[CONTRIBUTION FROM RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

Ferrocene and Related Organometallic π-Complexes. IV. Some Ullmann Reactions of Haloferrocenes[1]

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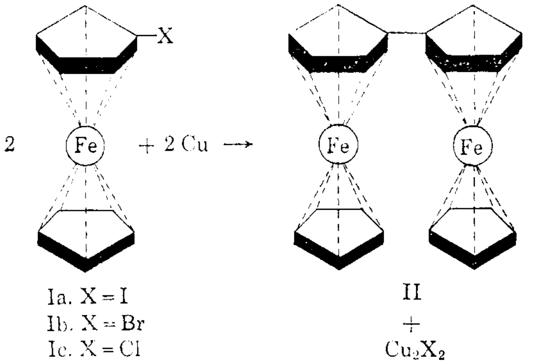
Haloferrocenes have been found to undergo the Ullmann coupling reaction readily. Iodoferrocene and copper bronze form biferrocenyl in quantitative yield at 150°. Both iodoferrocene and 1-iodo-2-nitrobenzene form coupling products in 95–100% yield at temperatures as low as 60°. A series of ferrocenyl aryl ethers have been prepared by the Ullmann condensation of iodoferrocene and potassium aryloxides.

Incidental to the synthesis of some trialkylsilylferrocenes from the reaction of ferrocenyllithium and trialkylchlorosilanes, trace amounts of a dark-orange, crystalline material were also isolated. An elemental analysis of this material indicated that it was biferrocenyl (II).[2] Structural assignment of the material as biferrocenyl has been made on the basis of infrared studies.[3] A subsequent unequivocal synthesis of biferrocenyl by means of Ullmann coupling of iodoferrocene (Ia) and copper bronze has further substantiated this assignment.[4]

In this paper, details of the formation of biferrocenyl from haloferrocenes are described, and some additional Ullmann reactions involving haloferrocenes and certain halobenzenes are reported.[5]



The Ullmann coupling reaction of halobenzenes and copper bronze is a well known procedure for the synthesis of biaryls, and the haloferrocenes might be expected to react as typical aryl halides in view of the aromatic nature of the ferrocene system.[6,7] Although attempts to prepare simple haloferrocenes directly *via* halogenation of ferrocene have not been successful, the haloferrocenes have recently become available by two indirect methods involving the reaction of halogens with chloromercuriferrocenes[8] and the reaction of cupric halides with ferrocenylboronic acids.[9]

Initial studies involved the reaction of iodoferrocene and copper bronze at *ca.* 150°. Biferrocenyl was formed readily under these conditions in yields of 96–100%. The reactions were normally run in the melt using an appreciable molar excess of copper bronze. Although varying reaction periods were employed, coupling appeared to be essentially complete in less than two hours. In one experiment in which biphenyl was used as a solvent and diluent, the yield of biferrocenyl was reduced to 76%. While dimethylformamide has been shown to be an excellent solvent and diluent for the Ullmann coupling reaction,[10] the interaction of iodoferrocene and copper bronze in dimethylformamide resulted primarily in dehalogenation with formation of ferrocene. Both bromoferrocene (Ib) and chloroferrocene (Ic) reacted with copper bronze to form biferrocenyl, although in the case of chloroferrocene the yield of the coupling product was appreciably lower. An attempted Ullmann coupling of iodoferrocene using powdered zinc in place of copper bronze afforded biferrocenyl in 17% yield.

Several attempts to synthesize arylferrocenes by mixed Ullmann couplings of iodoferrocene with iodobenzene, 2-iodobiphenyl and 1,4-diiodobenzene were not successful. The only products obtained

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[1] Presented in part at the 138th Meeting, American Chemical Society, Division of Organic Chemistry, New York, Sept. 11-16, 1960; see Abstracts of Papers, p. 54-P.

[2] M. Rausch, M. Vogel, H. Rosenberg, D. Mayo, and P. Shaw, Wright Air Development Center Technical Report 57-62, Part II, February, 1958; ASTIA Document No. 150979. This report has been released to the Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C., for sale to the general public.

[3] S. I. Goldberg and D. W. Mayo, *Chemistry and Industry*, 671 (1959).

