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The Influence of Catalysts on the Rearrangement of Acyldiazoethanes

By P. McC. Duggleby, G. Holt,* M. A. Hope, and A. Lewis, Department of Chemistry, University of Manchester Institute of Science and Technology, P.O. Box No. 88, Sackville Street, Manchester M60 1QD

Contrary to previous findings, decomposition of α -diazo-p-nitropropiophenone by silver oxide is slow at room temperature, and, rather than providing p-nitrophenyl vinyl ketone, yields 3-methyl-3,5-bis-p-nitrobenzoyl- Δ^2 -pyrazoline (VI). At higher temperatures, silver oxide-assisted Wolff rearrangement sets in. In contrast, decomposition by silver nitrate is much more rapid and leads to p-nitrophenyl vinyl ketone together with smaller amounts of the pyrazoline (VI) and 1-methyl-1,2-bis-p-nitrobenzoylcyclopropane (VII). When molar rather than catalytic quantities of silver nitrate are used, decomposition is virtually instantaneous and the unsaturated ketone is obtained in high yield. Other α -diazopropiophenones behave similarly. The fact that similar decompositions may be effected with silver trifluoroacetate, many metallic nitrates, and aniline hydrochloride, but not by silver benzoate or trimethylamine hydrochloride, suggests that the reaction is one of acid catalysis rather than specific silver catalysis. The results obtained by decompositions effected by nitric, perchloric, and formic acids support this view.

SILVER oxide and silver nitrate ¹ appear to be equally effective as catalysts for the rearrangement of acyldiazomethanes (I; $\mathbf{R}' = \mathbf{H}$). In contrast, the rearrangement of acyldiazoethanes (I; $\mathbf{R}' = \mathbf{M}e$) is usually brought about by pyrolytic procedures ^{2,3} since the silver oxide method leads to complex mixtures containing little rearrangement product. In these laboratories it was shown ⁴ that decomposition by silver nitrate in ethanol containing aniline, rather than providing Wolff rearrangement products, gave β -anilino-ketones (V). $\alpha\beta$ -Unsaturated ketones (IV), which were assumed to be intermediates, were, however, not isolated. It was therefore unexpected when Franzen⁵ reported that acyldiazoethanes (I; $\mathbf{R}' = \mathbf{M}\mathbf{e}$) when shaken with silver oxide in aqueous dioxan at room temperature gave $\alpha\beta$ -unsaturated ketones (IV) in high yield. We now report that all our attempts to reproduce his results have been unsuccessful. In particular, the decomposition of α -diazo-p-nitropropiophenone (I; $\mathbf{R} = p$ -NO₂·C₆H₄, $\mathbf{R}' = \mathbf{M}\mathbf{e}$) which, according to Franzen, readily provides p-nitrophenyl vinyl ketone (IV; $\mathbf{R} =$

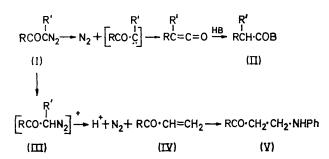
³ A. L. Wilds and A. L. Meader, J. Org. Chem., 1948, **13**, 763. ⁴ G. Baddeley, G. Holt, and J. Kenner, Nature, 1949, **163**, 766.

¹ See 'Org. Reactions,' vol. I, Wiley, New York, 1942, p. 38, for compilation of references.

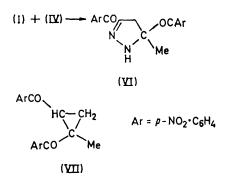
² B. Eistert, Angew. Chem., 1941, **54**, 124.

⁵ V. Franzen, Annalen, 1957, 602, 199.

p-NO₂·C₆H₄) (76%), proved to be extremely slow. No significant amount of p-nitrophenyl vinyl ketone



appeared to be present in the product, the major component of which proved to be the pyrazoline (VI), the structure of which was established by its i.r. and n.m.r. spectra and by its independent synthesis from p-nitrophenyl vinyl ketone (IV; R = p-NO₂·C₆H₄) and α diazo-p-nitropropiophenone (I; R = p-NO₂·C₆H₄, R' =Me). Presumably, the pyrazoline (VI) formed in the silver oxide decomposition arises by a similar 1,3-dipolar addition.



