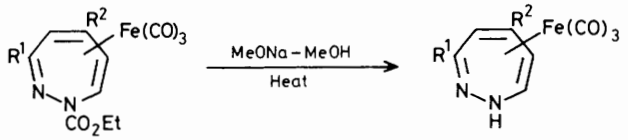
On the Reaction of Tricarbonyl (4—7-η-1*H*-1,2-diazepine)iron with Activated Acetylenes. Preparation of 1-Vinyl-1*H*-1,2-diazepine Derivatives

Makoto Nitta* and Hiroyuki Miyano
Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 160, Japan

Addition reactions of tricarbonyl(4—7-η-1*H*-1,2-diazepine)iron (**2a**) to the triple bond of dimethyl acetylenedicarboxylate (DMAD), methyl propiolate (MP), and dibenzoylacetylene (DBA) have been investigated. The stereochemical outcome is influenced by the solvent system and the acetylenic compounds employed. While the reaction of (**2a**) with DMAD in an aprotic solvent afforded the *syn*-adduct (**3a**) as the major product, in a protic solvent the reaction resulted in inversion of stereoselectivity to give predominantly the *anti*-adduct (**4a**). The reaction of (**2a**) with MP or with DBA exhibited a similar change in stereoselectivity, although MP has preferential *syn* selectivity and DBA has high *anti*-selectivity. The addition reactions of 3-methyl- and 5-methyl-derivatives of (**2a**) with DMAD have also been studied in order to confirm the mechanism of these reactions. The decomplexation reactions of several adducts have also been studied, with a view to the preparation of 1-vinyl-1*H*-1,2-diazepine derivatives.

1-Substituted 1*H*-1,2-diazepines have been synthesized photochemically from 1-iminopyridinium ylides, and 1,7-diazabicyclo[4.1.0]heptadienes have been postulated as intermediates in these reactions.[1] The utility of this method for the synthesis of 1-substituted 1*H*-1,2-diazepines has been limited by the existence of a competing and exclusive N–N bond cleavage of the ylides.[2] The acylation or alkylation of tricarbonyl (4—7-η-1*H*-1,2-diazepine)iron (**2a**) and subsequent decomplexation provides a new method of circumventing the above limitations.[3] Thermal and photochemical reactions of *N*-vinylpyridinium ylides have resulted in the formation of dihydropyrrolopyridines and pyrrolopyridines,[4] no 1-vinyl-1*H*-1,2-diazepine derivative having been synthesized to date.



(**1a–c**) (**2a–c**)

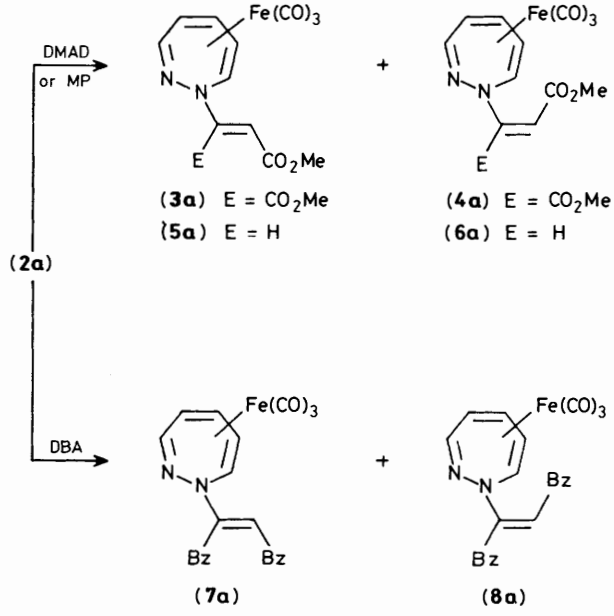
a; $R^1 = R^2 = H$; **b**; $R^1 = H$, $R^2 = Me$; **c**; $R^1 = Me$, $R^2 = H$

Scheme 1.

An interest in the synthesis and properties of 1-vinyl-1*H*-1,2-diazepines prompted us to study the nucleophilic addition of the tricarbonyl (4—7-η-1*H*-1,2-diazepine)iron derivatives (**2a—c**) to activated acetylenes such as dimethyl acetylenedicarboxylate (DMAD), methyl propiolate (MP), and dibenzoylacetylene (DBA). Theoretical studies have predicted that nucleophilic additions to unactivated acetylenes proceed *via* a single transition state to give *anti* addition products,[5] and this can be observed experimentally.[6] However, nucleophilic additions to activated acetylenes are known to give variable stereochemical results; *i.e.* both *syn* and *anti* addition products.[6] These observations are also comparable with recent theoretical studies, which indicate that the vinyl anions formed by nucleophilic addition to acetylenes are bent, but that the barrier to inversion is considerably lowered by electron-withdrawing substituents.[7] Therefore, addition reactions of (**2a—c**) were studied under various conditions in order to clarify the mechanism. The decomplexation of several adducts to provide 1-vinyl-1*H*-1,2-diazepine derivatives was also studied.

Results and Discussion

Tricarbonyl (4—7-η-1*H*-1,2-diazepine)iron complexes (**2a—c**) were prepared in excellent yields from (**1a—c**) by a modification of the method of Carty *et al.*[8] (Scheme 1).



Scheme 2.