[4] M. D. Rausch, *J. Am. Chem. Soc.*, **82**, 2080 (1960).

[5] O. A. Nesmeyanova and E. G. Perevalova [*Doklady Akad. Nauk S.S.S.R.*, **126**, 1007 (1959)] have recently reported that biferrocenyl can also be prepared in 1–6% yield from the reaction of diferrocenylmercury and palladium black.

[6] R. B. Woodward, M. Rosenblum, and M. C. Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952).

[7] M. D. Rausch, M. Vogel, and H. Rosenberg, *J. Chem. Ed.*, **34**, 268 (1957).

[8] A. N. Nesmeyanov, E. G. Perevalova, and O. A. Nesmeyanova, *Doklady Akad. Nauk S.S.S.R.*, **100**, 1099 (1955).

[9] A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Doklady Akad. Nauk S.S.S.R.*, **126**, 1004 (1959).

[10] N. Kornblum and D. L. Kendall, *J. Am. Chem. Soc.*, **74**, 5782 (1952).

were biferrocenyl and small amounts of biphenyl, 4-quaterphenyl and polyphenyl, respectively.

In view of the extraordinarily high reactivity of iodoferrocene and copper bronze at 150°, it was of interest to determine if this reaction could be accomplished under milder conditions. In a series of experiments carried out at 60° for sixty hours, biferrocenyl was obtained in 95–97% yield. A similar reaction was intercepted after only one hour, and in this case the yield of biferrocenyl was 22%. The facile formation of biferrocenyl from iodoferrocene at this temperature was rather surprising, since Ullmann coupling reactions are usually carried out at 200° or greater, and yields of coupling products are often only moderately satisfactory. Apparently, no studies of Ullmann reactions performed at temperatures as low as 60° have been reported.

A search of earlier literature on the Ullmann coupling reaction indicated that one of the most reactive compounds is 1-iodo-2-nitrobenzene. Iodo derivatives are generally the most reactive of the halobenzenes, and the *o*-nitro group is known to have a strong activating influence in this reaction.[11–13] Gore and Hughes were able to prepare 2,2′-dinitrobiphenyl in 96% yield by heating 1-iodo-2-nitrobenzene and copper bronze at 190–240°.[14] On the other hand, a *m*-nitro group is known to have little effect on the reactivity of an aryl halide under Ullmann conditions, and iodobenzene reacts only slowly and incompletely with copper bronze at 190°.[13]

As a means of comparison, a series of substituted iodobenzenes were likewise subjected to the Ullmann coupling reaction at 60°. The results are tabulated in Table I. Except in the case of the mixed coupling of iodoferrocene and 1-iodo-2-nitrobenzene, the yields given represent the average of two or more experiments.

TABLE I

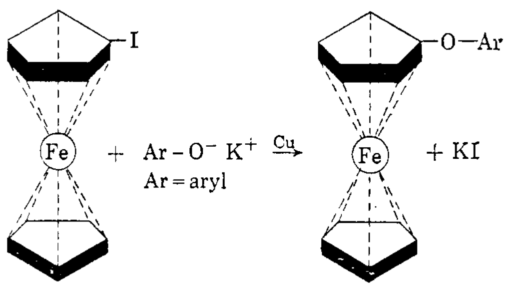
ULLMANN COUPLING REACTIONS OF IODOBENZENES AND IODOFERROCENE

(9 molar excess of copper; 60°; 60 hr.)

Halo-derivative	Coupling Product	Yield, %
1-Iodo-2-nitrobenzene	2,2′-Dinitrobiphenyl	>99
1-Iodo-3-nitrobenzene	3,3′-Dinitrobiphenyl	<1[a]
Iodobenzene	Biphenyl	0[a]
Iodoferrocene	Biferrocenyl	96
1-Iodo-2-nitrobenzene + iodoferrocene[b]	2,2′-Dinitrobiphenyl	—[c]
	Biferrocenyl	71
	2-Nitrophenylferrocene	7.5

[a] The starting materials were largely recovered from the reaction. [b] Equimolar mixture. [c] No attempt was made to isolate this product.

