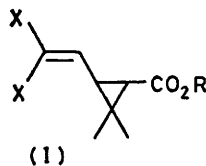


## Formation of 1,1-Dihalogeno-4-methylpenta-1,4-dienes by Reaction of Isobutene with Trihalogenoethylenes

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Isobutene reacts with trihalogenoethylenes in the gas phase at *ca.* 500° to give 1,1-dihalogeno-4-methylpenta-1,4-dienes which are precursors of photostable pyrethroid insecticides. The reaction appears suited to large scale continuous operation. The results are interpreted in terms of a free-radical chain mechanism.

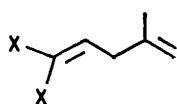
FOLLOWING the discovery, by Elliott *et al.*,<sup>1</sup> of the photostable pyrethroids, *e.g.* (Ib), intense effort has been devoted to devising suitable processes for the manufacture of these insecticides.<sup>2</sup> The acid moiety (Ia) of NRDC 143 (Ib) was originally prepared<sup>3</sup> from 1,1-dichloro-4-methylpenta-1,4-diene (II), which was in turn obtained from isobutene and chloral by a multistage synthesis<sup>3</sup> unsuitable for large scale operation. Our effort has been directed towards simple single stage processes for (II) using isobutene and readily available chloro-olefins. We have reported<sup>4</sup> on the oxidative coupling of isobutene with vinylidene chloride effected by palladium(II) salts. The present paper describes a vapour-phase reaction of isobutene with trichloroethylene to give (II) without the need of precious metal reagents.



a; R = H, X = Cl

b; R = CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>OPh-*m*, X = Cl

c; R = CH(CN)C<sub>6</sub>H<sub>4</sub>OPh-*m*, X = Br



(III) X = Br

### EXPERIMENTAL

**Materials.**—Isobutene (British Oxygen Co.), trichloroethylene (I.C.I. Mond Division), and peroxides (Laporte) were used as supplied. Tribromoethylene, (II), and 1,1-dibromo-4-methylpenta-1,4-diene (III) were prepared by literature methods.<sup>3,5</sup>

**General Procedure.**—The reactor system consisted of a vertical silica tube, of 30 ml capacity, mounted in a furnace. A stream of isobutene was passed down the tube continuously at atmospheric pressure at a rate of 30 ml min<sup>-1</sup> (as measured at 20°). Temperatures of individual runs are indicated in the Figure. Trihalogenoethylene (5.6 mmol) was injected continuously at a constant rate during 5 min, such that the liquid vaporised before reaching the reactor. Residence times were typically *ca.* 15 s. Peroxides (0.02 mmol), when used, were introduced as solutions in the trihalogenoethylene. Products were collected in an ice-cooled trap.

**Product Analysis.**—Products and recovered halogenoethylene were estimated by g.l.c. (2 m column of 30%

<sup>1</sup> M. Elliott, A. W. Farnham, N. F. Janes, P. H. Needham, D. A. Pulman, and J. H. Stevenson, *Nature*, 1973, **246**, 169.

<sup>2</sup> A. Bader, *Aldrichimica Acta*, 1976, **9**, 49.

<sup>3</sup> J. Farkas, P. Kourim, and F. Sorm, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2230.

ββ'-oxydipropionitrile on Embacel at 70°). The products (II), (IV), and (V) (Scheme) gave a single chromatographic peak and the distribution of these isomers was determined by <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy.

### RESULTS

**Product Stability.**—Following the general procedure, samples of (II) (10 μl) were introduced into the reactor in a flow of nitrogen (30 ml min<sup>-1</sup>) during 1 min. The results are tabulated. Similar treatment of *t*-butyl chloride (0.1 ml) at 500° gave a nearly quantitative yield of isobutene at 80% conversion.

#### Recovery of (II) at various temperatures

| Temperature (°C)   | 430 | 505 | 515 | 540 | 570 |
|--------------------|-----|-----|-----|-----|-----|
| Recovered (II) (%) | 95  | 70  | 60  | 40  | 40  |

**Identification of Products.**—With an isobutene flow of 100 ml min<sup>-1</sup>, trichloroethylene (0.100 mol) was introduced to the reactor at 540° during 15 min. Fractional distillation of the products gave (II) (0.013 mol) and *t*-butyl chloride (0.012 mol) both of which had <sup>1</sup>H n.m.r. and mass spectra identical to authentic samples. The isolated yields of (II) and *t*-butyl chloride were 65 and 60%, respectively, based on trichloroethylene consumed. 2,5-Dimethylhexa-1,5-diene (VI) was identified by its g.l.c. retention time and by mass spectroscopy. The results of other experiments with trichloroethylene are shown in the Figure.

Passage of tribromoethylene (0.2 ml) through the tube at 500°, in isobutene (40 ml min<sup>-1</sup>), gave a liquid product from which isobutene was allowed to evaporate. The residue contained a component having a g.l.c. retention time and <sup>1</sup>H n.m.r. and mass spectra identical to authentic (III). Of the total tribromoethylene passing through the reactor, 5% was converted into (III) and, of the tribromoethylene not recovered, 70% was converted into (III).

