Ultrasound in Cycloaddition Reactions: Sound-promoted Dipolar Cycloadditions of Nitrones with Unactivated Alkenes

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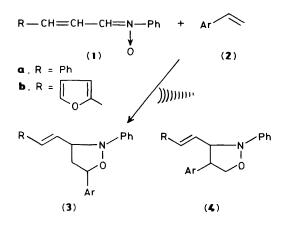
Ultrasound has been found to accelerate considerably the cycloaddition of unreactive conjugated nitrones with typical unactivated alkenes.

During the past few years ultrasound has proved to be a highly convenient and efficient way of accelerating slow reactions in heterogeneous media.¹ In particular its value has been well recognised in reactions, ³ and Reformatsky type reactions.⁴ During our work on this subject there have been few reports describing the use of this technique in cycloadditions.⁵ In particular we are not aware of any reports on the application of ultrasound to slow 1,3-dipolar cycloaddition reactions; we now describe our results in this area. Nitrones and in particular conjugated nitrones are somewhat unreactive dipoles because of considerable charge delocalisation. Therefore we chose to study conjugated nitrones and unactivated alkenes which require long times and drastic thermolytic conditions before they undergo cycloaddition.⁶ The conjugated nitrones (1) were prepared as reported earlier⁶ and their thermolytic reactions with alkenes under refluxing conditions were repeated. The same reactions under sonochemical conditions were successfully completed more quickly than the thermolytic reactions. All reactions were

Table 1. Comparison of sonochemical and thermal reactions.

Dipole	Dipolarophile	Sonochemical		Thermal ^a	
		Time	Yield, %	Time	Yield, %
(1 a)	Styrene	1 h	81	34 h	80
(1b)	Styrene	50 min	55	30 h	57
(1a)	Mesityl oxide	2.5 h	45	48 h	45
(1a)	4-Methylstyrene	50 min	72	24 h	70
(1a)	4-Chlorostyrene	55 min	75	24 h	75

^a Thermal reactions were carried out in refluxing benzene, since the use of toluene led to considerable amounts of resinous by-products.



conducted under homogeneous conditions. Yields and reaction times for the thermal and sonochemical reactions are in Table 1. A Virsonic cell disruptor with a direct immersed sonic horn was used as ultrasound source. The reaction mixture in toluene was sonified for 5 minutes and then left for 5 minutes during the times quoted. The maximum temperature of the isoxazolidine was obtained. In conclusion it appears that ultrasound should prove to be a useful technique in 1,3-dipolar cycloadditions, which are of considerable use in organic synthesis.

Received, 8th March 1988; Com. 8/00943K

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