1-Iodo-2-nitrobenzene was found to couple very readily at this low temperature, forming 2,2′-dinitrobiphenyl in essentially quantitative yield. 1-Iodo-3-nitrobenzene and iodobenzene, as might be expected, yielded little or no coupling products at this temperature. An attempted mixed Ullmann reaction involving equimolar amounts of iodoferrocene and 1-iodo-2-nitrobenzene produced a low yield of the unsymmetrical coupling product, 2-nitrophenylferrocene.



No rationalizations can be drawn at this time as to why iodoferrocene is so reactive under these conditions, since there is still considerable uncertainty regarding the mechanism of the Ullmann coupling reaction itself.[11,15] It can be concluded, however, that the ferrocenyl group activates a halogen in the Ullmann coupling reaction to an extent similar to that shown by the highly activating 2-nitrophenyl group.

Oxygen-substituted ferrocene derivatives were first prepared by an indirect procedure involving the reaction of 3-methyl-2-cyclopentenone with sodium amide and ferrous chloride in liquid ammonia.[16] Recently, the reaction of either ferrocenylboronic acid or bromoferrocene with cupric acetate has been reported to yield ferrocenyl acetate, and this compound has led to the formation of hydroxyferrocene and methoxyferrocene.[17,18] Since no aryloxyferrocenes have yet been described in the literature, it was of interest to investigate the possible Ullmann condensation of iodoferrocene and a variety of potassium aryloxides in the presence of copper. Ferrocenyl aryl ethers were formed in every case.[19,20] The properties, yields, and analyses of these ethers are given in Table II.

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(11) P. E. Fanta, *Chem. Rev.*, **38**, 139 (1946).

(12) W. Davey and R. W. Latter, *J. Chem. Soc.*, 264 (1948).

(13) J. Forrest, *J. Chem. Soc.*, 592 (1960).

(14) P. H. Gore and G. K. Hughes, *J. Chem. Soc.*, 1615 (1959).

(15) J. Forrest, *J. Chem. Soc.*, 594 (1960).

(16) R. E. Benson and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, 79, 5471 (1957).

(17) A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Tetrahedron Letters*, No. 17, 13 (1959).

(18) A. N. Nesmeyanov, V. A. Sazonova, and V. N Drozd, *Doklady Akad. Nauk S.S.S.R.*, **130**, 1030 (1960); 129, 1060 (1959).

(19) Other investigators (Refs. 8 and 18) have been unsuccessful in attempts to exchange a halogen atom in haloferrocenes for hydroxy, acyloxy, and similar groups in reactions with sodium hydroxide, sodium acetate, and similar salts of alkali metals under Ullmann conditions.

(20) The reaction of iodoferrocene and sodium mercaptides likewise yields ferrocenyl aryl sulfides (M. D. Rausch, unpublished studies).

TABLE II

FERROCENYL ARYL ETHERS

Compound	M.P.	Yield,[a] %	Calcd. C	Calcd. H	Calcd. Fe	Calcd. Mol. wt.	Found C	Found H	Found Fe	Found Mol. wt.
Ferrocenyl phenyl ether	93–93.5	28	69.10	5.07	20.08	278	69.27	4.99	19.90	294
Ferrocenyl 3-(3-phenoxyphenoxy)phenyl ether	74–74.5	50	72.74	4.80	12.08	462	72.63	5.01	12.31	473
Ferrocenyl 2-biphenylyl ether	141–142	62	74.60	5.12	15.77	354	74.50	5.10	16.25	345
Ferrocenyl 2-naphthyl ether	143–143.5	12	73.20	4.92	17.02	328	73.50	5.18	17.19	324
Ferrocenyl 4-bromophenyl ether[b]	87–87.5	22	53.83	3.67	15.64	357	53.70	3.65	15.73	355

[a] Based on iodoferrocene reacted. [b] Calcd.: Br, 22.38. Found: 22.19.

