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PHOTOCHEMICAL CYCLOADDITIONS OF THIOPARABANATES TO OLEFINS

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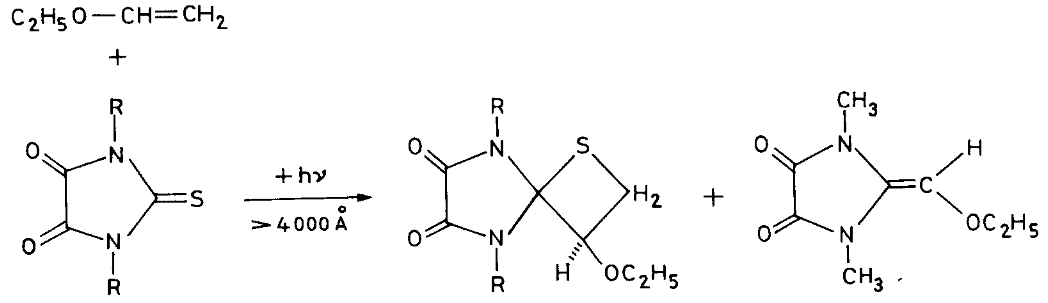
Diarylthioketones[1,2], thiophosgene[3], and thione carbonates[4] react with substituted alkenes under photochemical conditions to give thietanes and in some cases, 1,4-dithianes. It is known that thioparabanates, 1, undergo photoreduction in ethanolic solution[5]. However, the formation of a small amount (3%) of a thietane derivative has also been observed in the reaction of 1b with 2-methyl-2-butene[5]. In this communication, we would like to report that thioparabanates, 1, are highly reactive towards electron-rich and electron-poor olefins, if they are excited using light of proper wavelength.

It might be mentioned that the uv absorption spectrum (benzene) of 1,3-diphenyl-2-thioparabanate (1a) exhibits the n→π* transition of the C=S chromophore at 4450 Å (ε = 52), whereas, the long-wavelength π→π* transition lies at 3125 Å. Consequently, irradiation of 1 using light of wavelength >4000 Å allows a selective excitation of 1 to the n,π* state.

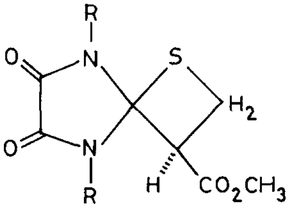


1a : R = C_6H_5 2a : R = C_6H_5 3

1b : R = CH_3 2b : R = CH_3

When a degassed benzene solution of 1a (0.014 m) and ethoxyethylene (0.32 m) was irradiated using >4000 Å light, colourless crystals of the spiro thietane derivative, 2a, were obtained in 88% yield, after recrystalization from methanol (2a: mp 198.5 - 200.5°; ir, 1745 cm^{-1} (C=O); nmr[6], τ = 8.79 (t, J = 7.1 Hz, CH_3), 7.73 (t, J = 8.5 Hz, CH), 7.28 (t, J = 8.5 Hz, CH), 6.44 (q, J = 7.1 Hz, OCH_2), 5.33 (t, J = 8.5 Hz, CH), 2.46 (mc, 2 C_6H_5); ms[7], *m/e* = 354 (M^+), 308 (M^+-CH_2S), 282 ($M^+-C_4H_8O$)). The peak at *m/e*, 308 strongly suggests that the ethoxy substituent is attached at the 3-position.

The photochemical reaction of 1b with ethoxyethylene, on the other hand, gave a mixture of 2b and 3 (65:35), in a 77% yield (2b: mp 138 - 139°; ir, 1738, 1720 cm^{-1} (C=O); nmr (C_6H_6), τ = 9.19 (t, J = 7.2 Hz, CH_3), 7.36 (d, J = 8.4 Hz, CH_2), 6.93 (q, J = 7.2 Hz, OCH_2), 7.03, 6.79 (2s, 2 NCH_3), 5.45 (t, J = 8.4 Hz, CH); ms, *m/e* = 230 (M^+), 184 (M^+-CH_2S), 158 ($M^+-C_4H_8O$); 3: mp 103-106° ; nmr, τ = 8.62 (t, J = 7.1 Hz, CH_3), 6.75, 6.44 (2s, 2 NCH_3), 5.95 (q, J = 7.1 Hz, OCH_2), 3.99 (s, =CH); ms, *m/e* = 184 (M^+)). The formation of 3 in this reaction may be rationalized in terms of the photofragmentation of 2b.