The reaction of the complex (**2a**) with DMAD took place slowly at room temperature to give the *syn*-adduct (**3a**) and the *anti*-adduct (**4a**) in good combined yields as shown in Scheme 2. The detailed reaction conditions and the results are summarized in Table 1. In aprotic solvents (Table 1, entries 1—3) at room temperature, the *syn*-adduct (**3a**) was the predominant isomer obtained. In aprotic solvents at elevated temperature (entries

Table 1. Results for the reaction of (**2a**) with DMAD

Entry	Solvent	Conditions		Product yield (%)		Ratio
		Temp.	Time (h)	(**3a**)	(**4a**)	(**3a**):(**4a**)
1	PhH	Room temp.	24	71	26	2.8:1.0
2	$CHCl_3$	Room temp.	24	72	25	2.8:1.0
3	MeCN	Room temp.	24	73	22	3.3:1.0
4	PhH	Reflux	1.0	83	13	6.3:1.0
5	$CHCl_3$	Reflux	1.0	81	19	4.4:1.0
6	MeCN	Reflux	1.5	87	13	7.6:1.0
7	Bu^{t}OH	Reflux	1.5	89	10	8.8:1.0
8	EtOH	Room temp.	24	28	71	1.0:2.5
9	MeOH	Room temp.	24	21	78	1.0:3.7
10	MeOH	Reflux	1.5	21	77	1.0:3.8

Table 2. Results for the reaction of (**2a**) with MP or DBA[a]

Entry	Acetylene	Solvent	Time (h)	Product yield (%)			
				(**5a**)	(**6a**)	(**7a**)	(**8a**)
1	MP	PhH	24	57[b]	0		
2	MP	MeOH	96	67	33		
3	DBA	PhH	14			15	64
4	DBA	MeOH	14			0	85

[a] Reactions were carried out at room temperature. [b] In this case, 36% of unchanged (**2a**) was recovered.

4—6), the reaction was fast and the ratio of (**3a**):(**4a**) increased to indicate predominant formation of (**3a**). In contrast, the reaction in protic solvents (entries 8—10) afforded the *anti*-adduct (**4a**) rather than the *syn*-adduct (**3a**). Interestingly, the protic nature of Bu^{t}OH has no effect on the reaction (entry 7) and the ratio of (**3a**):(**4a**) is similar to those in aprotic solvents.

Complex (**2a**) also reacted with MP very slowly, or with DBA at a modest rate, to give the *syn*-adduct (**5a**) and the *anti*-adduct (**6a**), or the *syn*-adduct (**7a**) and/or the *anti*-adduct (**8a**), respectively (see Scheme 2). The results and the reaction conditions are summarized in Table 2. In the reaction of MP, the stereoselectivity was also influenced by the solvent system (Table 2, entries 1 and 2), although MP exhibits a preferential *syn* selectivity (even in MeOH), as compared to DMAD. In contrast, DBA exhibits a considerable degree of *anti* selectivity (entries 3 and 4).

The structural assignments of these products were made on the basis of elemental analyses and mass, i.r., u.v., and n.m.r. spectra, all of which are summarized in the Experimental section. The *anti*-adduct (**4a**) was characterized by the downfield absorption (δ 5.88) of the β-vinyl proton of the trisubstituted olefin as compared to that of the *syn*-adduct (**3a**) (δ 5.48). This is, presumably, owing to the deshielding effect of the *cis* methoxycarbonyl group.[9,10] The stereochemistry of each of the isomers (**5a**) and (**6a**) was easily determined from the coupling constants [$J_{vic.}$ 14.1 Hz for (**5a**) and $J_{vic.}$ 10.5 Hz for (**6a**)] of the α,β-unsaturated ester moiety in the n.m.r. spectra. The downfield absorption (δ 7.68) of the β-vinyl proton in (**5a**), compared to that of (**6a**) (δ 6.68), is in accordance with that observed for (**3a**) and (**4a**). Compound (**7a**) was not purified completely, being contaminated with a trace of (**8a**) even after repeated t.l.c. on alumina. Elemental analyses as well as mass spectral data of oily (**7a**) were not therefore examined, and the structure of (**7a**) was deduced from the n.m.r. spectrum. The signal of (**7a**) due to the β-vinyl proton of the trisubstituted olefin also appeared at highfield (δ 6.03) compared to that of

Table 3. Results for the reaction of (**2b**) or (**2c**) with DMAD[a]

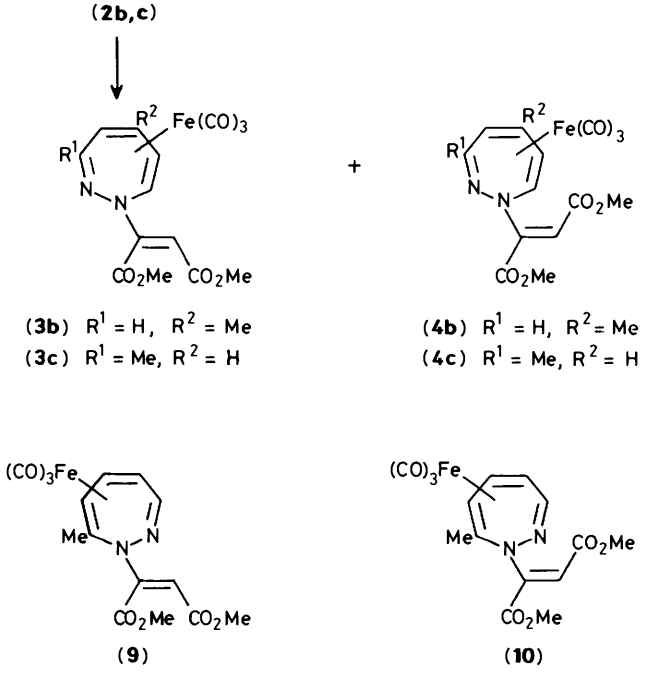
Entry	Compound	Solvent	Product yield		Recovery of (**2**) (%)	Ratio of (**3**):(**4**)
			(**3**)	(**4**)		
1	(**2b**)	PhH	89	10	0	8.7:1.0
2	(**2b**)	MeOH	24	76	0	1.0:2.7
3	(**2c**)	PhH	27	17	11	1.6:1.0
4	(**2c**)	MeOH	6	14	32	1.0:2.3

