be wise to take too seriously the numbers of ammonia and water ligands represented.

A sequence in which two chromium(II) ions successively attack the organic molecules would lead to intermediates IV and V. These might afford the aquopentamminechromium(III) ion (λ_{max} 480, 360 mμ).[12] There is no evidence that chromium is obtained in this form, either in the spectra of the products or their ion exchange behavior. However, formation of a binuclear chromium species from IV is not an impossibility.
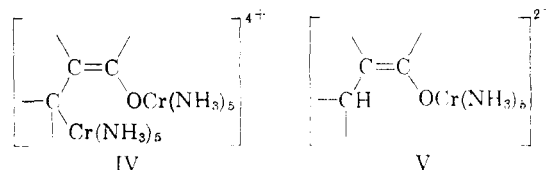
If improved methods of product isolation can be devised, the reduction of α,β-unsaturation by ammoniacal chromium(II) could prove a useful synthetic tool.

[Contribution from the Noyes Chemical Laboratory, University of Illinois, Urbana, Ill.]

Organic Chemistry of Ferrocene. III. 6-Methyl-6-hydroxy-2-phenylazofulvene[1]

By Richard E. Bozak and Kenneth L. Rinehart, Jr.

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The iron-free compound resulting from reaction of 1,1'-diacetylferrocene with benzenediazonium chloride has been shown to have the structure Id (6-methyl-6-hydroxy-2-phenylazofulvene), rather than one of the previously proposed structures Ia-c.

Ferrocene behaves somewhat anomalously toward aryldiazonium salts.[2] Although the organometallic undergoes extremely facile electrophilic substitution by many reagents (as in the Friedel–Crafts and Vilsmeier reactions),[2] it does not undergo the azo coupling reaction with aryldiazonium salts (eq. 1). Rather it gives mono- and heteroannular diaryl ferrocenes with accompanying loss of nitrogen[2]; an unusual oxidation–reduction scheme (eq. 2-3, involving phenyl radical formation and an intermediate ferricinium ion) has been proposed[2a] to account for this observed arylation.
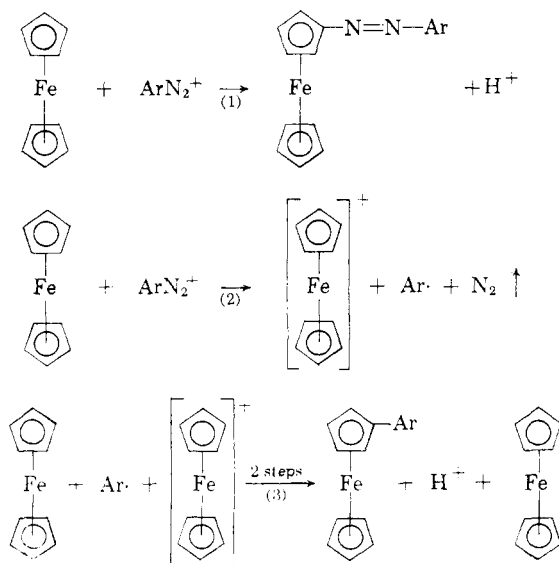
Of considerable interest, then, was the recent observation[3,4] that 1,1'-diacetylferrocene reacts by quite a different pathway with aryldiazonium salts (eq. 4), to give a product which does indeed contain the elements of the aryl azo group but no iron. In connection with a general study of the arylation reaction under way here, it seemed desirable to establish the structure of the diacetylferrocene–aryldiazonium salt product, and that structure constitutes the subject of the present paper.
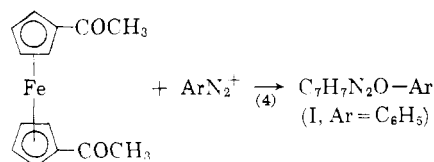
Of the three analogous compounds reported[3,4] from aryldiazonium salts and diacetylferrocene, the simplest (I, $C_{13}H_{12}N_2O$), from benzenediazonium chloride, was chosen for investigation (others were from p-nitrobenzene- and toluenediazonium chlorides) since it had been studied most extensively by the original investigators.[4] These workers assigned a 1,2,3-oxadiazine structure to the product, but did not distinguish among the isomers Ia, Ib and Ic, differing in double bond positions.[4] Their evidence for structures Ia-c rested on elemental analysis and molecular weight, on the synthesis of I by an alternative but similar route (eq. 5), and on the hydrogenation (eq. 6) of I to the pyrazole II (which was synthesized as the minor product of an authentic route, cf. eq. 7).

