Photochemical Interconversion of Some Diazo-amides and Diazirinecarboxamides

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The photoisomerisation of diazo-compounds by visible light to give diazirines appears to be restricted to α-diazo-amides. Mono- and di-substituted. alkyl- and aryl-diazirinecarboxamides as well as the parent diazirinecarboxamide have been made in this way. The photoisomerisation of the diazirinecarboxamides back to diazo-amides can be effected by irradiation at the frequency of the diazirine absorption band. The thermolysis of some diazirinecarboxamides has also been investigated.

DURING an investigation of the photochemistry of some α-diazo-amides, it was observed that the nature of the product depended upon the wavelength of the radiation used. *N*-Diazoacetylpiperidine (1; $R^1 = C_5H_{10}N$, $R^2 = H$), for example, when irradiated with a medium-pressure mercury lamp in a water cooled Pyrex vessel gave the β-lactam (2),[1] whereas irradiation with visible light gave the diazirinecarboxamide (3; $R = C_5H_{10}N$).[2] This observation prompted an investigation into the generality of the photoisomerisation of diazo-compounds with visible light.

Irradiation of diphenyldiazomethane[3] in carbon tetrachloride solution with a medium-pressure mercury lamp from which all radiation with wavelengths less than 400 nm was excluded, gave after 1 h a mixture of products shown by mass spectrometry to contain chlorine. The only product readily identified was 1,1,1,2-tetrachloro-2,2-diphenylethane, but the u.v. spectrum of the total photolysate did not contain the unusual but characteristically shaped diazirine absorption band.[4,5] Diphenyldiazirine however is known to isomerise spontaneously to diphenyldiazomethane.[6] Photolysis of diphenyldiazomethane in benzene solution with use of the 400 nm filter gave benzophenone azine as the sole product.

[1] D. M. Brunwin, G. Lowe, and J. Parker, *J. Chem. Soc.* (*C*), 1971, 3756; R. H. Earle, D. T. Hurst, and M. Viney, *ibid.*, 1969, 2093; F. Moll, *Arch. Pharm.*, 1968, **301**, 230.

[2] G. Lowe and J. Parker, *Chem. Comm.*, 1971, 1135.

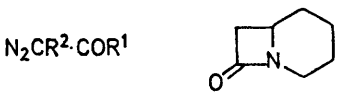
[3] J. B. Miller, *J. Org. Chem.*, 1959, **24**, 560; L. I. Smith and K. L. Howard, *Org. Synth.*, 1955, Coll. Vol. III, p. 351.

[4] H. M. Frey and I. D. R. Stevens, *J. Chem. Soc.*, 1963, 3514.

[5] W. H. Graham, *J. Amer. Chem. Soc.*, 1962, **84**, 1063.

[6] C. G. Overberger and J.-P. Anselme, *Tetrahedron Letters*, 1963, 1405.

Irradiation of diethyl diazomalonate [7] in carbon tetrachloride solution for 4 h with use of the 400 nm filter gave several chlorine-containing compounds, but again the u.v. absorption spectrum showed no trace of the characteristic diazirine absorption band.[4,5] Similarly ethyl



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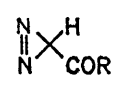

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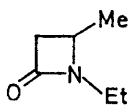

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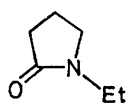

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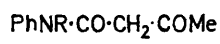

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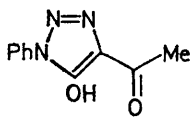

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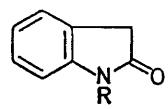


(8)

diazoacetate,[8] diazoacetone,[9,10] and diazoacetophenone,[9] when irradiated in carbon tetrachloride solution with use of the 400 nm filter each gave several chlorine-containing products, but no diazirine was evident.

In the light of these results, the irradiation of α-diazo-amides was explored further. Irradiation of *N*-(t-butoxycarbonyldiazoacetyl)piperidine (1; $R^1 = C_5H_{10}N$, $R^2 = CO_2Bu^t$), *N*-(t-butoxycarbonyldiazoacetyl)-L-proline benzyl ester (1; R^1 = Pro-OBzl, $R^2 = CO_2Bu^t$), and *N*-(ethoxycarbonyldiazoacetyl)pyrrolidine (1; R^1 = pyrrolidin-1-yl, $R^2 = CO_2Et$) in carbon tetrachloride solution with visible light did not generate the isomeric diazirines. It may be however that these disubstituted diazirines spontaneously revert to the corresponding diazo-compounds in order to release steric compression, as in the case of diphenyldiazirine.[6] Irradiation of *N*-diazoacetyl-L-proline benzyl ester (1; R^2 = Pro-OBzl, R^2 = H) and *N*-diazoacetyl-L-phenylalanine methyl ester (1; R^1 = Phe-OMe, R^2 = H) with visible light, gave the diazirinecarboxamides (3; R = Pro-OBzl and Phe-OMe), respectively. The photoisomerisation and diazo-compounds appears therefore to be restricted to α-diazo-amides in which one of the diazo-group substituents is a hydrogen atom.

Rando has shown that the photolysis of *NN*-diethyldiazoacetamide with u.v. light gives a mixture of the β- and γ-lactams (4) and (5).[11] Irradiation of *NN*-diethyldiazoacetamide in carbon tetrachloride solution with visible light gave the diazirinecarboxamide (3; R = NEt_2) in 22% yield as the only tractable product; there was no evidence of the β- and γ-lactams (4) and (5). The ethyl signals in the n.m.r. spectrum of the diazirinecarboxamide appeared as broad multiplets at 35° which became a sharp triplet and quartet at 70°, indicating rapid rotation about the C–N bond on the n.m.r. time scale; the ethyl groups in the n.m.r. spectrum of the diazo-amide (1; $R^1 = NEt_2$, R^2 = H) appeared as a single sharp triplet and quartet at 35°. The diazirine proton appeared as a sharp singlet at τ 8·0. The high field required to bring the diazirine proton into resonance has been ascribed to the large diamagnetic anisotropy of the diazirine ring.[5,12] The u.v. absorption spectrum showed the characteristically shaped diazirine absorption centred at 311 nm (ε 109).[4,5]

N-Methyldiazoacetamide (1; R^1 = NHMe, R^2 = H) was prepared by treatment of *p*-nitrophenyl diazoacetate with methylamine. *N*-Methyldiazoacetamide was not soluble in carbon tetrachloride, so the compound was irradiated in dioxan solution with visible light. The diazirine (3; R = NHMe) was isolated in 31% yield as the only tractable product.

Diazoacetamide (1; $R^1 = NH_2$, R^2 = H) is unstable and was not purified completely, but irradiation of a solution in dioxan with visible light gave the diazirinecarboxamide (3; R = NH_2), albeit in low yield. These experiments show that photoisomerisation of α-diazo-amides with visible light proceeds regardless of the degree of substitution of the amide nitrogen atom.