When the temperature was raised to 70° decomposition proceeded more rapidly, but again no p-nitrophenyl vinyl ketone could be isolated. In an attempt to trap any of the latter which may have been formed and subsequently lost by polymerisation, the reaction was carried out in the presence of aniline. The only product then isolated was α -p-nitrophenylpropionanilide (II; R = p-NO₂·C₆H₄, R' = Me, B = NHPh). Almost identical results were obtained when the reaction was carried out in the absence of catalyst except that a longer period of heating was required. It thus appears that the essential reaction here is a thermal Wolff rearrangement slightly accelerated by the presence of silver oxide.

This silver oxide-assisted Wolff rearrangement was not always so satisfactory with other acyldiazoethanes, since of those listed in the Table only p-chloro- α -diazopropiophenone (I; R = p-ClC₆H₄, R' = Me) and 2diazohexan-3-one (I; $R = Pr^n$, R' = Me) gave any appreciable quantity of Wolff product.

Reinvestigation of the silver nitrate-promoted decomposition confirmed the original findings⁴ and demonstrated that the conversion of α -diazopropiophenones (I; R' = Me) into β -anilino-ketones (V) is of

R in	NHPh in Ag ₂ O-EtOH- PhNH ₂ reaction	% RCO·CH ₂ ·CH ₂ · NHPh in AgNO ₃ -EtOH- PhNH ₂ reaction Reaction time	AgNO ₃ EtOH
RCO·CMeN,	ca. 6 h	20 min	2—3 min
Ph		49	80
p-NO, C,H₄	60	55	70
m-NO, C, H,	0	48	57
p-ClC ₆ H₄	35	54	
p-MeŎ•Ċ ₆ H₄		74	22
p-PhSO ₂ ·C ₆ H ₄	0	64	87
m-PhSO2.C6H	Tar		Unidentified
			oil
o-Phthalimido	0	Unidentified	
		products	
<i>p</i> -Phthalimido	0	Unidentified	
Pr ⁿ	64	0 products	

out silver nitrate-catalysed decompositions of α -diazo-pnitropropiophenone at 70° in the absence of aniline, when there resulted p-nitrophenyl vinyl ketone (IV; $R = p - NO_2 C_6 H_4$ (49%), the pyrazoline (VI) (2%), and the cyclopropane derivative (VII) (12.5%). When the reaction was carried out in dioxan at a lower temperature (25°), the pyrazoline (VI) became the major (58%) product, the yield of vinyl ketone fell to 35%, and the cyclopropane derivative (VII) could not be detected. The reaction time (ca. 6 h) contrasts sharply with the several days required when silver oxide is used as a catalyst. The cyclopropane derivative (VII) does not arise from thermal decomposition of the pyrazoline (VI) since the latter is stable at the temperature used. Further experiments on this aspect of the work are still in hand, since this appears to be the first recorded example of pyrazoline formation by the interaction of a diazoethyl ketone and an $\alpha\beta$ -unsaturated ketone.

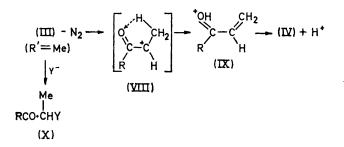
When α -diazo-p-nitropropiophenone was treated with molar amounts of silver nitrate rather than with the catalytic quantities previously employed, reaction was complete in 2 min, pyrazoline formation was largely avoided, and much improved yields of p-nitrophenyl vinyl ketone were obtained. Other α -diazopropiophenones gave similar results (Table), and these indicate that their silver nitrate-promoted decomposition provides a satisfactory general method for the preparation of aryl vinyl ketones and of the corresponding β -anilinoketones.