The conversion of I to II establishes the cyclopentane ring system of the compound and the relative positions of the erstwhile azo and acetyl groups. Alternative, isomeric structures were felt to be eliminated by the observation that the infrared spectrum of I contains no band in the O—H, N—H

(1) Paper II, K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, *J. Am. Chem. Soc.*, **79**, 3420 (1957). For the most recent communication in this series, *cf.* K. L. Rinehart, Jr., A. F. Ellis, C. J. Michejda and P. A. Kittle, *ibid.*, **82**, 4112 (1960).

(2) For reviews, *cf.* (a) P. L. Pauson, *Quart. Revs. (London)*, **9**, 391 (1955); (b) A. N. Nesmeyanov and E. G. Perevalova, *Uspekhi Khim.*, **27**, 3 (1958).

(3) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, N. A. Simukova and O. V. Starovski, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 638 (1957).

(4) A. N. Nesmeyanov, E. G. Perevalova, N. A. Simukova, Y. N. Sheinker, and M. D. Reshetova, *Doklad. Akad. Nauk S.S.S.R.*, **133**, 851 (1960).
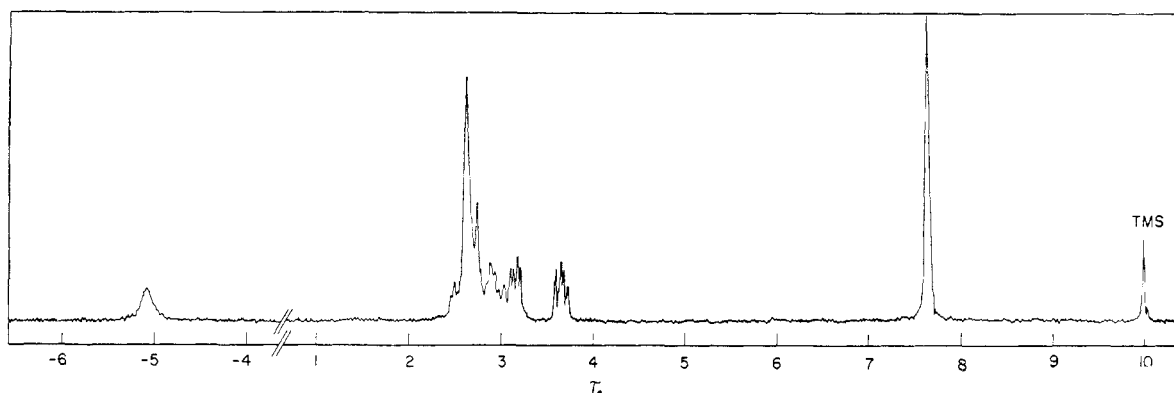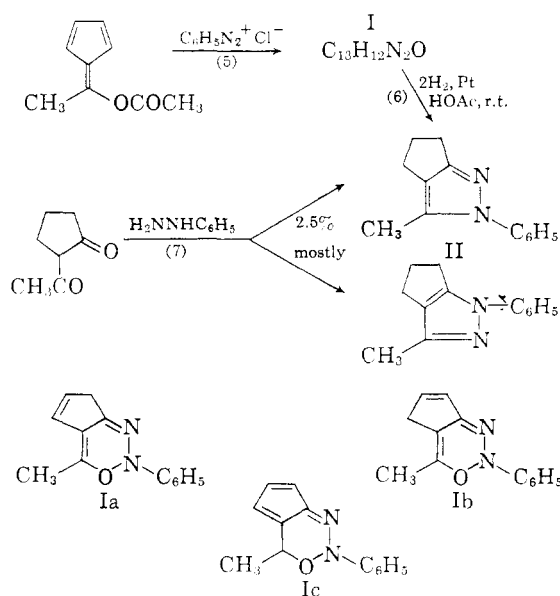
Fig. 1.—Nuclear magnetic resonance spectrum (CCl₄, 60 Mc.) of 6-methyl-6-hydroxy-2-phenylazofulvene.

or C=O stretching regions, and by negative tests for carbonyl (hydroxylamine, p-nitrophenylhydrazine and thiosemicarbazide), hydroxyl (unspecified) and enol (unspecified; however, cf. below for enol evidence) groups.


