the extreme photosensitivity and the line-broadening effect of the photolysis products on the n.m.r. spectrum, a sample was sublimed in the dark at 0.5 mm. immediately prior to spectral study. The resulting material was pure white; it was dissolved in methanol, stored at 0°, and protected from light.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Reduction of Unsaturated Compounds by Ammoniacal Chromium(II)

BY KENNETH D. KOPPLE

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Chromium(II) in concentrated aqueous ammonia has been shown to convert benzaldehyde and acetophenone to carbinols and to saturate the ethylenic double bond of cinnamic acid and mesityl oxide. Differences between this reagent and aquo chromium(II) are discussed.

Chromium(II), while stable in oxygen-free aqueous acid, has been observed to evolve hydrogen from alkaline solutions containing excess oligopolyethylenimines.[1] This observation suggested that it might be worthwhile to establish how other reducing properties of chromium(II) ammines differ from those of the aquo ion. Almost 100 years ago Berthelot reported that ammoniacal chromium(II) chloride converted acetylene to ethylene,[2] but with the exception of some experiments with chromium(II) hydroxide[3] subsequent studies of the action of divalent chromium on unsaturation have been limited to reaction in acidic solution.

Solutions of chromium(II) ion in concentrated aqueous ammonia may be stored under nitrogen for weeks without apparent decomposition, but they react almost instantaneously with a number of α,β-unsaturated carbonyl compounds that are unaffected by acidic solutions of chromium(II) salts. In their survey of the reactivity of the latter solutions toward carbonyl compounds,[4] Conant and Cutter found that while acetylenic derivatives, quinones and maleic and fumaric acids underwent two-electron reduction, where reaction occurred with other α,β-unsaturated carbonyl compounds one-electron products were obtained. For example, benzaldehyde and other aromatic aldehydes were converted to hydrobenzoins. (Acetophenone and saturated aliphatic aldehydes were not attacked.) Acrolein was reduced to 3,4-dihydroxy-1,5-hexadiene and benzalacetone to 4,5-diphenyl-2,7-octadione. (Mesityl oxide and cinnamic acid resisted attack.) In contrast, ammoniacal chromium(II) sulfate affords, upon extraction of the reaction mixture, two-electron products from benzaldehyde (benzylamine, isolated in 31% yield as the N-phenylurea), acetophenone (α-phenylethyl alcohol, isolated in 71% yield as the N-phenylcarbamate), mesityl oxide (methyl isobutyl ketone, isolated in 33% yield as the 2,4-dinitrophenylhydrazone) and cinnamic acid (hydrocinnamic acid, isolated in 45% yield). A related example, the reduction of cinnamic to hydrocinnamic acid by chromium(II) hydroxide, has been reported.[3] Other substances, not affected by the acidic solutions, that rapidly oxidize the ammoniacal reagent include acrylonitrile, acrylic acid and acrylamide. Neither reagent affects aliphatic ketones or cinnamyl alcohol.

When reaction occurs with the ammoniacal reagent, it is rapid and, where excess oxident is used, chromium(II) is consumed completely. Low yields of isolated product occur because of the formation of stable, unextractable chromium(III) complexes of the organic products. (A quantity of organic-soluble complex of hydrocinnamic acid was obtained; on decomposition it afforded an additional 17% of the acid.) Conant and Cutter apparently had the same difficulty with acidic chromium(II); they obtained cleaner organic products when vanadium(II) was used.

Experimental

Materials and Methods.—For reduction experiments on a preparative scale a 0.8 *M* solution of chromium(II) sulfate in 1.2 *N* sulfuric acid, obtained by zinc reduction of a chromium(III) sulfate solution, was employed. This was stored in a serum-capped flask, under nitrogen, and transferred by means of a hypodermic syringe to reaction vessels which were likewise capped. The contents of these flasks had been freed of air by flushing with nitrogen before addition of the reductant.

For other experiments a stable solution of chromium(II) chloride in concentrated aqueous ammonia was prepared by solution of the anhydrous salt in concentrated aqueous ammonia. Screening experiments were carried out in serum-capped test-tubes using this reagent. The occurrence of reaction was assumed to be indicated by a color change from deep blue to orange or violet.

Spectra were measured by means of a Cary model 14 spectrophotometer. Ammoniacal chromium(II) chloride was added to a serum-capped test-tube containing an excess of the pure oxidant. After reaction had occurred, the tube was immersed in a Dry Ice–acetone-bath until the contents were frozen and then mixed with sufficient 6 *N* HCl to give 1–2 *M* excess hydrogen ion. When an oxygen-free atmosphere was required the thawed contents of the reaction tubes were transferred by syringe to serum-capped, nitrogen-flushed cuvettes for measurement.

