

## Formation of Abnormal Products in the Aluminium Chloride-catalysed Ene Additions of Chloral and Bromal to Mono- and 1,2-Di-alkyl Ethylenes

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**Summary** The title reactions afford products of apparent Friedel-Crafts acylation of the olefins by the acyl halides  $X_2CHCOX$  ( $X=Cl$  or  $Br$ ) as well as the expected ene adducts in many cases; the two types of products appear to be formed from a common dipolar intermediate.

THE formation of by-products in the Lewis acid-catalysed ene additions to less reactive olefins (*i.e.*, alkyl olefins other than 1,1-dialkylethylenes) has been noted by Snider<sup>1</sup> and by ourselves.<sup>2</sup> These observations have an important bearing upon the synthetic potential of catalysed ene reactions and their possible mechanisms. Our preliminary results are presented here.

The ene addition of chloral to 1,1-dialkylethylenes will occur thermally. The reactions are also catalysed by Lewis acids to give the ene adducts cleanly, and in high yield.<sup>2</sup> Only the catalysed reactions are effective for alk-1-enes and 1,2-dialkylethylenes,  $AlCl_3$  being the reagent of choice.† In these cases g.l.c. or <sup>1</sup>H n.m.r. analysis of the reaction mixtures showed the presence of abnormal reaction products. A parallel study on the catalysed reactions of bromal (a less reactive enophile) revealed a similar picture (Table) except that the abnormal products were formed in greater amounts; reaction of bromal with the 1,2-dialkylethylenes has so far been unsuccessful.

Structural assignments follow from the spectroscopic and analytical data; for example (1) and (2), respectively, are the

TABLE. Product ratios (ene adduct: abnormal product) formed in the  $AlCl_3$ -catalysed addition of chloral and bromal to olefins.

Olefin	Chloral	Bromal
Propene <sup>a</sup>	50:50	15:85
But-1-ene <sup>a</sup>	—	60:40
Hex-1-ene <sup>a</sup>	70:30	60:40
Hept-1-ene <sup>a</sup>	—	60:40
Oct-1-ene <sup>a</sup>	70:30	60:40
Allyl benzene <sup>b</sup>	33:67	—
Allyl bromide <sup>c</sup>	ca. 0:100	—
<i>cis</i> -But-2-ene <sup>b</sup>	67:33	—
<i>trans</i> -But-2-ene <sup>b</sup>	17:83	—
Cyclopentene <sup>b</sup>	95:5	—
Cyclohexene <sup>b</sup>	67:33	—
Cycloheptene <sup>b</sup>	50:50	—
Cyclo-octene <sup>b</sup>	95:5	—

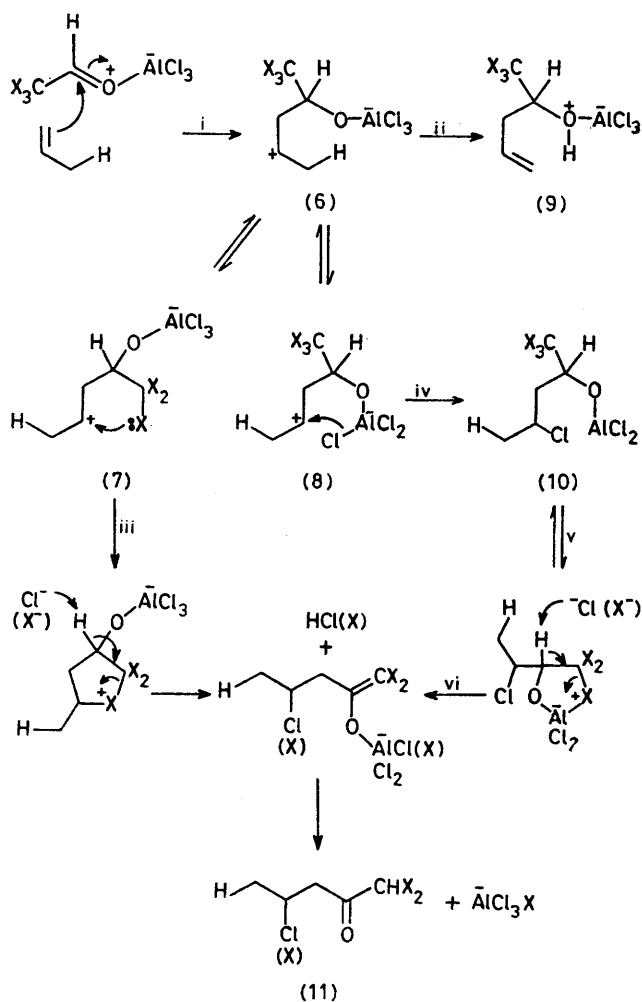
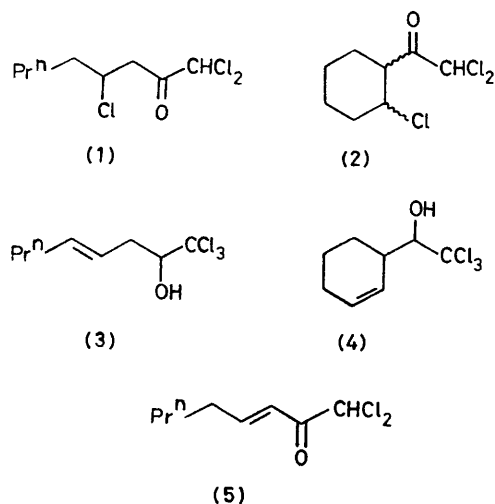
<sup>a</sup> 2 mol %  $AlCl_3$ . <sup>b</sup> 6 mol %  $AlCl_3$ . <sup>c</sup> 10 mol %  $AlCl_3$ .

abnormal products from reaction of chloral with hex-1-ene and with cyclohexene. The corresponding ene adducts have structures (3) and (4). The abnormal products are readily removed<sup>2</sup> (affording pure ene adducts), but are difficult to isolate because of their extreme sensitivity towards bases.‡ Even chromatography on silica gel is sufficient to convert (1) into (5); (3) and (5) are readily separated, as are related mixtures.

