

## Carbon Tetrachloride–Dimethyl Sulphone–Potassium Hydroxide–*t*-Butyl Alcohol: a Convenient New Reagent for *gem*-Dichloromethylenation of Alkenes

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The action of dimethyl sulphone–potassium hydroxide–*t*-butyl alcohol on carbon tetrachloride readily affords dichlorocarbene. In the presence of alkenes, *gem*-dichlorocyclopropanes are formed in moderate to high yields. The dichlorocarbene generated by this procedure adds stereospecifically to alkenes with retention of geometric configuration about the carbon–carbon double bond. Relative reactivities of alkenes towards the CCl<sub>4</sub>-derived dichlorocarbene parallel the nucleophilicities of the alkenes and indicate that free dichlorocarbene is probably involved.

Since the research of Hine<sup>1</sup> and of Doering and Hoffmann<sup>2</sup> three decades ago, various reagents designed for the generation of dichlorocarbene<sup>3</sup> have been described. In addition, several modifications<sup>4,5</sup> of the Doering–Hoffmann procedure<sup>2</sup> have appeared, of which the application of phase-transfer catalysis is a major improvement. In the course of these developments, the suitability of carbon tetrachloride as a precursor of dichlorocarbene was tested by several groups of workers,<sup>6–10</sup> using strong bases or organometallics as initiators. The results, though mechanistically interesting, offered at best marginal synthetic value for *gem*-dichloromethylenation of alkenes. We now report that carbon tetrachloride can be made into a useful dichlorocarbene progenitor by treatment with a mixture of potassium hydroxide, dimethyl sulphone, and *t*-butyl alcohol; this represents a new, inexpensive procedure for *gem*-dichloromethylenation of alkenes.

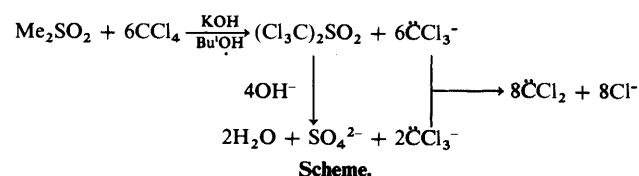
Our idea was formulated on the basis of the Meyers modification<sup>11–13</sup> of the Ramberg–Bäcklund rearrangement. In the Meyers procedure the reactions of a mixture of carbon tetrachloride, powdered potassium hydroxide, and *t*-butyl alcohol with sulphones containing  $\alpha$ -hydrogen atoms lead initially to  $\alpha$ -chloro-sulphones, which may be isolated or further transformed *in situ* into various types of product. The chlorination step is accompanied by the formation of dichlorocarbene, often regarded as undesirable. Although Meyers and his co-workers<sup>13</sup> suggested the modification of these reactions for *gem*-dichloromethylenation of alkenes, no full-scale exploration of this was performed. We undertook the present investigation to search for conditions under which the Meyers reaction might best be utilized as a method of dichlorocarbene generation.

### Results and Discussion

In the context of the Meyers reaction, the sulphone and the potassium hydroxide act as the agent releasing dichlorocarbene from carbon tetrachloride. In this capacity, the sulphone should ideally be a readily available compound, and itself be convertible into carbene-inert as well as easily removable co-products. Dimethyl sulphone was at once found to satisfy these requirements. It reacted exothermally with an excess of potassium hydroxide and carbon tetrachloride in *t*-butyl alcohol, decomposing almost exclusively into gaseous products and water-soluble substances in which the presence of sulphate ion was detected. A trace of organic residue contained mainly 2,2-dimethyl-1,1-dichlorocyclopropane.<sup>2</sup> Since alcohols have long been known to undergo dehydration under the conditions where dichlorocarbene is produced,<sup>14</sup> the observed *gem*-dichlorocyclopropane was simply an addition product from isobutene, which in turn originated from *t*-butyl alcohol.

In the presence of an alkene, the reagent CCl<sub>4</sub>–Me<sub>2</sub>SO<sub>2</sub>–KOH–Bu<sup>t</sup>OH effectively brought about dichloromethylenation at room temperature. The reaction was examined using cyclohexene as substrate; the best yield of 7,7-dichlorobicyclo-[4.1.0]heptane was obtained by employing a molar ratio (cyclohexene: CCl<sub>4</sub>: Me<sub>2</sub>SO<sub>2</sub>: KOH: Bu<sup>t</sup>OH) of 1:10:1:9:5. As expected, no noticeable reaction occurred without dimethyl sulphone.