Substances Screened.—The following substances, used in excess, reacted within seconds with ammoniacal chromium(II) chloride or sulfate: cinnamic acid, maleic acid, acrylic acid, acrylamide, acrylonitrile, benzaldehyde, acetophenone, mesityl oxide, *p*-benzoquinone. Unreactive on 24-hr. storage with the reagent were cinnamyl alcohol, hexamethylenetetramine, methyl ethyl ketone, diethyl ketone, phenetole.

In one experiment 0.5 ml. of freshly distilled acrylonitrile was shaken, under nitrogen, with 4 ml. of 0.1 *M* chromium(II) chloride in concentrated ammonia. The clear orange solution which resulted gradually reddened, and after 24 hr. was reddish-violet and still free of precipitate. It was acidified and dialyzed against water. Material remaining in the

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[1] K. D. Kopple, G. F. Svatos and H. Taube, *Nature*, **189**, 393 (1961).

[2] M. Berthelot, *Ann. chim.*, [4] **9**, 401 (1866).

[3] W. Traube and W. Passarge, *Ber.*, **49**, 1692 (1916).

[4] J. B. Conant and H. Cutter, *J. Am. Chem. Soc.*, **48**, 1016 (1926).

dialysis tubing after 24 hr. amounted to 30 mg. and lacked nitrile infrared absorption.

Ion Exchange Behavior of Cr(III) Product.—Portions (100 mg.) of 200–400 mesh Dowex 50-W sulfonic acid resin were saturated with $Cr(H_2O)^{+++}$, $Cr(en)_3{}^{+++}$, $Co(NH_3)_5(H_2O)^{+++}$, and the acidified products of oxidation of ammoniacal chromium(II) chloride by acrylamide, benzaldehyde and oxygen. Each loaded exchanger was washed several times with water and placed at the top of 1 g. of the same resin (H^+ form) in a 6 mm. i.d. column. Elution was carried out with 10 ml. of 1.0 *N* perchloric acid followed by 10 ml. of 0.2 *M* lanthanum perchlorate in 1.0 *N* acid, at a flow rate of about 0.5 ml./min. By this process the aquochromium(III) was completely washed off the column, the trisethylenediamine complex moved about one-third the length of the column, and the aquopentamminecobalt(III) moved one-half. None of the oxidation products of ammoniacal Cr(II) were dislodged from the original loaded portion of the column; the dividing line between the two segments of resin remained sharp.

Reduction of Cinnamic Acid.—To a solution prepared by mixing 50 ml. of the 0.8 *M* Cr(II) solution with 100 ml. of concentrated aqueous ammonia was added 1.5 g. (0.01 mole) of *trans*-cinnamic acid in 10 ml. of ammonia. After 5 minutes, the mixture was cooled while 150 ml. of 18 *N* sulfuric acid was added, atmospheric oxygen being excluded. Still in the absence of air, the mixture was heated at 80° until its brown color had turned to green—30 minutes—then extracted with three 50-ml. portions of ether. The ether, dried over magnesium sulfate, was concentrated to a purple oil that readily crystallized. This material was treated with 100 ml. of hot water, affording a colorless solution that upon evaporation yielded 0.62 g. (41%) of hydrocinnamic acid, m.p. 46–48°, mixed m.p. undepressed, plus a violet (λ_{max} 575, 415 mμ) ether-soluble, water-insoluble residue.

The original green reaction mixture was continuously extracted with chloroform to obtain an additional quantity of the organic-soluble violet material and this, combined with the first fraction, was digested with a solution of sodium pyrophosphate until complete solution resulted (18 hr.). Ether extraction of this solution, after acidification, yielded a further 0.25 g. (17%) of pure hydrocinnamic acid. No evidence for the presence of diphenyladipic acid in the chloroform extract was found.

In two other runs, identical except that air was not excluded and heat of neutralization not removed during acidification, the yields of uncomplexed hydrocinnamic acid were 45 and 42%. In a fourth experiment, the ammoniacal reaction mixture was heated at 80° for an hour, in the absence of air, and the still alkaline solution filtered from the green precipitate formed. No organic material could be extracted from this solution after acidification.