It is beyond dispute that the decomposition of the diazoethyl ketones discussed is brought about much more rapidly with silver nitrate than with silver oxide. Investigation of other silver salts showed that the trifluoroacetate is even more effective than the nitrate in decomposing α -diazo-p-nitropropiophenone to p-nitrophenyl vinyl ketone while, as Newman and Beal found,⁶

⁶ M. S. Newman and P. F. Beal, J. Amer. Chem. Soc., 1950, 72, 5163.

silver benzoate is ineffective. Again, the same diazoketone readily loses nitrogen when treated with copper-(II), iron(III), nickel(II), zinc(II), lead(II), or mercury(I) nitrate. The products of such reactions are usually more complex than those obtained when silver nitrate is used, but they always contain p-nitrophenyl vinyl ketone. All these results suggest strongly that the metal atoms are playing little significant part and that the decomposition is a consequence of the acidity of the salts involved. Support for this view is obtained from the observation that the presence of aniline in the already described silver nitrate decompositions brings about a marked retardation of the reaction. Further, the diazo-ketone is unaffected by triethylamine hydrochloride but rapidly decomposes with the more acidic aniline hydrochloride to give, albeit in poor yield, β anilino-p-nitropropiophenone. Direct comparison of the effects of nitric acid and silver nitrate is not easy since a solution of the former having the same pH as a given silver nitrate solution has a very different ionic strength. However, as with silver nitrate, the decomposition of the diazo-ketone is effected by a catalytic quantity (0.2)mol. equiv.) of nitric acid to provide the pyrazoline (VI) (78%). A similar catalytic decomposition is effected by perchloric acid. In both instances the yield of pyrazoline is greater, and that of $\alpha\beta$ -unsaturated ketone less, than when silver nitrate is used. Since the hydrogen ion activity of the nitric and perchloric acid solutions is certainly greater than that of the silver nitrate solution employed, it appears that pyrazoline formation from $\alpha\beta$ -unsaturated ketone and diazo-ketone is proton-catalysed. This view is supported by the observation that formic acid rapidly decomposes the diazo-ketone to give $\alpha\beta$ -unsaturated ketone but no pyrazoline.

These findings accord with the results of mechanistic studies by Dahn and his co-workers ⁷ that, in aqueous acid, secondary diazo-ketones (I; $\mathbf{R}' = alkyl$) are hydrolysed by irreversible protonation at the diazo carbon atom followed by unimolecular decomposition of the resulting diazonium ion (III) without intervention of a nucleophile. In super-acids one product of



this decomposition is the protonated form of the corresponding $\alpha\beta$ -unsaturated ketone, presumably formed as indicated [(III) \longrightarrow (VIII) \longrightarrow (IX)]. Only a catalytic quantity of H⁺ is required and the metallic salts used may simply be a convenient way of supplying this.

Whilst in these acid-catalysed reactions decomposition of the acyl diazonium ion (III) into $\alpha\beta$ -unsaturated ketone is the dominant process, products of nucleophilic intervention are formed to a limited degree with both nitric and formic acids [(III; $R = p-NO_2 \cdot C_6H_4$, R' =Me) \longrightarrow (X; $R = p-NO_2 \cdot C_6H_4$, $Y = O \cdot NO_2$ or OCHO, respectively)]. Not surprisingly, solvent is important in determining the mode of decomposition. For example, in acetic anhydride, α -diazo-p-nitropropiophenone reacts with toluene-p-sulphonic acid to give the product of nucleophilic intervention (X; R = $p-NO_2 \cdot C_6H_4$, $Y = O \cdot SO_2 \cdot C_6H_4Me-p$) in high yield. In aqueous dioxan, however, the yield of toluene-psulphonate is much reduced and the major products are $\alpha\beta$ -unsaturated ketone and pyrazoline.

Further investigations into these acid-catalysed decompositions are in hand.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 instrument and ¹H n.m.r. spectra on Perkin-Elmer R10 and Varian HA100 instruments. Gaseous volumes have been reduced to S.T.P. All the known compounds gave satisfactory analytical and i.r. data.

