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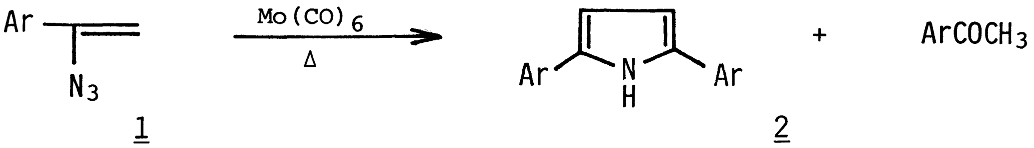
NOVEL TYPE OF TRANSFORMATIONS OF α-AZIDOSTYRENE DERIVATIVES AND 3-ARYL-2H-AZIRINES IN THE PRESENCE OF HEXACARBONYLMOLYBDENUM

Makoto NITTA* and Tomoshige KOBAYASHI
Department of Chemistry, School of Science and Engineering,
Waseda University, Shinjuku-ku, Tokyo 160

The reaction of α-azidostyrene derivatives with hexacarbonylmolybdenum was found to give 2,5-diarylpyrroles and acetophenone derivatives via a complexed 1-arylvinylnitrene intermediate, while that of 3-aryl-2H-azirines gave 2,4-diarylpyrroles in addition to acetophenone derivatives and 2,5-diarylpyrazines.

The reaction of 3-aryl-2H-azirines with group VI metal carbonyls [$M(CO)_6$; M= Cr, Mo, W] has been investigated to give 2,5-diarylpyrazines and/or isomeric dihydropyrazines.[1,2] The reaction mechanism are postulated to involve a complexed nitrile ylide intermediate[1] or a metathetic type reaction of C=N bond of the azirines.[2] In contrast, 2-alkenyl-3-aryl-2H-azirine is transformed into 2-arylpyrrole in excellent yield via the intramolecular cyclization of a complexed dienylnitrene intermediate, and the related reactions have been devised to synthesize isoxazoles and pyrazoles.[1] Although a series of bisphenylnitrene and diphenylurea-based complexes or the corresponding complexes of 1-phenylvinylnitrene have been isolated in the reaction of [$Fe(CO)_5$] or [$Fe_2(CO)_9$] with azidobenzene,[3] or α-azidostyrene and 3-phenyl-2H-azirines,[4,5] the related reaction of organic azide with [$Mo(CO)_6$] has not been studied. We now wish to report a novel type of reaction of α-azidostyrenes 1a-c with [$Mo(CO)_6$] giving 2,5-diarylpyrroles 2a-c and acetophenone derivatives 3a-c possibly via a complexed 1-arylvinylnitrene intermediate in good combined yields as shown in Scheme 1. Furthermore, 3-aryl-2H-azirines 4a,b, which stand as the isomer of 1-arylvinylnitrenes, were also studied to afford 2,4-diarylpyrroles 5a,b, along with 3a,b and 2,5-diarylpyrazines 6a,b. The formation of 5a,b from azirines 4a,b is novel and, has not been observed in a former study.[1]

A solution of α-azidostyrene 1 (1 mmol) and [$Mo(CO)_6$] (1 mmol) in 10 ml of solvent was heated at 60 °C for 24 h under a dry nitrogen atmosphere. The solu-



1 2 3

a: Ar = C_6H_5 b: Ar = p-CH_3-C_6H_4 c: Ar = p-Br-C_6H_4

Scheme 1.

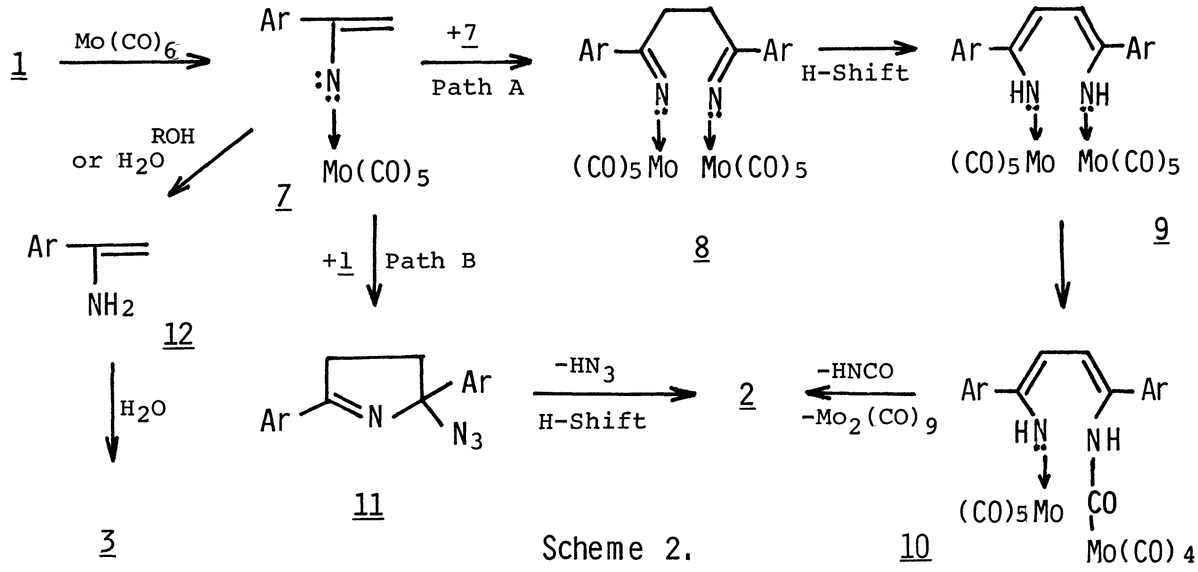
Table 1. Hexacarbonylmolybdenum-induced Reaction of α-azidostyrenes[a)]