[a] Reactions were carried out at 30 °C for 24 h.

(**8a**) (δ 6.89). This feature is also ascribed to the deshielding effect of the benzoyl group (*cis* to H) in (**8a**).

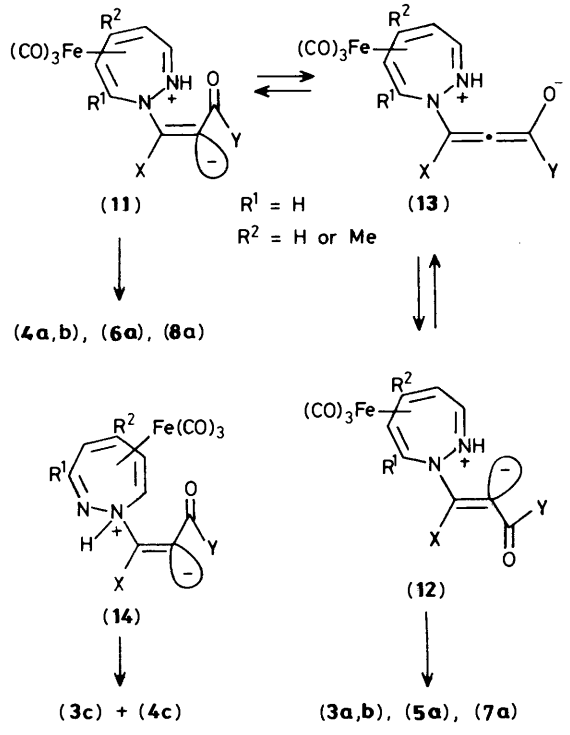
The degenerate rearrangement and fluxionality of the complexes (**2a,b**) has been established on the basis of the temperature dependence of their n.m.r. spectra.[8] The fluxionality involves intermolecular hydrogen transfer and diene–$Fe(CO)_3$ reorganization, in which the $Fe(CO)_3$ moiety moves over a five-carbon chain;[8] the hydrogen tautomerism is analogous to that in pyrazole. This behaviour of (**2a,b**), made it likely that nucleophilic addition of (**2**) to the triple bond would proceed by attack of N-2 followed by $Fe(CO)_3$ reorganization leading to (**11**) and then (**12**) (see Scheme 4). The reaction of 3,5-dimethylpyrazole with DMAD has been reported recently[9] to proceed *via* N-2 attack to a linear zwitterion.[11]

The reaction of the fluxional (**2b**) with DMAD afforded the *syn*- and *anti*-adducts, (**3b**) and (**4b**), in good yield. However, the reaction of the non-fluxional 3-methyl derivative (**2c**),[8] that in which the $Fe(CO)_3$ moiety is bonded to carbon atoms C(4)–C(7) and is stabilized, proceeded very slowly. The products isolated are the *syn*- and *anti*-adducts (**3c**) and (**4c**), and not the isomers (**9**) and (**10**) (see Table 3). This result and the low combined yields of the products, indicate that N-1 attack of (**2c**) occurs, presumably as a consequence of steric effects. The stereochemical preferences in Table 3 is analogous to that listed in Table 1.



Scheme 3.

The *syn*/*anti* ratio of the present addition reactions changes remarkably depending on the solvent system and acetylenic compounds employed. It was confirmed that no *syn*–*anti* stereoequilibrium occurs under the reaction conditions used. For example, independent reaction of (**3a**) or (**4a**) in benzene even under reflux for 1.5 h caused no isomerization and resulted in the recovery of unchanged (**3a**) or (**4a**). However, (**4a**) when heated under reflux for a prolonged period (24 h) was partially converted into (**3a**), while the latter after the same treatment, was recovered quantitatively. Thus, the *syn*-adduct (**3a**) is thermodynamically more stable than *anti*-adduct (**4a**). The above results can most resonably be explained by the mechanism shown in Scheme 4.

