Rhodium Carbenoid Mediated Cyclisations. Synthesis of 1,2-Diazetidinones (Aza-β-lactams).[1]

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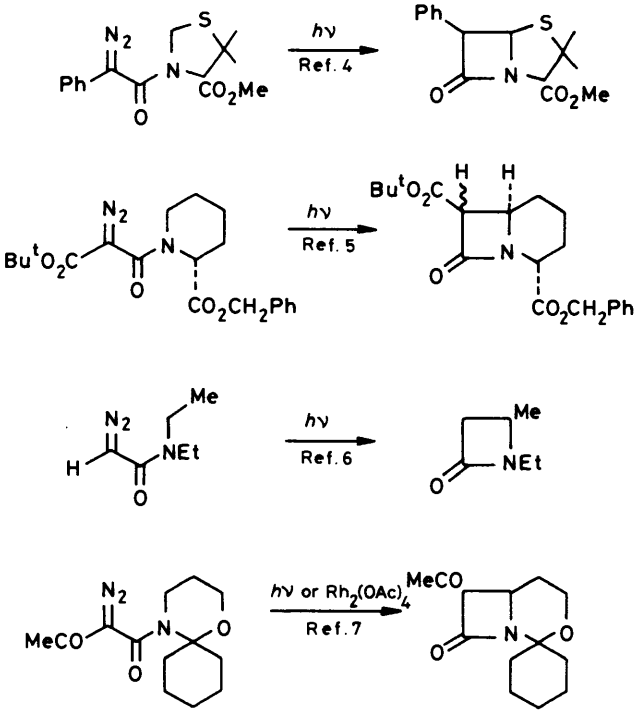
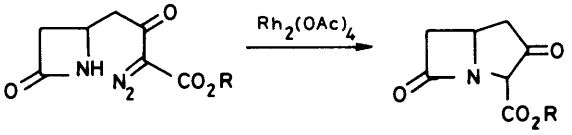
Decomposition of the diazo hydrazides (**1b—h**) in boiling benzene in the presence of a catalytic amount of rhodium(II) acetate gives the corresponding 1,2-diazetidinones (**2**) in good yield. The aza-β-lactams (**2**) exhibit the expected high frequency carbonyl stretch (1 783—1 820 cm^{-1}) in their i.r. spectra.

The decomposition of α-diazocarbonyl compounds has been widely investigated under thermal, photochemical, and transition-metal catalysed conditions,[2] and the intramolecular cyclisations of the resulting carbenes or carbenoids can be synthetically useful reactions.[3] For example, in the β-lactam field such reactions have been used in two contexts. First, the β-lactam ring itself can be formed by intramolecular C–H insertion reaction of the carbenes derived from α-diazo amides, and some examples are shown in Scheme 1,[4–7] although in the monocyclic series the yield of the β-lactam was low because of competing γ-lactam formation and Wolff rearrangement.[6]



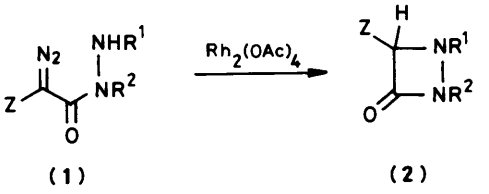
Scheme 1.

Secondly, intramolcular insertion of a carbene or carbenoid into the N–H bond of an azetidinone allows fusion of the second ring. This important reaction, originally developed as the key step in the Merck route to carbapenams[8] (Scheme 2), is now widely used in the synthesis of β-lactams. However, since the rhodium(II)-catalysed decompositon of diazo compounds is believed to involve a rhodium carbenoid intermediate rather than a free carbene,[9] this type of ring closure (Scheme 2) is probably better regarded as nucleophilic attack by the β-lactam NH on the rhodium carbenoid, rather than an insertion into the N–H bond.[10]



Scheme 2.