EXPERIMENTAL[21]

Materials. Iodoferrocene was prepared in 60–70% yield by the reaction of chloromercuriferrocene and iodine in xylene solution at 75–80°.[8] After several recrystallizations from methanol-water, the compound melted at 49–49.5° (reported[8] m.p. 44–45°). Bromoferrocene and chloroferrocene were obtained by the reaction of ferrocenylboronic acid with cupric bromide and cupric chloride, respectively.[9] Copper bronze was obtained from B. F. Drakenfeld and Co., Inc., New York, and was activated according to the procedure of Vogel.[22] Zinc dust was obtained from J. T. Baker Chemical Co., and activated according to the procedure of Cava and Mitchell.[23] 1-Iodo-2-nitrobenzene, 1-iodo-3-nitrobenzene, 2-phenylphenol, and 4-bromophenol were obtained from Distillation Products Industries, iodobenzene and 2-naphthol from the Matheson Co., and phenol from Allied Chemical Co. 3-(3-Phenoxyphenoxy)phenol was obtained from Dr. W. C. Hammann of This Laboratory; it was isolated as a by-product from the reaction of phenol, 3-chlorophenol and potassium hydroxide. G.E. lamp-grade nitrogen was used throughout this investigation.

Conversion of haloferrocenes to biferrocenyl. (A) *In melt.* A mixture of 0.936 g. (0.003 mole) of iodoferrocene and 1.90 g. (0.03 mole) of copper bronze was added to a Schlenk tube that had previously been flushed with nitrogen. A 2-ft. air condenser was inserted and the mixture was heated for 16 hr. in a bath of silicone oil maintained at 140–150°.[24] After cooling, the reaction products were extracted repeatedly with 25-ml. portions of boiling benzene until the extracts were colorless. The solvent was evaporated under reduced pressure, leaving a dark-orange, crystalline residue of biferrocenyl, 0.555 g. (100% yield), m.p. 238–239° dec. Careful recrystallization from heptane produced 0.510 g. of product, m.p. 239–240° dec., and a second crop (0.025 g.) of m.p. 233–236° dec.

Anal. Calcd. for $C_{20}H_{18}Fe$: C, 64.91; H, 4.90; Fe, 30.19; mol. wt. 370. Found: C, 64.99; H, 4.97; Fe, 30.09; mol. wt. 360.

In experiments in which less pure iodoferrocene was used, the yield of biferrocenyl was appreciably less than quantitative. Similar reactions in which iodoferrocene was replaced by bromoferrocene and chloroferrocene produced biferrocenyl in yields of 97% and 65%, respectively.

(B) *In solvent.* A mixture of 0.405 g. (0.0013 mole) of iodoferrocene, 0.83 g. (0.013 mole) of copper bronze, and 4 g. of biphenyl, m.p. 70–71°, was heated under nitrogen at 130° for 16 hr. and at 158–160° for an additional 3 hr. The reaction products were extracted well with boiling benzene and the benzene was evaporated. The residue was then extracted twice with 20-ml. portions of petroleum ether (b.p. 60–70°) at room temperature. The remaining dark-orange crystalline material amount to 0.130 g. of biferrocenyl, m.p. 237–239° dec. Chromatography of the petroleum ether extracts on alumina rapidly eluted the biphenyl, followed by an additional 0.053 g. of biferrocenyl, for a total yield of 76%.

In reactions in which dimethylformamide was utilized as the solvent and diluent according to the general procedure outlined by Kornblum and Kendall,[10] work-up of the reaction products yielded mostly ferrocene.

(C) *Using zinc.* The reaction was carried out as described in (A) using 0.405 g. (0.0013 mole) of iodoferrocene and 0.83 g. (0.013 mole) of zinc dust. After heating for 19 hr. at 145–150°, the residue was extracted with benzene, the benzene was evaporated, and the residue was chromatographed on an alumina column in petroleum ether-benzene solution. The first band yielded ferrocene, 0.13 g., m.p. 173–174°. Continued elution with benzene produced 0.04 g. (17% yield) of biferrocenyl, m.p. 237–240° dec.

