April, 1984] © 1984 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 57, 1035—1039 (1984) 1035

Nonacarbonyldiiron or Pentacarbonyliron Induced Decomposition of Organic Azides and an Azirine. Novel Reduction and Carbonyl Insertion of the Complexed Nitrene Intermediate in Protic Solvents

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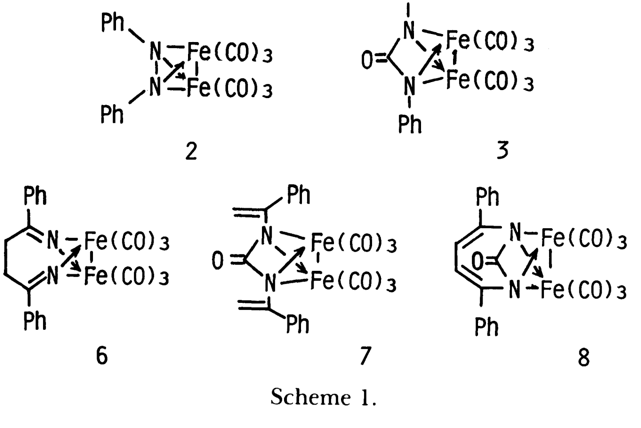
(Received June 20, 1983)

The thermal reactions of [Fe$_2$(CO)$_9$] or the photochemical reactions of [Fe(CO)$_5$] with organic azides and an azirine in protic media have been investigated. The thermal reaction of azidobenzene (**1**) with [Fe$_2$(CO)$_9$] in methanol under mild conditions gave aniline and methyl phenylcarbamate, along with *N,N′*-diphenylurea, while in the presence of water, **1** afforded aniline and *N,N′*-diphenylurea, in good combined yield. Similarly, the thermal reaction of α-azidostyrene (**4**) with [Fe$_2$(CO)$_9$] in methanol gave methyl 1-phenylvinylcarbamate and acetophenone which could be derived from the corresponding enamine, while in the presence of water, **4** gave only acetophenone in good yield. The photoirradiation of [Fe(CO)$_5$] with **1** or **4** also gave results similar to the [Fe$_2$(CO)$_9$]-induced reaction. However, the thermal reaction of 3-phenyl-2*H*-azirine (**5**) with [Fe$_2$(CO)$_9$] in methanol gave 2,5-diphenylpyrazine in low yield, in addition to acetophenone and methyl 1-phenylvinylcarbemate, although 5 afforded only acetophenone in the presence of water. The reaction pathways for the formation of the products are discussed on the basis of the formation of a complexed nitrene intermediate, reduction of which induces amine or enamine and carbonyl insertion to yield an organic isocyanate in protic media.

Reaction of azidobenzene (**1**) with [Fe$_2$(CO)$_9$] under mild conditions has been shown to give complexes such as bisnitrene complex **2** and urea-based complex **3** in benzene solution.[1,2] In the context of these reactions, the decomposition of **1** in the presence of [Fe(CO)$_5$] and acetic acid has been studied to give *N,N′*-diphenylurea.[3] The urea-based complex **3** , which could be derived from the complexed phenylnitrene intermediate,[1,4] is proposed as the possible precursor.

In contrast to these studies, transition-metal prompted reactions of the azirine ring system, which can be considered an isomer of vinylnitrene, have been widely studied from both the synthetic and mechanistic point of view.[5,6,7–14] Among these reactions, [Fe$_2$(CO)$_9$]-induced reaction of 3-phenyl-2*H*-azirine (**5**) in aprotic media has been shown to give complexes such as **6**, **7**, **8**, along with pyrrole and acetophenone albeit in low combined yield.[5] However, the [Fe$_2$(CO)$_9$][5] [Fe(CO)$_5$][6] prompted reaction of α-azidostyrene (**4**) in a similar media gives the complexes **6** and **7**, along with acetophenone or 3,6-diphenylpyridazine. The complexed 1-phenylvinylnitrene is proposed as a key intermediate in the reactions of **4** and **5**. However, the best explanation for the difference of the product composition resulting from the reaction of **4** and **5** could be a further intervention of the complexed azirine in the case of **5**.[5] No reaction of **4** or **5** with [Fe(CO)$_5$] or [Fe$_2$(CO)$_9$] in protic media has been investigated.