We have been interested in preparing 1,2-diazetidinones as aza analogues of β-lactams, and have developed a new route to this ring system based on the photochemical ring contraction of 4-diazopyrazolidine-3,5-diones.[11,12] However, this route has its limitations particularly when starting from unsymmetrical 4-diazopyrazolidine-3,5-diones, and therefore an alternative was sought. On the basis of the foregoing discussion of 'carbene insertion' routes to β-lactams, it seemed likely that aza-β-lactams (**2**) could be prepared by rhodium(II) acetate-catalysed decomposition of the diazo hydrazides (**1**) (Scheme 3). This method is attractive because, in principle, a great variation in substituents on the four-membered ring is possible, and because closure of the aza-β-lactam ring by nucleophilic attack by the NHR^1 group on the rhodium carbenoid intermediate should be considerably easier than the formation of β-lactams by C–H insertion (Scheme 1).

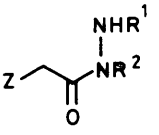


Scheme 3. See compound (3) for R^1, R^2, and Z

We have now shown that aza-β-lactams (**2**) can indeed be prepared in high yield from the diazo hydrazides (1),[1] and our results are reported in detail herein.

Results and Discussion

Synthesis of Diazo Hydrazides (1).—The diazo hydrazides (1) were prepared by diazo transfer[13] to the corresponding hydrazides (**3**), which are readily available by standard chemistry. Thus the known[14] diphenyl derivative (**3a**) was prepared by monoacylation of hydrazobenzene with ethoxycarbonylacetyl chloride, and the benzyl phenyl compound (**3b**) by a similar acylation of benzaldehyde phenylhydrazone followed by catalytic hydrogenation of the C=N bond.

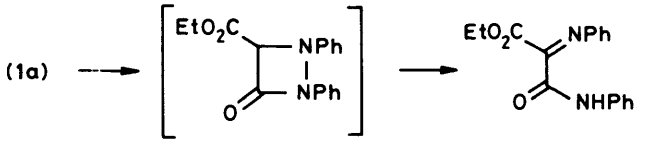


(3)

a; $R^1 = R^2 = Ph$, $Z = CO_2Et$
b; $R^1 = CH_2Ph$, $R^2 = Ph$, $Z = CO_2Et$
c; $R^1 = CO_2Bu^t$, $R^2 = CH_2Ph$, $Z = CO_2Et$
d; $R^1 = CO_2Bu^t$, $R^2 = CH_2Ph$, $Z = Ac$
e; $R^1 = CO_2Bu^t$, $R^2 = CH_2CO_2Et$, $Z = CO_2Et$
f; $R^1 = CO_2Bu^t$, $R^2 = CH_2CO_2Et$, $Z = Ac$
g; $R^1 = CO_2CH_2Ph$, $R^2 = CH_2CO_2Et$, $Z = CO_2Et$
h; $R^1 = CO_2CH_2Ph$, $R^2 = CH_2CO_2Et$, $Z = Ac$

The hydrazides (**3c**) and (**3d**) were prepared from the known[15] t-butyl 3-benzylcarbazate by acylation of the more basic nitrogen with ethoxycarbonylacetyl chloride or with diketene, and the hydrazides (**3e—h**) were similarly obtained by acylation of the known[16] ethyl (2-t-butyloxycarbonylhydrazino)acetate and the corresponding benzyloxycarbonyl derivative. In general, the hydrazides (**3**) were not completely characterised, but were directly converted into the corresponding diazo hydrazides (**1**) under the normal diazo-transfer conditions. The diazo compounds (**3**), which were isolated in variable yield (19—76%), were purified by chromatography, before being subjected to the cyclisation conditions.

Rhodium(II)*-catalysed Decomposition of the Diazo Hydrazides* (**1**).—When the diphenyl diazo compound (**1a**) was heated under reflux in benzene in the presence of a catalytic amount of rhodium(II) acetate, a single product was isolated in 59% yield. This product was not the expected 1,2-diazetidinone (**2a**), but the imine (**4**), which had previously been isolated during the attempted formation of the aza-β-lactam (**2a**) by photochemical ring contraction of 4-diazo-1,2-diphenylpyrazolidine-3,5-dione in the presence of ethanol.[11] Clearly the 1,2-diazetidinone (**2a**) is unstable with respect to cleavage of the N–N bond under both photochemical and thermal conditions.