From the outset of the present investigation, structures Ia–c seemed suspect from the mode of formation of I and its hydrogenation to II.[5] Moreover, a 2-phenyl-1,2,3-oxadiazine should have been no more than slightly colored, while compound I was reported to be bright red. From evidence described below the structure of I is shown, in fact, to be Id (6-methyl-6-hydroxy-2-phenylazofulvene).[6]

From three runs, in which modifications of the procedure[3] of Nesmeyanov, et al., were followed, compound I was obtained in 2–16% conversion.

These conversions are slightly below the 19% reported by the earlier workers,[3] but the physical properties of the compound (melting point, color, infrared spectrum) agree perfectly with literature values.[4] Evidence for the present structure (Id) is provided by its n.m.r., infrared and ultraviolet spectra and by its solubility behavior.
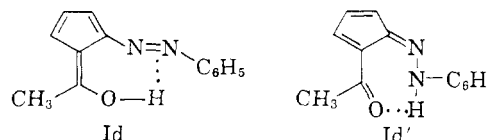
The nuclear magnetic resonance spectrum alone (Fig. 1) conclusively eliminates structures Ia–c. Both Ia and Ib would have, in addition to the methyl protons, two diallylic methylene protons (probably near τ[7] 7.10 as in cyclopentadiene)[8] while Ic would have a single allylic proton, α to oxygen (probably a quartet, near τ 5.89 like the 1-proton in 2-cyclohexenol).[8] Moreover, the methyl group of Ic would appear as a doublet. In fact (cf. Fig. 1), the methyl group produces a sharp singlet at τ 7.64, but no other aliphatic protons appear. The spectrum is well explained, however, by structure Id, since it contains, in addition to the methyl group, two fulvene ring protons at τ 3.20 and 3.66 (protons B and C: quartets, $J_{AB} = 2.5$ c.p.s., $J_{AC} = 3.9$ c.p.s., $J_{BC} = 4.3$ c.p.s.), five phenyl and one fulvene ring protons between τ 2.5 and 3.1 (a largely unresolved multiplet), and a very strongly hydrogen-bonded hydroxyl proton at τ −5.05 (broad). No further peaks are found, although the spectrum has been scanned to τ −27.6. As anticipated, the low-field peak disappears on subjecting I to deuterium oxide exchange, while the other peaks remain constant.

The strong hydrogen bonding found in the n.m.r. spectrum is also apparent in the infrared spectrum of I (Fig. 2,I). While no O–H stretching band is found in the usual region (3500–3100),[9] as noted by the earlier investigators,[4] a broad peak due to a very strongly hydrogen bonded hydroxyl does appear at 2690 cm.⁻¹. That this is due to OH is

(5) No simple 1,2,3-oxadiazine (as Ia–c) has been prepared [G. W. Stacy, in "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 798], though two 1,2,3-benzoxadiazines have been reported (cf. Stacy). Properties expected for Ia–c may be inferred, however, from those of related heterocycles, as 1,2,4-oxadiazines (Stacy) and 1,2-oxazines (N. H. Cromwell, in "Heterocyclic Compounds," Vol. 6, R. C. Elderfield, ed. John Wiley and Sons, Inc., New York, N. Y., 1957, p. 548).

(6) This structure (Id) was explicitly considered by the earlier workers (as was Id'),[4] but was rejected for the reasons cited in the preceding paragraph.

(7) G. V. D. Tiers, J. Phys. Chem., 62, 1151 (1958).

(8) G. V. D. Tiers, "Table of Characteristic Nuclear Magnetic Resonance Shielding Values," Minnesota Mining and Manufacturing Co., St. Paul, Minn.

