491. *The Homolytic Addition of Chloroacetone to Olefins.*

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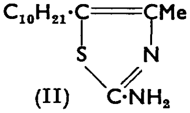
Chloroacetone adds homolytically to dec-1-ene to give 3-chlorotridecan-2-one, whose structure has been established by degradation. Addition proceeds less effectively with allylbenzene and ethyl undec-10-enoate, and fails with allylacetone, *cyclo*hexene, and ethyl crotonate. A chain mechanism is proposed.

CHLOROACETONE, under catalysis by benzoyl or *tert.*-butyl peroxide, adds homolytically to dec-1-ene, to give the chloro-ketone (I), whose constitution is established by the following evidence. (*a*) Reaction with thiourea gave the aminothiazole (II), characterised as the acetyl derivative, showing the adduct to be an α-chloro-ketone.[1] (*b*) Treatment with potassium hydroxide readily yielded the hydroxy-ketone (III) which was oxidised by potassium permanganate to decanoic acid. [Oxidation to decanoic rather than undecanoic acid might seem unexpected, but finds an analogy in a similar oxidation of the hydroxy-ketone (IV) to succinic acid in over 50% yield.[2]] The following chain mechanism for the addition is proposed :

$C_{10}H_{21}{\cdot}CHCl{\cdot}COMe$

(I)



(II)

$C_{10}H_{21}{\cdot}CH(OH){\cdot}COMe$

(III)

$Ph{\cdot}CO{\cdot}CH(OH){\cdot}[CH_2]_3{\cdot}CO_2H$

(IV)

(1) $CH_3{\cdot}CO{\cdot}CH_2Cl + R{\cdot}$ (from the peroxide) $\longrightarrow CH_3{\cdot}CO{\cdot}CHCl{\cdot} + RH$

(2) $CH_3{\cdot}CO{\cdot}CHCl{\cdot} + C_8H_{17}{\cdot}CH{=}CH_2 \longrightarrow C_8H_{17}{\cdot}\dot{C}H{\cdot}CH_2{\cdot}CHCl{\cdot}COMe$ (V) . (Initiation)

(3) (V) $+ CH_3{\cdot}CO{\cdot}CH_2Cl \longrightarrow$ (I) $+ CH_3{\cdot}CO{\cdot}CHCl{\cdot}$ . . . (Propagation)

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[1] Traumann, *Annalen*, 1888, **249**, 38; King and Hlavacek, *J. Amer. Chem. Soc.*, 1950, **72**, 3722; cf. Huang, *J.*, 1957, 1342.

[2] Huang and Williams, unpublished work.

That the initiating radical is $CH_3\cdot CO\cdot CHCl\cdot$ (reaction 1) and not $CH_3\cdot CO\cdot CH_2\cdot$ follows from the fact that the adduct is an α- and not a γ-chloro-ketone. This confirms previous findings that a hydrogen atom is more susceptible to attack by free radicals than is a chlorine atom, as in the cases of chloroacetic acid and chloroalkanes reported by Kharasch and his co-workers.[3] The structure of the adduct also shows that addition takes place initially at the end of the chain, to give the more resonance-stabilised intermediate radical (V), and thus conforms to the usual pattern of addition of other substances, *e.g.*, aliphatic aldehydes [4] and halogenated methanes,[5] to terminal double bonds, as that in oct-1-ene.

One marked departure from these known homolytic additions, however, is the relatively large quantities of catalyst required for any reasonable yield of the adduct. Thus 20 moles % of either peroxide gave only a 30% yield, the highest obtained. The yield dropped to 14—16% when only 10 moles % of benzoyl peroxide were used, under varied conditions, and moreover in each case at least a third of the olefin did not enter reaction despite presence of a large excess of chloroacetone. In all cases, considerable quantities of polymeric products were formed, although none of the " dimer " of chloroacetone (VI) was encountered. These results seem best explained by inefficient propagation rather than inadequate initiation, with some of the intermediate radicals undergoing telomerisation and dimerisation, instead of carrying on the chain.