### DISCUSSION

The vapour-phase condensation of isobutene with trichloroethylene provides an attractive, one-step, high yielding route to (II) from relatively inexpensive feedstocks. Although pass conversions are low (5–30%), the unchanged olefins can be distilled readily from (II) and recycled. In addition, the process is well suited for continuous operation at atmospheric pressure.

The main features of the reaction can be interpreted<sup>6</sup> in terms of the Scheme. The ready abstraction of atomic hydrogen from isobutene yields methallyl radicals. Reaction of this radical with trichloroethylene

<sup>4</sup> D. Holland, D. J. Milner, and H. W. B. Reed, *J. Organometallic Chem.*, 1977, **136**, 111.

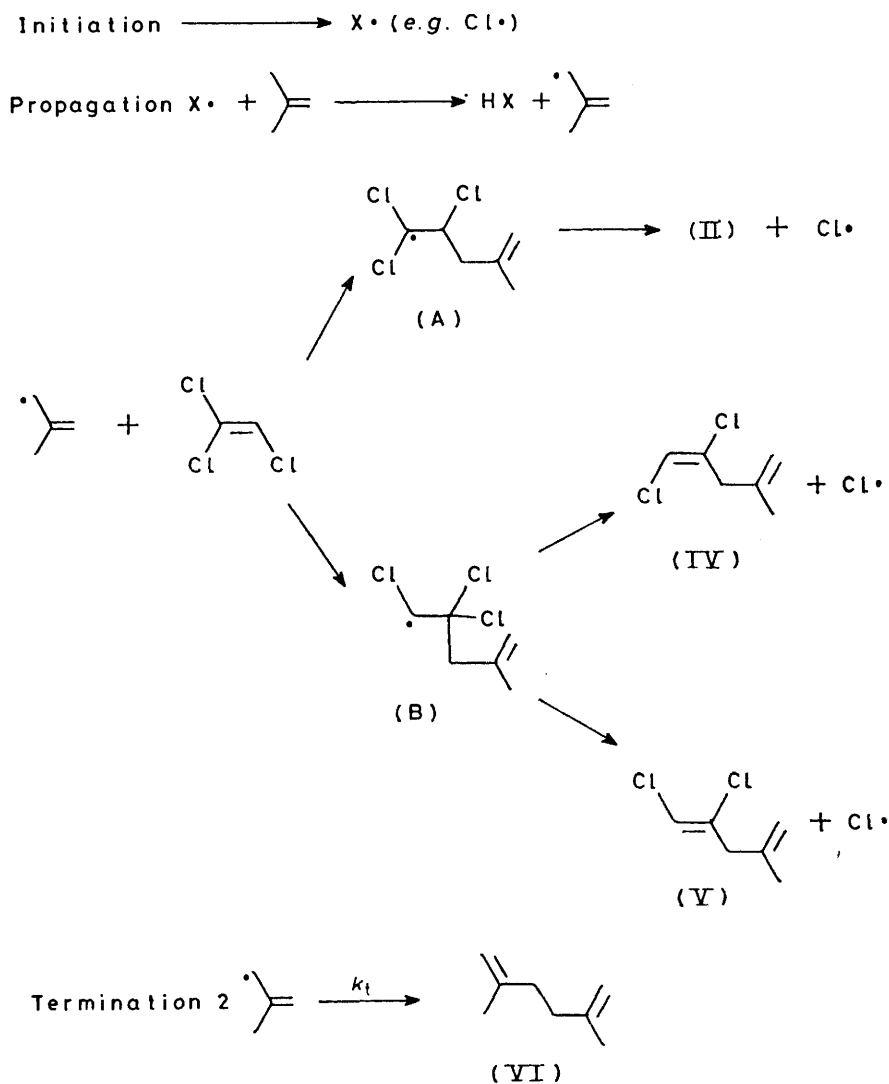
<sup>5</sup> W. H. Dehn, *J. Amer. Chem. Soc.*, 1912, **34**, 286.

<sup>6</sup> T. J. Hardwick, *Internat. J. Chem. Kinetics*, 1969, **1**, 325.

can give either species (A) or (B). Subsequent loss of atomic chlorine leads to (II), (IV), and (V) and to continuation of the chain reaction. The formation of (VI) suggests that termination is largely by dimerisation of methallyl radicals. The ratio [(II)]:[(IV) + (V)], determined by  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectroscopy, is 20:1, and this ratio may reflect the relative ease of formation of radical (A). Preferential formation of radical (A)

of *t*-butyl chloride through the reactor at  $500^\circ$  in a stream of nitrogen results in 80% conversion into isobutene. It is apparent, therefore, that *t*-butyl chloride is formed by addition of hydrogen chloride with unconsumed isobutene outside the heated reaction zone.