N-Aryl diazo-amides could not be synthesised by the reaction of aniline with *p*-nitrophenyl diazoacetate or by treatment of *N*-phenylcarbamoyl chloride with diazomethane. Instead the *N*-phenyldiazo-amides were prepared by way of the *N*-acetoacetanilides (*cf.* ref. 13). *N*-Methylaniline was acylated with diketen to give *N*-methylacetoacetanilide (6; R = Me) which was shown by its n.m.r. spectrum to be a tautomeric mixture. Triethylamine-catalysed diazo-exchange with methanesulphonyl azide gave the diazoacetoacetanilide (1; R^1 = NMePh, R^2 = Ac), which on treatment with sodium methoxide in absolute methanol gave *N*-methyldiazoacetanilide (1; R^1 = NMePh, R^2 = H). By the same synthetic procedure diphenylamine gave *N*-phenyldiazoacetanilide (1; $R^1 = NPh_2$, R^2 = H). However, diazoacetoacetanilide (1; R^1 = NHPh, R^2 = Ac) prepared in a similar manner from aniline gave on treatment with sodium methoxide in methanol the triazole (7) as the sole product.

Irradiation of *N*-methyldiazoacetanilide (1; R^1 = NMePh, R^2 = H) with visible light gave two compounds which were separated chromatographically. The major product was the diazirinecarboxamide (3; R = NMePh) and the minor one, *N*-methyloxindole (8; R = Me). Thermolysis of the diazirinecarboxamide (3; R = NMePh) in refluxing toluene rapidly gave a quantitative yield

[7] M. Rosenberger, P. Yates, J. B. Hendrickson, and W. Wolf, *Tetrahedron Letters*, 1964, 2285.
[8] N. E. Searle, *Org. Synth.*, 1963, Coll. Vol. IV, p. 424.
[9] F. Arndt and J. Amende, *Ber.*, 1928, **61**, 1122.
[10] C. E. McCauley and C. V. King, *J. Amer. Chem. Soc.*, 1952, **74**, 6221.
[11] R. R. Rando, *J. Amer. Chem. Soc.*, 1970, **92**, 6706.
[12] J. J. Uebel and J. C. Martin, *J. Amer. Chem. Soc.*, 1964, **86**, 4618.
[13] M. Regitz, J. Hocker, and A. Liedhegener, *Org. Synth.*, 1968, **48**, 36.

of *N*-methyloxindole. Irradiation of *N*-methyldiazoacetanilide (1; R^1 = NMePh, R^2 = H) with u.v. light in a Pyrex vessel gave a mixture of products from which *N*-methyloxindole was obtained.

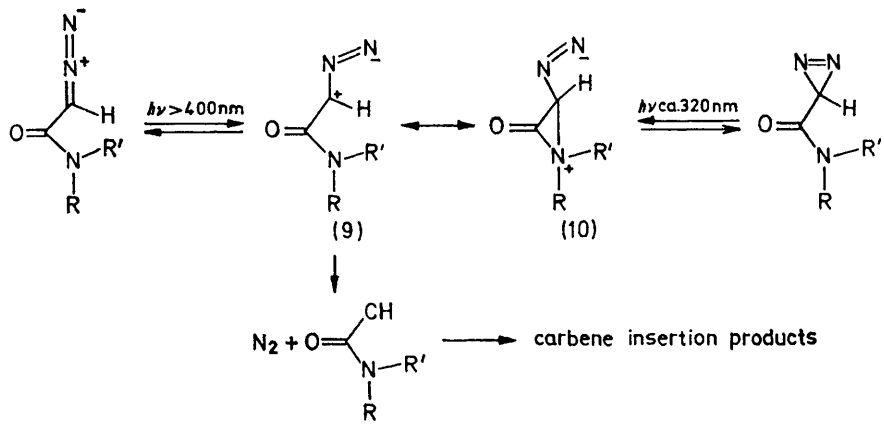
Irradiation of *N*-phenyldiazoacetanilide (1; R^1 = NPh_2, R^2 = H) with visible light gave the isomeric diazirinecarboxamide (3; R = NPh_2) and *N*-phenyloxindole (8; R = Ph). The diazirinecarboxamide (3; R = NPh_2) underwent thermolysis in refluxing toluene to give *N*-phenyloxindole. Irradiation of *N*-phenyldiazoacetanilide (1; R^1 = NPh_2, R^2 = H) with u.v. light in a Pyrex vessel gave a complex mixture of products from which *N*-phenyloxindole could be isolated.

The photolysis of simple diazirines in the gas phase has been extensively studied,[14,15] and a theoretical treatment of the excited states of diazirine and diazomethane has been described.[16] Generally, irradiation of diazirines gives carbenes, but diazomethane was detected [15] during the photolysis of diazirine at 320 nm.

Irradiation of the diazirinecarboxamide (3; R = NHMe) at 312 nm for 1 h (optimum period) produced a yellow photolysate which was shown by t.l.c. and by the i.r. spectrum to contain *N*-methyldiazoacetamide (1; R^1 = NHMe, R^2 = H) (*ca.* 30% yield), together with several other compounds. Similarly, irradiation of the diazirinecarboxamide (3; R = NPh_2) at 334 nm for 2·25 h (optimum period) produced *N*-phenyldiazoacetamide (1; R^1 = NPh_2, R^2 = H) (*ca.* 15% yield), together with other products as shown by t.l.c. When this diazirinecarboxamide (1; R^1 = NPh_2, R^2 = H) was irradiated at 312 nm, however, no diazo-amide was found. Although the diazirine absorption maximum is at about 310 nm, there is end absorption from the diphenylamide at this wavelength which probably accounted for this behaviour.

tronically excited nitrogen molecule.[16] Irradiation of diazo-amides with visible light however probably generates an excited state with relatively low vibrational energy, so allowing isomerisation to successfully compete with carbene formation. Since the photochemical isomerisation appears to be restricted to diazo-amides, it seems likely that the amide group participates in some way. If the excited state of the diazo-group is envisaged to have an electron distribution formally represented by the dipolar structure (9), this could be stabilised by a contribution from the canonical structure (10) to the resonance hybrid. The related canonical structure for the excited state of a diazo-ester would be expected to make a much less significant contribution to the resonance hybrid, and with a diazo-ketone none at all. The contribution of the canonical structure (10) to the excited state of diazo-amides would suppress fragmentation to nitrogen and a carbene and promote intramolecular attack by the di-imide anion to give the diazirinecarboxamide. This mechanism also suggests why diazo-amides of malonic half esters do not give diazirines, since the carbon atom undergoing substitution would be a tertiary centre. Similarly irradiation of a diazirinecarboxamide at a frequency near that of its absorption maximum would generate an excited state in which C–N bonds of the diazirine are weakened and from which either a carbene and nitrogen or a diazo-amide may be formed from the resonance-stabilised excited state [(9) ⟷ (10)] by essentially the reverse process. The ready thermolysis of diazirinecarboxamides leading to carbene insertion products probably involves the concerted breaking of the C–N bonds to give nitrogen and the carbene directly.