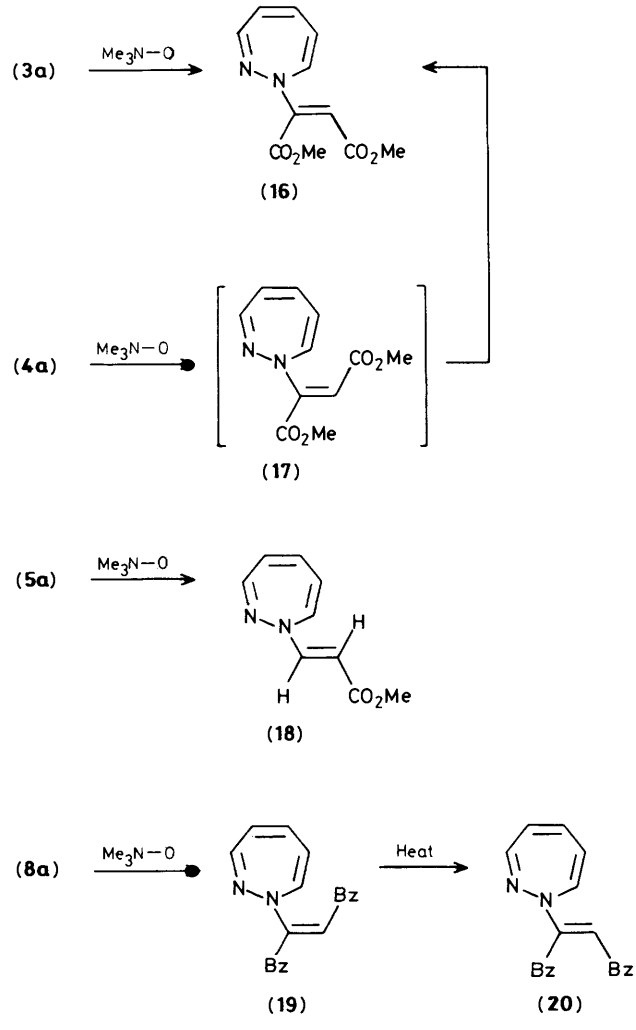


Scheme 4.

The nucleophilic addition of (**2a,b**) to the activated acetylenes would first give the kinetically preferred *anti* zwitterion (**11**).[7] If this species is rapidly protonated, or is highly stabilized by polar solvents, *anti* addition is favoured, resulting in the *anti*-adducts (**4a,b**) (Table 1, entries 8—10, and Table 3, entry 2). The intermediate (**11**) would equilibrate with *syn* zwitterion (**12**), presumably *via* a linear zwitterion (**13**), when protonation is slow and the barrier to inversion is sufficiently lowered,[7] although direct formation of (**12**) is not completely ruled out. Subsequent deprotonation–protonation sequences of (**12**) involving the possible intervention of a solvent molecule[7] give *syn*-adducts (**3a,b**) preferentially (Table 1, entries 1—3 and Table 3, entry 1). The temperature dependence of the *syn*/*anti* ratio (Table 1, entries 4—6) suggests acceleration of the pathway of (**11**)→(**12**). Furthermore, in the reaction in Bu^{t}OH (Table 1, entry 7), protonation of (**11**) seems to be slow, presumably because of steric hindrance by a solvent molecule.

Considering the geometrical constraints affecting the stabilities of the *syn* anion (**12**) and the *anti* anion (**11**), the degree of substitution of the acetylenic compounds could be expected to affect the *syn*/*anti* ratio. In the case of MP, the stereochemical preference is strongly *syn*, even in a protic solvent such as methanol. This may be ascribed to the low barrier of isomerization[7] as well as to the high degree of stability of (**12**) as compared to (**11**), in which considerable steric constraints exist. In contrast, the reaction of DBA exhibited a high degree of *anti* selectivity to give (**8a**). This suggests that the presence of the two bulky benzoyl groups is more destabilizing to the *syn* zwitterion (**12**) than to the *anti* zwitterion (**11**); this is not the case with DMAD or MP. Thus, the equilibration of the kinetically controlled anion (**11**) with (**12**) would be slow to compete with protonation of (**11**), even in an aprotic solvent such as benzene.

The reaction of (**2c**) with DMAD proceeded by attack of N-1. Thus the analogous reaction sequences involving the intermediate (**14**) in place of (**11**) would explain the results in Table 3, entries 3 and 4.



Scheme 5.

Decomplexation of the *syn*-adduct (**3a**) by trimethylamine oxide[12] afforded (**16**) in good yield, the first example of a 1-vinyl-1*H*-1,2-diazepine (Scheme 5). However, the decomplexation product of the *anti*-adduct (**4a**), which is a thermodynamically less stable isomer than (**3a**), is also (**16**), and not (**17**). This fact suggests that (**17**) is thermodynamically less stable than (**16**), to which it is isomerized under the reaction conditions used. Similarly, the addition products (**5a**) and (**8a**) afforded (**18**) and (**19**), respectively, in good yield. Compound (**19**) when heated under reflux in benzene gives its isomer (**20**), suggesting that the latter has greater thermal stability.

Compound (**18**) is thought to be more stable than the corresponding *cis* isomer, presumably because of steric hindrance.

The *syn*-adducts (**3a**—**c**), (**5a**), and (**7a**) are geometrically similar to the more stable isomers (**16**), (**18**), and (**20**), respectively. Therefore, the *syn*-adducts are suggested to be thermodynamically controlled products in the present addition reactions, the results of which are comparable with recent theoretical studies.[7]

In conclusion, we have demonstrated that the complex (**2**) can undergo addition reactions with the activated acetylenes, DMAD, MP, and DBA. These reactions should prove useful for the synthesis of 1-vinyl-1*H*-1,2-diazepines in good yields.