Biferrocenyl is appreciably less soluble in common organic solvents than is ferrocene. It can be sublimed, although less readily than ferrocene. In a sealed capillary under nitrogen, biferrocenyl melts with no noticeable decomposition and remains a clear orange fluid on heating to *ca.* 300° at which temperature appreciable darkening occurs. The infrared spectrum of biferrocenyl is quite similar to that of ferrocene, the most significant differences being a splitting of the band near 1100 cm.$^{-1}$, and increased absorption in the 800–850 cm.$^{-1}$ region. The two intense absorption bands near 1100 and 1000 cm.$^{-1}$ are in agreement with the presence of unsubstituted cyclopentadienyl rings. Biferrocenyl in ethanol solution exhibits absorption maxima at 455 mμ in the visible region and at 297 and 221 mμ in the ultraviolet region. Similar spectral data have been reported for biferrocenyl obtained from the reaction of ferrocenyllithium and trialkylchlorosilanes.[3] Maxima for ferrocene in ethanol solution have been reported at 440 and 326 mμ.[25]

Ullmann coupling reactions at 60°. (A) *Reaction of 1-iodo-2-nitrobenzene.* In a typical experiment, 4.98 g. (0.02 mole)

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[21] All melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. The molecular weight of biferrocenyl was determined cryoscopically in benzene by Mrs. G. Kratzer of This Laboratory. Molecular weights of the ferrocenyl aryl ethers were determined cryoscopically in camphor by Schwarzkopf Microanalytical Laboratory.

[22] A. I. Vogel, *A Textbook of Practical Organic Chemistry,* Longmans, Green and Co., London, 1954, p. 188.

[23] M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.,* 81, 5409 (1959).

[24] Conversion of iodoferrocene to biferrocenyl can also be readily accomplished by heating the reaction mixture in a sealed tube under nitrogen. In a comparative experiment in which 1-iodo-2-nitrobenzene was heated in a sealed tube at 150°, however, the tube exploded. For this reason, the sealed tube procedure is not recommended.

[25] G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Am. Chem. Soc.,* **74,** 2125 (1952); L. Kaplan, W. L. Kester, and J. J. Katz, *J. Am. Chem. Soc.,* **74,** 5531 (1952).

of 1-iodo-2-nitrobenzene and 12.7 g. (0.2 mole) of copper bronze were mixed and placed in a Schlenk tube under nitrogen. A 2-ft. air condenser was inserted and the tube was heated for 60 hr. in a silicone bath maintained at 60 ± 2°. A thermometer placed inside the tube indicated that the internal temperature likewise did not exceed 60°. The reaction product was then extracted three times with boiling benzene and the benzene was evaporated. The yellow crystalline residue amounted to 2.43 g. (99.6% yield) of 2,2'-dinitrobiphenyl, m.p. 124–125° (reported[26] m.p. 124°). Recrystallization produced 2.30 g. of product, m.p. 125°.

(B) *Reaction of 1-iodo-3-nitrobenzene.* In a reaction similar to that described in (A) involving 4.98 g. (0.02 mole) of 1-iodo-3-nitrobenzene and 12.7 g. (0.2 mole) of copper bronze, chromatography of the extraction residue on alumina produced 4.20 g. of unchanged 1-iodo-3-nitrobenzene and 0.03 g. (1% yield) of 3,3'-dinitrobiphenyl, m.p. 197–198° (reported[26] m.p. 200°).

(C) *Reaction of iodobenzene.* In a reaction similar to that described in (A) involving 20.4 g. (0.10 mole) of iodobenzene and 1.0 g. (63.5 g.) of copper bronze, distillation yielded 16.0 g. of unchanged iodobenzene and no trace of biphenyl.

(D) *Reaction of iodoferrocene.* In a reaction similar to that described in (A) involving 0.624 g. (0.002 mole) of iodoferrocene and 1.28 g. (0.02 mole) of copper bronze, evaporation of the benzene extracts left 0.360 g (97% yield) of biferrocenyl, m.p. 235–236° dec. Recrystallization from heptane gave 0.330 g. of product, m.p. 237–239° dec.

(E) *Reaction of iodoferrocene and 1-iodo-2-nitrobenzene.* In a reaction similar to that described in (A) involving 0.405 g. (0.0013 mole) of iodoferrocene, 0.324 g. (0.0013 mole) of 1-iodo-2-nitrobenzene, and 1.65 g. (0.026 mole) of copper bronze, chromatography of the extraction residue on alumina in petroleum ether-benzene solution produced 0.17 g. (71% yield) of biferrocenyl, m.p. 237–239° dec., and 0.03 g. (7.5% yield) of purple needles of 2-nitrophenylferrocene, m.p. 116–117° (reported[27] m.p. 112–114°). The infrared spectrum of 2-nitrophenylferrocene in potassium bromide exhibited strong absorption bands at 1520 and 1350 cm.$^{-1}$, indicative of nitro stretching vibrations, bands near 1100 and 1000 cm.$^{-1}$ indicative of an unsubstituted cyclopentadienyl ring, as well as characteristic phenyl absorption bands.