The photochemical interconversion of diazo-amides and diazirinecarboxamides is formally analogous to a



Applying simple symmetry arguments, Hoffmann concluded that diazomethane and diazirine in their first excited states decompose to methylene and an elec-

growing class of electrocyclic reactions involving three-membered rings, which includes the oxaziridine-to-nitrone,[17] aziridine-to-azomethine ylide,[18] epoxide-to-

[14] H. M. Frey, 'I.U.P.A.C. International Symposium on Organic Photochemistry,' Butterworths, London, 1964, p. 527, and references there cited; H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.* 1962 79.

[15] M. J. Amrich and J. A. Bell, *J. Amer. Chem. Soc.*, 1964, **86**, 292.

[16] R. Hoffmann, *Tetrahedron*, 1966, **22**, 539.

[17] J. S. Splitter, T-M. Su, H. Ono, and M. Calvin, *J. Amer. Chem. Soc.*, 1971, **93**, 4075.

[18] R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, 1967, **89**, 1753; J. H. Hall and R. Huisgen, *Chem. Comm.*, 1971, 1187; J. H. Hall, R. Huisgen, C. H. Ross, and W. Scheer, *ibid.*, p. 1188.

carbonyl ylide,[19] and azirine-to-nitrile ylide rearrangements.[20]

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. and u.v. spectra were measured on a Perkin-Elmer 257 grating spectrometer and a Carey model 14 spectrometer, respectively. ^{1}H N.m.r. spectra were recorded on Perkin-Elmer R10 and R14 instruments (operating at 60 and 100 MHz, respectively) and mass spectra on A.E.I. MS9 and Varian M.A.T. CH7 instruments. Microanalyses were determined by Dr Strauss and his staff in this laboratory. Absorbents used in t.l.c. and preparative layer chromatography (p.l.c.) were $HF_{254+366}$ and $PF_{254+366}$ silica gel (Merck), respectively. Harrington's neutral alumina (grade IV) and M60 silica gel were used for column chromatography. Anhydrous sodium sulphate was used to dry organic solvents. Light petroleum refers to the fraction b.p. 60—80°.

Apparatus.—The reaction vessel was a three-compartment apparatus. The inner compartment accommodated a Hanovia 450 W medium-pressure mercury lamp, type 2521, surrounded by a Pyrex probe through which cooling water was circulated. In the central compartment was placed the appropriate filter solution (described later). In the exterior compartment was placed the solution to be irradiated at concentrations of *ca.* 1% w/v. Dry nitrogen was bubbled through the solution during the irradiation.

Filter Solutions.[21]—(i) 400 *nm.* 9,10-Dibromoanthracene (0·2 g) and pyrene (0·2 g) in toluene (0·5 l). This filter solution excludes light below 400 nm and has an effective lifetime of *ca.* 18 h under irradiation conditions.

(ii) 334 *nm.* An aqueous solution of nickel sulphate (500 g l^{-1}) which was circulated through the Pyrex cooling probes to act both as a filter and as a coolant. In the filter solution compartment of the reaction vessel was placed a solution of naphthalene in iso-octane (12·8 g l^{-1}). This filter excludes light below 320 and above 360 nm.

(iii) 312 *nm.* Potassium chromate (1·6 g) and potassium carbonate (27·6 g) in water (4·0 l); this excludes light below 300 and between 325 and 420 nm.

N-*Diazoacetylpiperidine* (1; $R^1 = C_5H_{10}N$, $R^2 = H$).—This was available from a previous study.[1]

Photoisomerisation of N-*Diazoacetylpiperidine* (1; $R^1 = C_5H_{10}N$, $R^2 = H$).—*N*-Diazoacetylpiperidine (0·1 g) in carbon tetrachloride (100 ml) was irradiated for 1 h (400 nm filter). P.l.c. of the photolysate on a 1 m plate (ether as eluant) gave a trace of unchanged diazo-compound and *NN*-pentamethylenediazirine-3-carboxamide (3; R = $C_5H_{10}N$) (20 mg), $\lambda_{max.}$ (CCl_4) 303—312 nm (ε 110); $\nu_{max.}$ (CCl_4) 1655 cm^{-1} (amide); τ (CCl_4) 6·45br (4H, m, piperidine H-2 and H-6), 8·18 (1H, s, diazirine H), 8·34br (6H, m, H-3, -4, and -5); *m/e* 151 (Calc. for $C_7H_9N_3O$: *M*, 151).

Diphenyldiazomethane.—This was prepared by the literature method,[3] and was obtained as purple needles, m.p. 25—27° (lit.,[3] 29—30°).

Photolysis of Diphenyldiazomethane.—Diphenyldiazomethane (0·5 g) in carbon tetrachloride (175 ml) was irradiated for 0·75 h (400 nm filter). The photolysate did not show the characteristic u.v. absorption band for a diazirine. P.l.c. of the photolysate gave several fractions. From the least polar was obtained 1,1,1,2-*tetrachloro*-2,2-*diphenylethane* (0·28 g, 34%) as prisms, m.p. 86—87° (from methanol–chloroform) [Found: C, 52·3; H, 3·0; Cl, 44·1%; *m/e* 318, 320, 322, 324, and 326 in characteristic ratio for a Cl_4 compound. $C_{14}H_{10}Cl_4$ requires C, 52·5; H, 3·1; Cl, 44·3%; *M* (^{35}Cl), 318].

Diphenyldiazomethane (0·5 g) was irradiated in benzene (175 ml) for 2·5 h either with use of the 400 nm filter, or with four 200 W tungsten lamps. After removal of the solvent, the solid product was recrystallised to give benzophenone azine (0·34 g, 43%) as yellow needles, m.p. 166—167° (lit.,[22] 164—165°), *m/e* 360 (M^+) (Calc. for $C_{26}H_{20}N_2$: *M*, 360).