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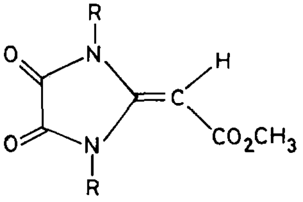

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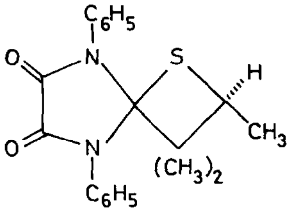
	R
a	C_6H_5
b	CH_3

Also, it has been observed that alkenes having electron-withdrawing substituents, react with 1 to give thietanes. Thus, irradiation of 1a in presence of methyl acrylate gave a mixture of 4a and 5a in a 45:55 ratio (4a: mp 122 - 124°; ir, 1750, 1726 cm^{-1} (C=O); nmr, τ = 7.56, 7.33 (2t, J = 9.0 Hz, CH_2), 6.28 (s, OCH_3), 5.44 (t, J = 9.0 Hz, CH), 2.46 (mc, 2 C_6H_5); ms, *m/e* = 368 (M^+), 322 (M^+-

CH_2S), 282 ($M^+-C_4H_6O_2$); 5a: mp 205 - 207°; ir, 1760, 1706, 1665 cm^{-1} (C=O); nmr, τ = 6.90 (s, OCH_3), 5.08 (s, $=CH_2$), 2.71 - 2.36 (m, 2 C_6H_5); ms, m/e = 322 (M^+)).

Similarly, the reaction of 1b with methyl acrylate yields a mixture of 4b (60%) and 5b (25%) (4b: mp 165.5 - 167°; ir, 1758, 1747, 1732 cm^{-1} (C=O); nmr, τ = 7.03 (t, J = 9.4 Hz, CH), 6.71, 6.66 (2s, 2 NCH_3), 6.46 (t, J = 9.4 Hz, CH), 6.30 (s, OCH_3), 5.26 (t, J = 9.4 Hz, CH); ms, m/e = 244 (M^+), 198 (M^+-CH_2S), 158 ($M^+-C_4H_6O_2$); 5b: mp 152 - 153°; nmr, τ = 6.70, 6.41 (2s, 2 NCH_3), 6.17 (s, OCH_3), 4.82 (s, =CH); ms, m/e = 198 (M^+)).

It has been reported that no photocycloaddition occurs between 1a and 2-methyl-2-butene[5]. In contrast, our findings show that the light-induced reaction of 1a in presence of 2-methyl-2-butene yields the 1:1-adduct, 6 in a 30% yield (6: mp 256 - 257°; ir, 1740 cm^{-1} (C=O); nmr, τ = 9.08 (d, J = 7.0 Hz, CH_3), 8.93, 8.85 (2s, 2 CH_3), 7.04 (q, J = 7.0 Hz, CH), 2.48 - 1.88 (m, 2 C_6H_5); ms, m/e = 352 (M^+), 292 ($M^+-C_2H_4S$), 282 ($M^+-C_5H_{10}$)).



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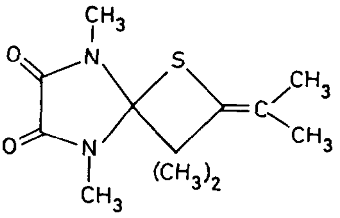

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Finally, the reaction of 1b with tetramethylallene under similar conditions gave a 22% yield of 7 (7: mp 207 - 208°; ir, 1740 cm^{-1} (C=O); nmr, τ = 8.52 (s, 2 CH_3), 8.36, 8.21 (2s, 2 CH_3), 6.56 (s, 2 NCH_3); ms, m/e = 254 (M^+), 168 ($M^+-C_4H_6S$), 158 ($M^+-C_7H_{12}$)).

The scope and mechanism of these photochemical cycloadditions are presently under investigation. All new compounds gave satisfactory analytical results.

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6. If not stated otherwise, the nmr spectra were taken in $CDCl_3$ with TMS as internal standard, on a Varian A60, spectrometer.
7. The mass spectra were determined using a AEI MS 902, mass spectrometer at 70 ev.