Experimental

I.r. spectra were recorded on a Shimadzu IR-400 spectrometer. N.m.r. spectra were recorded on a Hitachi R-24 or a JEOL PS-100 spectrometer and chemical shifts are given in p.p.m. (δ) relative to internal $SiMe_4$ standard. Mass spectral studies were conducted using Shimadzu GCMS-QP1000 and JEOL-DX300 (HR-MS) spectrometers. Microanalyses were performed at the Science and Engineering Research Laboratory of Waseda University. M.p.s were recorded on a Büchi apparatus and are uncorrected.

Preparation of the Tricarbonyl (4—7-η-1H-1,2-*diazepine*)*iron Compounds* (**2a**—**c**).—A solution of the tricarbonyl (4—7-η-1-ethoxycarbonyl-1,2-diazepine)iron derivatives (**1a**—**c**)[1] (10 mmol) and sodium methoxide (1 mmol) in anhydrous methanol (40 ml) was heated under reflux for 1.5—2.0 h under nitrogen. After removal of solvent, the residue was purified by passage through a short column packed with alumina using hexane–dichloromethane (1:1) as eluant to give (**2a**—**c**) in quantitative yield. The structures of (**2a**—**c**) were confirmed by comparison with literature spectral data.[8]

General Procedure for the Reaction of (**2a**) *with* DMAD.—A solution of (**2a**) (117 mg, 0.5 mmol) and DMAD (85 mg, 0.6 mmol) in an anhydrous solvent (5 ml) was stirred for various periods of time at room temperature or under reflux (see Table 1). After the removal of solvent, the residue was separated by t.l.c. on silica gel using benzene–ethyl acetate (10:1) as developer to give the products (**3a**) and (**4a**) (see Table 1). For (**3a**): m.p. 139—140 °C (decomp.) (from benzene); $\delta_H(CDCl_3)$ 3.39 (1 H, ddd, *J* 6.4, 6.0, 1.6 Hz), 3.67 (3 H, s), 3.83 (3 H, s), 4.62 (1 H, ddd, *J* 6.3, 4.7, 1.6 Hz), 4.93—5.28 (2 H, m), 5.48 (1 H, s), and 6.83 (1 H, d, *J* 6.4 Hz); $\nu_{max.}(CHCl_3)$ 2 075, 2 005, 1 744, and 1 704 cm^{-1}; $\lambda_{max.}$(EtOH) 305 and 345 nm (log ε 4.11 and 4.08); *m/z* 348 (M^+ − 28, 26%) and 260 (100) (Found: C, 44.75; H, 3.2; N, 7.6. $C_{14}H_{12}FeN_2O_7$ requires C, 44.71; H, 3.22; N, 7.45%). For (**4a**): m.p. 90—91 °C (decomp.) (from benzene); $\delta_H(CDCl_3)$ 3.44 (1 H, ddd, *J* 6.0, 6.0, 1.6 Hz), 3.69 (6 H, s), 4.54 (1 H, ddd, *J* 6.0, 4.6, 1.6 Hz), 4.93 (1 H, ddd, *J* 6.0, 4.6, 2.0 Hz), 5.14 (1 H, dd, *J* 6.0, 2.0 Hz), 5.88 (1 H, s), and 6.79 (1 H, d, *J* 6.0 Hz); $\nu_{max.}(CHCl_3)$ 2 064, 1 999, and 1 712 cm^{-1}; $\lambda_{max.}$(EtOH) 242sh, 281sh, and 370 nm (log ε 4.15, 3.82, and 3.84); *m/z* 376 (M^+, 4%) and 260 (100) (Found: C, 44.9; H, 3.2; N, 7.5. $C_{14}H_{12}FeN_2O_7$ requires C, 44.71; H, 3.22; N, 7.45%).

General Procedure for the Reaction of (**2a**) *with* MP.—A solution of (**2a**) (117 mg, 0.5 mmol) and MP (51 mg, 0.6 mmol) in anhydrous solvent (5 ml) was stirred for various periods of time at room temperature (see Table 2). After evaporation of solvent, the residue was separated by t.l.c. on silica gel using benzene–ethyl acetate (10:1) as developer to give the products, (**5a**) and (**6a**) (see Table 2). For (**5a**): m.p. 160—161 °C (decomp.) (from benzene); $\delta_H(CDCl_3)$ 3.42 (1 H, ddd, *J* 7.0, 6.5, 1.4 Hz), 3.74 (3 H, s), 4.50 (1 H, ddd, *J* 6.6, 4.5, 1.4 Hz), 5.12 (1 H, ddd, *J* 7.0, 4.5, 2.0 Hz), 5.35 (1 H, dd, *J* 6.6, 2.0 Hz), 5.56 (1 H, d, *J* 14.1 Hz), 7.02 (1 H, d, *J* 6.5 Hz), and 7.68 (1 H, d, *J* 14.1 Hz); $\nu_{max.}(CHCl_3)$ 2 068, 1 998, and 1 692 cm^{-1}; $\lambda_{max.}$(EtOH) 304, 341sh, and 419sh nm (log ε 4.20, 4.01, and 3.38); *m/z* 318 (M^+, 17%) and 262 (100) (Found: C, 45.4; H, 3.2; N, 8.65. $C_{12}H_{10}FeN_2O_5$ requires C, 45.31; H, 3.17; N, 8.81%). For (**6a**): m.p. 109—110 °C (decomp.) (from benzene); $\delta_H(CDCl_3)$ 3.35 (1 H, ddd, *J* 6.0, 6.0, 1.6 Hz), 3.70 (3 H, s), 4.71 (1 H, ddd, *J* 6.3, 4.3, 1.6 Hz), 4.90 (1 H, d, *J* 10.5 Hz), *ca.* 5.0 (1 H, m), 5.89 (1 H, dd, *J* 6.3, 2.0 Hz), 6.68 (1 H, d, *J* 10.5 Hz), and 6.85 (1 H, d, *J* 6.0 Hz); $\nu_{max.}(CHCl_3)$ 2 055, 1 993, and 1 696 cm^{-1}; $\lambda_{max.}$(EtOH) 307 and 346 nm (log ε 4.08 and 4.08); *m/z* 318 (M^+, 14%) and 290 (100) (Found: C, 45.35; H, 3.25; N, 8.55. $C_{12}H_{10}FeN_2O_5$ requires C, 45.31; H, 3.17; N, 8.81%).