N-(*t-Butoxycarbonyldiazoacetyl*)*piperidine* (1; $R^1 = C_5H_{10}N$, $R^2 = CO_2Bu^t$).—This was available from a previous study.[1]

N-(*t-Butoxycarbonyldiazoacetyl*)-L-*proline Benzyl Ester* (1; R^1 = Pro-OBzl, $R^2 = CO_2Bu^t$).—L-Proline benzyl ester, freed from its hydrochloride (4·5 g) with potassium carbonate solution, was stirred with t-butyl hydrogen malonate (3 g) [1] and dicyclohexylcarbodi-imide (4 g) in ethyl acetate (100 ml). After 1 h dicyclohexylurea was filtered off and the filtrate was washed with 0·5N-hydrochloric acid, saturated sodium hydrogen carbonate solution, and water, and dried. Removal of the solvent gave *N*-(t-butoxycarbonylacetyl)-L-proline benzyl ester (6 g) as a viscous colourless oil, $\nu_{max.}$ (CCl_4) 1740 (esters) and 1660 cm^{-1} (amide).

This material in acetonitrile (150 ml) was treated with toluene-*p*-sulphonyl azide (14 g) and diethylamine (2·5 ml) for 10 h at 20°. The solvent was removed and the residue taken up in benzene (100 ml) and washed with potassium hydroxide solution and brine. After removal of the solvent, the residue was chromatographed on silica gel (200 g). Elution with ether–light petroleum gave N-(*t-butoxycarbonyldiazoacetyl*)-L-*proline benzyl ester* (5 g) as pale yellow crystals, m.p. 92—93°. Recrystallisation from ether–light petroleum gave fine yellow needles, m.p. 93—94°, $[\alpha]_D^{20}$ −56·5° (*c* 1 in $CHCl_3$) (Found: C, 61·0; H, 6·3; N, 11·3. $C_{19}H_{23}N_3O_5$ requires C, 61·2; H, 6·2; N, 11·5%).

N-(*Ethoxycarbonyldiazoacetyl*)*pyrrolidine* (1; $R^1 = C_4H_8N$, $R^2 = CO_2Et$).—To a stirred solution of pyrrolidine (17 ml) in benzene (150 ml) at 5° was added ethyl chloroformylacetate [1] (12·5 g). After 1 h the solution was washed with 2N-hydrochloric acid, saturated sodium hydrogen carbonate solution, and brine, dried and evaporated to give a light yellow residue (11 g) which was essentially pure (t.l.c. and n.m.r.). A small sample was fractionally distilled to give the pure *amide*, b.p. 132° at 0·45 mmHg, $\nu_{max.}$ (CCl_4) 1740 (ester) and 1655 cm^{-1} (amide) (Found: C, 58·1; H, 8·0; N, 7·7. $C_9H_{15}NO_3$ requires C, 58·4; H, 8·1; N, 7·6%).

N-(Ethoxycarbonylacetyl)pyrrolidine (4 g) and toluene-*p*-sulphonyl azide (4 g) were dissolved in acetonitrile (50 ml); the solution was cooled to 0° and diethylamine (2·5 ml) was added. After 24 h at 0° the solvent was removed and the residue taken up in benzene. The solution was washed with potassium hydroxide solution and with water, dried and evaporated. The residue was chromatographed on silica gel (300 g). Elution with ether–light petroleum gave N-(*ethoxycarbonyldiazoacetyl*)*pyrrolidine* (3·4 g) as a thick yellow oil, $\nu_{max.}$ (CCl_4) 2120 (diazo), 1710 (diazo-ester), and

[19] H. Hamberger and R. Huisgen, *Chem. Comm.*, 1971, 1190; A. Dahman, H. Hamberger, R. Huisgen, and V. Markowski, *ibid.*, p. 1192.

[20] D. J. Anderson and A. Hassmer, *J. Amer. Chem. Soc.*, 1971, **93**, 4339.

[21] J. G. Calvert and J. N. Pitts, jun., 'Photochemistry,' Wiley, New York, 1966, p. 728.

[22] E. R. Blout, V. W. Eager, and R. M. Gofstein, *J. Amer. Chem. Soc.*, 1946, **68**, 1983.

1630 cm^{-1} (diazo-amide) (Found: C, 51·0; H, 5·9; N, 20·1. $C_9H_{13}N_3O_3$ requires C, 51·2; H, 6·1; N, 19·9%).

N-*Diazoacetyl-L-proline Benzyl Ester* (1; R^1 = Pro-OBzl, R^2 = H).—L-Proline benzyl ester [freed from its hydrochloride (4·5 g) with potassium carbonate solution] in ethyl acetate (50 ml) was stirred with *N*-benzyloxycarbonylglycine (4 g) and dicyclohexylcarbodi-imide (4 g) for 24 h. The mixture was filtered and the filtrate washed with 2N-hydrochloric acid, saturated sodium hydrogen carbonate solution, and water, dried and evaporated to give *N*-benzyloxycarbonylglycyl-L-proline benzyl ester (6 g) (pure by t.l.c.).

The protected dipeptide (1 g) was dissolved in a saturated solution of hydrogen bromide in glacial acetic acid (10 ml). When evolution of carbon dioxide ceased, dry ether (5 ml) was added and the resulting gum crystallised from methanol–ether to give *glycyl-L-proline benzyl ester hydrobromide* (0·6 g), which after recrystallisation from the same solvent had m.p. 149—151°, $[\alpha]_D^{20}$ −93·2 (*c* 1 in H_2O) (Found: C, 48·9; H, 5·3; Br, 23·1; N, 8·2. $C_{14}H_{19}BrN_2O_3$ requires C, 49·0; H, 5·5; Br, 23·3; N, 8·2%).

Glycyl-L-proline benzyl ester hydrobromide (5 g) in aqueous 2M-sodium acetate (40 ml) and glacial acetic acid (2 ml) was stirred at −2° while sodium nitrite (2 g) was added. Stirring was continued for 2 h and the solution extracted with dichloromethane (4 × 20 ml). The solution was dried and the solvent removed to give crystalline N-*diazoacetyl-L-proline benzyl ester* (1 g), which formed pale yellow prisms, m.p. 98—99° (from dichloromethane–light petroleum), $[\alpha]_D^{20}$ −103·8° (*c* 1 in $CHCl_3$), $\lambda_{max.}$ (EtOH) 250 (ε 20,000) and 378 nm (ε 20); $\nu_{max.}$ ($CHCl_3$) 2130 (diazo), 1740 (ester), and 1608 cm^{-1} (diazo-amide); τ ($CDCl_3$) 2·68 (5H, s, Ph), 4·83 (2H, s, C*H*$_2$Ph), 5·16 (1H, s, CHN_2), 5·50 (1H, m, H-2), 6·68 (2H, m, H-5), and 7·98 (4H, m, H-3 and -4) [Found: C, 61·3; H, 5·5; N, 15·2%; *m/e* 245 (M^+ − 28). $C_{14}H_{15}N_3O_3$ required C, 61·5; H, 5·5; N, 15·4%; *M*, 273).