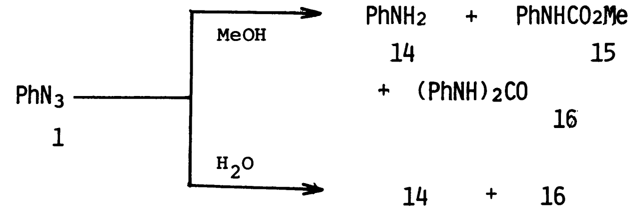
Scheme 1.

Previously the reaction of 3,5-disubstituted isoxazolines (**9**) with [Fe(CO)$_5$] or [Fe$_2$(CO)$_9$] in methanol has been shown to undergo the N–O and C$_4$–C$_5$ bond cleavage to give two fragments of aldehydes **10** and ketones **11** in good yields.[15] The complexed vinylnitrene species **12**, which could be reduced to the corresponding enamine **13** in protic media, is proposed as the precursor of the ketones. In connection with the above results, it seemed conceivable that [Fe(CO)$_5$] or [Fe$_2$(CO)$_9$] induced decomposition of organic azides in protic media might provide evidence for the behavior of the complexed nitrene species. This paper describes the reduction and carbonyl insertion of the complexed nitrene species which results from the reaction of azidobenzene (**1**), α-azidostyrene (**4**), and 3-phenyl-2*H*-azirine (**5**) with [Fe$_2$(CO)$_9$] or [Fe(CO)$_5$].

Scheme 2.

Results and Discussion

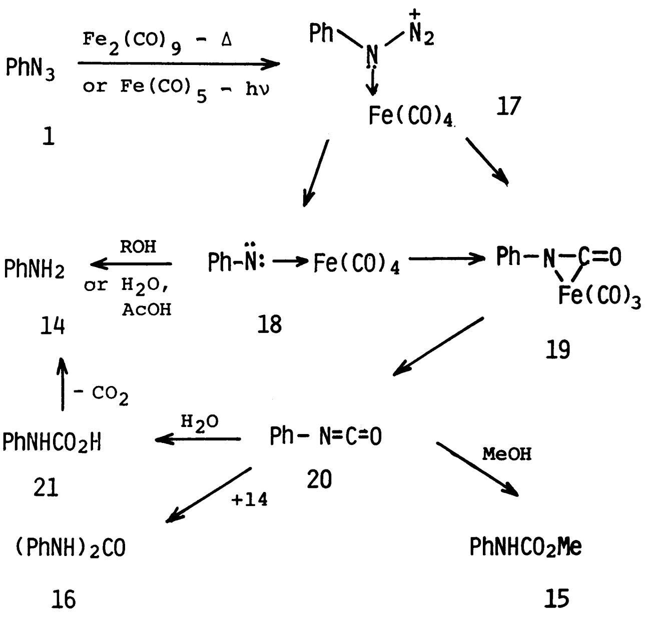
Treatment of azidobenzene (**1**) with [Fe$_2$(CO)$_9$] in anhydrous methanol at 50 °C afforded aniline (**14**), methyl phenylcarbamate (**15**), and *N,N′*-diphenylurea (**16**), in 21, 51, and 20% yields respectively (Table 1, entry 1). Use of acetonitrile containing water as the



Scheme 3.

reaction solvent gave **14** and **16** in 67 and 23% yields (entry 2). The combined yield of **14**—**16** for each case is very good; the reaction conditions and the products are summarized in Table 1. The structure of the products was identified by comparison of the spectral properties with those of authentic materials. The irradiation of a solution of **1** and $[Fe(CO)_5]$ in anhydrous methanol or in acetonitrile containing water gave results similar to the $[Fe_2(CO)_9]$-induced reactions (entries 3 and 4). However, the reaction of **1** with $[Fe(CO)_5]$ in anhydrous methanol at the refluxing temperature proceeded very slowly and, gave **15** and **16** in 11 and 3% yields, with the remainder being recovered starting material (entry 5). Thus the $[Fe(CO)_5]$ could not act effectively at the low temperature and phbtochemically genarated $[Fe(CO)_4]$ species[15—17] could be very effective to induce the decomposition of **1**. At high temperature, thermal reaction of **1** with $[Fe(CO)_5]$ in acetic acid also proceeded smoothly (entries 6 and 7).