(1a) (2a) (4)

Decomposition of the other diazo hydrazides (**1b—h**) in boiling benzene in the presence of a catalytic amount of rhodium(II) acetate, however, gave the expected 1,2-diazetidinones (**2**) in high yield (Table).

(1) (2)

With the exception of ethyl 1-benzyl-2-phenyl-3-oxo-1,2-diazetidine-4-carboxylate (**2b**), a crystalline solid which we had prepared previously, confirming its structure by *X*-ray crystallography,[12] the aza-β-lactams (**2c—h**) are colourless oils which exhibit the characteristic high frequency carbonyl stretch in their i.r. spectra and lowfield singlet for 4-H in their ^1H n.m.r. spectra (Table 1). The substituent on N-1 does have some effect on the i.r. frequency of the four-membered ring, an electron-withdrawing group raising the frequency. This may be a result of a reduced or suppressed α-effect of the N-1 lone pair on the amide resonance of the N-2 lone pair.

Thus the readily available hydrazides (**3**) can be converted into aza-β-lactams (**2**) in two steps by diazo transfer followed by rhodium(II)-catalysed decomposition of the diazo compounds (**1**). The rhodium(II) carbenoid mediated cyclisation step proceeds in high yield under relatively mild conditions and indicates the ease with which rhodium carbenoids undergo intramolecular nucleophilic attack, even when a small highly strained ring is being formed.

Experimental

For general points see ref. 11.

Preparation of the Hydrazides (**3**).—*1-(Ethoxycarbonylacetyl)-1,2-diphenylhydrazine* (**3a**). This was prepared from hydrazobenzene by the literature route.[14]

2-Benzyl-1-ethoxycarbonylacetyl-1-phenylhydrazine (**3b**). A stirred mixture of benzaldehyde phenylhydrazone (0.80 g, 4.1 mmol) and sodium hydride (50%; 0.15 g, 6.1 mmol) in dry THF (25 ml) was heated under reflux for 30 min. The deep red solution was cooled to 0 °C, ethoxycarbonylacetyl chloride (0.67 g, 4.4 mmol) was added, and the mixture was stirred at 0 °C for 30 min. It was then diluted with ether (50 ml), washed with water, dried, and evaporated. Flash chromatography of the residue gave *2-benzylidene-1-ethoxycarbonylacetyl-1-phenylhydrazine* (0.44 g, 35%), m.p. 92 °C (from ethanol) (Found: M^+, 310.1329. $C_{18}H_{18}N_2O_3$ requires *M*, 310.1317); $\nu_{max.}$(Nujol) 1 730 and 1 685 cm^{-1}; δ(90 MHz; $CDCl_3$) 1.26 (3 H, t), 3.98 (2 H, s), 4.25 (2 H, q), and 7.20—7.70 (11 H, m).

A solution of the above compound (0.20 g) in ethanol (25 ml) was hydrogenated over 10% palladium–charcoal (0.02 g) to give the *title compound* (**3b**) (0.19 g, 94%) as a colourless solid, m.p. 85.5 °C (from hexane–ethyl acetate) (Found: C, 69.0; H, 6.35; N, 8.95. $C_{18}H_{20}N_2O_3$ requires C, 69.2; H, 6.45; N, 9.0%); $\nu_{max.}$(Nujol) 3 290, 1 735, and 1 650 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.25 (3 H, t), 3.3 (1 H, s), 3.65 (1 H, s), 3.80 (1 H, d, *J* 16 Hz),

Table. Preparation of aza-β-lactams (**2**) by rhodium carbenoid mediated cyclisation

