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HOMOLYTIC DISPLACEMENT AT CARBON

VI *. SYNTHESIS OF TRICHLOROETHYLARENES FROM BENZYLCOBALOXIMES

PETER BOUGEARD, B. DASS GUPTA, and MICHAEL D. JOHNSON *

Department of Chemistry, University College, 20 Gordon St., London WC1H OAJ (Great Britain)

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Summary

Benzylbis(dimethylglyoximato)pyridinecobalt(III) reacts with bromotrichloromethane at from 50 to 90°C in chloroform to give good yields of trichloroethylbenzene, which are higher when imidazole is present in the reaction mixture. Methyl- and polymethyl-substituted benzylbis(dimethylglyximato)pyridinecobalt(III) complexes give higher yields of the corresponding trichloroethylarenes (85—90%), whereas 4-chlorobenzylbis(dimethylglyoximato)pyridinecobalt(III) gives a lower yield and 4-nitrobenzylbis(dimethylglyoximato)pyridinecobalt(III) only gives the 4-nitro-trichloroethylarene when imidazole is present during the reaction. Similar reactions were observed with benzylcobaloximes and trichloromethanesulphonyl chloride both thermally and under irradiation by tungsten lamps through all-pyrex apparatus. The reactions are interpreted as a direct attack of the trichloromethyl radical on the α-carbon of the benzyl ligand.

In previous papers we have described some reactions of allyl, propadienyl, and but-3-enyl metal complexes with some organic radical precursors [1—5]. We proposed that the reactions proceeded by a chain mechanism, briefly outlined in equations 1—3, a key step of which (equation 3) was the bimolecular homolytic displacement of a paramagnetic metal complex by attack of the organic radical at an unsaturated carbon of the axial organic ligand (e.g., equations 4—6). The displaced paramagnetic complex was then itself instrumental in the production of the organic radical from its precursor (equation 2). Similar homolytic

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* For part V see ref. 1.

displacements have also been proposed as steps in chain reactions involving allyltin(IV) compounds [6].

$$RM \rightleftharpoons \dot{R} + \dot{M} \qquad (1)$$

$$\dot{M} + XY \rightarrow MY + \dot{X} \qquad (2)$$

$$\dot{X} + RM \rightarrow RX + \dot{M} \qquad (3)$$

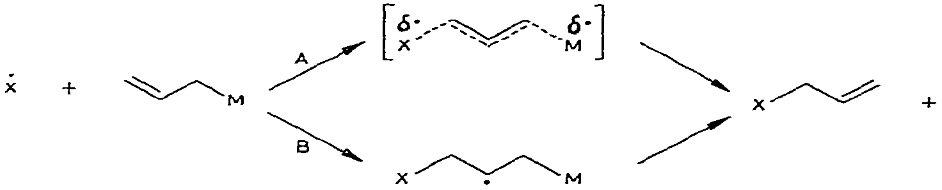
$$Cl_3\dot{C} + Me_2C:C:CHCo^{III}(dmgH)_2L \rightarrow Cl_3C \cdot CMe_2C{\equiv}CH + \dot{C}o^{II}(dmgH)_2L \qquad (4)$$

$$Ar\dot{S}O_2 + CH_2:CH \cdot CH_2CH_2Co^{III}(dmgH)_2py \rightarrow ArSO_2CH_2\overline{CH \cdot CH_2CH_2} + \dot{C}o^{II}(dmgH)_2py \qquad (5)$$

$$NC \cdot \dot{C}Cl_2 + CH_2:CPh \cdot CH_2Co^{III}(dmgH)_2py \rightarrow NC \cdot CCl_2CH_2CPh:CH_2 + \dot{C}o^{II}(dmgH)_2py \qquad (6)$$

In the above examples, we were unable to distinguish between a direct concerted displacement (e.g. equation 7; path A) and an addition-elimination process involving the formation of an intermediate organometallic radical (equation 7; path B). Whilst we favour the stepwise path B [7], the direct mechanism would have much greater credibility if such a reaction could also be identified at saturated carbon, for which such an addition-elimination process could be excluded (equation 8). At the start of this work, examples of displacement at saturated carbon were restricted to two cases, namely the gas-phase displacement at saturated carbon by trifluoromethyl radicals [8], and the displacement of halogen atoms from cyclopropane carbon atoms [9].