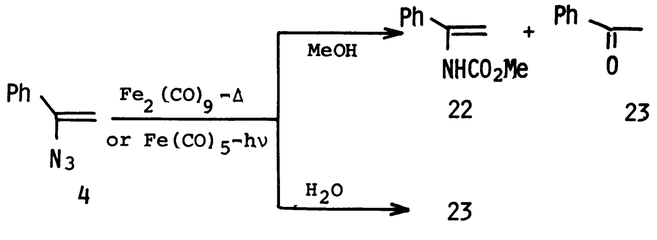
Possible pathways for the formation of the products, **14**, **15**, and **16** were shown in Scheme 4. The initial step in the present reactions is probably n-donor complexation of **1** to the thermally or photochemically generated $[Fe(CO)_4]$ species to give **17** followed by the elimination of a nitrogen molecule to give the phenylnitrene complex **18**.[1,2,5,6] In aprotic media, complexes such as **2** and **3** could be obtained from **18**.[1,2] However, the protonation and subsequent reduction of the phenylnitrene moiety of **18** by the central metal could occur in protic media such as methanol, acetonitrile containing water, or acetic acid, to give aniline **14**. The intramolecular insertion of ligand-carbonyl into metal-nitrogen bond of **18** could give the complex **19**, decomplexation of which could give phenyl isocyanate (**20**). The concerted formation of **19** from **17** may not be ruled out (*vide infra*). In contrast to the present reaction, the carbonylation of azidobenzene to give phenyl isocyanate has been shown to proceed possibly *via* free phenylnitrene under drastic conditions.[18] Phenyl isocyanate **20** is known to be trapped to give **15** in methanol, while in the presence of water, **20** would also give **14** *via* **21**. The formation of **16** can be rationalized on the basis of the reaction of **20** with **14**.[19]



Scheme 4.

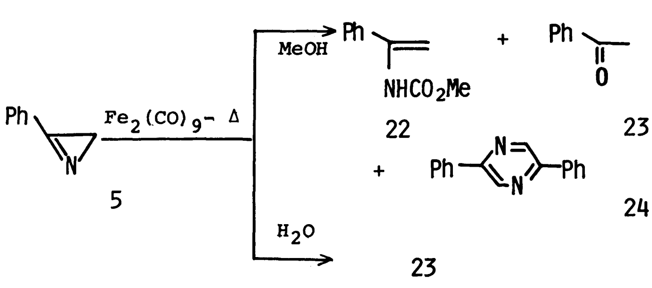
Previously, thermal reaction of aromatic azides with $[Fe(CO)_5]$ in acetic acid has been shown to give *N,N'*-diphenylurea. The urea-based complex, such as **3** in Scheme 1 is proposed as the reasonable intermediate.[3] However attempted thermal reaction of **1** with $[Fe(CO)_5]$ in acetic acid at 100 °C (entry 6) gave **14** and **16** in 33 and 52% yields similarly to the case of entries 2 and 4. On the other hand, the similar reaction of **1** with $[Fe(CO)_5]$ at 100 °C in a tenfold concentrated acetic acid solution gave only **16** in 67% yield (entry 7). Thus the formation of **16** in acetic acid seems dependent on the concentration of aniline **14** which is derived from the reduction of **18** in acetic acid.[20] In a concentrated media of acetic acid, **14** is actually trapped quickly by **20** (see Experimental section), thus only **16** could be obtained in entry 7.

Similarly to the above reactions, $[Fe_2(CO)_9]$ or $[Fe(CO)_5]$ induced reactions of **4** and **5** were studied in protic solvents. The reaction conditions and the products are summarized in Table 2. Treatment of **4** with $[Fe_2(CO)_9]$ in methanol at 50 °C afforded methyl 1-phenylvinylcarbamate (**22**)[21] and acetophenone (**23**) in 44 and 18% yields (Table 2, entry 1). The carbamate **22** is labile and it is hydrolysed by TLC on silica gel to give acetophenone. Accordingly the products, **22** and **23**, in Table 2 were isolated by distillation using a Kugelrohr apparatus. A similar result was also obtained by the photoirradiation of $[Fe(CO)_5]$ and **4** (entry 3). However, the thermal reaction of **4** with $[Fe(CO)_5]$ in methanol at the refluxing temperature proceeded very slowly, and 80% of **4** was recovered (entry 4). Similar to the case of **1**, reaction of **4** with $[Fe_2(CO)_9]$ or $[Fe(CO)_5]$ in acetonitrile containing water afforded only **23** in moderated yield (entries 2 and 5).



Scheme 5.

