have reported that the Ag(I) catalyzed reaction of exo,endo- and exo,exo-2,4-dimethylbicyclo[1.1.0]butane also provided an equal mixture of two isomeric dimers : see ref. 2f) and L. A. Paquette, Account Chem. Res., 4, 280 (1971).
- 8) P. G. Gassman, T. J. Atkins and F. J. Williams, J. Amer. Chem. Soc., 93, 1812 (1971); P. G. Gassman and T. Nakai, ibid., 93, 5897 (1971).
- 9) I. Murata, K. Nakasuji and H. Kume, Accompanying communication.