In this paper are described the reactions of benzyl- and substituted benzylcobaloximes with two trichloromethyl radical precursors under thermal and photochemical conditions, in an attempt to identify homolytic displacement reactions in solution at saturated carbon, and to develop syntheses for 2,2,2-trisubstituted halogenoethylbenzenes.



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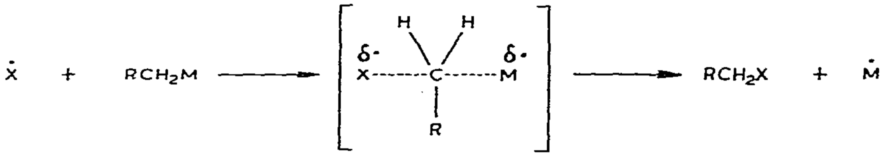

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Results

Reaction of benzylcobaloximes with bromotrichloromethane

Benzylbis(dimethylglyoximato)pyridinecobalt(III) reacted with an excess of bromotrichloromethane in $CHCl_3$ at 70°C for 2 h to give a mixture containing benzyl bromide (53% based on benzylcobaloxime), 2,2,2-trichloroethylbenzene (47%), hexachloroethane, and bromobis(dimethylglyoximato)pyridinecobalt(III), which were identified by NMR spectroscopy and GLC through comparison with authentic materials (Table 1). When imidazole was added to the mixture at the end of the reaction and the mixture heated at 70°C for a further 2 h, the products were the same except that benzyl bromide was replaced by *N*-benzylimidazole, However, when a four-fold excess of imidazole was present initially, little *N*-benzylimidazole or benzyl bromide was formed and the main organic product was 2,2,2-trichloroethylbenzene, which was isolated from the reaction mixture in 75% yield.

Similar reactions of substituted benzylbis(dimethylglyoximato)pyridinecobalt(III) complexes with bromotrichloromethane gave mixtures containing bromobis(dimethylglyoximato)pyridinecobalt(III), the substituted benzyl bromide, the substituted trichloroethylbenzene, and hexachloroethane. The proportions of products, shown in Table 1, were dependent on the nature of the substituent and whether imidazole was present. In all cases the presence of imidazole increased significantly the yield of the trichloroethylarene, and in the case of 4-nitrobenzylbis(dimethylglyoximato)pyridinecobalt(III), 4-nitrotrichloroethylbenzene was only obtained when imidazole was present during the reaction.

Several benzylbis(dimethylglyoximato)(ligand)cobalt(III) complexes were also treated with lower concentrations of bromotrichloromethane at ambient temperature under irradiation by tungsten lamps through all-pyrex apparatus. The products (Table 1) were similar to those formed in the thermal reactions except that small quantities of dibenzyl were also obtained.

Reactions of benzylcobaloximes with trichloromethanesulphonyl chloride

Benzylbis(dimethylglyoximato)pyridinecobalt(III) reacted with trichloromethanesulphonyl chloride at 50°C for 4—5 h to give mainly trichloroethylbenzene together with benzyl chloride, dibenzyl, and some α-toluenesulphonyl chloride. The inorganic products of this reaction were not investigated. The proportions of products are shown in Table 2. The same reaction was also carried out with a number of other benzylbis(dimethylglyoximato)(ligand)cobalt(III) complexes and with benzylbis(dimethylglyoximato)aquocobalt(III) in the presence of equivalent concentrations of a variety of monodentate ligands (Table 2), both thermally as above, and at ambient temperature under irradiation by tungsten lamps through all-pyrex apparatus.

