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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[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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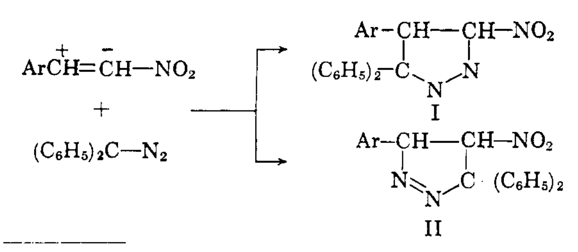
It has been shown by radio tracer studies that diphenyldiazomethane adds to 1-nitropropene to give a pyrazoline in which the diazonitrogen is attached to the *beta* carbon of the nitroolefin. This orientation of addition is the same as previously determined for the addition of diphenyldiazomethane to 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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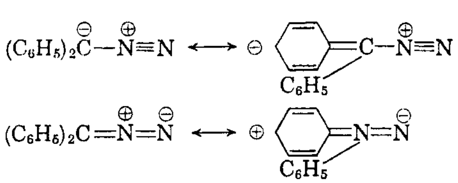
[1] E. I. duPont de Nemours and Co. summer fellow, 1959. From the Ph.D. Thesis of Henry G. Braxton, Jr., The University of Minnesota, 1960.

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

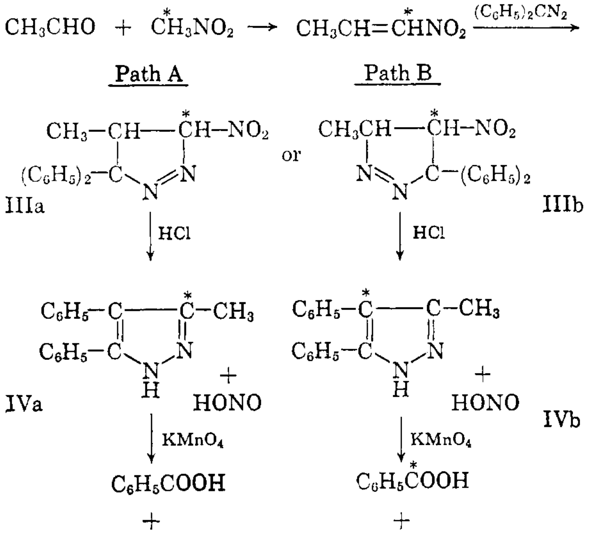
[3] *Cf.* (a) W. E. Parham and J. L. Bleasdale, *J. Am. Chem. Soc.*, **72**, 3843 (1950); (b) W. E. Parham and J. L. Bleasdale, *J. Am. Chem. Soc.*, **73**, 4664 (1951).



The decreased nucleophilic character of the diazocarbon atom and the increased nucleophilic character of the terminal nitrogen atom, in diphenyldiazomethane, as compared with diazomethane, is reasonable if one considers resonance interaction involving the attached phenyl groups.

Nevertheless, we felt that a check of the generality of this reaction should be made in which the aryl group of the conjugate system is replaced by an aliphatic group. Need for such confirmation was made further evident by the observation that the thermal decomposition of pyrazolines derived from aliphatic nitroolefins and diphenyldiazomethane affords nitrocyclopropane derivatives, while pyrolysis of analogous pyrazolines derived from aromatic nitroolefins do not. The course of these thermal decomposition reactions is discussed in the accompanying paper.

The olefin chosen was 1-nitropropene, and the synthetic and degradative scheme used in this work, both for tagged and untagged experiments, are outlined in the above series of equations.



The reaction[4] of diphenyldiazomethane with 1-nitropropene to give III was previously described, and is complicated by: (1) polymerization of the 1-nitropropene; (2) probable decomposition of diphenyldiazomethane to diphenylmethylene[5]; and (3) the instability of the adduct III. Although the yield of crude adduct, melting at 60–120°, is high, repeated recrystallization of the crude product was required for purification, and pure III was isolated in only 12% yield. Attempts to purify III by chromatography were unsuccessful, since the absorbants studied catalyzed the conversion III to IV. Repeated attempts were also made to isolate isomeric pyrazolines; however, only one isomer, m.p. 140–141°, was obtained.

