Nonacarbonyldiiron-Induced Reaction of 3-Azido-1,2,3-triphenylcyclopropene and 4,5,6-Triphenyl-1,2,3-triazine

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(Received January 6, 1987)

Synopsis. The [$Fe_2(CO)_9$]-induced reaction of 3-azido-1,2,3-triphenylcyclopropene (**1**) undergoes elimination of a nitrogen molecule and C-C bond cleavage to result in the formation of benzonitrile, diphenylacetylene, 2,3-diphenylinden-1-one, and 1,2,3-triphenylpropen-1-one. The similar reaction of 4,5,6-triphenyl-1,2,3-triazine, which is an isomer of **1**, undergoes reductive N-N bond cleavage to give 3,4,5-triphenylpyrazole in good yield.

Previously, we have found that [$Mo(CO)_6$], [$Fe(CO)_5$], and [$Fe_2(CO)_9$] can induce the reductive N-O bond cleavage of isoxazoles in protic media to give β-amino enones in good yields.[1] Application of this method for the synthesis of geiparvarin has been demonstrated.[2] Furthermore, our group[3] and other groups[4–10] have investigated the generation and chemical behaviors of the complexed nitrene intermediates which are derived from the reaction of organic azides with iron carbonyl. A series of these studies then raise the question whether the complexed nitrene intermediate, which is derived from 3-azido-1,2,3-triphenylcyclopropene (**1**) and [$Fe_2(CO)_9$], undergoes ring expansion to give azete (azacyclobutadiene) or complexed azete derivative or not. Thermal reaction of **1** has been reported to give 4,5,6-triphenyl-1,2,3-triazine (**2**).[11] The photochemical reaction of **2** has also been reported to give benzonitrile, diphenylacetylene, 2,3-diphenylquinoline, and 2,3,5,6,7,8-hexaphenyl-1,4-diazocine via postulated azete intermediate.[11,12] However, up to now, three azete derivatives, tris(dimethylamino)-,[13] tri-*t*-butylazete,[14] and 2-arylbenzazete,[15] have been isolated as the products of the thermal decomposition of the corresponding triazines. We report here the results for the [$Fe_2(CO)_9$]-induced reaction of **1** and **2**.

The reaction of **1** with [$Fe_2(CO)_9$] at ambient temperature in anhydrous benzene, acetonitrile, and aqueous acetonitrile afforded benzonitrile (**3**), diphenylacetylene (**4**), 2,3-diphenyl-1*H*-inden-1-one (**5**), and 1,2,3-triphenylpropen-1-one (**6**) as shown in Scheme 1. The product **3** was detected by GLC and IR, and the isolation was not carried out. The reaction conditions and the yields of the products except **3** are summarized in Table 1 (Entries 1—3). In contrast, the reaction of **1** and [$Fe_2(CO)_9$] in methanol gave mainly **6** and the complex **7** in addition to **3**, **4**, and **5** (Table 1, Entry 4).

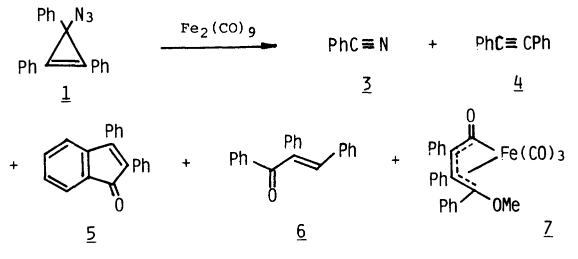
Table 1. Results of the Reaction of **1** with [$Fe_2(CO)_9$][a)]

Entry	Solvent	Product (yield/%)				
		3	**4**	**5**	**6**	**7**
1	PhH	b)	8	6	8	—
2	MeCN	b)	5	15	9	—
3	MeCN-H_2O[c)]	b)	3	4	10	—
4	MeOH	b)	1	1	67	13

