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Photodecarbonylation of 2,2,6,6-Tetrasubstituted Cyclohex-3-enones to Vinylcyclopropanes†

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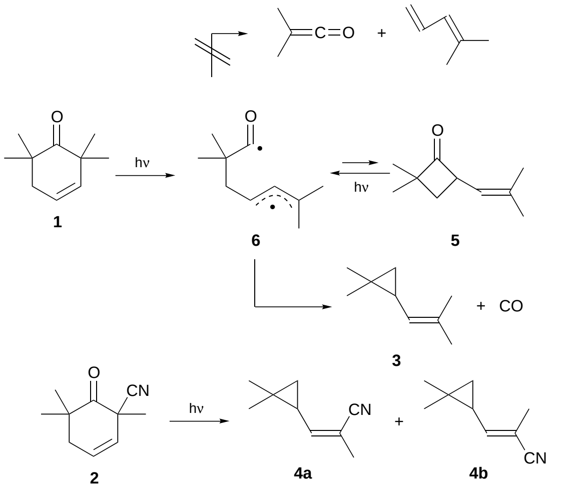
On irradiation ($\lambda = 300$ nm), 2,2,6,6-tetramethylcyclohex-3-enone (**1**) is cleanly converted into 1-(2,2-dimethylcyclopropyl)-2-methylpropene (**3**); similarly, 6-oxo-1,5,5-trimethylcyclohex-2-ene-1-carbonitrile (**2**) affords a mixture of (*Z*)- and (*E*)-3-(2,2-dimethylcyclopropyl)-2-methylpropenonitriles **4a** and **4b**.

The photorearrangement of bicyclooct-2-en-5-ones or bicyclohept-2-en-5-ones by a 1,3-acyl migration to yield (bicyclic) cyclobutanones occurs efficiently for a variety of systems, while subsequent photodecarbonylation has only been observed in a few cases.[1–5] Here we report the first examples of the light-induced conversion of monocyclic cyclohex-3-enones to vinylcyclopropanes.

2,2,6,6-Tetramethylcyclohex-3-enone (**1**) and 6-oxo-1,5,5-trimethylcyclohex-2-ene-1-carbonitrile (**2**) were obtained by methylation of 2,6,6-trimethylcyclohex-2-enone and 5,5-dimethyl-6-oxocyclohex-1-ene-1-carbonitrile, respectively. Irradiation of **1** in pentane up to total conversion affords **3** selectively in 75% yield, while irradiation of **2** affords a 4:1 mixture of **4a** and **4b**. Monitoring the irradiation of **1** in CD_3CN by ^1H NMR and GC–MS at a low degree of conversion ($<20\%$) indicated the formation of **3** (2/3) and an additional product **5** (1/3), the latter disappearing at higher degrees of conversion of **1**. Spectroscopic evidence allows the assignment of a cyclobutanone structure, *i.e.* the expected 1,3-acyl migration product, to **5**. From these findings it becomes evident that **5** is efficiently (photo)reconverted to its precursor, *i.e.* the biradical **6**, which undergoes only decarbonylation and subsequent 1,3-cyclization, to the exclusion of β-cleavage to dimethylketene and 4-methylpenta-1,3-diene (Scheme 1). This selectivity in the behaviour of **6** is most probably due to its (alkyl)substitution pattern,[6] the α-cleavage process (leading to **3**) being facilitated by the methyl groups on C(2) of the acyl–allyl biradical.

Experimental

NMR spectra (Bruker WM 400 spectrometer: ^1H, 400 MHz; ^{13}C, 100.62 MHz) were recorded in either $CDCl_3$ or CD_3CN as solvent. High-resolution mass spectra were recorded at 70 eV on a 311A (Varian MAT) spectrometer. Photolyses were run in a Rayonet RPR-100 photoreactor equipped with 300 nm lamps.



Scheme 1

Cyclohex-3-enones.—Treatment of 2,6,6-trimethylcyclohex-2-enone[7] with LDA–HMPT and MeI in THF,[8,9] and subsequent chromatography (SiO_2, pentane–diethyl ether, 15:1) afforded **1** in 47% yield as a colourless liquid, ^1H NMR and UV-spectrum identical to those reported;[10,11] δ_C ($CDCl_3$) 219.5 (C-1), 136.1 (C-4), 122.7 (C-3), 44.1 and 43.4 (C-2 and C-6), 38.5 (C-5), 27.0 and 25.6 (CH_3). Similarly, treatment of 5,5-dimethyl-6-oxocyclohex-1-ene-1-carbonitrile[12] and subsequent chromatography (SiO_2, pentane–ethyl acetate, 10:3) afforded **2** in 13% yield as a colourless oil; δ_H ($CDCl_3$) 6.02 (1 H), 5.76 (1 H), 2.38 (2 H), 1.58, 1.36 and 1.19 (CH_3); δ_C 206.2 (CO), 128.8 and 127.0 ($CH=CH$), 118.9 (CN), 44.2 and 42.3 ($>C<$), 39.2 (CH_2), 26.0, 25.2 and 23.8 (CH_3) (Found: M^+, 163.0997. $C_{10}H_{13}NO$ requires M_r 163.0996).

