A New, One-Pot Preparation of Alicyclic Ketones via Wolff Rearrangement

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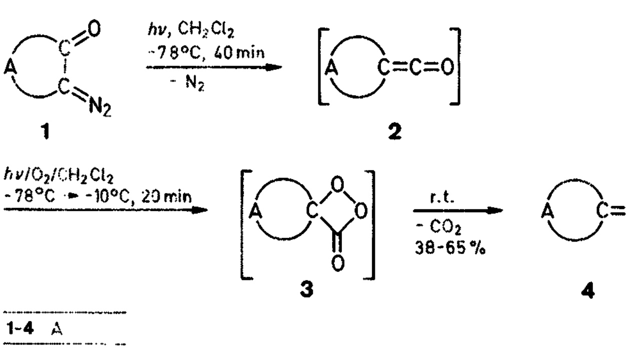
Photooxygenation of α-diazocycloalkanones leads to ring contraction via Wolff rearrangement to give cycloalkanones in moderate to good yields.

The Wolff rearrangement has found wide synthetic application[2] as well in the Arndt–Eistert synthesis[3] as in the ring contraction of cyclic α-diazo ketones[4] which, *inter alia*, gives access to unusual strained cyclic compounds.[5] It is known that singlet oxygen adds to electron-rich olefins to give relatively unstable 1,2-dioxetanes which decompose on warming to form carbonyl compounds.[6] The considerably less stable 3-oxo-1,2-dioxetanes (peroxy-α-lactones) can be obtained by reaction of ketenes with singlet oxygen.[7] Since α-diazo carbonyl compounds are readily accessible and rearrange upon irradiation to ketenes, we have combined the photolysis of cyclic α-diazo ketones **1** with the photooxygenation of the intermediary ketenes **2** in order to obtain ring-contracted cyclic ketones[8] **4** via intermediates **3**.



The photolyses of the α-diazo ketones **1a–d** were carried out in aprotic solvents at three different temperatures by irradiation with a Hanau TQ150 mercury lamp while passing oxygen through the reaction mixture. Best yields were obtained in dichloromethane at −78 °C (Table, conditions D). The use of other solvents (cyclohexane, petroleum ether, ether, chloroform, toluene, acetonitrile) or higher temperatures led to poorer yields. When the irradiation was carried out in the absence of oxygen and was followed by the addition of methanol, the methyl ester of the corresponding acid and a considerable amount of undefined material were obtained. That singlet oxygen is the oxidizing species was shown by the fact that under the same reaction conditions in the presence of 1,4-diazabicyclooctane, a singlet oxygen quencher,[10] only undefined material was obtained. Undefined material was obtained as the only product in a control experiment when oxygen was passed through the reaction solution in the dark after the solution had been irradiated for 45 min.

Table. Alicyclic Ketones **4** from Alicyclic α-Diazo Ketones **1**

1 → 4	Yield[a] (%) of 4				Identification of 4
	Reaction Conditions[b]				
	A	B	C	D	
a	14	27	36	42	GLC[c]
b	34	29	48	54	GLC[c]
c	72	43	64	65	mp 283–285 °C (Lit.[16] mp 285–286 °C)[c]
d	18	14	28	38	mp 210–212 °C (Lit.[17] mp 211–213 °C)[d]

[a] Yield of isolated and purified product.

[b] A: Oxygen is passed through the solution of **1** in benzene at room temperature from the beginning of irradiation.[9]
B: Oxygen is passed through the solution of **1** in CH_2Cl_2 at room temperature from the beginning of irradiation.[9]
C: Oxygen is passed through the solution of **1** in CH_2Cl_2 at −30 °C during the last 20 min of irradiation.
D: Oxygen is passed through the solution of **1** in CH_2Cl_2 at −78 °C during the last 20 min of irradiation.

[c] Comparison of IR, ^{1}H-, and ^{13}C-NMR spectra with those of authentic samples.

[d] IR, ^{1}H-, and ^{13}C-NMR-spectral data in accord with the published[16] data.

GLC analyses were carried out on a Varian Aerograph 1800 gas chromatograph (columns QF-1 or OV-101). Mass spectra were recorded on a Varian CH-7 mass spectrometer, IR spectra on a Perkin-Elmer 297 spectrophotometer, and ^{1}H- and ^{13}C-NMR spectra on a JEOL FX 90 FT spectrometer.

All solvents were dried and distilled before use. Silica gel (70–230 mesh) was purchased from Merck Chemical Co. Cyclohexanone and cycloheptanone were of commercial quality (Fluka Chemical Co). 4-Homoadamantanone[11] and 4-protoadamantanone[12] were prepared according to the published procedures and were characterized by spectroscopic means. The known α-diazo ketones **1a–c** were prepared as reported[13,14] and chromatographed on silica gel (0 → 30% Et_2O/pentane) immediately before use.

5-Diazo-4-protoadamantanone (1d):
Prepared by converting 4-protoadamantanone to the α-formyl ketone[15] and by treating this ketone with tosyl azide.[13] The structure proof is based on the spectrometric data.

$C_{10}H_{12}N_2O$	calc.	C 68.16	H 6.86	N 15.90
(176.2)	found	68.22	6.89	15.96

MS (70 eV): m/z = 176 (M^+, 37%); 148 (9); 120 (21); 105 (70); 92 (68); 91 (79); 79 (100).

IR (film): ν = 2940 (s); 2870 (m); 2070 (s); 1648 (s), 1372 (s); 1015 (s) cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.5–3.05 (m).

^{13}C-NMR ($CDCl_3$/TMS): δ = 31.49; 35.67; 35.72; 37.25; 38.15; 39.96; 41.76; 49.49; 65.35; 200.23.

Alycyclic Ketones 4a–d; General Procedure:
The α-diazo ketone **1a–d** (2 mmol) is dissolved in dry CH_2Cl_2 (80 mL) and this solution is cooled to −78 °C under N_2. Irradiation is performed with a Pyrex filter and a Hanau TQ150 high-pressure mercury lamp for 60 min. During the first 40 min, N_2 is bubbled through the solution and during the last 20 min a stream of O_2 (20 mL/min) is passed through the solution causing a rise in temperature to −10 °C. Evaporation of the solvent at room temperature and purification of the residue by column chromatography on neutral alumina (activity II/III) using 0 → 30% Et_2O/pentane as eluent affords the ketone **4** in > 97% purity (by GLC).

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