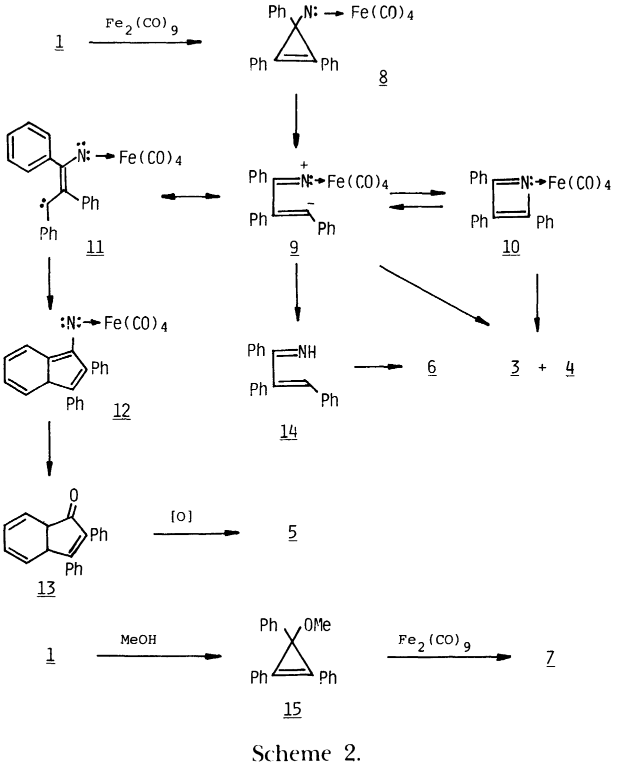
a) Reactions were carried out at ambient temperature for 24 h. b) Isolation was not carried out. c) 5.0 Molar equivalent amounts of water was added.

The postulated mechanistic pathways for the reaction are shown in Scheme 2. The reaction of **1** with [$Fe_2(CO)_9$] initially gives the complexed nitrene intermediate **8**.[3–10] Then, the C-C bond cleavage of **8** seems to occur to give **9**. The direct decomposition of **9** can give **3** and **4**. An alternative route involving an azete intermediate **10**, which can give **3** and **4**, might not be ruled out. However, no evidence has been obtained at this stage.

On the other hand, compound **9** would cyclize to **12**,



Scheme 1.

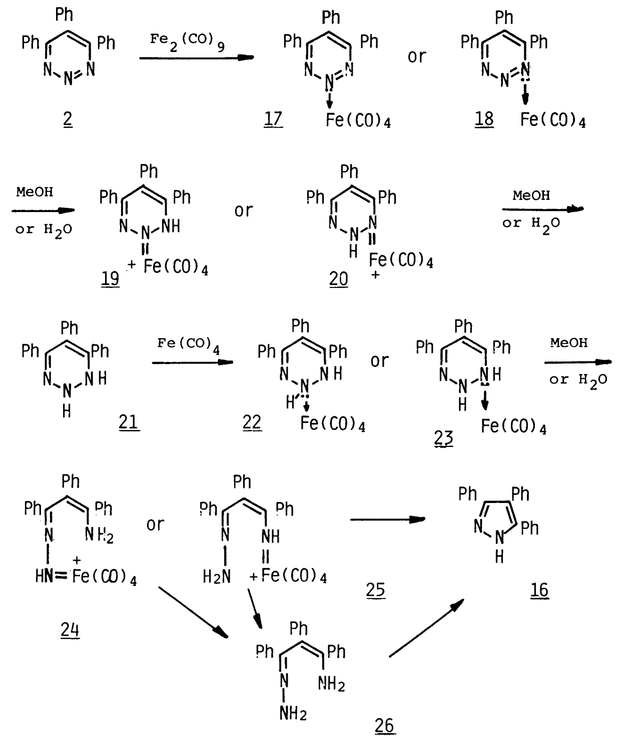


Scheme 2.