Photoisomerisation of N-*Diazoacetyl-L-proline Benzyl Ester* (1; R^1 = Pro-OBzl, R^2 = H).—*N*-Diazoacetyl-L-proline benzyl ester (0·5 g) in dichloromethane (200 ml) was irradiated (400 nm filter). After 10 h only a trace of diazo-compound remained. P.l.c. of the photolysate on a 1 m plate (two elutions with chloroform), gave two bands and material on the base-line. The least polar material was a trace of unchanged diazo-compound. The more polar material was extracted and gave the crystalline N-(*diazirin-3-ylcarbonyl*)-L-*proline benzyl ester* (3; R = Pro-OBzl). Recrystallisation from dichloromethane–light petroleum gave colourless needles, m.p. 98—100°, $[\alpha]_D^{20}$ −94·0° (*c* 1 in $CHCl_3$), $\lambda_{max.}$ (EtOH) 310 nm (ε 124); $\nu_{max.}$ ($CHCl_3$) 1745 (ester) and 1658 cm^{-1} (amide); τ ($CDCl_3$) 2·68 (5H, s, Ph), 4·88 (2H, s, C*H*$_2$Ph), 5·45 (1H, s, H-2), 6·17 (2H, m, H-5), 7·90 (4H, m, H-3 and -4), and 8·17 (1H, s, diazirine H) [Found: C, 61·3; H, 5·7; N, 15·4%; *m/e* 273 (M^+). $C_{14}H_{15}N_3O_3$ requires C, 61·5; H, 5·5; N, 15·4%; *M*, 273].

N-*Diazoacetyl-L-phenylalanine Methyl Ester* (1; R^1 = Phe-OMe, R^2 = H).—A sample of this material, provided by R. S. Bayliss and J. R. Knowles,[23] had m.p. 126—128° (from dichloromethane–ether), $[\alpha]_D^{20}$ +186 (*c* 1 in $CHCl_3$), $\nu_{max.}$ (Nujol) 2100 (diazo), 1730 (ester), and 1600 cm^{-1} (diazo-amide).

Photoisomerisation of N-*Diazoacetyl-L-phenylalanine Methyl Ester* (1; R^1 = Phe-OMe, R^2 = H).—The diazo-compound (0·2 g) in dichloromethane was irradiated (400 nm filter). After 4 h the solvent was removed from the photolysate and the residue purified by p.l.c. on two 20 × 20 cm plates (two elutions with chloroform). Extraction of the band at R_F 0·5 with chloroform gave the crystalline *N*-(diazirin-3-ylcarbonyl)-L-phenylalanine methyl ester (3; R = Phe-OMe), which formed colourless needles, m.p. 104—105° (from dichloromethane–light petroleum), $\lambda_{max.}$ (EtOH) 310 nm (ε 120); $\nu_{max.}$ ($CHCl_3$) 1720 cm^{-1} (ester); τ ($CDCl_3$) 2·80br (5H, s, Ph), 3·70br (1H, d, NH), 5·18 (1H, m, CH_2·C*H*, NH), 6·30 (3H, s, CH_3), 6·95 (2H, d, *J* 6 Hz, CH·C*H*$_2$Ph), and 8·40 (1H, s, diazirine H).

p-*Nitrophenyl Diazoacetate*.—This ester [24] was obtained (52%) as yellow plates, m.p. 87—90° (lit.,[4] 89—90°), $\nu_{max.}$ ($CHCl_3$) 1720 (CO_2R) and 2140 cm^{-1} (CN_2).

NN-*Diethyldiazoacetamide* (1; R^1 = NEt_2, R^2 = H).—This was prepared according to the procedure of Rando,[11] and was isolated chromatographically on neutral alumina. Benzene–ethyl acetate (4 : 1) eluted *NN*-diethyldiazoacetamide (2 g, 72%) as a yellow liquid, $\nu_{max.}$ (film) 1610 ($CONEt_2$) and 2140 cm^{-1} (CN_2); τ (CCl_4) 8·9 (6H, t, *J* 7 Hz, 2 × Me), 6·7 (4H, q, *J* 7 Hz, 2 × CH_2), and 4·9 (1H, s, CHN_2).

Photoisomerisation of NN-*Diethyldiazoacetamide* (1; R^1 = NEt_2, R^2 = H).—*NN*-Diethyldiazoacetamide (1·0 g) in dry carbon tetrachloride (160 ml) was irradiated (400 nm filter). The carbon tetrachloride was removed under reduced pressure to give a colourless oil which was chromatographed on two 1 m p.l.c. plates. Two bands were removed and eluted with ethyl acetate. The most polar band contained *ca.* 5 mg of the starting material. The other band contained an oil (250 mg) which was distilled at 125—130° (bath temp.) and 0·5 mmHg to give NN-*diethyldiazirine-3-carboxamide* (3; R = NEt_2) (220 mg, 22%) as a colourless oil, b.p. 97—100° at 1·3 mmHg, n_D^{20} 1·4618 (Found: C, 51·4; H, 7·7; N, 29·5. $C_6H_{11}N_3O$ requires C, 51·1; H, 7·9; N, 29·8%), $\lambda_{max.}$ (EtOH) 311 nm (ε 109); $\nu_{max.}$ (film) 1660 cm^{-1} (amide); τ (CCl_4; 35°) 8·8 (6H, m, 2 × Me), 8·0 (1H, s, diazirine H), 6·6 (4H, m, 2 × CH_2); τ (CCl_4; sealed tube at 70°), 8·8 (6H, t, *J* 7 Hz, 2 × Me), 8·0 (1H, s, diazirine H), and 6·6 (4H, q, *J* 7 Hz, 2 × CH_2).

N-*Methyldiazoacetamide* (1; R^1 = NHMe, R^2 = H).—*p*-Nitrophenyl diazoacetate (2·7 g) was suspended in aqueous 25% methylamine (100 ml), and the mixture was stirred at 20° for 1 h. The solution was concentrated under reduced pressure at 35° to give a solid which was chromatographed on neutral alumina. Benzene–ethyl acetate (7 : 3) eluted *N*-methyldiazoacetamide (1·0 g, 69%) which crystallised from ether as yellow spikes, m.p. 89—90° (lit.,[25] 89—89·5°), $\nu_{max.}$ ($CHCl_3$) 1640 (amide) and 2140 cm^{-1} (diazo); τ ($CDCl_3$) 7·15 (3H, d, *J* 5 Hz, CH_3), 5·12 (1H, s, diazo H), and 3·9br (1H, s, amide H).

Photoisomerisation of N-*Methyldiazoacetamide* (1; R^1 = NHMe, R^2 = H).—The diazo-amide (0·7 g) in purified dioxan (160 ml) was irradiated (400 nm filter) for 9·5 h. The dioxan was removed under reduced pressure to give a semi-solid, which was chromatographed on a 1 m p.l.c. plate with ether as eluant. Two bands were removed. The more polar band gave crystalline starting material (2 mg). From the less polar band was obtained N-*methyl-*

[23] R. S. Bayliss, J. R. Knowles, and G. B. Wybrandt, *Biochem. J.*, 1969, **113**, 377.