(1)/(2)	R^1	R^2	Z	Yield (%)	$\nu_{max.}$(cm^{-1})	δ (4-H)
a	Ph	Ph	CO_2Et	0	—	—
b	CH_2Ph	Ph	CO_2Et	87	1 783	4.57
c	CO_2Bu^t	CH_2Ph	CO_2Et	91	1 805	5.23
d	CO_2Bu^t	CH_2Ph	COMe	100	1 795	5.17
e	CO_2Bu^t	CH_2CO_2Et	CO_2Et	95	1 820	5.40
f	CO_2Bu^t	CH_2CO_2Et	COMe	75	1 820	5.32
g	CO_2CH_2Ph	CH_2CO_2Et	CO_2Et	93	1 820	5.43
h	CO_2CH_2Ph	CH_2CO_2Et	COMe	82	1 820	5.48

3.95—4.50 (3 H, m), 6.05 (1 H, br, D_2O exch.), and 7.15—7.50 (10 H, m); *m/z* 312 (M^+), 266, 207, 119, and 91 (base).

t-Butyl 2-benzyl-2-(ethoxycarbonylacetyl)hydrazine-1-carboxylate (**3c**). A solution of ethoxycarbonylacetyl chloride (1.65 g, 11 mmol) in benzene (15 ml) was added dropwise to a stirred ice-cooled mixture of t-butyl 3-benzylcarbazate[15] (2.22 g, 10 mmol) and triethylamine (1.4 ml, 10 mmol) in benzene (50 ml). The mixture was stirred at 0 °C for 1 h and then at room temperature for 19 h after which it was filtered and the filtrate evaporated. The residue was dissolved in ethyl acetate (50 ml), and the solution washed with dilute hydrochloric acid, water, and saturated aqueous sodium hydrogen carbonate, dried, and evaporated to give the title compound (**3c**) (2.27 g, 68%) as a pale brown oil, δ (90 MHz; $CDCl_3$) 1.27 (3 H, t), 1.45 (9 H, s), 3.52 (2 H, br s), 3.8—4.4 (4 H, br, incl. δ 4.21, 2 H, q), 6.54 (1 H, br), and 7.33 (5 H, s).

t-Butyl 2-acetoacetyl-2-benzylhydrazine-1-carboxylate (**3d**). Diketene (tech. grade; 0.78 ml, 10 mmol) was added dropwise to a stirred ice-cooled solution of t-butyl 3-benzylcarbazate[15] (2.22 g, 10 mmol) in benzene (20 ml). The mixture was stirred at 0 °C for 2 h and then at room temperature for 17 h; it was then diluted with ethyl acetate (50 ml). The organic solution was washed with water, dilute hydrochloric acid, water, and saturated aqueous sodium hydrogen carbonate, dried, and evaporated to give the title compound (**3d**) (2.67 g, 87%) as a yellow oil, δ (90 MHz; $CDCl_3$) 1.56 (9 H, s), 2.39 (3 H, s), 3.73 (2 H, br s), 3.8—4.5 (2 H, br), 6.54 (1 H, br s), and 7.41 (5 H, s).

t-Butyl 2-ethoxycarbonylacetyl-2-(ethoxycarbonylmethyl)-hydrazine-1-carboxylate (**3e**). Ethyl 2-(t-butoxycarbonylhydrazino) acetate[16] (2.0 g, 9.2 mmol) was acylated with ethoxycarbonylacetyl chloride (1.3 g, 9.2 mmol) using the conditions described for compound (**3c**) to give the title compound (**3e**) (2.95 g, 97%) as a yellow gum, δ (90 MHz; $CDCl_3$) 1.28 (6 H, t), 1.45 (9 H, s), 3.47 (2 H, s), 4.19 (4 H, q), 4.25—4.65 (2 H, m), and 7.2 (1 H, br s).