(9) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 96.
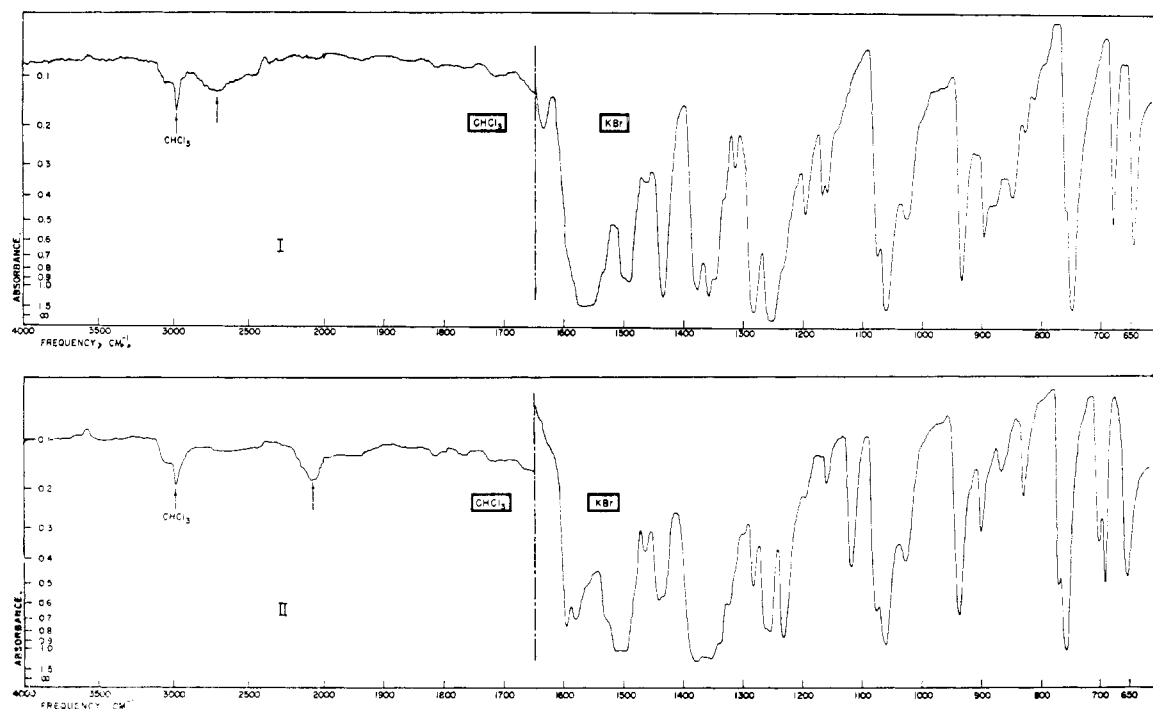
Fig. 2.—Infrared spectra (CHCl₃, 4000–1650 cm.⁻¹; KBr, 1650–600 cm.⁻¹): I, 6-methyl-6-hydroxy-2-phenylazofulvene; II, 6-methyl-6-deuterioxy-2-phenylazofulvene.

shown by its shift to 2060 cm.⁻¹ (theoretical 1960 cm.⁻¹) in the deuterium oxide exchanged product (Fig. 2,II). The strength of the hydrogen bond and its effect on the remainder of the molecule is seen by comparing Figs. 2,I and 2,II, where not only the O–H stretching band, but a number of other vibrational frequencies are shifted in the deuterium oxide exchanged product. This spectral behavior is also found in the o-azophenols (cf. below).[10]

Compound I displays many of the properties of an enol. It is insoluble in water and dilute acid, but dissolves in alkali and, while no dramatic change in color occurs upon addition of ferric chloride to the already red solution, the color deepens noticeably. Moreover, the ultraviolet spectrum of I (Fig. 3,I), essentially constant in neutral, acidic and pyridine solvents, undergoes in alkali a bathochromic shift (Fig. 3,II). Although the presence of the hydroxyl group is demonstrated by the above observations, it is surprisingly unreactive. For instance, treatment of I with either diazomethane or dimethyl sulfate in base failed to effect methylation, and attempts to acetylate or dinitrobenzoylate I under mild conditions also failed. This lack of hydroxyl reactivity (also noted by Nesmeyanov, et al., but interpreted differently[4]) is best explained by the strong hydrogen bond of I. Similarly torpid behavior has been observed for other strongly hydrogen-bonded hydroxyl groups, as in the failure of the α-hydroxyl groups of hypericin (III) to react with acetic anhydride or in the insolubility of the diacetate IV in aqueous alkali.[11]

As has been adumbrated above, I, in its proper-

(10) D. Hadzi, J. Chem. Soc., 2143 (1956).