[24] J. Schafer, P. Baronowsky, R. Laursen, F. Finn, and F. H. Westheimer, *J. Biol. Chem.*, 1966, **241**, 421.

[25] H. Chaimovich, R. J. Vaughan, and F. W. Westheimer, *J. Amer. Chem. Soc.*, 1968, **90**, 4088.

diazirine-3-carboxamide (3; R = NHMe) (0·22 g, 31%) which crystallised from chloroform–light petroleum as needles, m.p. 107—110° (with decomposition, and also sublimation at 90—100°) (Found: C, 36·1; H, 5·05; N, 41·9. $C_3H_5N_3O$ requires C, 36·4; H, 5·1; N, 42·4%), $\lambda_{max.}$ (EtOH) 311 nm (ε 93); $\nu_{max.}$ ($CHCl_3$) 1690 (amide) and 3400 cm^{-1} (NH); τ ($CDCl_3$) 8·3 (1H, s, diazirine H), 7·15 (3H, d, *J* 5 Hz, s after exchange with D_2O, CH_3), and 3·6br (1H, s, NH, exchanged with D_2O).

Irradiation of N-*Methyldiazirine-3-carboxamide* (3; R = NHMe) *with Light at* 312 *nm*.—The diazirine (50 mg) in benzene (160 ml) was irradiated with use of a filter solution to provide a window at 312 nm. After irradiation for 1 h, the benzene was removed. The i.r. spectrum of the residue showed a diazo-band at 2140 cm^{-1}. T.l.c. showed a spot corresponding to *N*-methyldiazoacetamide, together with several other spots. Irradiation for 2 h decreased the yield of diazoamide, as shown by the loss of intensity of the 2140 cm^{-1} band in the i.r. spectrum.

Diazoacetamide (1; $R^1 = NH_2$, R^2 = H).[26]—Ethyl diazoacetate (2·0 g) (prepared by diazotisation of ethyl glycinate hydrochloride with nitrous acid) [8] was treated at 0° with aqueous 25% ammonia (20 ml) and the mixture was shaken at 0—4° for 5 weeks. It was then filtered and the yellow filtrate was concentrated *in vacuo* at 20°. Trituration of the residue with cold ethanol gave a bright yellow solution and a brown insoluble solid. After filtration, the solvent was removed under reduced pressure at 20° to give a dark yellow semi-solid which began to decompose; $\nu_{max.}$ (film) 1650 (amide), 2120 (diazo), and 3300 cm^{-1} (amide NH); τ [$(CD_3)_2SO$] 4·4 (1H, s, diazo H) and 3·2br (2H, s, amide NH). This material (0·2 g) was dissolved in purified dioxan, and the solution was filtered from a small quantity of brown insoluble material, to give a yellow solution of the diazoacetamide.

Photoisomerisation of Diazoacetamide (1; $R^1 = NH_2$, R^2 = H).—The solution of diazoacetamide in dioxan (160 ml) was irradiated (400 nm filter) for 8 h. The photolysate contained a brown precipitate. The solution was decanted and the solvent removed under reduced pressure to give a brown semi-solid. Further solid was removed from the photolysis apparatus by washing with water. Removal of the water under reduced pressure gave a brown solid which was combined with the residue from the dioxan solution. Recrystallisation of the product (15 mg) from aqueous ethanol gave a pale brown solid, m.p. 110—120° (decomp.), which had all the spectroscopic properties of the expected diazirine-3-carboxamide (3; R = NH_2), $\lambda_{max.}$ (EtOH) 310 nm (ε 100); $\nu_{max.}$ (Nujol) 1690 (amide) and 3400 cm^{-1} (NH_2); τ [$(CD_3)_2SO$] 8·0 (1H, s, diazirine H) and 2·8br (2H, s, NH_2) (other signals also present).

N-*Methylacetoacetanilide* (6; R = Me).—Freshly redistilled *N*-methylaniline (10·7 g, 0·1 mol) in dry benzene (15 ml) was stirred at 20° while a solution of 50% diketen–acetone (18 g) in dry benzene (20 ml) was added during 0·5 h. The solution was heated under reflux for 1 h, the solvent was removed, and the residue was chromatographed on alumina. Elution with benzene gave N-*methylacetoacetanilide* (14 g, 73%) as a pale yellow liquid (Found: C, 69·2; H, 6·7; N, 7·5. $C_{11}H_{13}NO_2$ requires C, 69·1; H, 6·9; N, 7·3%), $\nu_{max.}$ (film) 1660 (CONMePh) and 1720 cm^{-1} (CH_3CO); τ (CCl_4) 8·3 (s, CH_3 of enol form), 7·9 (s, CH_3 of keto form), 6·8 (s, CH_2), 6·7 (s, NCH_3), 5·4 (s, =CH of enol form), and 2·7 (m, Ph).

2-*Diazo*-N-*methylacetoacetanilide* (1; R^1 = NMePh, R^2 = Ac).—*N*-Methylacetoacetanilide (5·0 g, 26 mmol) in dry methyl cyanide (50 ml) and triethylamine (2·65 g, 26 mmol) was stirred at 20°, and treated with methanesulphonyl azide (3·42 g, 26 mmol) in methyl cyanide (20 ml). The solution was stirred at 20° for 2·5 h, the solvents were removed under reduced pressure, and the residue was dissolved in ether. The ethereal solution was washed with water, dried, and concentrated to give a yellow liquid which was chromatographed on alumina. Elution with benzene gave 2-*diazo*-N-*methylacetoacetanilide* (4·8 g, 83%) as a yellow liquid (Found: C, 61·2; H, 5·3; N, 19·0. $C_{11}H_{11}N_3O_2$ requires C, 60·8; H, 5·1; N, 19·4%), $\nu_{max.}$ (film) 1650 (CONMePh), 1670 (CH_3·CO), and 2140 cm^{-1} (CN_2); τ (CCl_4) 7·7 (3H, s, NMe), 6·6 (3H, s, MeCO), and 2·7 (5H, m, Ph).

Diazo-N-*methylacetanilide* (1; R^1 = NMePh, R^2 = H).—2-Diazo-*N*-methylacetoacetanilide (4·1 g, 19 mmol) was dissolved in dry methanol (25 ml) and the solution was treated at 20° with a solution of sodium methoxide [from sodium (440 mg, 19 mmol)] in dry methanol (10 ml). The mixture was heated under reflux for 3 h, cooled, and poured into water. The product was extracted with ether, and the ether layer was washed with water, dried, and evaporated. The residue was chromatographed on alumina; elution with benzene gave *diazo*-N-*methylacetanilide* (2·8 g, 85%) as a yellow liquid (Found: C, 61·9; H, 5·0; N, 23·5. $C_9H_9N_3O$ requires C, 61·5; H, 5·2; N, 24·0%), $\nu_{max.}$ (film) 1630 (CONMePh) and 2100 cm^{-1} (CN_2); τ (CCl_4) 6·7 (3H, s, NCH_3), 5·5 (1H, s, CHN_2), and 2·7 (5H, m, Ph).