The conversion of III to IV was carried out in high yield (77–90%), as previously described,[4] by reaction with hydrochloric acid in ethanol. The structure of this rearranged product was previously established[4] as 3-methyl-4,5-diphenylpyrazoline; thus it was known that IVa would have to be formed by a double migration of groups, or IVb by a single migration of phenyl, during loss of nitrous acid.[6]

Exhaustive oxidation of 3-methyl-4,5-diphenylpyrazole (IV) with potassium permanganate in *t*-butyl alcohol and water gave carbon dioxide and benzoic acid (40–74% calculated for two moles). This oxidation was found suitable as a degradative scheme for determining the fate of the tagged carbon.

The objective of the C-14 study is readily apparent from the above equations, and is essentially the same as that used[2] in earlier studies in which derivatives of ω-nitrostyrene were employed as starting olefin. The nitropyrazoline resulting from the reaction of 1-C^{14}-1-nitropropene must have either structure IIIa or IIIb. If the pyrazoline has structure IIIa the derived pyrazole (IVa) must give, upon oxidation, nonradioactive benzoic acid and radioactive carbon dioxide. If the pyrazoline has structure IIIb, then oxidation of the derived pyrazole (IVb) would give radioactive benzoic acid and nonradioactive carbon dioxide.

The radioactivity of samples studied, expressed in counts per minute per sample (c./m.) were obtained by counting "infinitely thick" samples of barium carbonate and thus may be compared directly. Activities from the thick sample measurements are directly proportional to the specific activities of the compounds assayed. Details of the tracer studies are found in the Experimental section and are summarized in Table I.

TABLE I

RADIOACTIVITY MEASUREMENTS OF OXIDATION PRODUCTS OF IVb

	Calcd.	Observed
Benzoic acid	564 ± 8	549 ± 7
Carbon dioxide	0	354 ± 6

It can be seen that the counting rate of the benzoic acid should be 564 c./m. if the pyrazole has structure IVb, and 0 c./m. if the pyrazole has structure IVa. The near identity in activity of the

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(4) W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 799 (1954).

(5) W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 935 (1954).

(6) Parham and Hasek originally suggested that the pyrazoline has structure IIIa, and that IVa is formed by a twofold migration of groups. *Cf.* ref. (4).

pyrazole and benzoic acid clearly establishes structure IVb for the pyrazole and structure IIIb for the intermediate pyrazoline. The counting rate for carbon dioxide is the result of further oxidation of benzoic acid,[2] but is somewhat higher than expected.

These results establish the fact that the orientation of addition of diphenyldiazomethane to 1-nitropropene is the same as previously observed for the addition of diphenyldiazomethane to the aromatic nitroolefins. These results further support the previous conclusion[2] that disubstituted diazo compounds generally add to nitroolefins (and presumably other conjugated systems) in a manner just opposite to that generally observed with diazomethane and diazoacetic ester.

EXPERIMENTAL

5-Methyl-4-nitro-3,3-diphenylpyrazoline. This material, prepared from 1-nitropropene and diphenyldiazomethane[4] was originally thought to be 3-nitro-4-methyl-5,5-diphenylpyrazoline. However, as suggested by Parham, Serres, and O'Connor,[2] and confirmed in this report, the product is 5-methyl-4-nitro-3,3-diphenylpyrazoline.

A solution of 11.80 g. (0.1358 mole) of 1-nitropropene in petroleum ether (b.p. 30–60°, 30 ml.) was added to a solution of diphenyldiazomethane (18.4 g., 0.0948 mole) in petroleum ether (60 ml.). The mixture was cooled and allowed to stand in a refrigerator for 4 days. The product was a red tarry solid (m.p. 60–136°) weighing 23.13 g. (75.5% crude yield). The solid was washed immediately with diethyl ether to remove the red tars. Most of the remaining precipitate was dissolved in absolute ethanol, and a fine yellow insoluble solid was removed by filtration.

Anal. Found: C, 68.38; H, 5.79; N, 8.74, 8.67.

The identity of this material was not established; however, the infrared spectrum of this product did not show absorption at 1550 cm.$^{-1}$, characteristic of the nitro group,[7] but did show strong peaks at 1145 cm.$^{-1}$ and 1185 cm.$^{-1}$ which are not present in the spectra of 3-methyl-4-nitro-5,5-diphenylpyrazoline, 3-methyl-4,5-diphenylpyrazole, and 1-methyl-2-nitro-3,3-diphenylcyclopropane.[8]

The alcohol-soluble product was recrystallized several times from ethanol (with considerable loss) and finally washed with ether. Pure IIIb weighed 3.24 g. (12.2% yield), and melted at 140–141° (reported[4] 140–141°).

