Olefin Synthesis *via* Pyrolysis of *O*-t-Alkyl *N*-Toluene-*p*-sulphonylcarbamates

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Summary Pyrolysis of *O*-t-alkyl *N*-toluene-*p*-sulphonylcarbamates in bulk or in solution yields a mixture of *p*-tolylsulphonamide, CO_2, and olefins, which are partially isomerized under the reaction conditions.

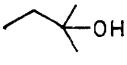
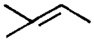
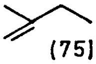
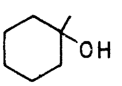
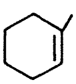
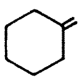
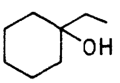
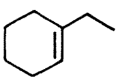
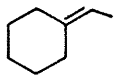
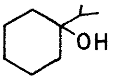
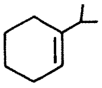
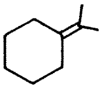
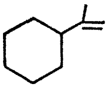
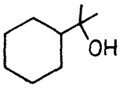
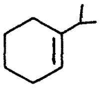
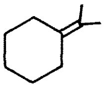
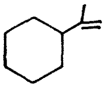
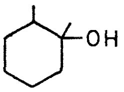
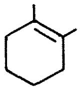
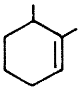
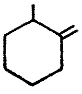
O-ALKYL *N*-TOLUENE-*p*-SULPHONYLCARBAMATES can be prepared in quantitative yield by the addition of toluene-*p*-sulphonyl isocyanate to alcohols.[1] We have observed that arylsulphonylcarbamate derivatives of tertiary alcohols exhibit poor thermal stability and cannot be stored at room temperature or recrystallized without noticeable decomposition. Therefore, the application of benzenesulphonyl isocyanates to the preparation of alcohol derivatives[2] should be undertaken with caution. Sulphonylcarbamate derivatives of tertiary alcohols should be prepared at low temperatures ($<10°$) and recrystallization should be omitted.

The thermal decomposition of alkyl toluene-*p*-sulphonylcarbamates proceeds slowly in the solid state but occurs rapidly in the melt at 100—150°. An analysis of the decomposition products obtained from t-pentyl toluene-*p*-sulphonylcarbamate (**1**) revealed that *p*-tolylsulphonamide, CO_2, and a mixture of 2-methylbut-1-ene (**2**) and 2-methylbut-2-ene (**3**) were formed in quantitative yield. The composition of the olefin mixture, as determined by g.l.p.c. and n.m.r., was 75% (**2**) and 25% (**3**). Since acid-catalysed dehydration of t-pentyl alcohol yields 98% (**3**), the thermal decomposition of the arylsulphonylcarbamates does not appear to depend upon the thermodynamic stability of the olefin formed.

Although the melt-pyrolysis technique minimizes the problems involved in product separation (the olefin is simply distilled from the mixture), the isolation of the arylsulphonylcarbamate is unnecessary. A solution of

0·02 mole tertiary alcohol in 20 ml of diglyme reacts with 0·021 mole of toluene-*p*-sulphonyl isocyanate (room temp., 30 min.) to give the corresponding alkyl toluene-*p*-sulphonylcarbamate: the solution is then heated to 150—170° to effect the decomposition of the carbamate. The olefin usually begins to distil from the solution when the pot temperature reaches 160° and is isolated in 50—60% yield. Arylsulphonylcarbamates derived from primary or secondary alcohols fail to decompose under these conditions but all the tertiary alcohols we have examined yield olefin mixtures (Table).

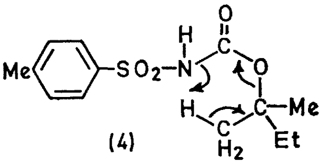
Thermal decomposition of t-alkyl toluene-*p*-sulphonylcarbamates

Alcohol	Olefin distribution[a] Saytzeff (%)		Hofmann (%)
	 (25)		 (75)
	 (95)		 (5)
	 (83·3)		 (16·7)
	 (83·6)	 (8·1)	 (8·3)
	 (58·1)	 (23·7)	 (18·2)
	 (36·4)	 (52·4)	 (11·2)

[a] Composition of olefin fraction determined with 10 ft. Ucon polar column at 95° and confirmed by n.m.r. spectroscopy.

The composition of the olefin mixture we obtained from *O*-t-pentyl *N*-toluene-*p*-sulphonylcarbamate (**1**) suggests that reaction is a concerted Hofmann elimination. A six-membered cyclic transition state (**4**) which favours the formation of the less-substituted olefin is consistent with this observation. A stepwise homolytic cleavage of the sulphonylcarbamate group is less likely because (**1**) failed to initiate the free-radical polymerization of methyl methacrylate when a solution of 30 mg of (**1**) in 3 ml of monomer was heated for 3 hr. at 100°. *The decomposition* of (**1**) was essentially complete under these conditions.

The results obtained from a series of cyclohexyl toluene-*p*-sulphonylcarbamates are not as conclusive. The more thermodynamically-stable olefin, Saytzeff product, is usually favoured and rearranged products are observed. In the case of methylcyclohexanol, the olefin distribution was similar to that observed in the dehydration catalysed by iodine or toluene-*p*-sulphonic acid,[3] which is known to proceed through a carbonium ion intermediate. The appearance of 2-cyclohexylpropene from 1-isopropylcyclohexanol requires a double-bond migration which probably involves intermediate carbonium ions. These results suggest that the decomposition of the sulphonylcarbamates occurs *via* an ion-pair intermediate (**5**) rather than a concerted cyclic mechanism. The ion-pair intermediate (**5**) could be converted by a hydride shift into (**6**), which would yield 2-cyclohexylpropene upon loss of a proton. Ion-pair intermediates have been suggested for similar low-temperature decompositions of alkyl derivatives including dialkyl oxalates,[4] alkyl hydrogen phthalate esters,[5] and dimethyl sulphoxide adducts.[6] The olefin compositions obtained from these ion-pair intermediates are comparable to the distribution reported in the Table, but there are some significant differences. For example, the major product obtained from the sulphonylcarbamate of 2-cyclohexylpropan-2-ol is 1-isopropylcyclohexene; this is definitely a minor component in the olefin mixtures obtained by the alternative procedures. The extent of exocyclic double-bond formation is also much lower than one would predict from a kinetically-controlled pyrolysis. It appears that the residual alkyl toluene-*p*-sulphonylcarbamate is catalysing the isomerization of the olefins to the Saytzeff product before we isolate them. This postulate was confirmed by equilibrating a mixture of 2-cyclohexylpropene (56%), isopropylidenecyclohexane (27·5%), and isopropylcyclohexene (16·5%) in diglyme (175°, 8 hr.) in the presence of *O*-isopropyl *N*-toluene-*p*-sulphonylcarbamate, which does not decompose under these conditions. Re-isolation of the olefin mixture by extracting the diglyme solution with pentane revealed that the Hofmann products had isomerized to produce the more thermodynamically favourable composition: isopropylcyclohexene (84%), 2-cyclohexylpropene (11%) and isopropylidenecyclohexane (5%). Therefore, a concomitant pyrolysis and olefin isomerization is occurring under our reaction conditions.



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