Photoisomerisation of Diazo-N-*methylacetanilide* (1; R^1 = NMePh, R^2 = H).—(a) *Irradiation with mercury lamp and* 400 *nm filter*.—Diazo-*N*-methylacetanilide (2 g) in dry carbon tetrachloride (or purified dioxan) (160 ml) was irradiated for 13 h (400 nm filter). After concentration of the photolysate solution, the resulting oil was chromatographed on two 1 m p.l.c. plates. Two bands were removed; the least polar fraction gave an oil, which was filtered through a small column of alumina in light petroleum–ether (1 : 1). Concentration of the eluate gave N-*methyl*-N-*phenyldiazirine-3-carboxamide* (3; R = NMePh) (0·42 g, 21%) as a pale yellow liquid. The diazirine decomposed during distillation at 90—95° and 0·1 mmHg; n_D^{20} 1·5482 (Found: C, 61·2; H, 5·1; N, 24·1. $C_9H_9N_3O$ requires C, 61·5; H, 5·2; N, 24·0%), $\lambda_{max.}$ (EtOH) 310 nm (ε 214); $\nu_{max.}$ (film) 1680 cm^{-1} (amide); τ (CCl_4) 8·6 (1H, s, diazirine H), 6·7 (3H, s, NCH_3), and 2·4br (5H, s, Ph).

From the second band was obtained an orange solid, which crystallised from light petroleum–ether to give *N*-methyloxindole (98 mg, 6%) as pale yellow needles, m.p. 87—88° (lit.,[27] 89°) (Found: C, 73·5; H, 6·3; N, 9·4%; *m/e* 147. Calc. for C_9H_9NO: C, 73·5; H, 6·2; N, 9·5%; *M*, 147), $\lambda_{max.}$ (EtOH) 277infl (ε 2840) and 252 nm (17,000); $\nu_{max.}$ ($CHCl_3$) 1720 cm^{-1} (oxindole); τ ($CDCl_3$) 6·8 (3H, s, NCH_3), 6·4 (2H, s, CH_2), and 2·6—3·3 (5H, m, aromatic protons).

(b) *With an incandescent light source*. Diazo-*N*-methylacetanilide (2 g) in dry carbon tetrachloride (160 ml) was irradiated with four 200 W tungsten lamps. After 34 h much of the starting material remained, but the n.m.r. spectrum of the total photolysate indicated that a 9% conversion into the diazirine had occurred.

Irradiation of Diazo-N-*methylacetanilide* (1; R^1 = NMePh, R = H) *with Pyrex-filtered Ultraviolet Light*.—The diazo-amide (0·2 g) in carbon tetrachloride (180 ml) was

[26] I. Curtius and J. Thompson, *Ber.*, 1906, **39**, 1383; I. Curtius, *Ber.*, 1885, **18**, 1284.

irradiated in a Pyrex vessel. After 45 min no starting material remained. The solvent was removed from the photolysate, which showed several spots on t.l.c. The least polar spot corresponded to *N*-methyloxindole. A portion (100 mg) of the product was chromatographed on one 20 × 20 cm p.l.c. plate. Removal of the top band, elution with chloroform, and concentration gave a solid, which after crystallisation from light petroleum–ether gave pure *N*-methyloxindole (20 mg, 18%), m.p. and mixed m.p. 87—88°.

Thermolysis of N-*Methyl*-N-*phenyldiazirine*-3-*carboxamide* (3; R = NMePh).—The diazirine (0·1 g) in toluene (10 ml) was heated under reflux for 1 min. The toluene was removed under reduced pressure to give *N*-methyloxindole in quantitative yield, m.p. 88°, identical (R_F on t.l.c., and i.r. spectrum) with the *N*-methyloxindole isolated before. The *N*-methyloxindole was also formed when the diazirine was distilled.

N-*Phenylacetoacetanilide* (6; R = Ph).—To freshly recrystallised diphenylamine (6·3 g, 37 mmol) in dry benzene (15 ml) was added to a solution of 50% diketen–acetone (8·0 g) in dry benzene (30 ml), and the mixture was heated under reflux for 1 h. The solvents were removed under reduced pressure to give a brown gum which crystallised slowly from ethyl acetate–light petroleum. Recrystallisation from ethyl acetate–light petroleum gave N-*phenylacetoacetanilide* (7 g, 75%) as colourless microcrystals, m.p. 78—79° (Found: C, 76·3; H, 6·0; N, 5·6. $C_{16}H_{15}NO_2$ requires C, 75·9; H, 6·0; N, 5·5%), $\nu_{max.}$ ($CHCl_3$) 1660 (amide) and 1720 cm^{-1} (ketone).

2-*Diazo*-N-*phenylacetoacetanilide* (1; R^1 = NPh_2, R^2 = Ac).—*N*-Phenylacetoacetanilide (2 g, 8 mmol) in methyl cyanide (50 ml) and triethylamine (0·8 g, 8 mmol) was treated at 20° with a solution of methanesulphonyl azide (1·05 g, 8 mmol) in methyl cyanide, and the solution was stirred at 20° for 12 h. The solvent was removed under reduced pressure and the residue dissolved in ether. The ethereal solution was washed with water, dried, and evaporated to give orange crystals. Recrystallisation from ethyl acetate–light petroleum gave 2-*diazo*-N-*phenylacetoacetanilide* (1·8 g, 80%) as yellow prisms, m.p. *ca.* 100—110° (decomp.) (Found: C, 68·8; H, 4·7; N, 15·0. $C_{16}H_{13}N_3O_2$ requires C, 68·5; H, 4·7; N, 15·0%), $\nu_{max.}$ ($CHCl_3$) 1640 (amide), 1660 (ketone), and 2140 cm^{-1} (diazo); τ ($CDCl_3$) 7·5 (3H, s, Ac) and 2·7 (10H, m, aromatic protons).