Synthesis of C^{14} *compounds. C-14-assay procedures.* The samples to be assayed were totally combusted using the Van Slyke-Folch wet oxidation method.[9] The counting rates were determined for "infinitely" thick uniform layers of barium carbonate.[10] The counting error is the standard deviation error for sample and background counting rates. The counting was done with a Nuclear Instrument and Chemical Corporation Scaling Unit, model 163, using a thin-window Geiger tube.

1-Nitro-1-C^{14}*-2-propanol.* This compound was prepared from freshly distilled nitromethane (61 g., 1 mole, containing 0.5 millicurie C^{14}) by a procedure adapted[11] from that of Henry[12] and Staub[13] with modifications by Hurd and Nilson[14] and Roy.[15] The yield was 37.4 g. (35.7%, n_D^{25} 1.4491, reported 52%, $n_D^{25.4}$ 1.4522).

1-Nitro-1-C^{14}*-2-propyl acetate.* This material (n_D^{27} 1.4305, reported n_D^{20} 1.4242) was prepared from 1-C^{14}-2-propyl alcohol (37.4 g.) in 84% yield by the procedure reported by Tindall.[16]

1-C^{14}*-1-nitropropene-1.* The procedure used was similar to that reported by Schmidt and Rutz.[17] A mixture of 1-nitro-C^{14}-2-propyl acetate (42.4 g., 0.303 mole) in ether (42.5 ml.) and sodium acetate trihydrate (425 g., 3.16 mole) in water (425 ml.) was shaken for 2 hr. at 35°. 1-C^{14}-1-nitropropene-1 (b.p. 37–45°/8–10 mm., 13.36 g., $n_D^{27.8}$ 1.4478) was obtained in 50.5% yield.

3-Methyl-4-nitro-4-C^{14}*-5,5-diphenylpyrazoline.* 1-C^{14}-1-nitropropene (13.05 g., 0.15 mole) in 50 ml. of ether was treated with diphenyldiazomethane as described earlier in this report. The 3-methyl-4-nitro-4-C^{14}-5,5-diphenylpyrazoline obtained (3.27 g., m.p. 138–139°) was diluted with 2.00 g. of inactive pyrazoline, and the mixture was recrystallized to m.p. 140.5–141.5°.

Radioactive assay: 1130 ± 11 c./m.

3-Methyl-C^{14}*-4,5-diphenylpyrazole.* The procedure used was a slight modification of that reported.[4] 3-Methyl-4-C^{14}-4-nitro-5,5-diphenylpyrazoline (1.88 g.) in absolute ethanol (50 ml.) was heated for 35 hr. using a total of 2.5 ml. of concd. hydrochloric acid. The crude product (1.21 g., m.p. 160–174°) was recrystallized from ethanol and sublimed. The pure pyrazole melted at 183–184° (reported[4] m.p. 183–184°). The structure of this pyrazole was previously established by 4,5-diphenylpyrazole-3-carboxylic acid and to 4,5-diphenylpyrazole.

Radioactive assay: 1092 ± 11 c./m.

This material (0.325 g.) was diluted with inactive pyrazole (0.3839 g.) prior to oxidation.

Radioactive assay: 494 ± 7 c./m.

Oxidation of 3-methyl-4-C^{14}*-4,5-diphenylpyrazole.* A mixture, over nitrogen and protected from the atmosphere by ascarite, of the pyrazole (0.70 g., assay 494 ± 6 c./m.), *t*-butyl alcohol (25 ml.), water (25 ml.), sodium hydroxide (0.013 g.), and potassium permanganate was heated just under the reflux temperature until the pink color disappeared (31 hr.). The solution was filtered to remove manganese dioxide and the precipitate was washed with hot water. The cold basic filtrate was acidified in a closed system, and the carbon dioxide liberated was collected in 0.25 n. sodium hydroxide. Addition of ammonium chloride and barium chloride gave a precipitate of barium carbonate weighing 0.386 g. This sample had an activity of 354 ± 6 c./m.

The strongly acidic solution was extracted with ether, the ether extract was dried (magnesium sulfate) and the ether was removed. The crude benzoic acid (58% yield) melted at 108–119°. After the benzoic acid (carbonyl C^{14}) was recrystallized from water and sublimed, it melted at 119–121°.

Radioactive Assay: 549 ± 7 c./m.

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