t-Butyl 2-acetoacetyl-2-(ethoxycarbonylmethyl)hydrazine-1-carboxylate (**3f**). Diketene (0.35 ml, 4.46 mmol) was added to a solution of ethyl 2-(t-butoxycarbonylhydrazino)acetate[16] (0.95 g, 4.38 mmol) in benzene (20 ml) containing triethylamine (2 drops). The mixture was heated under reflux for 16 h, evaporated, and the residue partitioned between dichloromethane (50 ml) and water (20 ml). The dichloromethane layer was separated, dried, and evaporated to give the title compound (**3f**) (1.22 g, 93%) as an orange oil, δ (90 MHz; $CDCl_3$) 1.30 (3 H, t), 1.49 (9 H, s), 2.29 (3 H, s), 3.60 (2 H, s), 4.0—4.5 (2 H, br), 4.26 (2 H, q), and 7.18 (1 H, br s).

Benzyl 2-ethoxycarbonylacetyl-2-(ethoxycarbonylmethyl)-hydrazine-1-carboxylate (**3g**). Ethyl 2-(benzyloxycarbonylhydrazino)acetate[16] (1.26 g, 5 mmol) was acylated with ethoxycarbonylacetyl chloride (0.83 g, 5.5 mmol) using the conditions described for compound (**3c**) to give the title compound (**3g**) (1.83 g, 100%) as an oil, δ (90 MHz; $CDCl_3$) 1.23 (6 H, t), 3.40 (2 H, s), 4.1 (4 H, 2 × q), 4.0—4.5 (2 H, br), 5.08 (2 H, s), and 7.18 (5 H, s).

Benzyl 2-acetoacetyl-2-(ethoxycarbonylmethyl)hydrazine-1-carboxylate (**3h**). Ethyl 2-(benzyloxycarbonylhydrazino)acetate[16] (570 mg, 2.26 mmol) was acylated with diketene (0.18 ml, 2.26 mmol) using the conditions described for compound (**3f**) to give the title compound (**3h**) (760 mg, 100%) as a brown oil, δ (60 MHz; $CDCl_3$) 1.27 (3 H, t), 2.16 (3 H, s), 3.53 (2 H, s), 4.17 (2 H, q), 4.0—4.5 (2 H, br), 5.16 (2 H, s), 7.35 (5 H, s), and 8.00 (1 H, br).

General Procedure for the Preparation of the Diazo Hydrazides (**1**).—A solution of the hydrazide (**3**) (2 mmol) and toluene-*p*-sulphonylazide (4 mmol) in dichloromethane (50 ml) was treated with triethylamine (2 mmol), and the mixture stirred at room temperature until t.l.c. indicated that the reaction was complete (usually ≥ 24 h). The solvent was evaporated, and the residue triturated with ether. The insoluble toluene-*p*-sulphonamide was filtered off, the filtrate evaporated, and the residue chromatographed (silica gel, dichloromethane eluant) to give unchanged tosyl azide, followed by the diazo hydrazide (**1**). The following compounds were thus prepared:

1-Ethoxycarbonyldiazoacetyl-1,2-diphenylhydrazine (**1a**) (56%), m.p. 137—138 °C (Found: C, 63.0; H, 4.9; N, 17.3. $C_{17}H_{16}N_4O_3$ requires C, 63.0; H, 4.9; N, 17.3%); $\nu_{max.}$(Nujol) 3 300, 2 130, 1 730, 1 710, 1 645, and 1 600 cm^{-1}; δ (60 MHz; $CDCl_3$) 1.30 (3 H, t), 4.25 (2 H, q), and 6.70—7.80 (11 H, m); *m/z* 324 (M^+), 278 (base), 256, 252, 183, 155, 149, and 119.