When the neutralization step was carried out in air at 0° (added ice) and the acidified solution shaken with air for several hours thereafter, thorough methylene chloride extraction yielded a non-crystallizable product, a portion of which (0.05 g.) was insoluble in ether. This ether-insoluble, bicarbonate-soluble material had m.p. 265–275°; recrystallized from ethanol–water it melted at 274–276°, in agreement with *meso*-β,γ-diphenyladipic acid.[5]

Reduction of Acetophenone.—A suspension of 1.0 ml. (0.0085 mole) of acetophenone in 50 ml. of concentrated aqueous ammonia was treated with 25 ml. of 0.8 *M* chromium(II) solution. The reaction mixture became rust colored on addition of the reductant and gradually turned violet. After an hour of occasional shaking it was extracted with four 30-ml. portions of methylene chloride. The extract was concentrated to a volume of 25 ml. by distillation and mixed with 1.0 ml. of phenyl isocyanate. After storage for a day, the remaining methylene chloride was removed under reduced pressure and the residual oil crystallized from 60° petroleum ether to yield 1.46 g. (71%) of α-phenethyl-N-phenylcarbamate, m.p. 88–90°. Recrystallization from carbon tetrachloride–petroleum ether afforded a product of m.p. 94°.[6]

Reduction of Benzaldehyde.—Benzaldehyde (1.0 ml.) was treated exactly as acetophenone, above. The product of reaction with phenyl isocyanate was 0.69 g. (31%) of N-benzyl-N′-phenylurea, m.p. 170–170.5°, undepressed when mixed with an authentic sample, after recrystallization from ethyl acetate–petroleum ether.

Reduction of Mesityl Oxide.—A suspension of 1.0 ml. (0.0085 mole) of mesityl oxide in 50 ml. of concentrated aqueous ammonia was treated with 25 ml. of the 0.8 *M* chromium(II) solution. The reaction mixture was allowed to remain for 20 hours, with occasional shaking during the first few hours, and then extracted with five 50-ml. portions of methylene chloride. The methylene chloride extract was concentrated by careful distillation under a Vigreux column to a volume of 5 ml. and then mixed with 50 ml. of dinitrophenylhydrazine reagent. The crude dinitriphenylhydrazone, 800 mg. (33%), was chromatographed on alumina to yield methyl isobutyl ketone dinitrophenylhydrazone, m.p. 94–95°,[7] undepressed when mixed with an authentic sample.

When this procedure was repeated, but the extraction carried out within 5 min. of mixing reactants, no saturated ketone derivative and only 60 mg. of mesityl oxide dinitrophenylhydrazone, m.p. 203°,[7] was isolated.

Discussion

The two-electron reduction products reported here may arise because the free radicals formed by one-electron transfer, although not readily reduced in acid solution, are, in the presence of ammine, reduced by a second chromium before they can dimerize. If radicals sufficiently reactive toward disproportionation or further reduction are formed in the first step, two-electron reduction may also occur in acid solution. It may be asked, however, whether chromium(IV), implicated in the reaction of ammoniacal chromium(II) with oxygen,[8] is not involved in the formation of two-electron reduction products in aqueous ammonia, *i.e.*, whether reaction in ammonia proceeds *via* one-, rather than two-step reduction of the substrate.

Immediately upon mixing the deep blue (λ_{max} 580 mμ) ammoniacal chromium(II) solution with excess of any of the reactive substrates mentioned above there is produced a yellow-orange solution that gradually becomes deep violet. The orange color persists for hours when mesityl oxide or cinnamic acid is the oxidant, for minutes in the cases of acetophenone and benzaldehyde, and for seconds only with the acrylic derivatives mentioned. The violet species, too, is unstable in the alkaline solution; eventually it becomes a precipitate of chromic oxide. Solutions of the orange intermediate, derived by reaction of cinnamic acid and of benzaldehyde, were examined. The orange color is associated with a relatively intense ($\epsilon \approx$ 300, based on total Cr in solution) absorption maximum in the near ultraviolet, at 352 mμ in the case of cinnamic acid (curve 1, Fig. I) and 340 mμ in the case of benzaldehyde. Although its stability in the absence of air is not appreciably different in acidified solution from what it is in the original reaction mixture, the intermediate is rapidly destroyed by oxygen (curve 2, Fig. 1). These properties suggest that it contains a C–Cr(III) bond, by analogy to pentaaquobenzylchromium(III) ion, which Anet and Leblanc prepared by action of chromium(II) perchlorate on benzyl chloride.[9] Their product possessed a strong absorption at 358 mμ and was destroyed by oxygen; on heating or storage it dissociated to chromium(II) and benzyl radicals (bibenzyl). The pre-

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(5) M. P. Oommen and A. I. Vogel, *J. Chem. Soc.*, 2148 (1930).