Several additional features of the cyclohexene–CCl<sub>4</sub>–Me<sub>2</sub>SO<sub>2</sub>–KOH–Bu<sup>t</sup>OH system are noteworthy. First, although the amount of *t*-butyl alcohol used could be varied,<sup>13</sup> its omission seriously impeded the generation of dichlorocarbene. Secondly, so long as both the hydroxide and carbon tetrachloride were maintained in excess, cyclohexene required less than an equimolar amount of dimethyl sulphone for reaction. In a separate experiment run with the molar ratio of (cyclohexene: CCl<sub>4</sub>: Me<sub>2</sub>SO<sub>2</sub>: KOH: Bu<sup>t</sup>OH) 8:10:1:9:5, 3.3 mol equiv. of pure 7,7-dichlorobicyclo[4.1.0]heptane were isolated. These results clearly suggested that polychlorination of the sulphone occurred, thereby releasing from carbon tetrachloride a proportional number of trichlorocarbanions and thence dichlorocarbene. In principle, an eight-fold molar quantity of dichlorocarbene could be produced by the process depicted in the Scheme. The formation of sulphate ion noted








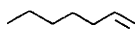
earlier suggests that some perchlorination occurs in the overall reaction, although the key intermediate bis(trichloromethyl) sulphone<sup>15</sup> has eluded isolation. Finally, as in the generation of dichlorocarbene by phase-transfer catalysis,<sup>4</sup> the present reaction does not require anhydrous conditions. In fact, addition of water (20% v/v) to the *t*-butyl alcohol did not appreciably lower the yield of the cyclohexene–dichlorocarbene adduct.

The reaction was extended to other alkenes, using the molar ratio (alkene: CCl<sub>4</sub>: Me<sub>2</sub>SO<sub>4</sub>: KOH: Bu<sup>t</sup>OH) 1:10:1:9:5. The results are summarized in Table 1. The yields of cyclopropane products range from moderate to high and compare favourably with those reported in most published procedures. However, as with other base-catalysed *gem*-dichloromethylenations of alkenes, extremely poor reactivity was encountered with those having feebly nucleophilic double bonds<sup>16</sup> (e.g. tetrachloroethene and *trans*-stilbene) or having base-sensitive function-

**Table 1.** *gem*-Dichlorocyclopropanes prepared by the reaction of alkenes with CCl<sub>4</sub>-Me<sub>2</sub>SO<sub>2</sub>-KOH-Bu'OH

Alkene	Dichlorocyclopropane	% Yield of isolated product based on alkene
2,3-Dimethylbut-2-ene	1,1-Dichloro-2,2,3,3-tetramethylcyclopropane	80
<i>cis</i> -Hex-2-ene	<i>cis</i> -1,1-Dichloro-2-methyl-3-propylcyclopropane	51
<i>trans</i> -Hex-2-ene	<i>trans</i> -1,1-Dichloro-2-methyl-3-propylcyclopropane	48
3-Ethylpent-2-ene	1,1-Dichloro-2,2-diethyl-3-methylcyclopropane	60
Hept-1-ene	1,1-Dichloro-2-pentylcyclopropane	77
Oct-1-ene	1,1-Dichloro-2-hexylcyclopropane	45
Non-1-ene	1,1-Dichloro-2-heptylcyclopropane	88
Cyclopentene	6,6-Dichlorobicyclo[3.1.0]hexane	58
Cyclohexene	7,7-Dichlorobicyclo[4.1.0]heptane	72
Cycloheptene	8,8-Dichlorobicyclo[5.1.0]octane	63
Cyclo-octene	9,9-Dichlorobicyclo[6.1.0]nonane	73
Styrene	1,1-Dichloro-2-phenylcyclopropane	77
$\alpha$ -Methylstyrene	1,1-Dichloro-2-methyl-2-phenylcyclopropane	75
1,1-Diphenylethene	1,1-Dichloro-2,2-diphenylcyclopropane	93

**Table 2.** Relative reactivities of alkenes towards the CCl<sub>4</sub>-derived dichlorocarbene at 50  $\pm$  1 °C

Alkene structure	Relative reactivity
	18.0
	7.8
	4.0
	1.3
	1.0
	0.2 <sup>a</sup>

<sup>a</sup> Hept-1-ene was run against styrene and the resulting value was re-normalized to cyclohexene.

alities<sup>17</sup> (e.g. allyl alcohol, allyl chloride, and vinyl acetate). In this respect, the present reagent is perhaps less versatile than phenyl(bromodichloromethyl)mercury.<sup>18</sup>

In line with expectation, the insertion of dichlorocarbene into alkenes, under the conditions of the Meyers reaction, occurred in a stereospecific manner, as in the Doering-Hoffmann reaction. Thus, the reactions of *cis*- and *trans*-hex-2-ene led to *cis*- and *trans*-1,1-dichloro-2-methyl-3-propylcyclopropane, respectively. The individual products were uncontaminated by each other within the limits of detection by g.l.c.