Preparative Irradiations.—An Ar-degassed solution of **1** (760 mg, 5 mmol) in pentane (50 ml) was irradiated for 6 h. After distillation of the solvent through a Vigreux column the residue was bulb-to-bulb distilled at 130 °C to give 1-(2,2-dimethylcyclopropyl)-2-methylpropene (**3**), 465 mg (75%), with ^1H and ^{13}C NMR spectra identical with those reported.[13] Similarly, an Ar-degassed solution of **2** (815 mg, 5 mmol) in pentane (50 ml) was irradiated for 8 h. After distillation of the solvent as above the residue, a 4:1 mixture of **4a** and **4b**, was separated by chromatography (SiO_2, pentane–diethyl ether 15:1) to afford first (*Z*)-3-(2,2-dimethylcyclopropyl)-2-methylpropenonitrile (**4a**), $R_f = 0.47$, as a colourless liquid, δ_H ($CDCl_3$ 5.79 (1 H), 1.93 (3 H), 1.73 (ddd, *J* 5.1, 8.4, 10.4 Hz), 1.30 and 1.10 (CH_3), 0.97 (dd, *J* 4.6, 8.4 Hz), 0.56 (t, *J* 4.8 Hz) (Found: M^+, 135.1041. $C_9H_{13}N$ requires M_r 135.1040), and then the *E*-diastereoisomer (**4b**), $R_f = 0.37$ as a colourless liquid, δ_H ($CDCl_3$) 6.00 (1 H), 1.91 (3 H), 1.44 (ddd, *J* 4.9, 8.1, 10.2 Hz), 1.23 and 1.21 (CH_3), 0.96 (dd, *J* 4.8, 8.1 Hz), 0.61 (t, *J* 4.9 Hz) (M^+, 135.1039. $C_9H_{13}N$ requires M_r 135.1040).

Detection of 2-(2-*Methylprop*-1-*enyl*)-4,4-*dimethylcyclobutanone* (**5**).—An Ar-degassed solution of **1** (1.52 mg, 1×10^{-2} mmol) in CD_3CN (1 ml) was irradiated for 10 min. Besides **1** (80%) and **3** (12%) there were ^1H NMR signals for **5**, δ_H 5.15 (1 H), 4.25 (1 H), 2.18 (t, *J* 11.7 Hz), 1.71 and 1.63 (CH_3), 1.58 (dd, *J* 8.1, 11.7 Hz), 1.22 (6 H). GC–MS analysis gave (M^+, 152.1341. $C_{10}H_{16}O$ requires M_r 152.1340).

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References

1 J. Salaün, in *Methods of Organic Chemistry (Houben-Weyl)*, ed. A. de Meijere, Thieme, Stuttgart, 1997, vol. E17, p. 1156.
2 V. Singh, B. Thomas and U. Sharma, *Tetrahedron Lett.*, 1995, **36**, 3421.
3 S. Katayama and M. Yamauchi, *Chem. Lett.*, 1995, 311.
4 J. Meinwald and P. J. van Vuuren, *J. Chem. Soc., Chem. Commun.*, 1971, 1460.
5 H. D. Scharf and W. Küsters, *Chem. Ber.*, 1971, **104**, 3016.
6 K. Hobel and P. Margaretha, *Res. Chem. Intermed.*, 1989, **12**, 263.
7 M. Baumann, W. Hoffmann and A. Nürrenbach, *Liebigs Ann. Chem.*, 1979, 1945.
8 G. Stork and R. l. Danheiser, *J. Org. Chem.*, 1973, **38**, 1775.
9 G. M. Rubottom and H. D. Juve Jr, *J. Org. Chem.*, 1983, **48**, 422.
10 W. Cocker, K. J. Crowley and K. Srinivasan, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2485.
11 R. K. Murray Jr. and D. L. Goff, *J. Chem. Soc., Chem. Commun.*, 1973, 881.
12 S. Andresen and P. Margaretha, *J. Chem. Res. (S)*, 1994, 332.
13 B. J. Fahie and W. J. Leigh, *Can. J. Chem.*, 1989, **67**, 1859.

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