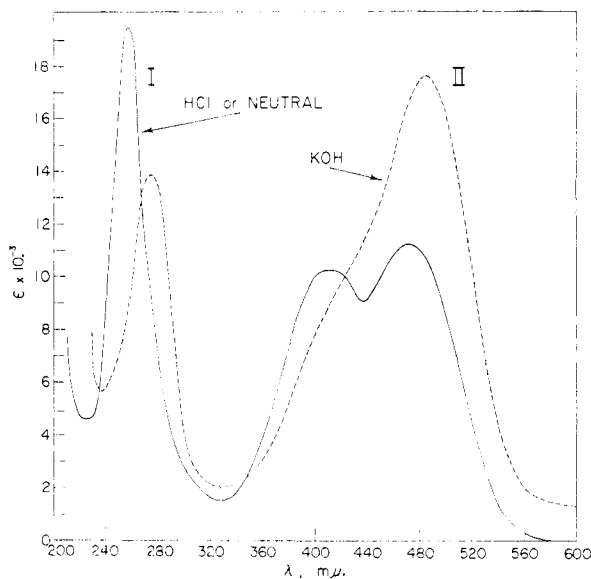(11) H. Brockmann, E. H. von Falkenhausen, R. Neeff, A. Dorlars and G. Budde, Ber., 84, 865 (1951).

Fig. 3.—Ultraviolet spectra (95% ethanol) of 6-methyl-6-hydroxy-2-phenylazofulvene: I, 0.02 N hydrochloric acid; II, 0.93 N potassium hydroxide.

ties, resembles the o-phenylazophenols.[10] In the infrared spectrum of o-phenylazophenol itself, the O–H stretching band is found at about 2800 cm.⁻¹,[10] and the usual near-infrared hydroxyl overtone band is missing.[12] Although o-phenylazophenol and p-phenylazophenol exist largely in the hydroxy-azo form (as V), other closely related compounds exist predominantly in the keto-hydrazone form (as VI), and some (as VII and VIII) may exist as

(12) S. B. Hendricks, O. R. Wulf, G. E. Hilbert and U. Liddell, J. Am. Chem. Soc., 58, 1991 (1936).

mixtures whose proportions are frequently dependent on solvent.[13] The precise structures of these compounds have been the subjects of considerable

III, R = H,
IV, R = Ac

III $\xrightarrow{\text{Ac}_2\text{O}}$ IV

V

VI

VII

VIII

water   hexane

IX
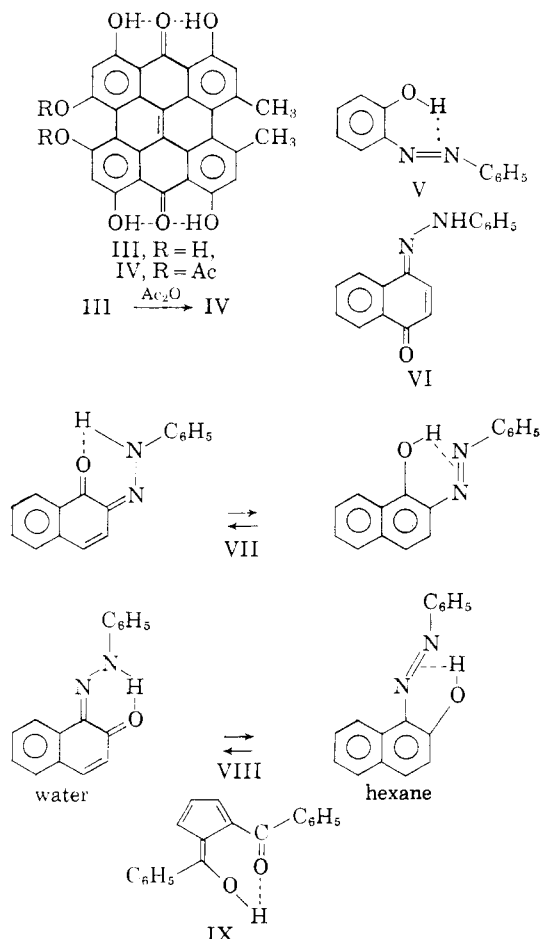
discussion. Although the alternate keto-hydrazone form Id for I cannot be eliminated completely, and would in any event differ from Id principally in the O–H and N–H bond distances, structure Id' is considered extremely unlikely due to its color and since no carbonyl absorption is found in the infrared spectrum above 1600 cm.$^{-1}$. The lowest frequency for the carbonyl band of the keto-hydrazone form reported by Hadzi[10] was 1612 cm.$^{-1}$.