probably through intermediarily formed **11**. The reduction of the nitrene moiety of **12** to enamine followed by hydrolysis under workup conditions would give **13**.[1,3] The oxidation of **13** seems to occur easily to give **5**. Furthermore, the protonation and reduction of the nitrogen moiety of **9** giving **14** followed by hydrolysis would give **6**.[16] The compound **6** was obtained even in anhydrous solvents (Table 1, Entries 1 and 2). Even in the reaction in anhydrous solvents, the possibility of stray water can not be ruled out. The compound **6** was obtained in good yield in methanol (Table 1, Entry 4). This fact would be attributable to the effective reduction and protonation of **9** in methanol.[16] The complex **7** has already been isolated in the reaction of iron carbonyls with 3-methoxy-1,2,3-triphenylcyclopropene (**15**).[17] Actually, the reaction of **1** with methanol afforded **15** in a quantitative yield, therefore the formation of **7** would be rationalized. Thus, the complexed cyclopropenylnitrene **8** was demonstrated to undergo easy cleavage of the bent C-C bond. The intervention of the complexed azete **10** is not supported by experimental evidence.

On the other hand, the reaction of **2** with [$Fe_2(CO)_9$] in methanol or in aqueous acetonitrile under reflux afforded 3,4,5-triphenylpyrazole (**16**) in 80 or 77% yield, respectively.

The reaction is formally explained by the pathways shown in Scheme 3. The initial step should be an n-donor complexation of **2** to the [$Fe(CO)_4$] species[1] to give **17** [or **18**]. The peroxy acid oxidation of 1,2,3-triazine derivatives gives 1-oxides and/or 2-oxides.[18] No evidence is available to distinguish between the N1 and N2 complexation to give **18** and **17** at the present reaction. The back donation of the d-electron from the iron to the complexed 1,2,3-triazine **17** [or **18**] and subsequent protonation gives **19** [or **20**] and then **21** in protic media. The further complexation of **21** with another [$Fe(CO)_4$] species giving **22** [or **23**] followed by reductive ring opening gives **24** [or **25**], cyclization of which then affords the pyrazole **16**. The reduction-protonation sequences of **24** [or **25**] seems also possible to give **26** which would give **16**.[11] Although the catalytic hydrogenation of **2** has been known to give **16** in good yield,[11] the present reaction could provide the first example of [$Fe_2(CO)_9$]-induced reductive cleavage of the triazine ring system.



Scheme 3.

Experimental

The IR spectra were recorded on a Shimadzu IR-400 spectrometer. The NMR spectra were recorded on a Hitachi R-24 spectrometer and the chemical shifts are given in ppm (δ) relative to the internal $SiMe_4$ standard. The mass spectral studies were conducted using Shimadzu GCMS QP-1000 spectrometer. [$Fe_2(CO)_9$] was prepared by the standard method.[19] All of the [$Fe_2(CO)_9$]-induced reactions were carried out under a nitrogen atmosphere. The desired compounds, 3-azido-1,2,3-triphenylcyclopropene (**1**)[11] and 4,5,6-triphenyl-1,2,3-triazine,[20] were prepared according to the literatures. All of the melting points are uncorrected.

General Procedure for the Reaction of 1 with [$Fe_2(CO)_9$]. A solution of **1** (309 mg, 1 mmol) and [$Fe_2(CO)_9$] (728 mg, 2 mmol) in a solvent (20 cm^3) was stirred for 24 h at ambient temperature. Then, the solution was filtered through Celite to remove insoluble materials, and the filtrate was concentrated in vacuo. The residue contained benzonitrile **3** which was detected by GLC and IR. The residue was separated by column chromatography on silica gel. The fractions eluted with hexane afforded **4**, the mixture of **5** and **6**, and **7**. The mixture was further separated by TLC on silica gel using CCl_4 as a developer to give **5** and **6**. The reaction conditions and the yields of the products are summarized in Table 1. For **5**: mp 145—146 °C (from MeOH) (lit,[21] 149—151 °C); IR ($CHCl_3$) 1709, 1604 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.19—7.63 (14H, m). For **6**: mp 96—97 °C (from benzene-hexane) (lit,[21] 96.5—97.5 °C). For **7**: mp 131—133 °C (decomp) (from benzene-hexane) (lit,[17] 133—135 °C); IR ($CHCl_3$) 3075, 3033, 2961, 2065, 1998, 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.79 (3H, s), 6.77—7.36 (15H, m); *m/z* (rel intensity), 466 (M^+—28, 3), 105 (100).

