Intramolecular Homolytic Displacement of Bromine Atoms from Carbon in the Reaction of But-3-enyl Bromides with Radicals

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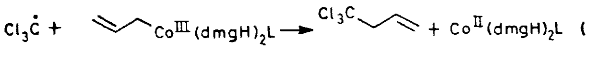
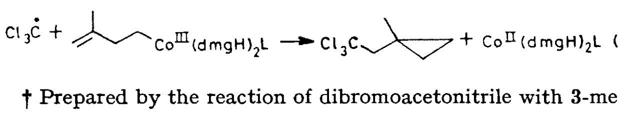
Summary The homolytic displacement of bromine atoms from 1-bromo-1-cyano-2,2-dimethylbut-3-ene by trichloromethyl radicals takes place by a stepwise mechanism in which a trichloromethyl radical attacks carbon-4 to give an intermediate radical which can undergo an intramolecular cyclisation with loss of a bromine atom or a radical transfer reaction with the addend.

In 1949, Kharasch described the formation of 4,4,4-trichlorobut-1-ene as a by-product in the reaction of bromotrichloromethane with allyl bromide under free radical conditions [equation (1)].[1] In our studies of the homolytic displacement of transition metal complexes from organometallic substrates by conventional free radicals, we observed a similar, but higher-yield, regiospecific reaction of trichloromethyl radicals with allylcobalt(III) complexes [equation (2)][2] (dmgH$_2$ = dimethylglyoxime) and extended the work to high-yield regiospecific reactions of trichloromethyl radicals with but-3-enylcobalt(III) complexes [equation (3)].[3] In neither of the latter two cases was it evident whether the displacement was concerted or proceeded through an intermediate adduct radical. We now describe some novel reactions which show that the attack of trichloromethyl radicals on but-3-enyl compounds can lead to intermediate radicals which can either react further with the trichloromethyl radical precursor or undergo an intramolecular cyclisation.

(1)

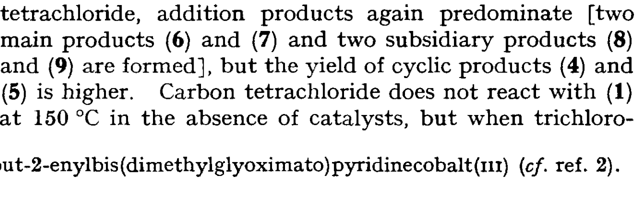


(2)



(3)

Thus, 1-bromo-1-cyano-2,2-dimethylbut-3-ene (**1**)† reacts with bromotrichloromethane at 110 °C in the presence of catalysts (FeCl$_3$–BuNH$_2$ or benzoyl peroxide)[4] to give two diastereoisomeric addition products (**2**) and (**3**), with only a trace of the cyclic products (**4**) and (**5**) [equation (4)]. In the corresponding catalysed reaction of (**1**) with carbon tetrachloride, addition products again predominate [two main products (**6**) and (**7**) and two subsidiary products (**8**) and (**9**) are formed], but the yield of cyclic products (**4**) and (**5**) is higher. Carbon tetrachloride does not react with (**1**) at 150 °C in the absence of catalysts, but when trichloro-



(4)

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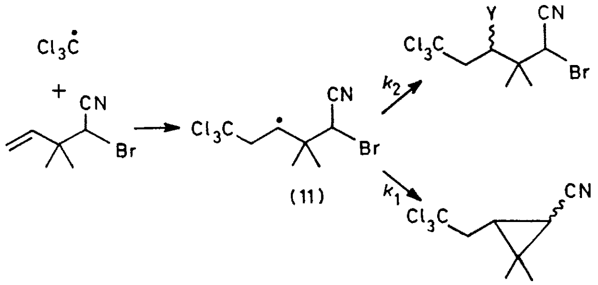
† Prepared by the reaction of dibromoacetonitrile with 3-methylbut-2-enylbis(dimethylglyoximato)pyridinecobalt(III) (*cf.* ref. 2).

methanesulphonyl chloride (**10**)[5] reacts with (**1**) in carbon tetrachloride or in heptane at 150 °C, the yield of cyclic products (**4**) and (**5**) not only increases as the concentration of (**10**) is decreased, but rises as high as 65% under optimum conditions. In all cases one isomer, presumed to be the *trans*-isomer (**5**), predominates.