Ferrocenyl aryl ethers. All compounds listed in Table II were prepared by essentially the same procedure. The preparation of ferrocenyl 2-naphthyl ether is given as a typical example. A mixture of 1.44 g. (0.01 mole) of 2-naphthol and 0.28 g. (0.005 mole) of potassium hydroxide was placed in a Schlenk tube under nitrogen and the tube was heated at 150° until all the potassium hydroxide had dissolved. After cooling, 0.936 g. (0.003 mole) of iodoferrocene and 0.02 g. of copper bronze was added, a 2-ft. air condenser was inserted, and the reaction mixture was heated for 16 hr. at 155°. After cooling, the contents was washed with 10% potassium hydroxide solution, water, and then extracted repeatedly with boiling benzene until the extracts were colorless. After evaporation of the solvent, the residue was taken up in a minimum amount of 1:1 petroleum ether benzene and chromatographed on alumina. Elution with this solvent developed two distinct bands. From the first band there was collected 0.11 g. of ferrocene, m.p. 173–174°. The second band deposited 0.15 g. of yellow crystals, m.p. 139–141°. Two recrystallizations from heptane produced 0.12 g. of analytically pure ferrocenyl 2-naphthyl ether, m.p 143–143.5°.

All ferrocenyl aryl ethers exhibited strong absorption bands in the 1270–1230 cm.$^{-1}$ region, indicative of an aryloxy group, as well as bands near 1100 and 1000 cm.$^{-1}$ When heated in sealed capillaries under nitrogen, the ethers did not appear to undergo visual change at temperatures up to *ca.* 300°, although appreciable decomposition was noted in air at this temperature.

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[26] F. Ullmann and J. Bielecki, *Ber.*, **34**, 2174 (1901).

[27] G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 367 (1955).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Reaction of Diazo Compounds with Nitroolefins. VI. The Reaction of Diphenyldiazomethane with 1-Nitropropene

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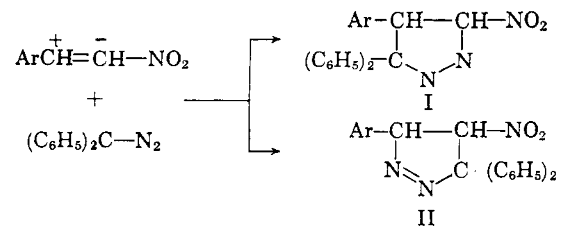
It has been shown by radio tracer studies that diphenyldiazomethane adds to 1-nitropropene to give a pyrazoline in which the diazonitrogen is attached to the *beta* carbon of the nitroolefin. This orientation of addition is the same as previously determined for the addition of diphenyldiazomethane to aromatic nitroolefins, and just opposite to the orientation observed for additions involving diazomethane and diazoacetic ester. These results substantiate the conclusion that disubstituted diazo compounds add in an "inverse manner" to conjugated systems.

We have recently[2] shown that diphenyldiazomethane adds to certain derivatives of ω-nitrostyrene to give pyrazolines (II) in which the diazonitrogen atom is attached to the β-carbon atom of the conjugate system.



This orientation of addition, which was suggested to be general for additions involving diphenyldiazomethane, is just opposite to that observed when diazomethane[3] or diazoacetic ester reacts with conjugate systems.

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[1] E. I. duPont de Nemours and Co. summer fellow, 1959. From the Ph.D. Thesis of Henry G. Braxton, Jr., The University of Minnesota, 1960.

[2] W. E. Parham, Carl Serres, Jr., and P. R. O'Connor, *J. Am. Chem. Soc.*, **80**, 588 (1958).

[3] *Cf.* (a) W. E. Parham and J. L. Bleasdale, *J. Am. Chem. Soc.*, **72**, 3843 (1950); (b) W. E. Parham and J. L. Bleasdale, *J. Am. Chem. Soc.*, **73**, 4664 (1951).