(6) A. Klages and P. Allendorf, *Ber.*, **31**, 1004 (1898).

(7) C. F. H. Allen, *J. Am. Chem. Soc.*, **52**, 2955 (1930).

(8) T. B. Joyner and W. K. Wilmarth, *ibid.*, **83**, 516, (1961).

(9) F. A. L. Anet and E. Leblanc, *ibid.*, **79**, 2649 (1957).

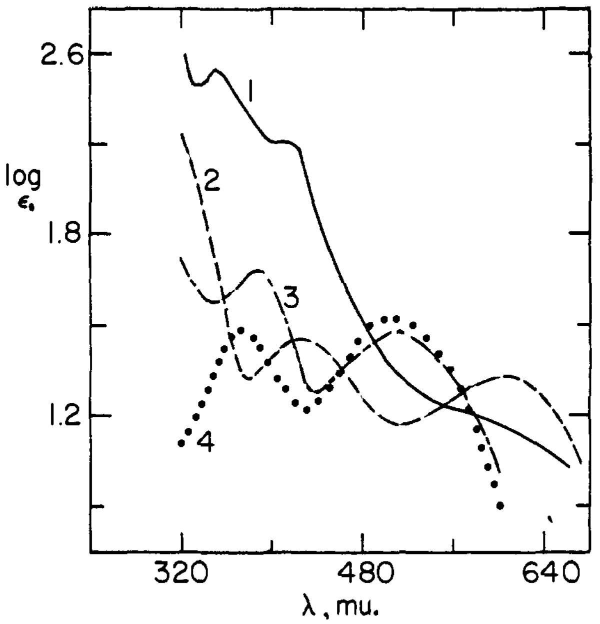

Fig. 1.—Spectra of acidified reaction mixtures: 1, oxidation product of ammoniacal Cr(II) by excess cinnamic acid; 2, same solution after exposure to air for several hours; 3, oxidation product of ammoniacal Cr(II) by excess acrylamide; 4, oxidation product of ammoniacal Cr(II) by air; extinction coefficients are based on total chromium in solution.

ferred mode of decomposition of the intermediate in the present case would appear to be hydrolysis. A dimeric product from a cinnamic acid reduction mixture was isolated, but only in very low yield and only from a run in which the intermediate was decomposed in the presence of air. If it were possible to draw valid conclusions from the presence of a trace product when half of the total product is unaccounted for, this would suggest that dissociation of the orange cinnamic acid intermediate provides a reaction path only when a driving force, such as the oxidation of the chromium(II) formed, is available. However, the form of trivalent chromium produced on air oxidation of the intermediate in hydrochloric acid solution appears to be the $CrCl^{++}$ ion (λ_{max} 425, 610 mμ[10]; see curve 2, Fig. 1) suggesting that substitution-labile chromium(II) is available from the complex.

In view of the substitution lability to be expected of a chromium(IV) species,[11] it is unlikely that the orange intermediate just discussed contains this oxidation state, but intermediation of Cr(IV) at some stage is suggested by the properties of the violet complexes formed in the reaction mixtures.

When the oxidation of ammoniacal chromium(II) is carried out by excess acrylic acid or acrylamide, after a transient orange coloration there results a red-violet solution that gradually becomes bluish (λ_{max} 530 → 565 mμ). If the reaction mixture is acidified within minutes of mixing, a species, stable in acid, with the absorption spectrum shown in curve 3, Fig. 1 (λ_{max} 385, 513 mμ), is obtained. This probably represents an immediate product of hydrolysis of the orange species. The bathochromic shift which occurs on its continued storage in the alkaline ammoniacal solution is probably the result of replacement of ammonia by water in the chromium(III) coördination sphere. Because of this hydrolysis, the 513 mμ species cannot be obtained from reaction mixtures in which the orange intermediate possesses appreciable stability. Absorption of the acid solution at 513 mμ might correspond to a mixture of $Cr(NH_3)_3(H_2O)_3^{3+}$ and $Cr(NH_3)_2(H_2O)_4^{3+}$ ions[12]; however, the colored product in this solution cannot be eluted from Dowex-50 cation exchanger by 0.2 *M* lanthanum perchlorate, which suggests the presence of a more highly charged, and therefore binuclear, species.