Initiation involves thermolysis of either trichloroethylene (which is stable below  $400^\circ$ ) or of added initiator. Thus, the presence of peroxide allows some



SCHEME

relative to (B) is expected both in terms of greater mesomeric stabilisation by adjacent chlorines in (A), and on the basis of lower steric repulsion for a methallyl radical attacking the less chlorinated carbon.<sup>7</sup>

Most of the hydrogen chloride eliminated in the coupling reaction appears in the products as *t*-butyl chloride. A calculation, based on group additivity tables,<sup>8</sup> indicates that *t*-butyl chloride is unstable towards loss of hydrogen chloride above  $200^\circ$ , and passage

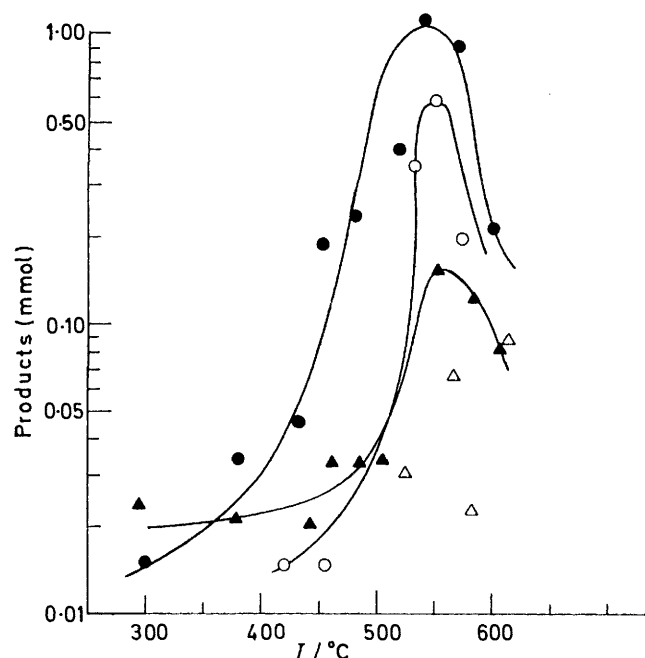
reaction to occur even at  $300^\circ$  (Figure). However, chain propagation is not sustained below *ca.*  $450^\circ$ . Following Hardwick's observations,<sup>6</sup> it seems likely that the displacement of chlorine atoms from trichloroethylene is the rate-limiting step in the chain.

Below  $520^\circ$ , the quantity of (VI) formed is nearly equivalent to the peroxide added. Above  $520^\circ$ , there is a fairly sharp increase in the formation of (VI) which probably results from initiation by decomposition of

<sup>7</sup> E. Sanhueza, I. C. Hisatsune, and J. Hecklen, *Chem. Rev.*, 1976, **76**, 801.

<sup>8</sup> S. W. Benson, 'Thermochemical Kinetics,' Wiley, London, 1968.

trichloroethylene. Thus, the yield of (VI) is a measure of the degree of initiation, and the ratio  $[(\text{II})] : [(\text{VI})]$  is



Products from trichloroethylene (5.6 mmol) in isobutene (30 ml  $\text{min}^{-1}$ ):  $\circ$ , (II);  $\triangle$ , (VI). Effect of t-butyl hydroperoxide (0.02 mmol):  $\bullet$ , (II);  $\blacktriangle$ , (VI)

proportional to the kinetic chain length  $k_p/k_t$ . At a peroxide level of 0.4% in the trichloroethylene, this ratio increases from 0.6 at 300 to 11.6 at 515°. These ratios,

<sup>9</sup> C. D. Wagner, *J. Phys. Chem.*, 1960, **64**, 231.

<sup>10</sup> S. W. Benson, A. N. Bose, and P. Nangia, *J. Amer. Chem. Soc.*, 1962, **85**, 1388.

and values for intermediate temperatures, closely follow the Arrhenius expression and give  $E_p - E_t$   $70 \pm 5$   $\text{kJ mol}^{-1}$ . At temperatures above 515°, both (II) and (VI) become increasingly unstable and  $[(\text{II})] : [(\text{VI})]$  no longer reflects values of  $k_p/k_t$ . Since termination by radical dimerisation has a very low activation energy,<sup>9</sup>  $E_p$  is ca. 70  $\text{kJ mol}^{-1}$ . As expected, this is much higher than the  $E_p$  of 21  $\text{kJ mol}^{-1}$  found<sup>6</sup> for the rate-limiting addition of cyclopentyl radicals to trichloroethylene. The difference between these activation energies is attributable to the mesomeric stabilisation of the methallyl radical, for which Benson<sup>10</sup> estimates a resonance energy of 50  $\text{kJ mol}^{-1}$ . This stabilisation of the methallyl radical appears to be completely lost in the transition state for chain propagation.

Reaction temperature and residence time are critical for the efficient synthesis of (II); with a given residence time, there is a narrow useful temperature range within which a sustained chain reaction occurs and the resulting (II) remains largely undecomposed (Figure).

Schmerling reported<sup>11</sup> that bromo-olefins are very much less reactive than are chloro-olefins towards radical substitution in the liquid phase at 130° due to the bulky bromine atoms. However, we find that isobutene reacts with tribromoethylene in the gas phase to yield (III), a precursor of NRDC 161 (Ic) and that the temperature dependence and conversions observed for this reaction are similar to those found for trichloroethylene.

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<sup>11</sup> L. Schmerling, *J. Org. Chem.*, 1975, **40**, 2430; U.S.P. 2,562,369/1968.