Attempted Repetition of Franzen's Experiment.-When α -diazo-p-nitropropiophenone (10 g) in purified dioxan (80 ml) and water (20 ml) was shaken with freshly prepared silver oxide at 23°, erratic results were obtained. In a few instances the reaction failed to start and in all the others nitrogen evolution was slow, e.g. 32% after 24 h and 50-55% after 2-3 days. Separation of the silver-silver oxide and removal of the solvent under reduced pressure provided a deep yellow oil which usually solidified. p-Nitrophenyl vinyl ketone could not be isolated from this material, m.p. 159-163° (from ethanol). Yields varied from ca. 35 to 60%. Recrystallisation from acetonitrile gave yellow plates of 3-methyl-3,5-bis-p-nitrobenzoyl- Δ^2 pyrazoline (VI) (Found: C, 56.8; H, 4.0; N, 14.8. C₁₈H₁₄N₄O₆ requires C, 56.5; H, 3.7; N, 14.7%), m.p. 165—166° (decomp.), v_{max} 3258m (NH), 1697s (CO), 1619m (CN), and 1600m (CC) cm⁻¹, τ [(CD₃)₂SO] 0.17 (1H, s, NH), 1.75 (8H, m, aromatic), 6.60 (2H, ABq, J_{AB} 17 Hz, CH₂), and 8.40 (3H, s, Me). The pyrazoline (0.5 g) with acetic anhydride (6 ml) at 100° for 30 min provided a crude acetyl derivative (0.4 g), m.p. 150-171°, which gave yellow plates (from acetonitrile) of N-acetyl-3-methyl-3,5bis-p-nitrobenzoyl- Δ^2 -pyrazoline (Found: C, 56.7; H, 4.0; N, 13.4. C₂₀H₁₆N₄O₇ requires C, 56.5; H, 3.8; N, 13.2%), m.p. 170-171°. Its i.r. spectrum showed no NH band.

Interaction of α -Diazo-p-nitropropiophenone and p-Nitrophenyl Vinyl Ketone.—The unsaturated ketone (0.43 g, 2.44 mmol) and the diazo-ketone (0.5 g, 2.44 mmol) in carbon tetrachloride (20 ml) were kept at 21—22° until t.l.c. showed that the diazo-compound was no longer present (72 h). Removal of the solvent under reduced pressure gave a sticky orange solid which was chromatographed on silica gel (180 g; 2.7 × 43 cm). Elution with toluene provided 1-methyl-1,2-bis-p-nitrobenzoylcyclopropane (VII) (0.28 g, 33%) (Found: C, 61.2; H, 3.7; N, 7.9. C₁₈H₁₄N₂O₆ requires C, 61.0; H, 4.0; N, 7.9), m.p. 147— 148° (from ethanol), ν_{max} 1690m (CO), 1678s (CO), 1600m

⁷ C. Wentrup and H. Dahn, Helv. Chim. Acta, 1970, 53, 1637.

(CC), and 1000m cm⁻¹, τ (CDCl₃) 1.75 (8H, m, aromatic), 7.97 and 8.30 (double AB quartets, two non-identical protons, J 4.5 Hz, CH₂ each coupled [J 7.5 and 6.0 Hz] with one proton [quartet at τ 6.43] on an adjacent asymmetric centre, CH), and 8.56 (3H, s, Me). When the cyclopropane derivative had been removed, elution with toluene-chloroform (1:1) provided the pyrazoline (VI) (0.62 g, 66.5%), identical (mixed m.p., i.r., and n.m.r. spectra) with that already described.

Wolff Rearrangement of Diazoethyl Ketones .- a-Diazo-pnitropropiophenone (5 g), aniline (3 g), and silver oxide (0.2 g) were stirred at 70° in ethanol (60 ml) until nitrogen evolution was complete (6.5 h). The hot solution was filtered and the solvent removed to leave a sticky solid which was shaken with chloroform and dilute hydrochloric acid. The aniline-free organic layer was washed with water, dried, and concentrated; the crude product crystallised from benzene to provide 2-(p-nitrophenyl)propionanilide (4 g, 62%), m.p. 158-159° (lit.,3 159°). A similar result was obtained when the silver oxide was omitted but the reaction time was then 8.5 h. When dioxan was used as solvent the corresponding reaction times were 14 and 20 h. Subsequent experiments were carried out at threefold dilution, under which conditions 2-diazohexan-3-one gave 2-methylvaleranilide (64%), m.p. 96° [from light petroleum (b.p. 60-80°)] (lit.,⁸ 94·5-95·0°). p-Chloro-αdiazopropiophenone similarly yielded 2-(p-chlorophenyl)propionanilid e(35%), m.p. 152-153° (lit., 154.5-155.0°).