In an effort to understand better the nature of the CCl<sub>4</sub>-derived dichlorocarbene, we conducted a series of competitive experiments to determine the relative reactivities of various alkenes. Thus, 12 mol equiv. each of an alkene and cyclohexene were allowed to compete at 50  $\pm$  1 °C for the dichlorocarbene generated from carbon tetrachloride by the action of 1 mol equiv. of dimethyl sulphone and an excess of potassium hydroxide. Comparison of the amounts of the resulting *gem*-dichlorocyclopropane pairs by g.l.c. yielded the data in Table 2. These values correlate in general with the nucleophilicities of the olefinic double bonds and parallel the data reported by

Seyferth and his co-workers for the olefin-mercurial and olefin-sodium trichloroacetate systems<sup>18b,20</sup> studied at higher temperatures. In this context, the species produced by the present reagent may reasonably be regarded as 'free' dichlorocarbene.

### Experimental

Reagent-grade dimethyl sulphone, potassium hydroxide pellets, t-butyl alcohol, and carbon tetrachloride were used without further purification. Low-boiling alkenes were redistilled at atmospheric pressure except *cis*- and *trans*-hex-2-ene (Fluka, 99% purity by g.l.c.) which were used as purchased; styrene was freshly redistilled from calcium hydride under reduced pressure. Mass spectra were measured with a VG Micromass 7070F instrument. High resolution (300 MHz) <sup>1</sup>H n.m.r. spectra for *cis*- and *trans*-1,1-dichloro-2-methyl-3-propylcyclopropane were recorded at the University of Pittsburgh; peak assignments were based on decoupling results. Elemental analyses were performed by the Australian Microanalytical Service, Port Melbourne, Victoria.

*General Procedure for the gem-Dichloromethylenation of Alkenes by CCl<sub>4</sub>-Me<sub>2</sub>SO<sub>2</sub>-KOH-Bu'OH.*—Into a round-bottomed flask equipped with condenser and magnetic stirrer bar was placed a mixture of the alkene, carbon tetrachloride, dimethyl sulphone, and t-butyl alcohol in the molar ratio 1:10:1:5, respectively. To the stirred mixture finely pulverized potassium hydroxide (9 mol equiv.) was then added in one portion. In most cases, an exothermic reaction commenced within 15 min, causing the mixture to boil and gradually turning the contents into a thick paste. After the reaction subsided (1–1.5 h), water was added and the mixture was extracted with pentane. The combined extracts were successively washed with water, 5% hydrochloric acid, and water. The organic layer was dried (MgSO<sub>4</sub>) and evaporated *in vacuo* at room temperature. The residue was distilled either under atmospheric pressure or under appropriately reduced pressure to furnish the *gem*-dichlorocyclopropane. Representative preparations are illustrated below.

*7,7-Dichlorobicyclo[4.1.0]heptane.* To a stirred mixture of cyclohexene (3.28 g, 0.04 mol), dimethyl sulphone (3.76 g, 0.04 mol), carbon tetrachloride (38.5 ml, 0.4 mol), and t-butyl alcohol (19 ml, 0.2 mol) was added finely pulverized potassium hydroxide (22.4 g of the hydrate, 0.35 mol of KOH) in one portion. After 1.5 h (when the exothermic reaction had subsided) the mixture was cooled and water (200 ml) was added. The resulting mixture was extracted with pentane (3  $\times$  80 ml)

and the combined extracts were successively washed with water, 5% hydrochloric acid, and water. The dried ( $\text{MgSO}_4$ ) organic solution was concentrated *in vacuo* and the residue was vacuum-distilled over a short Vigreux column to give 7,7-dichlorobicyclo[4.1.0]heptane (4.75 g, 72%), b.p. 74–75 °C (11 mmHg),  $n_D^{24}$  1.5018 [lit.,<sup>4</sup> b.p. 78–79 °C (15 mmHg),  $n_D^{23}$  1.5014].