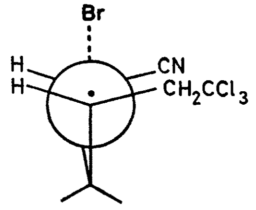
The cyclic products (**4**) and (**5**) could not be obtained from any of the addition products under the conditions of the above reactions, but were obtained by dehalogenation of a mixture of (**2**) and (**3**) with a zinc–copper couple in dimethylformamide. The products (**2**)—(**5**) were separated by h.p.l.c. and characterised by ^{1}H n.m.r. spectroscopy and elemental analysis. The products (**6**)—(**9**) were partially separated by h.p.l.c. but could not be purified sufficiently to establish with certainty the exact sequence and character of the five halogen atoms in the minor products (**8**) and (**9**).

The above results are consistent with a free radical chain process in which attack of a trichloromethyl radical at the δ-carbon of the butenyl group gives an intermediate (**11**) which can react further by either of the two paths shown in equation (5).‡ The choice between the two paths is a function of the concentration and character of the radical precursor Cl_3CX. Thus, with bromotrichloromethane in high concentration the abstraction of a bromine atom to give (**2**) and (**3**) takes place readily, whereas with trichloromethanesulphonyl chloride, especially at low concentrations, the atom abstraction process {rate = k_2[(**10**)][(**11**)]} is not favoured, and the intramolecular cyclisation {rate = k_1[(**11**)]} proceeds by default.

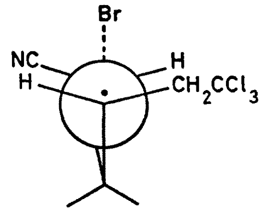


(5)

By analogy with our work on the displacement of cobalt(II) from but-3-enylcobalt(III) complexes,[3] we suppose that the predominant cyclic product is the *trans*-isomer (**5**) because of the greater steric hindrance between the cyano group and the trichloroethyl group in the transition state (**12**), leading to the *cis*-isomer (**4**), than in the transition state (**13**), leading to (**5**).

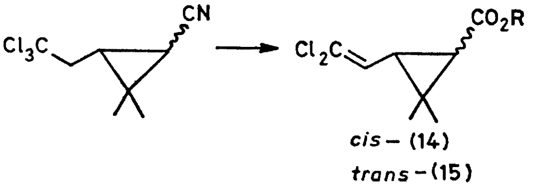


(**12**)



(**13**)

These results are of particular interest as a means of synthesis of esters of the type (**14**) and (**15**), which are potent and commercially important insecticides, although it is the *cis*-isomer (**14**) which is the more active.[6]



(6)

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‡ Minor products, formed as a result of reaction of the liberated bromine atoms, were not characterised.

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[2] A. Bury, C. J. Cooksey, T. Funabiki, B. D. Gupta, and M. D. Johnson, *J. Chem. Soc., Perkin Trans.* 2, 1979, 1050.

[3] M. R. Ashcroft, A. Bury, C. J. Cooksey, A. G. Davies, B. D. Gupta, M. D. Johnson, and H. Morris, *J. Am. Chem. Soc.*, submitted for publication.

[4] K. Kondon, K. Matsui, and A. Negishi in 'Synthetic Pyrethroids,' ed. M. Elliott, Amer. Chem. Soc. Symposium series No **42**, p. 128.

[5] We have used trichloromethanesulphonyl chloride as a convenient source of trichloromethyl radicals in these and related homolytic displacement reactions: A. E. Crease, B. D. Gupta, M. D. Johnson, E. Bialkowska, K. N. V. Duong, and A. Gaudemer, *J. Chem. Soc., Perkin Trans.* 1, 1979, 2611.

[6] M. Elliott, ref. 4 p. 1.