Reaction of (**2a**) *with* DBA *in Benzene*.—A solution of (**2a**) (140 mg, 0.6 mmol) and DBA (154 mg, 0.66 mmol) in anhydrous benzene (6 ml) was stirred for 14 h at room temperature. After the addition of hexane (4 ml) to the reaction mixture, the precipitate was filtered to give (**8a**) (180 mg, 64%), m.p. 192—193 °C (decomp.) (from benzene); $\delta_H(CDCl_3)$ 3.39 (1 H, ddd, *J* 6.4, 6.1, 1.6 Hz), 4.71 (1 H, ddd, *J* 6.1, 4.7, 1.6 Hz), 5.12 (1 H, ddd, *J* 6.4, 4.7, 1.6 Hz), 5.45 (1 H, dd, *J* 6.1, 1.9 Hz), 6.85 (1 H, d, *J* 6.1 Hz), 6.89 (1 H, s), 7.3—7.6 (6 H, m), and 7.8—8.1 (4 H, m); $\nu_{max.}(CHCl_3)$ 2 059, 1 977, and 1 684 cm^{-1}; $\lambda_{max.}$(EtOH) 256 and 405 nm (log ε 4.40 and 4.32); *m/z* 384 (M^+ − 84, 100%) (Found: C, 61.55; H, 3.4; N, 5.7. $C_{24}H_{16}FeN_2O_5$ requires C, 61.56; H, 3.44; N, 5.98%).

The filtrate was purified by t.l.c. on alumina using chloroform as developer to give (**7a**) as an oil (*ca.* 42 mg, 15%), contaminated with a trace of (**8a**). Repeated purification of (**7a**) by t.l.c. on alumina failed to give a pure sample. However, the n.m.r. spectrum of (**7a**) was assigned as follows: $\delta_H(CDCl_3)$ 3.03—3.35 (1 H, m), 4.79—5.00 (2 H, m), 5.13—5.35 (1 H, m), 6.03 (1 H, s), 6.61 (1 H, d, *J* 6.1 Hz), 7.2—7.6 (6 H, m), and 7.7—8.1 (4 H, m).

Reaction of (**2a**) *with* DBA *in Methanol*.—A solution of (**2a**) (140 mg, 0.6 mmol) and DBA (154 mg, 0.66 mmol) in anhydrous methanol (6 ml) was stirred for 14 h at room temperature. After the addition of hexane (4 ml) to the reaction mixture, the precipitate was filtered off to give (**8a**) (238 mg, 85%). When the filtrate was purified by t.l.c. on alumina however, no (**7a**) was obtained.

General Procedure for the Reaction of (**2b**,**c**) *with* DMAD.—A solution of (**2b**) or (**2c**) (0.3 mmol) and DMAD (0.36 mmol) in anhydrous solvent (4 ml) was stirred for 24 h at 30 °C. After removal of solvent, the residue was separated by t.l.c. on silica gel using hexane–ethyl acetate (5:1) to give the products (**3b**,**c**) and (**4b**,**c**) (see Table 3). Since compounds (**4b**,**c**) are viscous oils and not distillable, no correct elemental analyses were obtained. However, the structures were assessed by comparison of the spectral data with those of related compounds in this paper. For (**3b**): m.p. 115—116 °C (decomp.) (from benzene–hexane); $\delta_H(CDCl_3)$ 1.96 (3 H, s), 3.41 (1 H, dd, *J* 6.1, 1.9 Hz), 3.70 (3 H, s), 3.86 (3 H, s), 4.60 (1 H, dd, *J* 6.3, 1.9 Hz), 4.99 (1 H, d, *J* 6.3 Hz), 5.47 (1 H, s), and 6.88 (1 H, d, *J* 6.1 Hz); $\nu_{max.}(CHCl_3)$ 2 064, 1 998, 1 745, and 1 700 cm^{-1}; $\lambda_{max.}$(EtOH) 305 and 346 nm (log ε 4.19 and 4.18); *m/z* 362 (M^+ − 28, 25%) and 334 (100) (Found: C, 46.0; H, 3.4; N, 7.4. $C_{15}H_{14}FeN_2O_7$ requires C, 46.18; H, 3.62; N, 7.18%). For (**4b**): oil; $\delta_H(CDCl_3)$ 1.93 (3 H, s), 3.53 (1 H, dd, *J* 6.4, 1.7 Hz), 3.76 (6 H, s), 4.64 (1 H, dd, *J* 6.2, 1.7 Hz), 5.07 (1 H, d, *J* 6.2 Hz), 5.85 (1 H, s), and 6.89 (1 H, d, *J* 6.4 Hz); $\nu_{max.}(CHCl_3)$ 2 067, 1 999, and 1 714 cm^{-1}; $\lambda_{max.}$(EtOH) 242sh, 281sh, and 370 nm (log ε 4.09, 3.73, and 3.77); *m/z* 334 (M^+ − 56, 65%) and 274 (100). For (**3c**): m.p. 136—137 °C (decomp.) (from benzene–hexane); $\delta_H(CDCl_3)$ 2.08 (3 H, s),