*cis*-1,1-Dichloro-2-methyl-3-propylcyclopropane. To a mixture of *cis*-hex-2-ene (2.75 g, 0.033 mol), dimethyl sulphone (3.10 g, 0.033 mol), carbon tetrachloride (32 ml, 0.33 mol), and *t*-butyl alcohol (16 ml, 0.17 mol) was added finely pulverized potassium hydroxide (18.5 g of the hydrate, 0.28 mol of KOH) in one portion. After 1.5 h the mixture was worked up as before. Distillation over a short Vigreux column afforded pure *cis*-1,1-dichloro-2-methyl-3-propylcyclopropane (2.78 g, 51%), b.p. 161–162 °C;  $n_D^{23}$  1.4592;  $\delta(\text{CDCl}_3)$  0.97 (t, 3 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.10 (d, 3 H, 2-Me), 1.28–1.56 (m, 5 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$  overlapped with the H-3 signal), and 1.61 (dq, 1 H, H-2);  $m/z$  170 [( $M+4$ )<sup>+</sup>, trace], 168 [( $M+2$ )<sup>+</sup>, 1.5%], 166 ( $M^+$ , 2.2), 127 [( $M-\text{CH}_2\text{CH}_2\text{CH}_3+4$ )<sup>+</sup>, 2.5], 125 [( $M-\text{CH}_2\text{CH}_2\text{CH}_3+2$ )<sup>+</sup>, 14.9], 123 [( $M-\text{CH}_2\text{CH}_2\text{CH}_3$ )<sup>+</sup>, 23.4], 114 [( $M-\text{CHCH}_2\text{CH}_2\text{CH}_3+4$ )<sup>+</sup>, 10.2], 112 [( $M-\text{CHCH}_2\text{CH}_2\text{CH}_3+2$ )<sup>+</sup>, 63.4], and 110 [( $M-\text{CHCH}_2\text{CH}_2\text{CH}_3$ )<sup>+</sup>, base] (Found: C, 50.2; H, 7.5; Cl, 42.8.  $\text{C}_7\text{H}_{12}\text{Cl}_2$  requires C, 50.3; H, 7.2; Cl, 42.4%), identical (b.p., n.m.r., i.r., and g.l.c.) with that obtained by reaction of *cis*-hex-2-ene with  $\text{CHCl}_3\text{-KOBu}^t$ .

*trans*-1,1-Dichloro-2-methyl-3-propylcyclopropane.\* Under the same reaction conditions and using the same isolation procedure as for *cis*-hex-2-ene, *trans*-hex-2-ene (2.75 g, 0.033 mol) gave *trans*-1,1-dichloro-2-methyl-3-propylcyclopropane (2.65 g, 48%), b.p. 156–157 °C;  $n_D^{23}$  1.4550;  $\delta(\text{CDCl}_3)$  0.96 (t, 3 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.00–1.08 (m, 1 H, H-3), 1.10–1.20 (m, 1 H, H-2), 1.27 (d, 3 H, 2-Me), and 1.40–1.63 (m, 4 H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ );  $m/z$  170 [( $M+4$ )<sup>+</sup>, trace], 168 [( $M+2$ )<sup>+</sup>, 0.9%], 166 ( $M^+$ , 1.3), 127 [( $M-\text{CH}_2\text{CH}_2\text{CH}_3+4$ )<sup>+</sup>, 3.0], 125 [( $M-\text{CH}_2\text{CH}_2\text{CH}_3+2$ )<sup>+</sup>, 17.0], 123 [( $M-\text{CH}_2\text{CH}_2\text{CH}_3$ )<sup>+</sup>, 27.4], 114 [( $M-\text{CHCH}_2\text{CH}_2\text{CH}_3+4$ )<sup>+</sup>, 10.3], 112 [( $M-\text{CHCH}_2\text{CH}_2\text{CH}_3+2$ )<sup>+</sup>, 64.6], and 110 [( $M-\text{CHCH}_2\text{CH}_2\text{CH}_3$ )<sup>+</sup>, base] (Found: C, 50.6; H, 7.5.  $\text{C}_7\text{H}_{12}\text{Cl}_2$  requires C, 50.3; H, 7.2%), identical (b.p., n.m.r., i.r., and g.l.c.) with that obtained by reaction of *trans*-hex-2-ene with  $\text{CHCl}_3\text{-KOBu}^t$ .

*Competitive Experiments.*—The competitive experiments were carried out in a round-bottomed flask equipped with condenser, internal thermometer, and stirring bar, and immersed in a bath containing briskly circulating water drawn from a large reservoir thermostatted at 50 °C. In a typical run, a mixture of an alkene (0.040 mol), cyclohexene (0.040 mol), dimethyl sulphone (3.3 mmol), carbon tetrachloride (0.2 mol), and *t*-butyl alcohol (0.085 mol) was treated with finely pulverized potassium hydroxide (0.1 mol). After 1–1.5 h, the mixture was worked up by addition of water and extraction with pentane. After concentration of the combined extracts under slightly reduced pressure at 15–20 °C, samples of the residue were analysed by g.l.c. using a 6 ft column of 10% SE-30 on Gas-Chrom Q under appropriate conditions where the two *gem*-dichlorocyclopropanes were clearly separated. Relative reactivities were determined by comparing the peak areas on the chromatograms. In the case of hept-1-ene, a clear separation of its dichlorocarbene adduct from 7,7-dichlorobicyclo[4.1.0]heptane could not be obtained. Consequently, hept-1-ene was run against styrene and the resulting relative reactivity value was re-normalized to cyclohexene.

The thermal conductivity detector of the chromatograph was calibrated with adduct pairs the individual components of which had been previously purified by preparative g.l.c. All competitions were carried out at least in duplicate, and the results reported in Table 2 are the averaged values.

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\* This compound was reported by Starks,<sup>4b</sup> but its physical constants and elemental analyses were not given.