In surveying the scope of this reaction, addition to different types of olefins was studied, under the optimum conditions found above. *cyclo*Hexene gave very little if any of the adduct, some polymeric products, and in contrast to dec-1-ene, much unchanged olefin, indicating inadequate propagation but excluding telomerisation as a major chain-breaking process. It is of interest that aliphatic aldehydes (*e.g.*, butanal) also add sluggishly to *cyclo*hexene.[4] Ethyl crotonate behaved similarly; although with this olefin the ready addition of butanal (77% yield) [6] presents a striking contrast.

To explore possible applications in synthesis the addition of chloroacetone to substances containing a terminal double bond and another functional group was investigated. Allylbenzene and ethyl undec-10-enoate afforded only modest yields of the adducts (VII) and (VIII), while allylacetone gave none of the expected (IX) under a variety of conditions. In contrast addition of butanal to these substances gave fair yields of the adducts (X), (XI), and (XII) respectively, although no attempts were made to ascertain the optimum conditions.

$(CH_3\cdot CO\cdot CHCl\cdot)_2$
(VI)

$Ph\cdot[CH_2]_3\cdot R$
(VII) $R = \cdot CHCl\cdot COMe$
(X) $R = \cdot CO\cdot C_3H_7$

$EtO_2C\cdot[CH_2]_{10}\cdot R$
(VIII) $R = \cdot CHCl\cdot COMe$
(XI) $R = \cdot CO\cdot C_3H_7$

$Me\cdot CO\cdot[CH_2]_4\cdot R$
(IX) $R = \cdot CHCl\cdot COMe$
(XII) $R = \cdot CO\cdot C_3H_7$

EXPERIMENTAL

Addition of Chloroacetone to Dec-1-*ene*.—(*a*) Benzoyl peroxide (2·9 g., 0·012 mole) was added in 4 portions during 6 hr. to a mixture of dec-1-ene (n_D^{21} 1·4201; 8·9 g., 0·064 mole) and chloroacetone (46 g., 0·48 mole) at 70—75° under nitrogen. Heating was continued for 3 hr. more, for the last hr. at 85—90°. There was some evolution of hydrogen chloride during the last stages of heating. Excess of chloroacetone was removed under reduced pressure (b. p. 52°/70 mm.), and the product diluted with ether and washed five times with 5% aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated. Distillation then gave (i) a forerun, from which benzoic acid separated (*ca.* 0·2 g.; m. p. and mixed m. p.); (ii) 3-*chlorotridecan*-2-*one*, b. p. 102°/1 mm., $n_D^{21\cdot5}$ 1·4546 (4·8 g., 30%); and (iii) a residue (4·0 g.), which did not distil at 175° (bath)/1 mm. Further distillation of fraction (ii) gave a pure sample, b. p. 100° (bath)/0·5 mm., n_D^{20} 1·4521 (Found: C, 67·4; H, 10·7; Cl, 15·2. $C_{13}H_{25}OCl$ requires C, 67·1; H, 10·75; Cl, 15·3%). With semicarbazide and sodium acetate in aqueous ethanol it gave low yields of a solid, m. p. *ca.* 150—160°, which appeared to be a mixture of semicarbazones.

[3] Kharasch, Urry, and Jensen, *J. Amer. Chem. Soc.*, 1945, **67**, 1626; *J. Org. Chem.*, 1945, **10**, 386; Kharasch and Büchi, *J. Amer. Chem. Soc.*, 1951, **73**, 632.

[4] Kharasch, Urry, and Kuderna, *J. Org. Chem.*, 1949, **14**, 248.

[5] Kharasch, Jensen, and Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1100.

[6] Huang, *J.*, 1956, 1749.

(*b*) Under the same conditions but with 10 mole % of benzoyl peroxide and a 5 mole excess of chloroacetone, dec-1-ene (21 g.) gave a product which on distillation yielded : (i) unchanged decene, b. p. 48°/50 mm. (6·5 g.); (ii) material of b. p. 108—113°/4 mm. (*ca.* 1·5 g.); (iii) 3-chlorotridecan-2-one, b. p. 113°/4 mm., n_D^{20} 1·4546 (3·7 g., 14% yield, calc. on decene consumed); and (iv) a residue (7 g.).

(*c*) Using the same quantities of reactants as in (*b*) but adding the catalyst in 3 portions during 20 hr., and heating the mixture at 70° for a total of 26 hr., gave a 16% yield of adduct.

