Homolytic Displacement at Saturated Carbon: Synthesis of Trichloroethylbenzenes

By Takuzo Funabiki, B. Dass Gupta, and Michael D. Johnson*
(*Department of Chemistry, University College,* 20 *Gordon Street, London* WC1H OAJ)

Summary Benzylcobaloximes react with bromotrichloromethane thermally and photochemically to give good yields of trichloroethylbenzenes; the reaction is believed to involve a chain sequence in which one of the propagation steps involves the homolytic displacement of cobaloxime(II) by attack of trichloromethyl radicals at the α-carbon.

Though there are a great many examples of electrophilic and nucleophilic attack at saturated carbon, examples of homolytic attack have proved particularly elusive.[1] In the only case previously reported for a reaction in solution, the displacement of cobaloxime(II) from alkylcobaloxime(III) complexes by other cobaloxime(II) reagents[2] [equation (1)†], the attacking radical bears only partial resemblance to conventional organic radicals. Following our report[3] that homolytic displacement of cobaloxime(II) from allylcobaloxime(III) complexes can also be achieved by regiospecific attack of trichloromethyl radicals at the unsaturated γ-carbon [equation (2)],[4] we now report the first example of homolytic displacement by attack of an organic radical at saturated carbon.

$$\mathrm{py(dmgH)_2Co^{II} + RCo^{III}(chgH)_2py \rightleftharpoons py(dmgH)_2Co^{III}R + Co^{II}(chgH)_2py} \quad (1)$$

$$\mathrm{Cl_3C\cdot + R^1R^2C{=}CR^3CH_2Co(dmgH)_2py \longrightarrow Cl_3CCR^1R^2CR^3{=}CH_2 + Co^{II}(dmgH)_2py} \quad (2)$$

Thus, the products of reaction of benzylbis(dimethylglyoximato)pyridinecobalt(III) (**1**; Ar = Ph) (1m) and bromotrichloromethane (2m) in chloroform after 6 h at 55 °C were bromobis(dimethylglyoximato)pyridinecobalt(III) and a mixture of βββ-trichloroethylbenzene and benzyl bromide (Table). The corresponding reactions of substituted benzylbis(dimethylglyoximato)pyridinecobalt(III) complexes gave from 0 to *ca.* 55% yield of the corresponding

---

† dmgH and chgH are the conjugate bases of dimethylglyoxime and cyclohexanedionedioxime, respectively.

TABLE. Organic products from the reaction of $XC_6H_4CH_2Co(dmgH)_2B$ with $BrCCl_3$ in $CHCl_3$.[a]

X	B	Temp/°C	Time/min	Main products (yield/%)[b]
4-NO_2	Pyridine	55	360	$ArCH_2Br(\leqslant 90)$
4-NO_2	Imidazole[c]	55	360	$ArCH_2CCl_3(50)$, $ArCH_2Br(50)$
4-Cl	PPh_3	90	15	$ArCH_2CCl_3(70)$, $ArCH_2Br(30)$
4-Cl	Pyridine	55	360	$ArCH_2CCl_3(35)$, $ArCH_2Br(65)$
4-Cl	Imidazole[d]	55	360	$ArCH_2CCl_3(70)$, $ArCH_2Br(30)$
4-Br	Pyridine*d*	28	120	$ArCH_2CCl_3(30)$, $ArCH_2Br(70)$
H	Pyridine	70	60	$ArCH_2CCl_3(50)$, $ArCH_2Br(50)$
H	Imidazole[c]	70	60	$ArCH_2CCl_3(\geqslant 85)$[e]
4-Me	Pyridine	55	240	$ArCH_2CCl_3(55)$, $ArCH_2Br(45)$
4-Me	Imidazole	55	240	$ArCH_2CCl_3(\geqslant 85)$

[a] 0·5—1M organocobalt, 1—2M $BrCCl_3$. [b] Determined by ^1H n.m.r. spectroscopy and g.l.c. [c] Pyridine complex in the presence of an excess of imidazole. [d] Irradiated with 2 × 150 W tungsten bulbs at 10 cm; water-cooled glass apparatus. [e] Isolated in > 70% yield.

trichloroethylbenzene on changing from the 4-nitro- to the 4-methyl-derivative, respectively; in each case the benzyl bromide was the other main organic product (Table).‡ Studies of the halogen-substituted benzylbis(dimethylglyoximato)triphenylphosphinecobalt(III) complexes showed that the product distribution was essentially the same for reaction temperatures from 45 to 90 °C (in sealed tubes). The reaction time was only a few minutes at the highest temperature and was greatly reduced when the reaction mixture was irradiated by tungsten lamps through all-glass water-cooled apparatus at 28 °C. In all cases, the yield of the trichloroethylbenzene was greatly increased when imidazole (2M) was present in solution (Table), the small amount of benzyl bromide being converted into the *N*-benzylimidazole; pure trichloroethylbenzene was isolated in > 70% yield from this reaction on a large scale.