3.35 (1 H, dd, *J* 7.0, 1.8 Hz), 3.69 (3 H, s), 3.86 (3 H, s), 4.76 (1 H, ddd, *J* 6.4, 4.6, 1.8 Hz), 5.03—5.32 (2 H, m), and 5.44 (1 H, s); $\nu_{max.}(CHCl_3)$ 2 061, 1 995, 1 741, and 1 697 cm^{-1}; $\lambda_{max.}$(EtOH) 306 and 352 nm (log ε 4.16 and 4.13); *m/z* 362 ($M^+ - 28$, 40%) and 306 (100) (Found: C, 46.3; H, 3.45; N, 7.25. $C_{15}H_{14}FeN_2O_7$ requires C, 46.18; H, 3.62; N, 7.18%). For (**4c**): oil; $\delta_H(CDCl_3)$ 2.06 (3 H, s), 3.35 (1 H, dd, *J* 7.0, 1.9 Hz), 3.73 (3 H, s), 3.74 (3 H, s), 4.63 (1 H, ddd, *J* 6.2, 4.5, 1.9 Hz), 4.98 (1 H, ddd, *J* 7.0, 4.5, 2.0 Hz), 5.14 (1 H, dd, *J* 6.2, 2.0 Hz), and 5.70 (1 H, s); $\nu_{max.}(CHCl_3)$ 2 068, 1 994, and 1707 cm^{-1}; $\lambda_{max.}$(EtOH) 251sh, 315sh, and 373 nm (log ε 4.17, 3.77, and 3.78); *m/z* 334 ($M^+ - 56$, 71%) and 274 (100).

Thermal Isomerization of (**3a**).—A solution of (**3a**) (75 mg, 0.2 mmol) in benzene (2 ml) was heated under reflux for 24 h under a nitrogen atmosphere after which the mixture was evaporated and the residue purified by t.l.c. on silica gel using benzene–ethyl acetate (5:1) as developer to give unchanged (**3a**) (72 mg, 96%).

Thermal Isomerization of (**4a**).—A solution of (**4a**) (75 mg, 0.2 mmol) in benzene (2 ml) was heated under reflux for 24 h under nitrogen after which the mixture was evaporated and the residue separated by t.l.c. on silica gel using benzene–ethyl acetate (5:1) as developer to give (**4a**) (46 mg, 61%) and (**3a**) (19 mg, 25%).

Decomplexation of (**3a**) *with Trimethylamine Oxide.*—A solution of (**3a**) (113 mg, 0.3 mmol) and anhydrous trimethylamine oxide (113 mg, 1.5 mmol) in acetone (5 ml) was stirred at room temperature for 6 h. After the addition of hexane (3 ml) to the reaction mixture, it was filtered through Celite to remove insoluble material. The filtrate was concentrated and the residue was purified by t.l.c. on silica gel using benzene–ethyl acetate (5:1) as developer to give (**16**) (62 mg, 88%) as a red oil; $\delta_H(CCl_4)$ 3.60 (3 H, s), 3.78 (3 H, s), 5.23 (1 H, s), 5.53—5.96 (2 H, m), 6.03—6.66 (2 H, m), and 7.23 (1 H, dd, *J* 3.0, 1.0 Hz); $\nu_{max.}(CHCl_3)$ 1 740 and 1 696 cm^{-1}; $\lambda_{max.}$(EtOH) 223sh, 255sh, 305, and 374sh nm (log ε 3.81, 3.71, 4.19, and 3.04); *m/z* 236 (M^+, 86%), 145 (100) [HR-MS 236.0798. $C_{11}H_{12}N_2O_4$ requires 236.0797].

Decomplexation of (**4a**) *with Trimethylamine Oxide.*—A solution of (**4a**) (113 mg, 0.3 mmol) and anhydrous trimethylamine oxide (113 mg, 1.5 mmol) in acetone (5 ml) was stirred at room temperature for 20 min. Work-up similar to that described above afforded (**16**) (26 mg, 37%) and unchanged (**4a**) (5 mg, 4%).