Control reactions indicate that the ene adduct: abnormal product ratios are independent of reaction time and of relative quantities or concentrations of the reactants

† Reactions were conducted in dry  $CCl_4$  or  $CH_2Cl_2$ . Yields of crude products were frequently > 80%.

‡ Isolation of the abnormal products from reactions of bromal with propene (g.l.c.) and with hex-1-ene (chromatography on aged silica gel) have been achieved (ene adducts and abnormal products co-distil *in vacuo*). Micro-analytical data have been obtained for the dinitrophenylhydrazone derivative of (1).



SCHEME. X = Cl or Br. For i—vi, see text.

(including, within limits, the  $\text{AlCl}_3$ ), nor are the two compounds interconverted under the reaction conditions. Such variations in solvent as are possible to study<sup>§</sup> indicated a small, but significant increase in the relative yield of the ene adduct with increasing solvent polarity for the bromal-hex-1-ene- $\text{AlCl}_3$  reaction. The two products are therefore formed by independent reaction pathways. Since (1) is not formed and dichloroacetyl chloride is recovered largely unchanged when treated with hex-1-ene and 2 mol %  $\text{AlCl}_3$  under the above reaction conditions, it follows that the abnormal products are not the result of the acylation of the alkenes by pre-formed  $\text{X}_2\text{CHCOX}$  ( $\text{X}=\text{Cl}$  or  $\text{Br}$ ) (abnormal product can be detected when 1 equiv. of  $\text{AlCl}_3$  is used at  $-78^\circ\text{C}$ ).

The variation in the product ratios (Table) appears to indicate the importance of both steric and electronic effects in determining the predominant reaction pathway. Assuming that the  $\text{AlCl}_3$ -catalysed ene additions of chloral or bromal to the 1,1-dialkylethylenes are concerted,<sup>¶</sup> it is envisaged that reaction of the less reactive olefins proceeds through the formation of a dipolar intermediate (e.g., 6). The ene adduct (9) or the abnormal product (11) could then arise as shown in the Scheme.

There is some evidence for the reactions at the beginning and end of the Scheme. Reaction of 3,3-dimethylbut-1-ene (which lacks the allylic H atom necessary to an ene reaction) with bromal- $\text{AlCl}_3$  afforded a mixture of the stereoisomeric 2-tribromomethyl-4,5,5-trimethyltetrahydrofurans (neopentyl rearrangement and ring closure) and no abnormal product. Similarly, 3-methylbut-1-ene (sterically hindered allylic H atom) gave no ene adduct but the analogous tetrahydrofurans (resulting from 1,2-hydride migration and ring closure) and a small quantity of the abnormal product (ca. 20%). Reaction of chloral- $\text{AlCl}_3$  with  $\alpha$ -pinene affords only products of skeletal rearrangement.<sup>2</sup> Carbonium ions are

<sup>§</sup> Solvents with appreciable Lewis basicity (e.g.,  $\text{Et}_2\text{O}$ ) preferentially complex the  $\text{AlCl}_3$  and prevent reaction; solvent variations were limited to seven chloro-alkanes (dielectric constants 2.24—10.36).

<sup>¶</sup> The lack of skeletal rearrangement (e.g., with  $\beta$ -pinene) or of double bond migration (e.g., with 2-methylbut-1-ene; see ref. 2) during the catalysed ene addition of chloral (or bromal) militates against dipolar or diradical intermediates in such reactions of 1,1-dialkylethylenes.

\*\* There is a reasonable alternative pathway from (10) by way of the dihalogeno-epoxide ( $\text{AlCl}_2\text{X}$  elimination) followed by epoxide-ketone rearrangement.

<sup>1</sup> B. B. Snider, *J. Org. Chem.*, 1976, **41**, 3061; B. B. Snider, L. A. Brown, R. S. E. Conn, and T. A. Killinger, *Tetrahedron Letters*, 1977, 2831.

<sup>2</sup> G. B. Gill and B. Wallace, *J.C.S. Chem. Comm.*, 1977, 380, 382.

<sup>3</sup> 'Friedel-Crafts and Related Reactions,' ed. G. A. Olah, Vol. I, Interscience, New York, 1963, p. 686.

implicated in each of these processes (cf. i, Scheme), and it appears that the energetically worthwhile Wagner-Meerwein type shifts are faster than steps ii—iv (Scheme). The intermediate (10) can, in principle, be generated from the halogeno-alcohol and  $\text{AlCl}_3$  (cf.  $\text{MeOH} + \text{AlCl}_3 \rightarrow \text{MeOH}\cdot\text{AlCl}_3 \xrightarrow{\text{heat}} \text{MeOAlCl}_2 + \text{HCl}$ ).<sup>3</sup> Reaction of dihydro-(3) with  $\text{AlCl}_3$  in  $\text{CCl}_4$  at reflux gave  $\text{HCl}$  and the dichloromethyl ketone, although the reaction was not very efficient. This result provides some evidence for steps v and vi (Scheme).\*\*

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