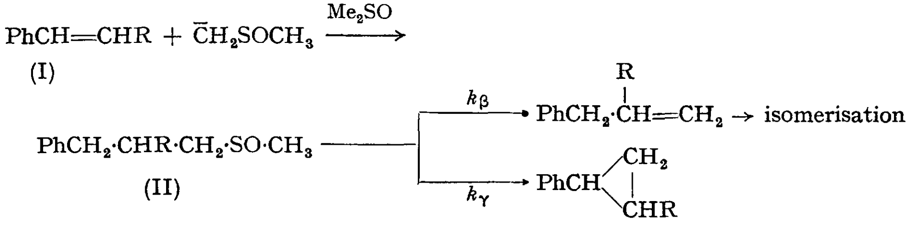
Formation of Cyclopropanes in γ-Elimination Reactions of Sulphoxides

By R. BAKER and M. J. SPILLETT
(*Chemistry Department, The University, Southampton*)

THE effect of leaving group in γ-eliminations has been examined previously.[1] We have found that both substituent and medium effects are extremely important factors in the competition between β- and γ-elimination reactions.

A number of 3-phenyl-2-alkylpropyl sulphoxides

(II), prepared by the reaction of β-alkylstyrenes (I) with the sodium salt of the anion of dimethyl sulphoxide ("dimsyl sodium"),[2] were allowed to react in dimethyl sulphoxide with a large excess (15 : 1) of dimsyl sodium for 48 hr. at 70°, and also with potassium amide in triethylamine for 24 hr. at 75°.



(1)

R = H, Me, Et, Pr^i, Bu^t.

The Table summarises the yields (%) of 1-phenyl-2-alkylcyclopropanes and olefins obtained from the reactions.

TABLE

R	$\overset{+}{Na}\overset{-}{C}H_2{\cdot}SO{\cdot}CH_3/Me_2SO$		KNH_2/Et_3N	
	Cyclopropane[a]	Olefin	Cyclopropane[a]	Olefin
H	0	3	0	32
Me	17	5	22	42
Et	50	19	13	51
Pr^i	67	8	32	50
Bu^t	97	0	38	50

[a] All cyclopropanes had *trans*-stereochemistry

The sulphoxide formed from 1,1-diphenylethylene[2] was also treated with base and shown to give 36% and 23% 1,1-diphenylcyclopropane in dimethyl sulphoxide and triethylamine respectively. The products were separated by distillation and gas-phase chromatography, and characterized by infrared, ultraviolet, and nuclear magnetic resonance spectra.

Some polymerisation of the olefin products probably occurred with the first two members of the series. The major components in the olefin fractions were those of the type PhCH=C(Me)R, *e.g.*, in Et_3N, where R = Bu^t and Pr^i, the yields were 50% and 41% respectively. Formation of small amounts of saturated products also occurred.

Particularly noteworthy is the quantitative yield of *trans*-1-phenyl-2-t-butylcyclopropane. Generally higher yields of cyclopropanes are formed in dimethyl sulphoxide ($\epsilon = 49$) than in triethylamine ($\epsilon = 3$). This would support the evidence already found that the β-elimination of sulphoxides proceeds essentially by an *E*2 process,[3] whereas the γ-elimination probably proceeds by an *E*1c*B* mechanism.[4] Dimethyl sulphoxide is known to favour ionic reactions since carbanions, although stable, are poorly solvated (*i.e.*, active); ion-pairing in this medium can have only minor importance.[5]

Reactions with sodamide in triethylamine were found to be slow, but the elimination of the sulphoxide (II; R = Pr^i) in dimethyl sulphoxide with dimsyl potassium has been studied; the yield of *trans*-1-phenyl-2-isopropylcyclopropane was 49%. Dependence of the yield of cyclic product upon the nature of the metal cation probably reflects the smaller selectivity of dimsyl potassium to β- and γ-eliminations, compared with that of the weaker base dimsyl sodium.

The decrease of β-elimination products with increasing size of alkyl group in the sulphoxide can be attributed to unfavourable inductive effects, increasing difficulty of the sulphoxide to achieve a favourable conformation for a *trans*-elimination, and factors which favour the cyclisation reaction. The formation of *trans*-1-phenyl-2-t-butylcyclopropane occurs so readily that 60% is produced in 3 hr. by the reaction of β-t-butylstyrene, in dimethyl sulphoxide, with dimsyl sodium at 60°. This, and the increase of cyclopropane formation with size of alkyl group, is in line with predictions based on the Thorpe–Ingold effect.[6]

(*Received, September* 13*th*, 1966; *Com.* 684.)

---

[1] C. L. Bumgardner, *Chem. Comm.*, 1965, 374.
[2] C. Walling and L. Bollyky, *J. Org. Chem.*, 1964, **29**, 2699.
[3] J. E. Hofmann, T. J. Wallace, and A. Schriesheim, *J. Amer. Chem. Soc.*, 1964, **86**, 1561.
[4] C. L. Bumgardner, *J. Amer. Chem. Soc.*, 1961, **83**, 4423.
[5] A. J. Parker, *Quart. Rev.*, 1962, **16**, 163.
[6] See T. C. Bruice and W. C. Bradbury, *J. Amer. Chem. Soc.*, 1965, **87**, 4838, for pertinent references.