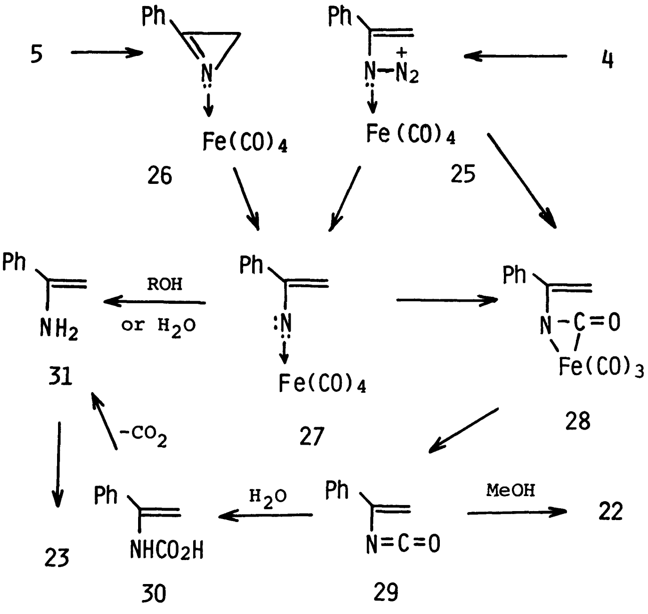
The thermal reaction of **5** with $[Fe_2(CO)_9]$ in methanol at 50 °C, on the other hand, afforded **22** and **23** in 14 and 34% yields, along with 2.2% of 2,5-diphenylpyrazine (**24**) (entry 6). It is notable that the major product from **4** in methanol is carbamate **22**, while that from **5** is acetophenone. Use of acetonitrile



Scheme 6.

containing water as the reaction solvent **5** afforded only acetophenone **23** in 72% yield (entry 7) as in the case of entries 2 and 5 in Table 2. However, irradiation of a solution of **5** with or without [$Fe(CO)_5$] in methanol resulted in the complete disappearance of **5** and afforded **24** in 42 or 35% yield, respectively. Thus the formation of **24** might be explained by the photochemical C–C bond cleavage of the azirine ring to give nitrile ylide.[22]

The reaction pathways for **4** and **5** are very similar to the case of **1**. The carbamate **22** would arise from **4** and **5** *via* methanol-addition of 1-phenylvinyl isocyanate (**29**), which could be derived from carbonyl insertion of the complexed 1-phenylvinylnitrene **27** *via* **25** or **26**.[5,6] The protonation and the subsequent reduction of vinylnitrene moiety of **27** may occur in protic media to give enamine **31**, which may be decomposed by stray water to give **23**. This fact and the lability of **22** to hydrolysis even on TLC plates could explain the previous studies shown in Scheme 2. Another pathway for the formation of **23** would be H_2O-addition of **29** to give **30** followed by decarboxylation to give **31**. Thus in the presence of water, only **23** could be obtained. In the reaction of **4** in methanol (entries 1 and 3) **22** predominates over **23**, while in that of **5**, **23** predominates over **22** (entry 6). This fact may be explained by the direct carbonylation of **25** to give **28**. A minor amount of 2,5-diphenylpyrazine **24** may arise from addition of **27** with **26** or from dimerization of **26**,[9] in the reaction of **5**. However, C–C and/or C=N bond cleavage of the azirine ring can not be ruled out to lead to **24**.[8,9]



Scheme 7.

In conclusion, the decomposition of **1**, **4**, and **5** with iron carbonyl species afford complexed nitrene intermediates under mild conditions. In a protic solvent this intermediate undergoes reduction to give an amine and carbonyl insertion to give an organic isocyanate in good combined yield. No complexes, such as **2**, **3**, **6**, **7**, and **8** were obtained in protic media.

Experimental

General. Solvents were purified and dried by standard methods. All reactions were carried out under a dry nitrogen atmosphere. Photoirradiations were carried out using Rayonet photoreactor (MGR-100) fitted with RPR-350 nm lamps through a Pyrex filter. The thermal reactions were carried out under unlighted conditions. Azidobenze (**1**),[23] α-azidostyrene (**4**),[24] and 3-phenyl-2*H*-azirine (**5**)[24] were synthesized according to the literature-procedures. All of the products are known compounds and were identified by comparison of the spectral data with those of authentic samples.

*Thermal Reaction of **1** with [$Fe_2(CO)_9$].* A mixture of **1** (119 mg, 1 mmol) and [$Fe_2(CO)_9$] (364 mg, 1 mmol) in 10 cm^3 of anhydrous methanol or acetonitrile containing water (1 mmol) was stirred at 50 °C for a period indicated in Table 1. The solution was filtered through Celite and the filtrate was evaporated. The residue was separated by TLC on silica gel using benzene or dichloromethane as the eluent to give the products, which are summarized in Table 1.