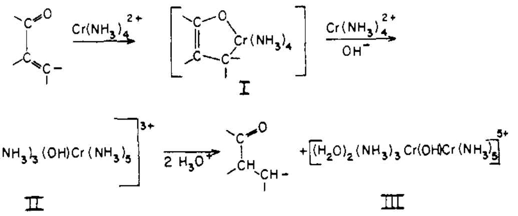

Fig. 2.—Reduction of α,β-unsaturated carbonyl compounds by chromium(II) in concentrated aqueous ammonia.

The formation of a binuclear chromium(III) species in oxidations of chromium(II) has been taken as good evidence for the intermediation of chromium(IV)[8,13]; from the oxygenation of ammoniacal chromium(II) the rhodo ion $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ is isolated in 30–60% yield.[8] Comparison of curve 3 with curve 4, Fig. 1, the spectrum of the air oxidized ammoniacal chromium(III) solution, shows that the spectrum of the acrylamide-oxidized product is shifted to the red. (The absorption of the pure rhodo ion is given as λ_{max} 500, 370 mμ.[14]) If this shift is owing to partial replacement of ammonia by water in a binuclear complex ion, then the scheme of Fig. 2 may be a fair generalized description of the overall process of reduction of α,β-unsaturated carbonyl derivatives by chromium(II) in ammonia.

In the scheme of Fig. 2, I represents an initial transient species in which chromium has the formal oxidation state IV; it may also be considered a complex of Cr(III) and an organic radical. Further reduction by Cr(II), through a bridged intermediate, occurs to afford complex II, identified with the orange species, which in turn is hydrolyzed to the reduced organic product, and III, identified with the 513 mμ species. This last is unstable in alkaline solution and undergoes further hydrolysis. The isolation of organic products by simple extraction of the reaction mixture indicates that both bonds to chromium of the organic ligand in II must be broken, at least to some extent. The low yields, however, suggest that this process is not always complete. There may well be other paths for the reduction, and in particular it would not

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[10] Spectrum identical to $CrCl^+$ eluted from Dowex 50 by 1 *N* hydrochloric acid.

[11] A. E. Ogard and H. Taube, *J. Phys. Chem.*, **62**, 357 (1958).

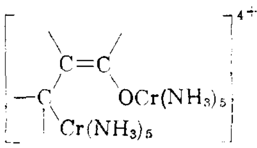
[12] R. I. Colmar and F. W. Schwartz, *J. Am. Chem. Soc.*, **54**, 3204 (1932).

[13] M. Ardon and R. A. Plane, *ibid.*, **81**, 3197 (1959).

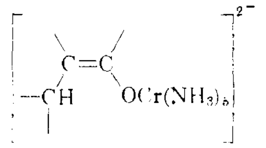
[14] C. E. Schaffer, *J. Inorg. and Nuclear Chem.*, **8**, 149 (1958).

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.



IV



V

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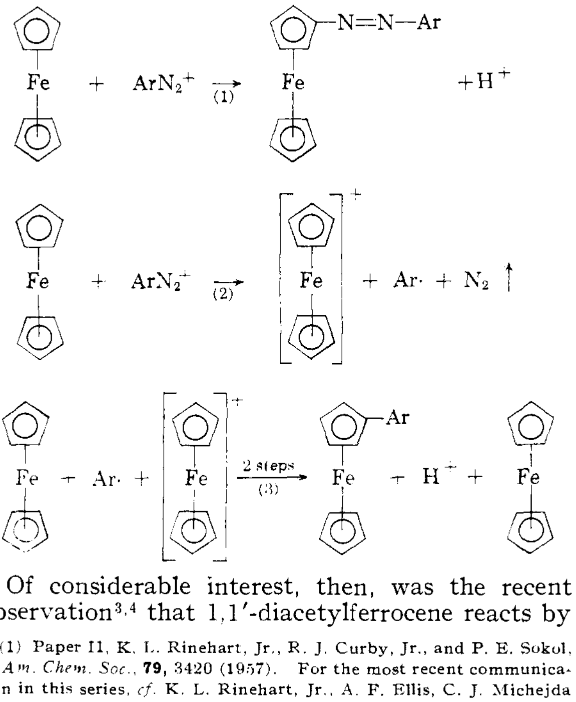
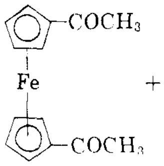
The iron-free compound resulting from reaction of 1,1'-diacetylferrocene with benzenediazonium chloride has been shown to have the structure Id (6-methyl-6-hydroxy-2-phenylazofulvene), rather than one of the previously proposed structures Ia-c.

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.



$$+ ArN_2^+ \xrightarrow[(4)]{} C_7H_7N_2O{-}Ar \quad (I,\ Ar = C_6H_5)$$

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

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[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).