Of particular note in carbonyl band comparisons is 6-hydroxy-1-benzoylfulvene (IX), whose phenyl-conjugated, hydrogen-bonded carbonyl band was found at 1639 cm.$^{-1}$.[14] Unfortunately for the total comparison the position of the O–H stretching band was not given in the report on this interesting compound. However, in other respects as well it resembles I. In particular, it is soluble in sodium hydroxide and its n.m.r. spectrum contains a chelated enolic proton at very low field (−8 p.p.m. relative to water, ca. τ −2.8).

The rationale for the formation of I is somewhat unclear. However, it is likely due to the intermediate electron density of the rings in diacetylferro-

cene. Ferrocene itself has been suggested to react with benzenediazonium chloride by an oxidation–reduction pathway, as noted above, in which ferrocene acts initially as an electron donor to the benzene-diazonium ion (eq. 2). The electron poorer diacetylferrocene is known from chronopotentiometric determinations[15] to be less readily oxidized than ferrocene and does not undergo this reaction (2), hence may react in the standard electrophilic substitution pathway (eq. 1). The phenylazodiacetylferrocene formed (or the intermediate σ-complex) is apparently unstable (probably due to the presence of three electron-withdrawing groups) and decomposes to I. Although it is initially surprising that only the o-diazophenyl product is obtained, this may be due to a failure to isolate the isomeric β-substituted product (easily allowed by the low yield obtained). In any event the α-isomer probably should be favored since, as reported by Richards and Curphey,[16] the small amount of homoannular diacetylferrocene obtained from Friedel–Crafts acetylation of ferrocene is the 1,2-isomer, and the α-isomer predominates in the similar acetylation of phenyl- and diphenylferrocenes.[17]

Ferrocenes substituted with still stronger electron-withdrawing groups apparently do not undergo readily either reaction pathway (1 or 2) with aryldiazonium salts, since in the present study nitroferrocene was recovered largely unchanged from reaction with benzenediazonium chloride.

Experimental[18]

6-Methyl-6-hydroxy-2-phenylazofulvene. A. Preparation. Run I.—Benzenediazonium chloride (0.2 mole) was prepared by a standard method.[19] Excess nitrous acid was decomposed at 0–5° with urea and the solution was neutralized to pH 4 with sodium acetate, then added rapidly to a similarly cooled solution of 10.8 g. (0.04 mole) of 1,1'-diacetylferrocene (m.p. 130–131°, lit.[20] m.p. 130–131°) in 80 ml. of glacial acetic acid. The resultant mixture was stirred under nitrogen and allowed to warm to room temperature during 20 minutes; warming was accompanied by vigorous evolution of nitrogen. Additional glacial acetic acid (80 ml.) was added to effect complete solution and stirring was continued at room temperature for 3.5 hours. At the end of this time the reaction mixture was a brown, tarry mass.

Petroleum ether (b.p. 30–60°) extraction of approximately three-fourths of this mass in a liquid–liquid extractor yielded 5.60 g. of red oil. Chromatography of the oil over an alumina (Merck, chromatographic grade) column gave as the major product 6 - methyl - 6 - hydroxy - 2 - phenylazofulvene, eluted in a broad orange band by petroleum ether–benzene (4:1). Evaporation of the eluate gave 1.03 g. (ca. 16%) of the crude reddish-orange solid, m.p. 62–67°, which on recrystallization from petroleum ether yielded 710 mg. (ca. 11%) of the analytical sample as bright red needles, m.p. 72–73° (lit.[4] m.p. 72–73°).