2-Benzyl-1-ethoxycarbonyldiazoacetyl-1-phenylhydrazine (**1b**) (49%), yellow oil, $\nu_{max.}$(neat) 3 280, 2 125, 1 725, 1 680, and 1 640 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.10 (3 H, t), 3.95 (2 H, s), 4.00 (2 H, q), 5.40 (1 H, br s), and 7.10—7.25 (10 H, m); *m/z* 338 (M^+), 310, 207, 196, 191, 117 (base), and 91.

t-Butyl 2-benzyl-2-(ethoxycarbonyldiazoacetyl)hydrazine-1-carboxylate (**1c**) (19%), yellow oil (Found: M^+, 362.1601. $C_{17}H_{22}N_4O_5$ requires *M*, 362.1590); $\nu_{max.}$(neat) 3 320, 2 140, 1 730, and 1 660 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.31 (3 H, t), 1.42 (9 H, s), 4.30 (2 H, q), 4.82 (2 H, br s), 7.30 (1 H, br s), and 7.35 (5 H, s); *m/z* 362 (M^+).

t-Butyl 2-acetodiazoacetyl-2-benzylhydrazine-1-carboxylate (**1d**), (76%), m.p. 73.5 °C (from ethanol–hexane) (Found: C, 57.85; H, 6.1; N, 16.8. $C_{16}H_{20}N_4O_4$ requires C, 57.8; H, 6.1; N, 16.9%); $\nu_{max.}$(Nujol) 3 280, 2 120, 1 740, and 1 650 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.39 (9 H, s), 2.41 (3 H, s), 4.71 (2 H, br s), 6.93 (1 H, s), and 7.27 (5 H, s).

t-Butyl 2-ethoxycarbonyldiazoacetyl-2-(ethoxycarbomethyl)-hydrazine-1-carboxylate (**1e**) (28%), m.p. 73.5 °C (from ethyl acetate–light petroleum) (Found: C, 46.8; H, 6.2; N, 15.45. $C_{14}H_{22}N_4O_7$ requires C, 46.9; H, 6.2; N, 15.6%); $\nu_{max.}$(Nujol) 3 320, 2 135, 1 740, 1 700, and 1 640 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.39 (3 H, t), 1.44 (3 H, t), 1.48 (9 H, s), 4.27 (4 H, q), 4.40 (2 H, m), and 7.62 (1 H, br s); *m/z* 358 (M^+).

t-Butyl 2-acetodiazoacetyl-2-(ethoxycarbonylmethyl)hydrazine-1-carboxylate (**1f**) (53%), yellow oil (Found: M^+, 328.1382. $C_{13}H_{20}N_4O_6$ requires *M*, 328.1383); $\nu_{max.}$(neat) 3 300, 2 140, 1 740, and 1 660 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.32 (3 H, t), 1.50 (9 H, s), 2.50 (3 H, s), 4.28 (4 H, m), and 7.38 (1 H, br s); *m/z* 328 (M^+).

Benzyl 2-ethoxycarbonyldiazoacetyl-2-(ethoxycarbonylmethyl)hydrazine-1-carboxylate (**1g**) (27%), yellow oil (Found: M^+, 392.1329. $C_{17}H_{20}N_4O_7$ requires *M*, 392.1332); $\nu_{max.}$(neat) 3 320, 2 135, 1 730, and 1 700 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.25 (6 H, t), 4.21 (4 H, 2 × q), 4.39 (2 H, br s), 5.15 (2 H, s), 7.28 (5 H, s), and 7.95 (1 H, br s); *m/z* 392 (M^+) and 91 (base).

Benzyl 2-acetodiazoacetyl-2-(ethoxycarbonylmethyl)hydrazine-1-carboxylate (**1h**) (50%), yellow oil (Found: M^+, 362.1224. $C_{16}H_{18}N_4O_6$ requires *M*, 362.1226); $\nu_{max.}$(Nujol) 3 280, 2 125, 1 745, and 1 660 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.28 (3 H, t), 2.43 (3 H, s), 4.24 (2 H, q), 4.48 (2 H, br s), 5.21 (2 H, s), 7.38 (5 H, s), and 7.84 (1 H, br s); *m/z* 362 (M^+), 292, 251, and 91 (base).

