Cycloaddition of Arylchlorocarbenes using Ultrasound

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An alternative method for the generation of arylchlorocarbenes using ultrasound is described.

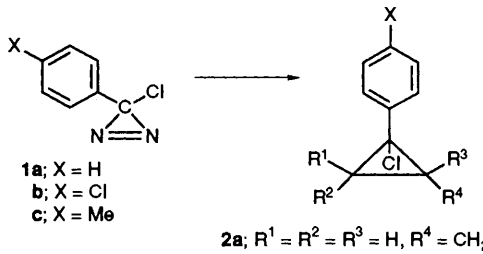
The use of ultrasound has its widest applications in heterogeneous reactions particularly in the field of organometallic chemistry.[1,2] However, there have been only a few reports on the application of sonochemistry in the area of carbenes. The generation of dichlorocarbene from NaOH–$CHCl_3$ in a two-phase system has been reported.[3] The major advantage of this new dichlorocarbene generation lies in the avoidance of phase-transfer catalysts. Cyclopropanation of diphosphenes with sonochemically generated halogenocarbenes using haloform and KOH pellets in hexane has been recently noted.[4]

We now report a procedure for the generation of carbenes by the ultrasonically induced decomposition of the corresponding diazirines. In the presence of olefin substrates, these carbenes may be trapped as cyclopropanes. As a result, this procedure should find broad application in small-scale preparations of cyclopropanes.

The arylchlorodiazirines[5] used in the present work display highly characteristic absorption in the accessible ultraviolet region, with a long wavelength band in the range of 330 to 390 nm. In addition, in the IR absorption spectrum, the N=N stretching frequency is very characteristic (1560–1580 cm^{-1}).

The procedure for the generation of carbene is extraordinarily simple. A solution of diazirine (0.5 mol dm^{-3}) and 2,3-dimethylbut-2-ene (1.0 mol dm^{-3}) in hexane solvent was placed in a round-bottomed flask equipped with a mechanical stirrer. The flask was immersed in a sonic cleaner (Fisher Scientific Solid State Ultrasound FS-9) and irradiated with ultrasound for 2 h. The temperature of the bath was 40 °C, a temperature at which all the diazirines were thermally stable. Analysis of the products were carried out by ^1H NMR, GC–MS, GC and also by comparison with authentic samples of cyclopropanes. The yields for cyclopropanes (Table 1) based on diazirines were calculated from the integrated areas of the components in the GC analysis using naphthalene as

Table 1 Arylchlorocarbene addition to olefins



2a; $R^1 = R^2 = R^3 = H$, $R^4 = CH_2Br$, X = H
b; $R^1 = R^4 = CO_2Et$, $R^2 = R^3 = H$, X = H
c; $R^1 = R^2 = R^3 = R^4 = Me$, X = H
d; $R^1 = R^2 = R^3 = H$, $R^4 = CH_2Br$, X = Cl
e; $R^1 = R^2 = R^3 = R^4 = Me$, X = Cl
f; $R^1 = R^4 = Cl$, $R^2 = R^3 = H$, X = Cl
g; $R^1 = R^2 = R^3 = H$, $R^4 = CH_2Br$, X = Me
h; $R^1 = R^2 = R^3 = R^4 = H$, X = Me
i; $R^1 = R^4 = Cl$, $R^2 = R^3 = H$, X = Me
j; $R^1 = R^4 = CO_2Et$, $R^2 = R^3 = H$, X = Me

Diazirine (0.5 mol dm^{-3})	Olefin substrate	Product	Yield (%) Photolysis	Ultrasound
1a	Allyl bromide (neat)	**2a** (*cis* + *trans*)	40	52
1a	Diethyl fumarate (1.0 mol dm^{-3})	**2b**	82	85
1a	2,3-Dimethylbut-2-ene (1.0 mol dm^{-3})	**2c**	90	63
1b	Allyl bromide (neat)	**2d** (*cis* + *trans*)	42	50
1b	2,3-Dimethylbut-2-ene (1.0 mol dm^{-3})	**2e**	90	67
1b	*trans*-Dichloroethylene (neat)	**2f**	80	64
1c	Allyl bromide (neat)	**2g** (*cis* + *trans*)	40	50
1c	2,3-Dimethylbut-2-ene (1 mol dm^{-3})	**2h**	85	75
1c	*trans*-Dichloroethylene (neat)	**2i**	80	74
1c	Diethyl fumarate (1 mol dm^{-3})	**2j**	78	82

internal standard. It is evident that the cyclopropane yields in the ultrasound experiments are similar to the yields obtained in photolysis.

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