 β -Anilino-ketones.—(a) To α -diazo-p-nitropropiophenone (5 g) and aniline (3 g) in ethanol (60 ml) at 70° was added 10% aqueous silver nitrate (5 ml). When nitrogen evolution was complete (15 min) the solution was filtered hot and the filtrate on cooling deposited orange needles of β -anilinop-nitropropiophenone (3.7 g, 55%) (Found: C, 67.0; H, 5.3; N, 10.2. Calc. for $C_{15}H_{14}N_2O_3$: C, 66.7; H, 5.2; N, 10.4%), m.p. 131-132° (from methanol) (lit., 131-132°).

When the experiment was repeated except that the aniline was not added until the evolution of nitrogen was complete (5 min) a similar yield of the β -anilino-ketone was obtained. When the aniline present in experiment (a) was increased to 25 g the yield of β -anilino-ketone was 54% but it was necessary to add a second portion of silver nitrate solution to effect complete decomposition of the diazoketone (1.5 h). In a dilution experiment the diazo-ketone (5 g) in ethanol (400 ml) containing aniline (15 g) was decomposed by addition of aqueous 10% silver nitrate (20 ml). The reaction took ca. 45 min and β -anilino-pnitropropiophenone (5.2 g, 80%) was isolated.

(b) General procedure. On the basis of the experience gained in (a) the following general procedure was developed. To a stirred solution of the diazo-ketone (10 mmol) and aniline (20 mmol) in ethanol (75 ml) at 70°, aqueous 10% silver nitrate (1.5 ml, 1.0 mmol) was added. When nitrogen evolution was complete (10-30 min) the hot solution was filtered and the β -anilino-ketone which precipitated on cooling was separated. By this procedure the following β-anilino-ketones were prepared (yields in the Table). R in RCO·CH₂·CH₂·NHPh: Ph, m.p. and mixed m.p.¹⁰ 116° (from petroleum); p-MeO·C₆H₄, m.p. and mixed m.p.¹⁰ 129° (from ethanol); m-NO₂·C₆H₄, m.p. 124— 125° (from petroleum) (lit., 122-123°); p-ClC₆H₄, m.p.

8 R. Ya. Levina and Yu. S. Shabarov, Doklady Akad. Nauk

¹⁰ J. Kenner and F. S. Statham, J. Chem. Soc., 1935, 299.

123-124° (from ethanol) (lit., 11 122-123°); p-PhSO₂·C₆H₄ (β-anilino-p-phenylsulphonylpropiophenone) (Found: С. 69.0; H, 5.2; N, 4.0. C₂₁H₁₉NO₃S requires C, 69.0; H, 5.2; N, 3.8%), m.p. 181-182° (from benzene).

Catalysed Decomposition of a-Diazo-p-nitropropiophenone in the Absence of Aniline.-(a) To a-diazo-p-nitropropiophenone (5 g) in ethanol (60 ml) at 70° was added aqueous 10% silver nitrate (5 ml). When nitrogen evolution was complete (5 min) the solution was filtered hot and the filtrate on cooling deposited crude p-nitrophenyl vinyl ketone (1.34 g), m.p. 72-80° [85-87° from light petroleum (b.p. 60-80°)]. The filtrate from which this material had separated was concentrated to provide a sticky solid (3.46 g), which was chromatographed on silica gel (200 g; 47×2.7 cm). Elution with toluene provided crude p-nitrophenyl vinyl ketone (0.79 g), m.p. 73-81°, followed by the cyclopropane derivative (VII) (0.54 g, 12.4%), m.p. 143-146°. Subsequent elution with toluene-chloroform (1:1) gave two fractions, neither of which was crystalline, but t.l.c., i.r. and n.m.r. spectroscopy indicated that the major component of the more mobile one (0.09 g, 1.8%) was α -diazo-pnitropropiophenone, and that of the less mobile one (0.09 g,1.9%) was the pyrazoline (VI). The total yield (2.13 g) of the vinyl ketone was 49%.

(b) To the diazo-ketone (2.05 g) in dioxan (20 ml) at $21-22^{\circ}$ was added silver nitrate (0.16 g) in water (4 ml). The mixture was stirred until nitrogen evolution (179 ml) was complete (6 h). After filtration to remove silver, water (40 ml) was added and the oily mixture on cooling overnight at 0-5° deposited a yellow solid (1.76 g), m.p. 68-130° (decomp.). The dried solid was extracted (Soxhlet) with light petroleum (b.p. 40-60°) to remove the p-nitrophenyl vinyl ketone (0.61 g, 35%), m.p. 73-83°. The petroleum-insoluble residue (1.10 g, 58%), m.p. 132-140° (decomp.) on crystallisation from acetonitrile (Norit) provided the pyrazoline (VI), m.p. and mixed m.p. 164-165° (decomp.).