Entry	α-Azidostyrene	Solvent	Product (Yield/%)	
1	1a	CH_3CN	2a (64),	3a (23)
2	1b	CH_3CN	2b (54),	3b (21)
3	1c	CH_3CN	2c (57),	3c (17)
4	1a	CH_3OH	2a (63),	3a (34)
5	1a	CH_3CN-H_2O	2a (53),	3a (37)
6	1a	THF	2a (40),	3a (13)
7[b)]	1a	CH_3CN	1a (81),	4a (11)

a) All of the reactions were carried out under reflux for 24 h.
b) Heated at 60 °C for 24 h in the absence of $[Mo(CO)_6]$.

tion was filtered through Celite and the filtrate was separated by TLC on silica gel to give the products which are summarized in Table 1. All of the α-azidostyrenes 1a-c[6)] and the products[4)] are known compounds and were identified on the basis of the physical properties. In the present reactions, the solvent seems to be important in the formation of pyrroles 2a-c. In anhydrous acetonitrile, the best yield of 2a as compared to the yield of acetophenone 3a was obtained (entry 1). In protic solvent such as methanol or moist acetonitrile, 1a gave 2a and 3a, with the increased yield of 3a (entries 4 and 5). However in THF (tetrahydrofuran) solution, 1a gave 2a and 3a in low combined yield (entry 6). Although the thermal reaction of 1a at room temperature for 1 month has been shown to give 2a along with many other products,[7)] heating of 1a in the absence of $[Mo(CO)_6]$ afforded azirine 4a in an 11% yield with the remainder beeing unchanged starting material 1a in an 81% yield (entry 7). Thus the $[Mo(CO)_6]$ is indispensable for the formation of 2 and 3.

The present reactions are best explained by the mechanism in Scheme 2. This mechanism is speculative since no intermediate has been isolated. The complexed nitrene 7 could be formed initially. Path A represents the dimerization of 7 at β-vinyl carbon atom to give 8 followed by the 1,3-migration of hydrogens and the ligand migration to lead to 10 which then collapses to give 2. An alternative



Scheme 2.

pathway is the 1,3-dipolar-type cycloaddition (path B) of 7 with 1 giving 11, which could afford 2 through elimination of HN_3 and the subsequent migration of a hydrogen atom. However, attempted reactions of 1a with $[Mo(CO)_6]$ in the presence of a large excess of dipolarophiles, such as vinyl acetate and acrylonitrile, afforded 2a (16-49%), 3a (7-16%), and no 1,3-dipolar cycloadduct of 7 with the dipolarophile.8) Therefore path A seems to be favored over path B and, would explain the regioselective formation of 2. Acetophenone derivatives 3 would arise from the enamine 12, which could be derived from the reaction of the complexed nitrene intermediate 7 in the presence of protic solvents (entries 4 and 5) or in the presence of stray water.9)

Similar mechanistic pathways involving carbonyliron complexes corresponding to 8, 9, and 10 have been postulated in the reaction of 3-aryl-2H-azirines with $[Fe_2(CO)_9]$ in aprotic media to give 2,5-diarylpyrroles albeit in low yield, along with several complexes.4) On the other hand, $[Mo(CO)_6]$-induced reaction of 3-aryl-2H-azirines has been shown to give 2,5-diarylpyrazines and isomeric dihydropyrazines.1) With this in mind, the reaction of 3-aryl-2H-azirines 4a and 4b (Scheme 3) was also studied under the conditions similar to the case of 1a-c. The reaction conditions and the results are summarized in Table 2. The reaction in THF at room temperature would not proceed and the starting material was recovered in good yield (entries 1 and 2) unlike in the case of the former study.1) Under reflux in THF, on the other hand, 4a or 4b afforded 2,4-diarylpyrrole 5a10) or 5b,11) acetophenone derivative 3a or 3b, along with 2,5-diarylpyrazine 6a or 6b (entries 3 and 4). In the reaction of 4a in acetonitrile, the formation of 5a was supressed and 2,5-diarylpyrrole 2a was also obtained in low yield (entry 5). However, in acetonitrile containing water, the formation of acetophenone 3a was increased and the yield of 5a was decreased instead (entry 6).