General Procedure for the Rhodium(II) Acetate-catalysed Decomposition of the Diazo Hydrazides (**1**).—A solution of the diazo compound (**1**) (*ca.* 100—200 mg) in benzene (25—50 ml) was heated under reflux in the presence of rhodium(II) acetate (*ca.* 5—10 mg) until t.l.c. indicated that the diazo compound (1), which is strongly u.v. active, had been consumed. The catalyst was filtered off and the filtrate evaporated to give the product, which was purified by chromatography if necessary.

Decomposition of the Diazo Compound (**1a**).—Decomposition of the diazo compound (**1a**) (300 mg) in refluxing benzene for 0.5

h gave after chromatography, the imine (**4**) (160 mg, 59%) identical with a previously prepared sample.[11]

Decomposition of the Diazo Compound (**1b**).—Decomposition of the diazo compound (**1b**) (350 mg) in refluxing benzene (30 ml) for 2 h gave, after chromatography, *ethyl 1-benzyl-2-phenyl-3-oxo-1,2-diazetidine-4-carboxylate* (**2b**) (280 mg, 87%), m.p. 71.5 °C (Found: C, 69.5; H, 5.8; N, 8.9. $C_{18}H_{18}N_2O_3$ requires C, 69.7; H, 5.8; N, 9.0%); $\nu_{max.}$(Nujol) 1 783 and 1 750 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.20 (3 H, t), 4.16 (2 H, 2 overlapping q), 4.21 (2 H, AB, *J* 13 Hz), 4.57 (1 H, s), 7.18 (1 H, m), and 7.25—7.50 (9 H, m); *m/z* 310 (M^+), 282, 191, 118, 116, 105, and 91 (base), identical with a previously prepared sample.[12]

Decomposition of Diazo Compound (**1c**).—Decomposition of the diazo compound (**1c**) (128 mg) in refluxing benzene (30 ml) for 0.5 h gave *ethyl 2-benzyl-3-oxo-1-t-butoxycarbonyl-1,2-diazetidine-4-carboxylate* (**2c**) (107 mg, 91%) (Found: C, 60.9; H, 6.7; N, 8.3. $C_{17}H_{22}N_2O_5$ requires C, 61.1; H, 6.6; N, 8.4%); $\nu_{max.}$(neat) 1 805 and 1 750 br cm^{-1}; δ (90 MHz; $CDCl_3$) 1.26 (3 H, t), 1.48 (9 H, s), 4.27 (2 H, q), 4.78 (2 H, br s), 5.23 (1 H, s), and 7.37 (5 H, s); δ_c (62.9 MHz; $CDCl_3$) 13.9, 27.9, 51.6, 62.3, 75.8, 83.8, 128.0, 128.4, 128.6, 134.5, 158.0, 161.5, and 162.8; *m/z* 334 (M^+) and 234 (base).

Decomposition of the Diazo Compound (**1d**).—Decomposition of the diazo compound (**1d**) (210 mg) in refluxing benzene (50 ml) for 0.25 h gave *4-acetyl-2-benzyl-1-t-butoxycarbonyl-1,2-diazetidin-3-one* (**2d**) (192 mg, 100%) (Found: C, 63.0; H, 6.7; N, 9.25. $C_{16}H_{20}N_2O_4$ requires C, 63.1; H, 6.6; N, 9.2%); $\nu_{max.}$(neat) 1 795 and 1 725 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.48 (9 H, s), 1.91 (3 H, s), 4.66 (2 H, AB, *J* 15 Hz), 5.17 (1 H, s), and 7.28 (5 H, s); δ_c (62.9 MHz; $CDCl_3$) 27.5, 28.0, 51.8, 82.2, 84.1, 128.3, 128.7, 129.0, 134.8, 158.7, 161.6, and 196.1; *m/z* 304 (M^+), 204, 91, 85, 77, and 57 (base).