Decomplexation of (**5a**) *with Trimethylamine Oxide.*—A solution of (**5a**) (64 mg, 0.2 mmol) and anhydrous trimethylamine oxide (75 mg, 1 mmol) in acetone (4 ml) was stirred at room temperature for 6 h. Work-up similar to that described above afforded (**18**) (32 mg, 90%) as a red oil; $\delta_H(CCl_4)$ 3.37 (3 H, s), 5.22 (1 H, d, *J* 13.5 Hz), 5.61 (1 H, ddd, *J* 7.1, 5.1, 1.1 Hz), 5.83 (1 H, d, *J* 7.1 Hz), 6.11 (1 H, ddd, *J* 12.2, 3.2, 1.1 Hz), 6.46 (1 H, m), 7.25 (1 H, dd, *J* 3.2, 0.5 Hz), and 7.61 (1 H, d, *J* 13.5 Hz); $\nu_{max.}(CHCl_3)$ 1 690 cm^{-1}; $\lambda_{max.}$ 224sh, 254, 304, 381sh, and 403sh (log ε 3.60, 3.62, 4.15, 3.14, and 2.98); *m/z* 178 (M^+, 100%) [HR-MS 178.0751. $C_9H_{10}N_2O_2$ requires 178.0742].

Decomplexation of (**8a**) *with Trimethylamine Oxide.*—A solution of (**8a**) (187 mg, 0.4 mmol) and hydrated trimethylamine oxide (222 mg, 2 mmol) in acetone (10 ml) was stirred at room temperature for 2 h. Work-up similar to that described above afforded (**19**) (114 mg, 87%), m.p. 133—134 °C (decomp.) (from benzene); $\delta_H(CDCl_3)$ 5.77 (1 H, ddd, *J* 7.0, 5.5, 1.8 Hz), 6.03 (1 H, dd, *J* 7.0, 0.7 Hz), 6.23—6.68 (2 H, m,), 6.72 (1 H, s), 7.21—7.57 (7 H, m), and 7.77—8.13 (4 H, m); $\nu_{max.}(CHCl_3)$ 1 682 cm^{-1}; $\lambda_{max.}$(EtOH) 256 and 362 nm (log ε 4.35 and 4.32); *m/z* 328 (*M*, 68%) and 223 (100%) (Found: C, 76.25; H, 4.75; N, 8.65. $C_{21}H_{16}N_2O_2$ requires C, 76.81; H, 4.91; N, 8.53%).

Thermal Isomerization of (**19**) *to* (**20**).—A solution of (**19**) (164 mg, 0.5 mmol) in benzene (4 ml) was heated under reflux for 1.5 h under a nitrogen atmosphere. The reaction mixture was cooled and the precipitate was filtered to give (**20**) (138 mg, 84%), m.p. 183—185 °C (from benzene–hexane); $\delta_H(CDCl_3)$ 5.57—6.08 (3 H, m), 6.46—6.64 (2 H, m), 6.90—7.11 (1 H, m), 7.27—7.54 (6 H, m), and 7.73—8.04 (4 H, m); $\nu_{max.}(CHCl_3)$ 1 676 cm^{-1}; $\lambda_{max.}$(EtOH) 259 and 347 nm (log ε 4.10 and 4.00); *m/z* 328 (M^+, 85%) and 300 (100) (Found: C, 77.2; H, 4.85; N, 8.7. $C_{21}H_{16}N_2O_2$ C, 76.81; H, 4.91; N, 8.53%).

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research No. 56540312 from the Ministry of Education, Science, and Culture and by an Annual Project organized by Waseda University 1983—1984.

References

1 J. Streith, *Heterocycles*, 1977, **6**, 2021; M. Nastasi, *ibid.*, 1976, **4**, 1509 and references cited therein,
2 V. Snieckus, *Chem. Commun.*, 1969, 831; K. T. Potts and R. Dugas, *ibid.*, 1970, 732; V. Snieckus and G. Kan, *ibid.*, 1970, 172; C. W. Bird, I. Partridge, and D. Y. Wong, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1020.
3 D. J. Harris and V. Snieckus, *J. Chem. Soc., Chem. Commun.*, 1976, 844.
4 T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, 1972, **37**, 3106.
5 E. C. Dykstra, J. E. Arduengo, and T. Fukunaga, *J. Am. Chem. Soc.*, 1978, **100**, 6007; R. W. Stozier, P. Caramella, and K. N. Houk, *ibid.*, 1979, **101**, 1340.
6 J. I. Dickstein and S. I. Miller in 'Chemistry of the Carbon–Carbon Triple Bond Part 2,' ed. S. Patai, John Wiley and Sons, Chichester, New York, Brisbane, Toronto, 1978, p. 813 and references cited therein.
7 P. Caramella and K. N. Houk, *Tetrahedron Lett.*, 1981, **22**, 819; K. N. Houk, W. R. Stozier, M. Rozenboom, and S. Nagase, *J. Am. Chem. Soc.*, 1982, **104**, 323.
8 A. J. Carty, R. F. Hobson, H. A. Patel, and V. Snieckus, *J. Am. Chem. Soc.*, 1973, **95**, 6835; A. J. Carty, C. R. Jablonski, and V. Snieckus, *Inorg. Chem.*, 1976, **15**, 601.
9 J. Elguero, A. de la Hoz, and C. Pardo, *J. Chem. Soc., Perkin Trans. 2*, 1985, 427.
10 K. Hayakawa, Y. Kamikawaji, A. Wakita, and K. Kanematsu, *J. Org. Chem.*, 1984, **49**, 1985.
11 R. Huisgen, B. Giese, and H. Huber, *Tetrahedron Lett.*, 1967, 1883.
12 Y. Shvo and E. Hazum, *J. Chem. Soc., Chem. Commun.*, 1974, 336.

Received 21*st June* 1985; *Paper* 5/1043