TABLE 1. REACTION OF AZIDOBENZENE IN THE PRESENCE OF [$Fe_2(CO)_9$][a] OR [$Fe(CO)_5$][b]

Entry	Metalcarbonyl	Solvent	Reaction conditions	Reaction time/h	Yield of product/%			
					14	15	16	1
1	$Fe_2(CO)_9$	MeOH	50 °C	3	21	51	20	
2	$Fe_2(CO)_9$	MeCN-H_2O[c]	50 °C	3	67	—	23	
3	$Fe(CO)_5$	MeOH	*hν*	4	10	53	20	
4	$Fe(CO)_5$	MeCN-H_2O[c]	*hν*	8	47	—	40	
5	$Fe(CO)_5$	MeOH	Reflux	8	—	11	3	>30[f]
6[d]	$Fe(CO)_5$	AcOH	100 °C	3	33	—	52	
7[e]	$Fe(CO)_5$	AcOH	100 °C	6	—	—	67	

a) An equimolar quantity of [$Fe_2(CO)_9$] was used. b) 1.2 molar equivalent amount of [$Fe(CO)_5$] was used. c) Contained an equivalent amount of water. d) 1 mol of $Ph-N_3$ and 2 mol of [$Fe(CO)_5$] was dissolved in 5 cm^3 of AcOH. e) 10 mmol of $Ph-N_3$ and 20 mmol of [$Fe(CO)_5$] was dissolved in 5 cm^3 of AcOH. f) This compound is volatile under the workup conditions and the yield is low.

TABLE 2. REACTION OF α-AZIDOSTYRENE AND 3-PHENYL-2H-AZIRINE IN THE PRESENCE OF $[Fe(CO)_9]^{a)}$ OR $[Fe(CO)_5]^{b)}$

Entry	Compound	Metalcarbonyl	Solvent	Reaction conditions	Reaction time/h	Yield of product/%		
						22	**23**	Others
1	4	$Fe_2(CO)_9$	MeOH	50 °C	3	44	18	—
2	4	$Fe_2(CO)_9$	$MeCN-H_2O^{c)}$	50 °C	3	—	71	—
3	4	$Fe(CO)_5$	MeOH	*hν*	24	53	30	—
4	4	$Fe(CO)_5$	MeOH	Reflux	8	14	5	80 (**4**)
5	4	$Fe(CO)_5$	$MeCN-H_2O^{c)}$	*hν*	24	—	67	—
6	5	$Fe_2(CO)_9$	MeOH	50 °C	7	14	34	2.2 (**24**)
7	5	$Fe_2(CO)_9$	$MeCN-H_2O^{c)}$	50 °C	24	—	72	—
8	5	None	MeOH	h*ν*	2.5	—	—	42 (**24**)
9	5	$Fe(CO)_5$	MeOH	h*ν*	2.5	—	—	35 (**24**)

a) An equivalent amount of $[Fe_2(CO)_9]$ was used. b) 1.2 molar equivalent amount of $[Fe(CO)_5]$ was used. c) Contained an equivalent amount of water.

Photoirradiation of 1 with $[Fe(CO)_5]$. A solution of **1** (119 mg, 1 mmol) and $[Fe(CO)_5]$ (232 mg, 1.2 mmol) in 20 cm^3 of anhydrous methanol or acetonitrile containing water (1 mmol) was irradiated for a period indicated in Table 1. The solution was concentrated and filtered through Celite. The filtrate was evaporated and the residue was separated by TLC on silica gel using benzene or dichloromethane as the eluent to give the products, which are summarized in Table 1.

Thermal Reaction of 1 with $[Fe(CO)_5]$ in Methanol. A solution of **1** (119 mg, 1 mmol) and $[Fe(CO)_5]$ (232 mg, 1.2 mmol) in 10 cm^3 of anhydrous methanol was refluxed for 8 h. The solution was concentrated and chromatographed on Florisil to give the products, which are listed in Table 1.

Photoirradiation of 15 with $[Fe(CO)_5]$. A solution of **15** (151 mg, 1 mmol) and $[Fe(CO)_5]$ (232 mg, 1.2 mmol) in 20 cm^3 of anhydrous methanol was irradiated for 5 h. The photolysate was filtered through Celite and the filtrate was evaporated. The resulting residue was recrystallized to give **15** in 100% yield.