(*d*) Dec-1-ene (14 g., 0·10 mole), chloroacetone (56 g., 0·60 mole), and di-*tert.*-butyl peroxide (2·9 g., 0·02 mole) were heated together at 125—130° under reflux in nitrogen for 44 hr. After removal of the volatile fractions and of excess of chloroacetone, the product on distillation gave 3-chlorotridecan-2-one, b. p. 106—108°/*ca.* 2 mm., $n_D^{21\cdot5}$ 1·4508 (7·0 g., 30%). There was an undistillable residue (6·8 g.).

Reaction with Thiourea.—The above adduct (1·0 g.) and thiourea (0·33 g.) were refluxed in absolute ethanol (*ca.* 10 c.c.) for 20 hr. Most of the ethanol was distilled off and the residue treated with concentrated aqueous ammonia (20 c.c.), and the oil which separated taken up in ether, washed with water, dried, and after removal of the solvent heated with acetic anhydride (10 c.c.) and acetic acid (1 c.c.) at 90° for 6 hr., and boiled for 5 min. The solution was poured on ice, and the solid which separated was recrystallised from aqueous ethanol, then from methanol, giving 2-*acetamido*-5-*decyl*-4-*methylthiazole*, needles, m. p. 75° (0·8 g.) (Found: N, 9·3; S, 10·9. $C_{16}H_{28}ON_2S$ requires N, 9·4; S, 10·8%).

Degradation.—(*a*) 3-Chlorotridecan-2-one (1 g.) was unaffected by potassium acetate (1 g.) in acetic acid (10 c.c.) at 80° for 16 hr.

(*b*) The chloro-ketone (2·6 g.) in absolute ethanol (*ca.* 5 c.c.) was mixed with potassium hydroxide (0·75 g.) in the same solvent (10 c.c.). The mixture became warm, darkened, and soon deposited a yellow precipitate. After 24 hr. at room temperature, acetic acid (0·5 c.c.) was added, the solid filtered off, and the filtrate concentrated by distillation, then poured on ice, and extracted with ether. After being washed with aqueous sodium hydrogen carbonate and water, dried, and freed from solvent, the product was distilled, to give two fractions of the same refractive index, n_D^{21} 1·4481, b. p. 100—110° (bath)/0·4 mm. (1·5 g., 68%). A sample of this gave a good yield of 3-*hydroxytridecan*-2-*one semicarbazone*, needles (from aqueous ethanol), m. p. 173—174° (Found : C, 62·0; H, 10·65; N, 16·0. $C_{14}H_{29}O_2N_3$ requires C, 61·95; H, 10·8; N, 15·5%).

The above hydroxy-ketone (1·0 g.) in acetone (20 c.c.) was treated [7] with potassium permanganate (1·6 g.) and magnesium sulphate (0·6 g.) in water (20 c.c.). A slight rise in temperature was noted. The mixture was heated under reflux for 90 min., then filtered, and the colourless filtrate concentrated on the steam-bath to *ca.* 25 c.c. 20% Aqueous sodium carbonate (5 c.c.) was added, and the solution washed with ether, then acidified with 5N-sulphuric acid, and the oil which separated was taken up in ether and dried. On removal of ether, the oily acid obtained was converted *via* the acid chloride into the decananilide, needles (from aqueous ethanol), m. p. and mixed m. p. 69—70° (0·5 g.) (Found : N, 5·44. Calc. for $C_{16}H_{25}ON$: N, 5·66%). When mixed with a sample of undecananilide of m. p. 68°, it melted at 59—62°.

Other Addition Reactions of Chloroacetone.—(a) *Ethyl undec*-10-*enoate.* This ester (21 g., 0·10 mole; n_D^{22} 1·4375) with chloroacetone (46 g., 0·50 mole) and benzoyl peroxide (2·4 g., 0·01 mole) gave, by procedure (a), fractions : (i) unchanged ester, b. p. 83—84°/1 mm., n_D^{22} 1·4393 (10·6 g.); (ii) a pale yellow liquid, b. p. *ca.* 158°/1 mm., n_D^{22} 1·4615 (1·5 g.); (iii) undistillable residue (10·0 g.). Fraction (ii) on further distillation gave *ethyl* 12-*chloro*-13-*oxotetradecanoate*, b. p. 150° (bath)/0·5 mm., n_D^{21} 1·4612 (Found: Cl, 11·2. $C_{16}H_{29}O_3Cl$ requires Cl, 11·6%).