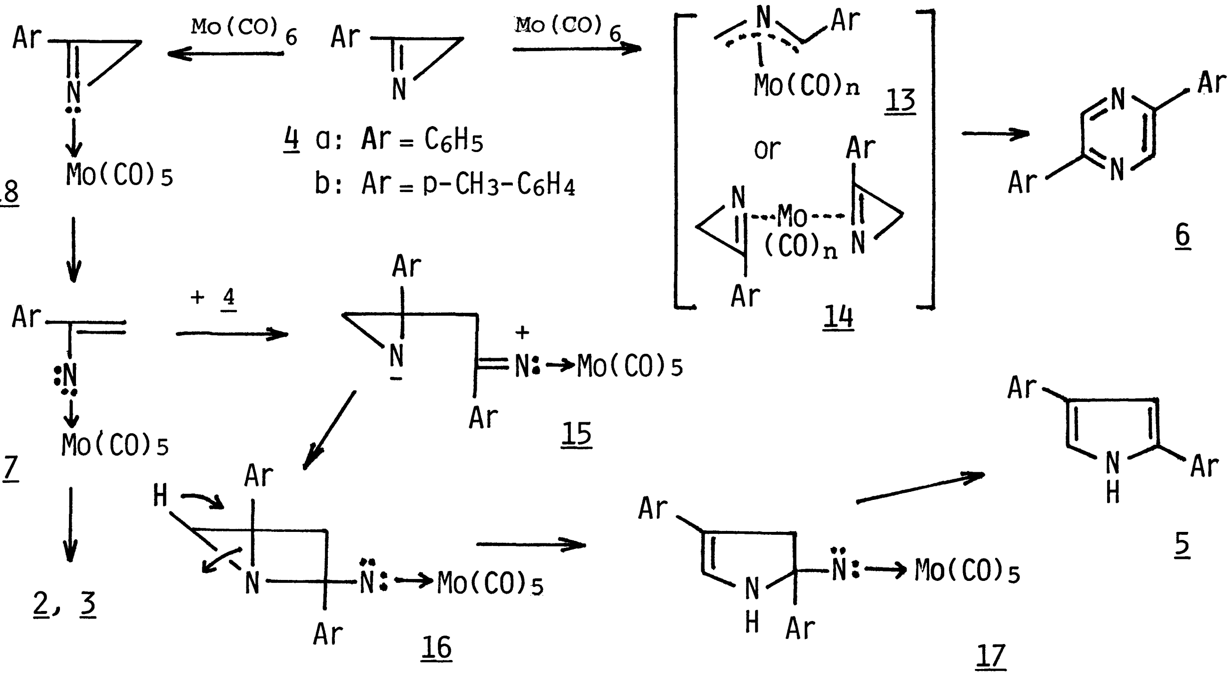
The formation of 2,5-diarylpyrazine 6 could be explained by the intervention of a complexed nitrile ylide 131) or a metathetic type reaction via the complex 14.2) Novel point of the reaction summarized in Table 2 is the formation of acetophenone derivatives 3a,b, 2,5-diarylpyrrole 2a, and 2,4-diarylpyrroles 5a,b. The formation of 2a and/or 3a,b is similar to the reaction of 1a-c. Furthermore, the increased yield of 3 as well as the decreased yield of 5 in entry 6 in Table 2 is suggestive of the common intermediate of a complexed nitrene 7, which would also be derived from the C-N bond cleavage of 4. Therefore we assume that 2,4-diaryl-

Table 2. Hexacarbonylmolybdenum-induced Reaction of 3-Aryl-2H-azirines 4a,ba)

Entry	Compound	Reaction time / h	Solvent	Product				
				2	3	4	5	6
1b)	4a	24	THF	0	0	97	0	0
2b)	4b	24	THF	0	0	85	0	0
3	4a	2	THF	0	10	0	39	3
4	4b	2	THF	0	3	0	36	5
5	4a	2	CH_3CN	4	3	0	17	2
6	4a	2	CH_3CN-H_2O	0	35	0	4	5

a) Heated at 75-80 °C in the presence of an equivalent amount of $[Mo(CO)_6]$.
b) The reaction was carried out at room temperature.

pyrrole 5a,b could be derived from the complex 7 with the azirines 4a,b, via 15, 16, and 17. The reaction of 4a,b is very rapid as compared to those of 1a-c (cf. Tables 1 and 2). Furthermore the reaction of 7 with 4 could be rapid as compared to the dimerization of 7 leading to 2 via 8, 9, and 10. The solvent seems also to affect the formation of 2 and 5 (entries 3 and 5). Further confirmation of the mechanistic aspect of the reactions is in progress.



Scheme 3.

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