Photochemical Addition of Sulphonyl Cyanides to Olefins

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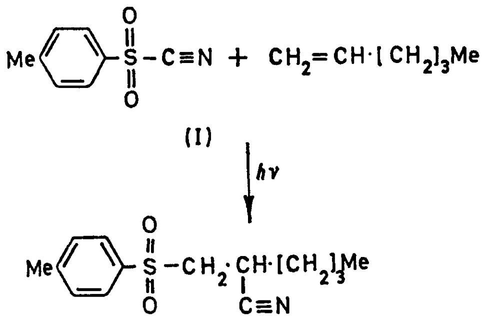
Summary The photochemical addition of toluene-*p*-sulphonyl cyanide to hex-1-ene, cyclohexene, and norbornadiene is reported.

RECENTLY, syntheses[1–3] and some chemistry[4–8] of the sulphonyl cyanide group have been reported. We now report a method for preparing *β*-cyanosulphones by the photoaddition of toluene-*p*-sulphonyl cyanide (I) to olefins; the first photochemical reaction of a sulphonyl cyanide group.

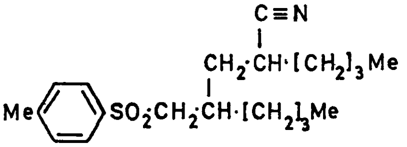
Toluene-*p*-sulphonyl cyanide (5·0 g) [λ_{max} (hexane) 236 (ϵ 15,900) and 268 nm (1220)] was dissolved in hex-1-ene–benzene (1 : 3 v/v; 100 ml) and irradiated under nitrogen in a Griffin–Srinivasan reactor at 2537 Å for 24 h to give 2-(tolyl-*p*-sulphonylmethyl)hexanenitrile (II).

In addition to the spectral data (see Table), further evidence for the addition of the sulphonyl function to the terminal carbon atom of the olefin was obtained by complexation with $Eu(fod)_3$ (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione).[9] After complexation, the average chemical shift of the non-equivalent methylene protons is *ca.* 0·5 p.p.m. downfield from the shift of the methine proton. Irradiation of (I) in neat hex-1-ene gave some chain-transfer product (III) as shown by the n.m.r. and mass spectra. Irradiation of (1) in cyclohexene–benzene (1 : 3) and in norbornadiene (1 : 3) gave *trans*-2-(tolyl-*p*-

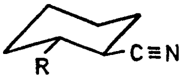


(I)

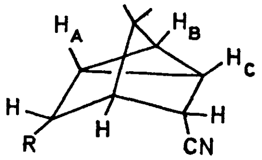
(II)



(III)



(IV)



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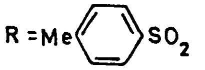

TABLE

Physical and spectral properties of the photoadducts of (I) *with olefins*

Olefin	Yield (%)	M.p. (°C)[a]	ν_{max}/cm^{-1}	(*m/e*)	N.m.r., δ/p.p.m.[b]
Hex-1-ene	77	38—40	2237 (C=N) 1321 (asym SO_2) 1135 (sym SO_2)	265 (parent ion)	0·9 (3H, m, aliphatic Me) 1·0—2·0 (6H, m, $[CH_2]_3$) 2·46 (3H, s, aromatic Me) 3·25, 3·40 (2H, m, $CH_2{\cdot}SO_2$) 3·10 (1H, m, CH·CN) 7·35, 7·82 (4H, m, ArH)
Cyclohexene	72	133—135	2283 (C=N) 1282 (asym SO_2) 1140 (sym SO_2)	263 (parent ion)	1·2—2·5 (8H, m, $[CH_2]_4$) 2·46 (3H, s, ArH) 2·90 (1H, m, CH·CN) 3·23 (1H, m, $CH{\cdot}SO_2$) 7·38, 7·81 (4H, m, ArH, $J_{CH{\cdot}CH}$ *ca.* 9·3 Hz)
Norbornadiene	22	202—204	2241 (C=N) 1287 (asym SO_2) 1152 (sym SO_2)	273 (parent ion)	1·75 (3H, m, $H_AH_BH_C$) 1·85, 2·59 (2H, m, CH_2) *ca.* 2·45 (2H, m, CH·CH·CN) 3·03 (1H, m, $CH{\cdot}SO_2$) 2·46 (3H, s, aromatic Me) 7·36, 7·78 (4H, m, ArH)

[a] All compounds reported gave satisfactory analyses.
[b] All n.m.r. data was obtained in $CDCl_3$ solution with tetramethylsilane.

sulphonyl)cyclohexanecarbonitrile (IV) and 5-(tolyl-*p*-sulphonyl)tricyclo[2,2,1,$0^{2,6}$]heptane-3-carbonitrile (V), respectively † The irradiation of (I) and 1-methylcyclohexene gave a complex mixture The reaction failed with acetylenes

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† No reaction was observed between (I) and cyclohexene when heated at 110 °C (sealed ampoule) for 20 h Heating (I) under reflux in cyclohexene without excluding oxygen leads to the formation of (IV)

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