Photoirradiation of 16 with $[Fe(CO)_5]$. A solution of **16** (212 mg, 1 mmol) and $[Fe(CO)_5]$ (232 mg, 1.2 mmol) in 20 cm^3 of anhydrous methanol was irradiated for 5 h. The photolysate was filtered through Celite and the filtrate evaporated. The resulting residue was recrystallized to give 100% of **16**.

Thermal Reaction of 1 with $[Fe(CO)_5]$ in AcOH. A solution of **1** (119 mg, 1 mmol) and $[Fe(CO)_5]$ (392 mg, 2 mmol) in 5 cm^3 of AcOH was heated at 100 °C for 3 h. The solution was diluted with 50 cm^3 of benzene and then neutralized with aqueous sodium hydrogencarbonate solution. The organic layer was separated and dried over sodium sulfate. After evaporation of the solvent, the residue was separated by TLC on silica gel using dichloromethane as the eluent to give **14** (31 mg, 33%) and **16** (55 mg, 52%).

Thermal Reaction of 1 with $[Fe(CO)_5]$ in AcOH (Concentrated Conditions). A solution of **1** (1.19 g, 10 mmol) and $[Fe(CO)_5]$ (392 mg, 20 mmol) in 5 cm^3 of AcOH was heated at 100 °C for 6 h. After addition of 10 cm^3 of water to this solution, the precipitated colorless crystals were collected to give **16** (782 mg, 67%). The filtrate was neutralized with aqueous sodium hydrogencarbonate solution and extracted with benzene. Evaporation of the solvent gave no other product.

Reaction of 14 with 20 in AcOH. Phenyl isocyanate **20** (101 mg, 1 mmol) was added dropwise to a stirred solution of **14** (93 mg, 1 mmol) in 5 cm^3 of AcOH. After stirring for 5 min, the solvent was evaporated and the residue was collected to give 210 mg (98%) of **16**.

Thermal Reaction of 4 with $[Fe_2(CO)_9]$. A solution of **4** (145 mg, 1 mmol) and $[Fe_2(CO)_9]$ (364 mg, 1 mmol) in 10 cm^3 of anhydrous methanol or acetonitrile containing water (1 mmol) was heated at 50 °C for 7 h. The solution was filtered through Celite and the filtrate was concentrated. The resulting residue was distilled *in vacuo* using a Kugelrohr apparatus to give the products, which are summarized in Table 2.

Photoirradiation of 4 with $[Fe(CO)_5]$. A solution of **4** (145 mg, 1 mmol) and $[Fe(CO)_5]$ (236 mg, 1.2 mmol) in 20 cm^3 of anhydrous methanol or acetonitrile containing water (1 mmol) was irradiated. The solution was concentrated and filtered through Celite. The filtrate was evaporated and the residue was distilled as described above to give the products.

Thermal Reaction of 4 with $[Fe(CO)_5]$. A solution of **4** (145 mg, 1 mmol) and $[Fe(CO)_5]$ (236 mg, 1.2 mmol) in 10 cm^3 of anhydrous methanol was refluxed for 7 h. The solution was concentrated and chromatographed on Florisil. The fraction eluted with hexane gave 116 mg (80%) of **4**. Then, the first fraction eluted with benzene gave 6 mg (5%) of **22**, and the second fraction gave 24 mg (13%) of **23** (Table 2, entry 4).

Thermal Reaction of 5 with $[Fe_2(CO)_9]$. A solution of **5** (117 mg, 1 mmol) and $[Fe_2(CO)_9]$ (364 mg, 1 mmol) in 10 cm^3 of anhydrous methanol or acetonitrile containing water (1 mmol) was heated at 50 °C for a period indicated in Table 2. The solution was filtered through Celite and the filtrate was evaporated. The residue was distilled as described above to give the products, **22** and/or **23**. After the distillation, the residual oil was purified by TLC on silica gel to give **24**: mp 196—197 °C (from EtOH).[8)]

Photoirradiation of 5 without $[Fe(CO)_5]$. A solution of **5** (117 mg, 1 mmol) in 10 cm^3 of anhydrous methanol was irradiated for 2.5 h. The evaporation of the solvent and the following separation by TLC on silica gel gave **24** (42 mg, 41%).

Photoirradiation of 5 with $[Fe(CO)_5]$. A solution of **5** (117 mg, 1 mmol) and $[Fe(CO)_5]$ (232 mg, 1.2 mmol) in 10 cm^3 of anhydrous methanol was irradiated for 2.5 h. The evaporation of the solvent and the following separation by TLC on silica gel gave **24** (41 mg, 35%).

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