Diazo-N-*phenylacetanilide* (1; R^1 = NPh_2, R^2 = H).—2-Diazo-*N*-phenylacetoacetanilide (3·0 g, 10·5 mmol) in dry methanol (25 ml) was treated at 4° with a solution of sodium methoxide [from sodium (0·25 g, 10·5 mmol)] in methanol (10 ml). The solution was then heated under reflux for 3 h, cooled, and poured into water. The product was extracted with ether; the organic layer was washed with water, dried, and concentrated to give a yellow solid. Recrystallisation from ethyl acetate–light petroleum gave *diazo*-N-*phenylacetanilide* (1·8 g, 72%) as bright yellow prisms, m.p. 85—87° (slight decomp.) (Found: C, 70·6; H, 4·7; N, 17·6. $C_{14}H_{11}N_3O$ requires C, 70·3; H, 4·7; N, 17·7%), $\nu_{max.}$ ($CHCl_3$) 1630 (amide) and 2100 cm^{-1} (diazo); τ ($CDCl_3$) 5·4 (1H, s, diazo H) and 2·7br (10H, s, aromatic protons).

Photoisomerisation of Diazo-N-*phenylacetanilide* (1; R^1 = NPh_2, R^2 = H).—The diazo-amide (1·0 g) in dry carbon tetrachloride (160 ml) was irradiated with light of wavelength greater than 400 nm as before for 8·5 h. The solvent was removed under reduced pressure and the residue chromatographed on two 1 m p.l.c. plates [light petroleum–ether (3 : 2) as eluant]. Two bands were removed. From the less polar band was isolated NN-*diphenyldiazirine*-3-*carboxamide* (3; R = NPh_2) (160 mg, 16%), which crystallised from ethyl acetate–light petroleum as fine colourless needles, m.p. 82—83° (Found: C, 70·5; H, 5·0; N, 17·7. $C_{14}H_{11}N_3O$ requires C, 70·3; H, 4·7; N, 17·7%), $\lambda_{max.}$ (EtOH) 310 (ε 358) and 240 nm (16,800); $\nu_{max.}$ ($CHCl_3$) 1680 cm^{-1} (amide); τ ($CDCl_3$) 8·4 (1H, s, diazirine H) and 2·7 (10H, m, aromatic protons).

From the more polar band was obtained *N*-phenyloxindole (75 mg, 4%), which crystallised from chloroform–ether as needles, m.p. 121—122° (lit.,[27] 121°) (Found: C, 79·4; H, 5·5; N, 6·7. Calc. for $C_{14}H_{11}NO$: C, 79·5; H, 5·3; N, 6·7%), $\nu_{max.}$ ($CHCl_3$) 1720 cm^{-1} (oxindole); τ ($CHCl_3$) 6·3 (2H, s, CH_2) and 2·7 (9H, m, aromatic H).

Irradiation of Diazo-N-*phenylacetanilide* (1; R^1 = NPh_2, R^2 = H) *with Pyrex-filtered Ultraviolet Light.*—The diazo-amide (0·5 g) was irradiated in a Pyrex vessel for 40 min. *N*-Phenyloxindole (0·08 g, 15%) was isolated chromatographically; m.p. and mixed m.p. 121—122° (from chloroform–ether).

Irradiation of NN-*Diphenyldiazirine*-3-*carboxamide* (3; R = NPh_2) *at* 334 *nm.*—The diazirine (0·1 g) in dry benzene (160 ml) was irradiated for 2·25 h (optimum period) with use of the 334 nm filter. After removal of the solvent the residue on t.l.c. showed several spots, one of which was identified as diazo-*N*-methylacetanilide. The i.r. spectrum of the photolysate showed a diazo-band at 2100 cm^{-1}.

2-*Diazoacetoacetanilide* (1; R^1 = NHPh, R^2 = Ac).—To aniline (9·5 g, 102 mmol) in benzene (20 ml) was added 50% diketen–acetone (18 g) in benzene (20 ml) and the mixture was refluxed for 1 h. The solvents were removed under reduced pressure, and the residue was dissolved in hot 50% ethanol–water. On cooling in ice, acetoacetanilide (14·2 g, 78%) was obtained as white flakes, m.p. 82—83° (lit.,[28] 84—85°).

Acetoacetanilide (5 g, 28·2 mmol) in acetonitrile (50 ml) and triethylamine (2·84 g, 28·2 mmol) was treated with toluene-*p*-sulphonyl azide (5·55 g, 28·2 mmol) with stirring at 20°. The mixture was stirred for 2·5 h, the solvents were removed under reduced pressure, and the residue was dissolved in ether. The ethereal solution was washed with aqueous potassium hydroxide solution (5 g in 50 ml) and with water. The ethereal layer was dried, the solvent removed under reduced pressure, and the residue filtered through neutral alumina [light petroleum–ether (1 : 1) as eluant]. Concentration of the eluate and recrystallisation from light petroleum gave 2-*diazoacetoacetanilide* (3·4 g, 60%) as pale yellow needles, m.p. 117—118° (Found: C, 58·7; H, 4·6; N, 20·1. $C_{10}H_9N_3O_2$ requires C, 59·1; H, 4·5; N, 20·6%), $\nu_{max.}$ ($CHCl_3$) 1605 (amide), 1680 (ketone), and 2150 cm^{-1} (diazo); τ ($CDCl_3$) 7·6 (3H, s, CH_3), 2·6 (5H, m, aromatic protons), and −0·1br (1H, s, amide H).

Treatment of 2-*Diazoacetoacetanilide with Sodium Methoxide.*—To diazoacetoacetanilide (2 g, 9·8 mmol) in dry methanol (50 ml) was added a solution of sodium methoxide [from sodium (225 mg, 9·8 mmol)] in dry methanol (10 ml) while the temperature was kept at 0—5°. The mixture was stirred at 0—5° for 1 h and poured into water (200 ml).

[27] R. Stollé, R. Bergdoll, M. Luther, A. Auerhahn, and W. Wacker, *J. prakt. Chem.*, 1930, **128**, 1; R. Stollé, Ger. Pat. 335,673 (*Chem. Abs.*, 1923, **17**, 1802).

[28] J. W. Williams and J. A. Krynitsky, *Org. Synth.*, 1955, Coll. Vol. III, p. 10.

The pH was adjusted to 7 by dropwise addition of 2N-hydrochloric acid. The water and methanol were removed under reduced pressure, and the resultant white solid was extracted with hot ethyl acetate. On cooling, a white solid separated. Recrystallisation from hot ethanol gave *4-acetyl-1-phenyl-1,2,3-triazol-5-ol* (7) (1·44 g, 72%) as needles, m.p. 192—195° (with softening at 190°) (Found: C, 59·1; H, 4·5; N, 20·7. $C_{10}H_9N_3O_2$ requires C, 59·1; H, 4·5; N, 20·7%), $\lambda_{max.}$ (EtOH) 298 (ε 9150) and 242 nm (14,800); $\nu_{max.}$ (Nujol) 1680 (CO) and 3500 cm^{-1} (OH); τ [$(CD_3)_2SO$] 7·6 (3H, s, CH_3), 6·6 (1H, s, OH), and 2·0—2·6 (5H, m, Ph); violet colour with iron(III) chloride solution.

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