Anal. Calcd. for C$_{13}$H$_{12}$N$_2$O: C, 73.56; H, 5.69; N, 13.19. Found: C, 73.61; H, 5.74; N, 13.12.

(13) A. Burawoy, A. G. Salem and A. R. Thompson, *J. Chem. Soc.*, 4793 (1952).

(14) W. J. Linn and W. H. Sharkey, *J. Am. Chem. Soc.*, **79**, 4970 (1957).

(15) D. E. Bublitz, G. Hoh and T. Kuwana, *Chemistry & Industry*, 635 (1959).

(16) J. H. Richards and T. J. Curphey, *ibid.*, 1456 (1956).

(17) M. Rosenblum and W. G. Howells, 140th Natl. Am. Chem. Soc. Mtg., Chicago, Ill., Sept. 3–8, 1961; *cf.* Abstracts, p. 34Q.

(18) Melting points were determined on a Kofler micro-hot-stage and are uncorrected. Ultraviolet spectra were determined by Mr. P.-K. Hon, nuclear magnetic resonance and infrared spectra by Messrs. O. W. Norton and D. H. Johnson and their associates, microanalyses in the Microanalytical Laboratory, under Mr. J. Nemeth.

(19) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., rev., D. C. Heath and Co., Boston, Mass., 1957, p. 197.

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

The compound is soluble in ether, ethanol, pyridine, glacial acetic acid, insoluble in water, 0.1 N hydrochloric acid, and saturated bicarbonate, slightly soluble in dilute and soluble in concentrated aqueous potassium hydroxide. From the latter solvent it is reprecipitated on acidification as a red powder, m.p. 71–73°, undepressed on admixture with authentic starting material. Addition of dilute ferric chloride solution to an ethanolic solution of the compound produces definite darkening of the solution's original red color.

Run II.—In another run which employed 2.7 g. (10 mmoles) of diacetylferrocene and 80 mmoles of benzenediazonium chloride, the same procedure was followed, except that the brown, tarry mass (2.7 g.) was not purified in a liquid–liquid extractor, but was chromatographed directly over alumina (Merck). Gradient elution with pentane–benzene–ether removed the crude fulvene, while elution with chloroform gave 1.61 g. (60%) of recovered 1,1'-diacetylferrocene (m.p. 121–126°, infrared spectrum identical to that of starting material). A second chromatography of the first band over alumina (Merck) employing pentane–benzene (5:1) eluent gave 29 mg. (1% conversion, 3% yield based on unrecovered diacetylferrocene) of 6-methyl-6-hydroxy-2-phenylazofulvene, m.p. 55–65°.

Run III.—In a third run 5.48 g. (20 mmoles) of diacetylferrocene and 100 mmoles of benzenediazonium chloride were employed. The reaction was carried out as in runs I and II, but the work-up procedure consisted of two pentane–water extractions (separatory funnel) of the brown, tarry mass. The pentane layer yielded after washing, drying and evaporation 0.95 g. of red oil. Gradient elution (pentane–benzene) of this material from an alumina (Merck) column gave 77 mg. (2%) of the crude fulvene, m.p. 62–67°; recrystallization from petroleum ether gave 28 mg. (1%) of red needles, m.p. 71.0–72.3°.

B. Spectra.—Nuclear magnetic resonance spectra (Fig. 1) were determined at 60 Mc. on carbon tetrachloride solutions containing internal tetramethylsilane standards employing a Varian high resolution spectrometer (model V-4300B) equipped with super stabilizer.

Infrared spectra were determined with a Perkin–Elmer recording spectrophotometer, model 21B, with sodium chloride optics. Potassium bromide pellets, carbon tetrachloride and chloroform solutions were employed. The best spectra obtained in two spectral regions are presented in Fig. 2.

Ultraviolet spectra were determined on a Cary recording spectrophotometer, model 14. A number of solvents were employed; representative spectra are given in Fig. 3; these and other spectral data are summarized in Table I.