Vinyl Ketones .-- General procedure. To a stirred solution of the diazo-ketone (0.1 mol) in ethanol (250 ml) at 70° was added silver nitrate (21.3 g, 0.125 mol) in water (35 ml) as rapidly as the vigorous evolution of nitrogen permitted (2-5 min). The hot solution was filtered, cooled rapidly, and diluted with water (700 ml) and the unsaturated ketone was separated. In those instances where no solid separated, the solution was extracted with chloroform (3×100) ml) and the ab-unsaturated ketone was isolated by distillation of the residue obtained by concentrating the dried chloroform extract. (With p-methoxyphenyl vinyl ketone there was considerable resinification during the distillation.) The identity of the liquid $\alpha\beta$ -unsaturated ketones was confirmed by their i.r. spectra and by the m.p.s of the derivatives formed with aniline and with phenylhydrazine. By these procedures the following vinyl ketones (IV) were obtained: (1) phenyl, b.p. $64-72^{\circ}$ at 0.5 mmHg [β anilino-ketone, m.p. 116° (from ethanol) (lit., 10 116°); pyrazoline, m.p. 152—153° (from ethanol) (lit., 12 153·5— 154.0°)]; (2) 4-methoxyphenyl, b.p. 93-98° at 0.5 mmHg [β -anilinoketone, m.p. 130—132° (from ethanol) (lit.,¹⁰ 130°); pyrazoline, m.p. 140—142° (from ethanol) (lit.,¹² 139.5-141°)]; (3) 4-nitrophenyl, m.p. 88-90° [from light petroleum (b.p. 60-80°)] (lit.,⁵ 91°); (4) 3-nitrophenyl,

971. ¹² A. V. Dombrovskii and M. I. Shevchuk, Zhur. obshchei Khim., 1964, 34, 192 (Chem. Abs., 1964, 60, 10581g).

S.S.S.R., 1952, 84, 709 (Chem. Abs., 1953, 47, 3219f).
F. Nerdel and G. Kresze, Chem. Ber., 1952, 85, 168.

¹¹ D. Hodson, G. Holt, and D. K. Wall, J. Chem. Soc. (C), 1970,

m.p. 106—107° [from light petroleum (b.p. 60—80°)] (lit.,¹³ 102—103°); (5) 4-phenylsulphonylphenyl vinyl ketone, m.p. 110—112° [from light petroleum (b.p. 60—80°)] (Found: C, 66·0; H, 4·6. $C_{15}H_{12}O_3S$ requires C, 66·1; H, 4·4%), v_{max} 3100m, 1605s, 1325s, and 1160s cm⁻¹.

 v_{max} 3100m, 1605s, 1325s, and 1160s cm⁻¹. When, under the conditions described, the silver nitrate was replaced by copper nitrate, α-diazo-*p*-nitropropiophenone (1.03 g) lost its diazo nitrogen almost instantly. Chromatography of the crude product on silica gel (80 g; 2 × 33 cm) (toluene as eluant) provided *p*-nitrophenyl vinyl ketone (36%), m.p. and mixed m.p. 81—84°. Nickel(II), zinc(II), lead(II), iron(III), and mercury(I) nitrates all brought about rapid decomposition of the diazo-ketone. The organic products of the reaction were not investigated in detail but t.l.c. showed that they all contained both αβ-unsaturated ketone and pyrazoline. The use of an equivalent quantity of aniline hydrochloride in place of these metallic salts provided a complex mixture from which was isolated β-anilino-*p*-nitropropiophenone (17%), m.p. and mixed m.p. 132—133°.

