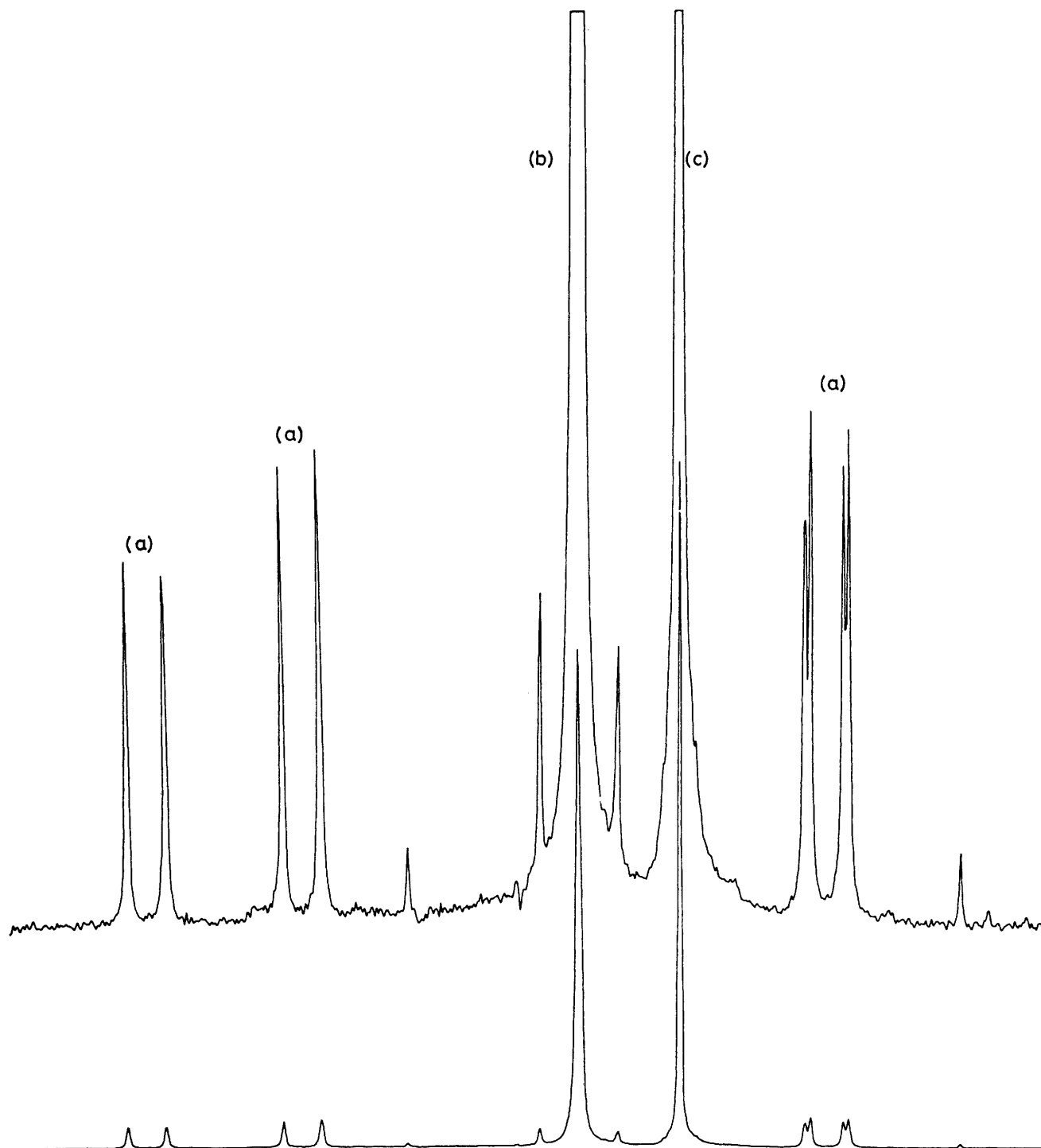




The reaction of 1,1'-diphenylethene with  $\text{OsO}_4$  was followed by  $^1\text{H}$  n.m.r. spectroscopy (400 MHz) at  $20^\circ\text{C}$  in  $\text{CDCl}_3$ , with particular reference to the olefinic region of the spectrum (Figure 1). On addition of  $\text{OsO}_4$ , the reaction mixture turned dark yellow, and the olefinic proton resonance,  $\delta$  5.45 (s, 2H) was seen to decay slowly as a resonance at  $\delta$  5.53 (s) corresponding to the osmium(vi) ester complex product developed. In addition to these two resonances four doublets could be clearly observed at  $\delta$  5.83, 5.72, 5.355, and 5.35 (all  $J$  11 Hz).

Irradiation at  $\delta$  5.83 led to the collapse of the doublet at  $\delta$  5.355 to a singlet, whilst irradiation at  $\delta$  5.72 led to the collapse of the doublet at  $\delta$  5.35 to a singlet. Likewise, irradiation of the two doublets centred at  $\delta$  5.35 led to the collapse of the other two doublets to singlets. In addition, the integrals of each of these doublets confirm that these resonances are due to two species in solution, each responsible for two doublets. After 2 h, the singlet at  $\delta$  5.45 due to free alkene had disappeared, and after 24 h the four doublets of the intermediate species



**Figure 1.**  $^1\text{H}$  N.m.r. spectrum (400 MHz) of reaction solution of  $\text{OsO}_4$  with 1,1-diphenylethene in  $\text{C}(\text{D}_2)\text{Cl}_3$  at  $20^\circ\text{C}$ : (a) asymmetric intermediate, (b) osmium(vi) ester product, (c) free alkene.

had decayed, leaving a singlet at  $\delta$  5.53 for the final dark-brown osmium(VI) product. During the course of the reaction, the phenyl region of the spectrum was too complex to be assigned with any confidence. Addition of pyridine to the above reaction solutions led to quenching of the intermediate species.

The spectral data described above are fully consistent with the formation in solution of low concentrations of two asymmetric intermediate species which we assign as involving four-membered ring species with an osmium to carbon bond, (5) and (6). The chemical shifts for protons  $H_\alpha$  and  $H_\beta$  are consistent with these structures, large downfield shifts being expected for these protons, as is observed for some substituted metallocyclobutane derivatives.<sup>10</sup> Attempts to obtain <sup>13</sup>C n.m.r. spectra of (5) and (6) have been dogged by concentration and relaxation problems associated with these species.

We have investigated the reaction of OsO<sub>4</sub> with a range of other disubstituted alkenes (*trans*-1,2-diphenylethene, *cis*-but-2-ene, and 2-methylprop-1-ene). Although the <sup>1</sup>H n.m.r. spectra obtained show features consistent with the formation of intermediates analogous to (5) and (6), low concentrations of side-products, presumably formed *via* carbon-carbon bond cleavage, or in the case of methyl substitution, by  $\beta$ -elimination reactions, complicate and hinder assignment of these spectra. This notwithstanding, our results with 1,1-diphenylethene are consistent with the formation of intermediate organometallic species, as previously proposed by Sharpless and co-workers,<sup>7</sup> and indicate a complexity of reactivity of alkenes with OsO<sub>4</sub> that has generally not been fully appreciated.

We thank the S.E.R.C. for financial support, and Professor Sir Jack Lewis and Dr W. P. Griffith for helpful advice and encouragement.

Received 14th April 1982; Com. 414

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