As in the case of the reactions of allylcobaloximes with bromotrichloromethane, the rates of reaction are rather variable, depending upon the purity of the substrate and the presence of added or adventitious initiators. We therefore ascribe the formation of the trichloroethylbenzenes to a short-chain reaction in which trichloromethyl radicals and cobaloxime(II) are the propagating species [equations (4) and (5)]. Initiation may be achieved by an initial thermolysis or photolysis of the carbon–cobalt bond [equation (3)]. The key step [equation (5)] involves a homolytic displacement of the cobaloxime(II) by attack of trichloromethyl radicals at the α-carbon of the benzyl group. Since no bibenzyl and little hexachloroethane‡ were formed, the trichloroethylbenzene cannot have been formed significantly from combination of benzyl and trichloromethyl radicals.

Initiation:

$$\underset{(\mathbf{1})}{ArCH_2Co(dmgH)_2B} \rightleftharpoons ArCH_2\cdot + \cdot Co^{II}(dmgH)_2B \qquad (3)$$

Propagation:

$$\cdot Co^{II}(dmgH)_2B + BrCCl_3 \longrightarrow BrCo^{III}(dmgH)_2B + Cl_3C\cdot \qquad (4)$$

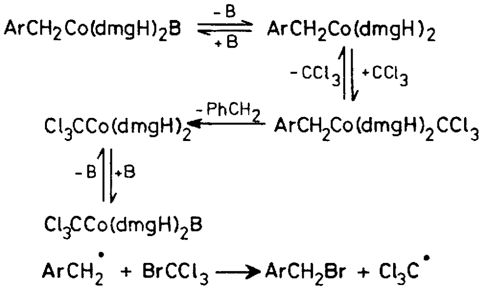
$$Cl_3C\cdot + ArCH_2Co^{III}(dmgH)_2B \longrightarrow Cl_3CCH_2Ar + \cdot Co^{II}(dmgH)_2B \qquad (5)$$

Termination:

$$2Cl_3C\cdot \longrightarrow Cl_3CCCl_3 \qquad (6)$$

$$Cl_3C\cdot + \cdot Co^{II}(dmgH)_2B \rightleftharpoons Cl_3CCo^{III}(dmgH)_2B \qquad (7)$$

The increase in the yield of trichloroethylbenzene in the presence of imidazole may be due to one or both of the following two effects. By co-ordinating more strongly to the metal[5] it may (i) enhance the rate of reaction (5), and (ii) prevent an alternative pathway in which the trichloromethyl radicals attack the metal and lead to the benzyl bromide through the sequence in the Scheme. The latter is supported by the longer reaction times necessary when imidazole is present.



SCHEME

Besides the mechanistic interest of these first examples of homolytic substitution at a saturated carbon atom, these reactions provide a useful synthetic route not only to trichloroethylbenzenes, some of which have not previously been prepared, but also, using other polyhalogenomethanes and related substrates, to a variety of other *βββ*-trisubstituted ethylbenzenes.

We thank the S.R.C. for support and Messrs M. W. Read, K. Older, and C. Neuberger for experimental assistance.

(*Received*, 30*th May* 1977; *Com.* 524.)

---

‡ The products were determined from the ^1H n.m.r. spectra of the reaction solutions, by g.l.c., and by isolation of the trichloroethylbenzenes. Hexachloroethane was determined by g.l.c.

[1] K. U. Ingold and B. P. Roberts, 'Free Radical Substitution Reactions,' Wiley-Interscience, New York, 1970.

[2] D.Dodd, M. D. Johnson, and B. L. Lockman, *J. Amer. Chem. Soc.*, 1977, **99**, 3664.

[3] T. Funabiki, B. D. Gupta, and M. D. Johnson, *J. Amer. Chem. Soc.*, 1976, **98**, 6697.

[4] Regiospecific attack of trichloromethyl radicals at the γ-carbon of allenylcobaloximes such as $Me_2C{=}C{=}CHCo(dmgH)_2py$ also proceeds in good yield: T. Funabiki, B. D. Gupta, and M. D. Johnson, unpublished work.

[5] D. Dodd and M. D. Johnson, *J. Organometallic Chem.*, 1973, **52**, 1.