TABLE I

Solvent	λmax, mμ (εmax)		
Isoöctane	471 (13,500)	415 (12,000)	257 (19,400)
EtOH (95%)	472 (10,600)	412 (9,400)	257 (17,200)
EtOH (50%)	474	410	257 ....[a]
Pyridine	469 (12,600)	423 (11,900)	Solvent absorbs
HCl (0.02 N, in 95% EtOH)	471 (11,200)	411 (10,300)	257 (19,400)
KOH (0.93 N, in 95% EtOH)	485 (17,600)	Sh. 398–420 (7600–9800)	275 (13,900)

[a] Concentration not determined.

C. Deuterium Exchange.—A solution of 67 mg. of 6-methyl-6-hydroxy-2-phenylazofulvene in 30 ml. of absolute ether containing 1 ml. of 99.5% deuterium oxide was heated for 4 hours under reflux, then cooled, dried and evaporated to yield the red solid deuterated compound, m.p. 71–73°,

undepressed on admixture with starting material. The nuclear magnetic resonance spectrum showed greatly reduced resonance at τ-5.05, but otherwise remained the same as that of Fig. 1. The infrared spectrum (composite of chloroform solution and potassium bromide pellet) is shown in Fig. 2,II.

D. Attempted Acetylation.—A solution of 67 mg. (0.31 mmole) of 6-methyl-6-hydroxy-2-phenylazofulvene (m.p. 72–73°) and 1.5 ml. (20 mmoles) of acetyl chloride in 30 ml. of pyridine–ether (1:1) was stirred for 5 hours under argon at 0°. Water was added, then sodium bicarbonate, and the resulting mixture was separated. The ether layer was washed, dried and evaporated to give a red solid whose infrared spectrum was essentially identical to that of starting material.

E. Attempted preparation of a 3,5-dinitrobenzoyl derivative under mild conditions (pyridine, room temperature)[21] gave recovered starting material, while more vigorous conditions (heating with solid dinitrobenzoyl chloride)[21] gave only an intractable black tar.

F. Attempted Methylation. 1. Diazomethane.—A solution of 157 mg. (0.74 mmole) of 6-methyl-6-hydroxy-2-phenylazofulvene and excess (5 mmoles) ethereal diazomethane[22] was allowed to stand for 24 hours at room temperature. Acetic acid was added and the solution was washed repeatedly, dried, and evaporated to yield 158 mg. of red semi-crystalline solid. This was eluted in a broad orange band from an alumina (Merck) column by petroleum ether–benzene (4:1); concentration gave 95 mg. of recovered starting material, m.p. 69–71°.

2. Dimethyl Sulfate.—A mixture of 95 mg. (0.45 mmole) of the azofulvene, 100 mg. of solid potassium carbonate, 5 ml. of dimethyl sulfate and 75 ml. of acetone was heated overnight under reflux. A slight excess of ammonium hydroxide was added and the supernatant solution was decanted, concentrated to one-third volume, poured into water and extracted repeatedly with ether. The combined ether extracts were washed, dried and evaporated to 128 mg. of a thick red oil. Elution of the oil from an alumina (Merck) column with petroleum ether–benzene (4:1) gave 82 mg. (86%) of recovered starting material, m.p. 62–68°, undepressed on admixture with authentic starting material.

Treatment of Nitroferrocene with Benzenediazonium Chloride.—Benzenediazonium chloride (2 mmoles) was prepared by the method of Fieser[19] and added to a cooled solution of 100 mg. (0.43 mmole) of nitroferrocene (m.p. 129.5–130.5°, lit.[23] m.p. 130°) in approximately 100 ml. of absolute ether. The resultant mixture warmed to room temperature during 30 minutes and stood an additional 90 minutes at room temperature. The ether layer was then removed, washed with water and dried. Removal of ether left a brown solid which, when chromatographed over an alumina (Merck) column, gave only recovered nitroferrocene, m.p. 126–127° after recrystallization from cyclohexane.

(21) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 212.

(22) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 165.

(23) H. Grubert and K. L. Rinehart, Jr., *Tetrahedron Letters*, No. **12**, 16 (1959).