Decomposition of the Diazo Compound (**1e**).—Decomposition of the diazo compound (**1e**) (110 mg) in refluxing benzene (50 ml) for 1 h gave *ethyl 2-ethoxycarbonylmethyl-3-oxo-1-t-butoxycarbonyl-1,2-diazetidine-4-carboxylate* (**2e**) (96 mg, 95%) (Found: M^+, 330.1423. $C_{14}H_{22}N_2O_7$ requires *M*, 330.1427); $\nu_{max.}$(neat) 1 820, 1 750, and 1 730 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.28 (3 H, t), 1.36 (3 H, t), 1.50 (9 H, s), 4.25 (2 H, 2 × q), 4.32 (2 H, m), 4.36 (2 H, m), and 5.40 (1 H, s); δ_c (62.9 MHz; $CDCl_3$) 13.9 (2 carbons), 27.9, 49.6, 61.9, 62.5, 76.1, 84.1, 158.1, 162.5, 163.2, and 166.4; *m/z* no M^+, 230, 202, 157, 129, 115, and 57 (base).

Decomposition of the Diazo Compound (**1f**).—Decomposition of the diazo compound (**1f**) (164 mg) in benzene (30 ml) for 1 h gave *4-acetyl-2-ethoxycarbonylmethyl-1-t-butoxycarbonyl-1,2-diazetidin-3-one* (**2f**) (112 mg, 75%) (Found: C, 52.4; H, 6.3; N, 8.8. $C_{13}H_{20}N_2O_6$ requires C, 52.0; H, 6.7; N, 9.3%); $\nu_{max.}$(neat) 1 820 and 1 750 br cm^{-1}; δ (90 MHz; $CDCl_3$) 1.25 (3 H, t), 1.50 (9 H, s), 2.40 (3 H, s), 4.20 (2 H, q), 4.26 (2 H, m), and 5.32 (1 H, s); δ_c (62.9 MHz; $CDCl_3$) 13.9, 27.4, 27.9, 49.6, 61.9, 82.5, 84.1, 158.8, 163.2, 166.5, and 195.6; *m/z* 300 (M^+), 227, 202, 200, 127, 85, and 57 (base).

Decomposition of the Diazo Compound (**1g**).—Decomposition of the diazo compound (**1g**) (100 mg) in refluxing benzene (25 ml) for 0.5 h gave *ethyl 1-benzyloxycarbonyl-2-ethoxycarbonylmethyl-3-oxo-1,2-diazetidine-4-carboxylate* (**2g**) (88 mg, 93%) (Found: M^+, 364.1280. $C_{17}H_{20}N_2O_7$ requires *M*, 364.1271); $\nu_{max.}$(neat) 1 820 and 1 745 cm^{-1}; δ (90 MHz; $CDCl_3$) 1.24 (3 H, t), 1.29 (3 H, t), 4.18 (2 H, q), 4.26 (2 H, q), 4.30 (2 H, s), 5.20 (2 H, s), 5.43 (1 H, s), and 7.30 (5 H, s).

Decomposition of the Diazo Compound (**1h**).—Decomposition of the diazo compound (**1h**) (200 mg) in refluxing benzene (40 ml) for 0.5 h gave *4-acetyl-1-benzyloxycarbonyl-2-ethoxycarbonylmethyl-1,2-diazetidin-3-one* (**2h**) (152 mg, 82%) (Found: C, 57.3; H, 5.4; N, 8.4. $C_{16}H_{18}N_2O_6$ requires C, 57.5; H, 5.4; N, 8.4%); $\nu_{max.}$(neat) 1 820 and 1 740br cm^{-1}; δ (90 MHz; $CDCl_3$) 1.28 (3 H, t), 2.45 (3 H, s), 4.26 (2 H, q), 4.34 (2 H, m), 5.28 (2 H, s), 5.48 (1 H, s), and 7.40 (5 H, s); δ_c (62.9 MHz; $CDCl_3$) 14.0, 27.5, 50.0, 62.2, 69.2, 82.9, 128.5, 128.77, 128.82, 134.7, 159.9, 163.3, 166.6, and 195.1.

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