Acid-catalysed Decompositions of a-Diazo-p-nitropropiophenone.—(a) With nitric acid. To the diazo-ketone (2.05 g)in pure dioxan (20 ml) and water (3 ml) at 21° was added 0.5m-nitric acid (2 ml). There was an initially brisk evolution of nitrogen which subsided after about 30 min. It was necessary to add two similar portions of nitric acid before the i.r. spectrum of the mixture indicated that decomposition was complete (2.25 h). Water (50 ml) was then added and the solution was neutralised with sodium hydrogen carbonate, then extracted with chloroform $(3 \times 50 \text{ ml})$. The water-washed chloroform extracts were dried $(MgSO_4)$ and evaporated to provide a yellow oil which was chromatographed on silica gel (100 g; 37×2 cm). Elution with toluene gave a yellow oil (0.6 g, 25%), which t.l.c. showed to be a single substance, apparently α -methyl $p\text{-nitrophenacyl nitrate, }\nu_{max.}$ 1708s (C=O), 1640s (O·NO₂, asym.), 1605m (aromatic C=C), 1525s (NO₂, asym.), and 1345s cm⁻¹ (NO₂, sym.), τ 1.6 (4H, ABq, aromatic), 3.7 (1H, q, CO·CHMe·ONO₂), and 8·3 (3H, d, Me). Subsequent elution with toluene-chloroform (1:1) provided a fraction (1.49 g, 78%), m.p. 143-148° (decomp.), which on crystallisation from acetonitrile proved to be identical [mixed m.p. 160-162° (decomp.), i.r. and n.m.r. spectra] with the pyrazoline (VI).

(b) With perchloric acid. To the diazo-ketone (2.05 g,

10 mmol) in dioxan (30 ml) and water (20 ml) at 21° was added 0.464M-perchloric acid (2.5 ml, 1.2 mmol). There was a steady evolution of nitrogen which was complete in 3 h, after which diazo-ketone was no longer present. The solution was neutralised with sodium hydrogen carbonate, diluted with water (50 ml), and extracted with chloroform (3 \times 50 ml). The water-washed chloroform extracts were dried (MgSO₄) and evaporated to provide a yellow oil, which was chromatographed on silica gel (80 g; 2×48 cm). Elution with 1:1 toluene-light petroleum (b.p. 60-80°) gave a yellow solid (0.38 g, 21%), m.p. 75-81°, which after recrystallisation from light petroleum (b.p. 60-80°) proved to be identical (mixed m.p. and i.r. spectrum) with p-nitrophenyl vinyl ketone. Subsequent elution with toluene-chloroform (1:1) gave an orange-coloured solid (1.62 g, 84%), m.p. 136-148° (decomp.), which after recrystallisation from acetonitrile (Norit) proved to be identical (mixed m.p. and i.r. spectrum) with the pyrazoline (VI).

(c) With aqueous formic acid. When the diazo-ketone (2.05 g) was added to aqueous 70% formic acid (50 ml) at 21-22°, nitrogen evolution was complete in 2 min. Dilution of the mixture with water (180 ml) and cooling to 5° produced a solid (1.33 g), m.p. 69-82°. A further crop (0.83 g) of this material was obtained from the aqueous solution by extraction with chloroform. The combined material was chromatographed on silica gel (80 g; 2×33 cm). Elution with toluene-light petroleum (b.p. 60-80°) gave a yellow solid (1.1 g, 62%), m.p. 79-85°, which, after crystallisation from light petroleum (b.p. 60-80°), proved to be identical (mixed m.p., i.r. and n.m.r. spectra) with p-nitrophenyl vinyl ketone. Subsequent elution with toluene-chloroform (1:1) gave a pale yellow solid (0.91 g)40%), m.p. 94-99°. Recrystallisation from ethanol provided a-methyl-p-nitrophenacyl formate, m.p. 99-102° (Found: C, 54.0; H, 4.3; N, 6.2. C₁₀H₉NO₅ requires C, 53.8; H, 4.05; N, 6.25%), v_{max} 1729s, 1715s, 1699s, 1600m (aromatic C=C), 1524s (NO₂, asym.), and 1352s cm⁻¹ (NO₂, sym.), 7 (CDCl₃) 1.72 (4H, m, aromatic), 1.83 (1H, s, HCO·O), 3.91 (1H, q, CH), and 8.41 (3H, d, Me).

[2/1092 Received, 21st July, 1972]

¹³ I. Sheng Kao et al., Sci. Sinica, 1957, **6**, 1031 (Chem. Abs., 1960, **54**, 4457g).