Formation of 15 in Methanol. A solution of **1** (160 mg, 0.5 mmol) in anhydrous methanol (5 cm^3) was stirred for 24 h at ambient temperature. After the methanol was evaporated, the residue was extracted with ether. The organic layer was dried over Na_2SO_4, and evaporated to give 90% of **15**: mp 67—68 °C (lit,[22] 69—70 °C); IR ($CHCl_3$) 1812 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.40 (3H, s), 7.18—7.59 (10H, m), 7.63—7.89 (5H, m).

General Procedure for the Reaction of 2 with [$Fe_2(CO)_9$]. A solution of **2** (309 mg, 1 mmol) and [$Fe_2(CO)_9$] (728 mg, 2 mmol) in methanol (20 cm^3) was refluxed for 2 h. The solution was filtered through Celite to remove insoluble materials. The filtrate was concentrated and the residue was purified by column chromatography on Florisil using benzene as the eluant to give **16** in an 80% yield. The reaction carried out in moist acetonitrile containing 5 molar equivalent amounts of water also afforded **16** in a 77% yield. The structure of **16** was confirmed by comparison of the spectral data with those of authentic specimen.[11,23]

References

1) M. Nitta and T. Kobayashi, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 1401.

2) P. G. Beraldi, A. Barco, S. Benetti, M. Guareri, S. Manfredini, G. P. Pollini, and D. Simoni, *Tetrahedron Lett.*, **26**, 5319 (1985); B. H. Lipshutz, *Chem. Rev.*, **86**, 795 (1986).

3) M. Nitta and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, **57**, 1035 (1985).

4) M. Decker and G. R. Knox, *Chem. Commun.*, **1967**, 1243.

5) C. D. Campbell and C. W. Rees, *Chem. Commun.*, **1969**, 537.

6) A. F. M. Iqubal, *Helv. Chim. Acta*, **56**, 655 (1976).

7) T. A. Mannuel, *Inorg. Chem.*, **1**, 1703 (1964).

8) J. A. J. Javis, B. E. Job, B. T. Kilbourn, R. H. B. Mals, P. G. Oweston, and P. F. Todd, *Chem. Commun.*, **1967**, 1149.

9) H. Alper and J. E. Prickett, *Inorg. Chem.*, **16**, 67 (1977).

10) Y. Nakamura, K. Bachmann, H. Heimgartner, and H. Schmid, *Helv. Chim. Acta*, **61**, 589 (1978).

11) E. A. Chandross and G. Smolinsky, *Tetrahedron Lett.*, **1960**, 19.

12) E. M. Burgess and J. P. Sanchez, *J. Org. Chem.*, **38**, 176 (1973).

13) G. Seybold, U. Jersak, and R. Gompper, *Angew. Chem.*, **85**, 918 (1973).

14) U.-J. Vogelbacher, M. Regitz, and R. Mynott, *Angew. Chem., Int. Ed. Engl.*, **25**, 842 (1986).

15) B. M. Adger, M. Keating, C. W. Rees, and R. C. Storr, *J. Chem. Soc., Chem. Commun.*, **1973**, 19.

16) M. Nitta and T. Kobayashi, *J. Chem. Soc., Perkin Trans., 1*, **1984**, 2103; and references cited therein.

17) J. Klimes and E. Weiss, *Chem. Ber.*, **115**, 2606 (1982).

18) A. Ohsawa, H. Arai, H. Ohnishi, and H. Igeta, *J. Chem. Soc., Chem. Commun.*, **1980**, 1182.

19) R. B. King, *Org. Synth.*, Vol. 1, 93 (1965).

20) H. Neunhoeffer, H.-D. Vöter, and H. Ohl, *Chem. Ber.*, **105**, 3695 (1972).

21) J. O. Stoffer and J. T. Bohanon, *J. Chem. Soc., Perkin Trans. 2*, **1978**, 692.

22) R. Breslow and C. Yuan, *J. Am. Chem. Soc.*, **80**, 5991 (1958).

23) P. Yates and E. M. Levi, *J. Org. Chem.*, **40**, 441 (1975).