(b) *Allylbenzene.* Allylbenzene (12 g., 0·10 mole), chloroacetone (58 g., 0·63 mole), and benzoyl peroxide (4·8 g., 0·02 mole) after 20 hr. at 65° and 1 hr. at 85° gave, on fractionation, 3-*chloro*-6-*phenylhexan*-2-*one*, b. p. 97—102°/1 mm. (1·0 g.), n_D^{20} 1·5258 (Found: Cl, 16·9. $C_{12}H_{15}OCl$ requires Cl, 16·8%).

(c) *Allylacetone* (n_D^{21} 1·4193; see Schechter *et al.*[8]). No adduct was obtained by using (*a*) benzoyl peroxide (10 or 20 mole%) or (*b*) *tert.*-butyl peroxide.

Addition of Butanal to Ethyl Undec-10-*enoate.*—The ester (24 g., 0·11 mole), butanal (40 g., 0·55 mole), and benzoyl peroxide (1·5 g., 0·006 mole) were refluxed under nitrogen for 20 hr.

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[7] Cf. Clarke and Howes, *J.*, 1956, 1152.

[8] Schechter, Green, and La Forge, *J. Amer. Chem. Soc.*, 1949, **71**, 3165.

After removal of excess of butanal by distillation, the product was taken up in ether and washed with aqueous sodium hydrogen carbonate, dried, and distilled. Unchanged ester (4 g.) was thus recovered. The residue slowly deposited *ethyl 12-oxopentadecanoate*, rods (9·5 g., 35%), which after recrystallisation from 90% ethanol had m. p. 41° (Found : C, 72·0; H, 11·2. $C_{17}H_{32}O_3$ requires C, 71·8; H, 11·3%). The semicarbazone, needles (from aqueous ethanol), melted at 69—71° (Found : N, 12·0. $C_{18}H_{35}O_3N_3$ requires N, 12·3%). Ultraviolet irradiation (Towers lamp) of the same mixture (peroxide being omitted) gave small quantities of the adduct (0·8 g.) after 23 hr., most of the reactants being recovered.

The above product (0·6 g.) was hydrolysed by potassium carbonate (1 g.) in boiling 50% ethanol (10 c.c.) for 4 hr., giving *12-oxopentadecanoic acid*, needles (from ethanol), m. p. 127° (Found : C, 69·9; H, 10·8. $C_{15}H_{28}O_3$ requires C, 70·3; H, 11·0%).

Addition of Butanal to Allylacetone.—Allylacetone (5·0 g., 0·05 mole), butanal (22 g., 0·30 mole), and benzoyl peroxide (1·1 g., 0·005 mole) by the same procedure gave *decane-2 : 7-dione*, b. p. 80—82°/1 mm., n_D^{18} 1·4415 (4·5 g., 53%) (Found : C, 70·0; H, 10·6. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·7%). The bis-semicarbazone, obtained by refluxing the diketone (0·6 g.) with semicarbazide hydrochloride (1·5 g.) and sodium acetate (1·5 g.) in 50% ethanol (20 c.c.) for 20 min., was crystallised from aqueous ethanol, then from methanol, and had m. p. 166—168° (Found : N, 28·9. $C_{12}H_{24}N_6$ requires N, 29·5%).

Addition of Butanal to Allylbenzene.—Allylbenzene (17 g., 0·15 mole), butanal (67 g., 0·9 mole), and benzoyl peroxide (2·4 g., 0·01 mole) by the same procedure gave (i) unchanged allylbenzene (12 g.) and (ii) *1-phenylheptan-4-one*, b. p. 111°/2 mm. (4·5 g., 56% yield calc. on allylbenzene consumed), n_D^{22} 14970 (Found : C, 82·0; H, 9·7. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5%). Attempts to prepare solid derivatives with semicarbazide and 2 : 4-dinitrophenylhydrazine were unsuccessful.

Microanalyses were by Dr. W. Zimmermann, Melbourne.

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