Discussion

The thermal reaction of benzylcobaloximes with bromotrichloromethane almost certainly proceeds by a mixture of mechanisms. The formation of significant quantities of benzyl bromide when imidazole is not present is indicative of

(Continued on p. 216)

TABLE 1

PRODUCTS OF REACTION OF SUBSTITUTED BENZYLBIS(DIMETHYLGLYOXIMATO)(LIGAND)COBALT(III) [$ArCH_2Co(dmgH)_2L$] WITH BROMOTRICHLOROMETHANE (WITH AND WITHOUT ADDED IMIDAZOLE) IN CHLOROFORM

Ar	L	[Imidazole] (*M*)	[Substrate] (*M*)	[$BrCCl_3$] (*M*)	Conditions	Benzylic products (%)[a]	
						$ArCH_2CCl_3$	$ArCH_2Br$
Ph	Py		0.25	2.5	2 h, 70° C	47	53
Ph	Py	1.0	0.25	2.5	8 h, 70° C	92	8
Ph	PPh_3		0.05	0.1	5 h, 55° C	19	77[b]
Ph	$P(OMe)_3$		0.05	0.1	5 h, 55° C	27	73[c]
2-MeC_6H_4	Py		0.25	2.5	2 h, 55° C	60	35
2-MeC_6H_4	Py	1.0	0.25	2.5	5 h, 55° C	sole	
3-MeC_6H_4	Py		0.25	2.5	5 h, 55° C	55	45
3-MeC_6H_4	Py	1.0	0.25	2.5	3 h, 70° C	95	5
4-MeC_6H_4	Py		0.25	2.5	4 h, 55° C	54	40[c]
4-MeC_6H_4	Py	1.0	0.25	2.5	1 h, 70° C	85	15
4-ClC_6H_4	Py		0.25	2.5	9 h, 55° C	35	65
4-ClC_6H_4	Py	1.0	0.25	2.5	6 h, 70° C	85	15
4-ClC_6H_4	PPh_3		0.25	2.5	1 h, 90° C	70	30
4-$NO_2C_6H_4$	Py		0.25	2.5	11 h, 55° C		sole[d]
4-$NO_2C_6H_4$	Py	1.0	0.25	2.5	5 h, 70° C	50	50[d]
3,5-Me_2-C_6H_4	Py		0.25	2.5	5 h, 50° C	sole	
2,5,6-Me_3-C_6H_4	Py		0.25	2.5	5 h, 50° C	95	5
Ph	$P(OMe)_3$		0.25	0.25	1.5 h, 15° C[e]	38	50[b]
Ph	$P(OMe)_3$		0.25	0.10	1.5 h, 15° C[e]	27	72[b]
Ph	PPh_3		0.25	0.5	1.5 h, 15° C[e]	15	82[b]

[a] Percentage of organic benzylic products. Reaction substantially complete. [b] Some dibenzyl also formed. [c] Other products unidentified (⩽7%). [d] Reaction substantially incomplete. [e] Photochemical reactions.

TABLE 2

PRODUCTS OF REACTION OF BENZYLBIS(DIMETHYLGLYOXIMATO)LIGANDCOBALT(III) [$PhCH_2Co(dmgH)L$] WITH TRICHLOROMETHANESULPHONYL CHLORIDE IN THE PRESENCE OF ADDED LIGANDS L′ IN CHLOROFORM (a) AT 18°C WITH IRRADIATION BY 4 X 150 WATT TUNGSTEN LAMPS AND (b) AT 50°C FOR 4.5 H

[$Cl_3C \cdot SO_2Cl$] (*M*)	[Substrate] (*M*)	L	L′	[L′] (*M*)	Benzylic products (%) [c]		
					$PhCH_2CCl_3$	$PhCH_2Cl$	$(PhCH_2)_2$ [d]
0.05	0.05 [a]	Py			59	19	19
0.10	0.05 [a]	Py			57	29	14
0.20	0.20 [a]	Py			52	33	9
0.20	0.20 [a]	Py	Py	0.20	45	34	17
0.35	0.35 [a]	Py	Py	0.35	42	47	6
0.35	0.35 [a]	Aq	Py	0.35	45	49	14
0.40	0.40 [a]	Py			44	44	12
0.05	0.05 [a]	4-MePy			57	12	25
0.10	0.05 [a]	4-MePy			56	32	12
0.05	0.05 [b]	Aq	4-MePy	0.05	29	40	31
0.05	0.05 [a]	Aq	Imidazole	0.05	57	21	18
0.05	0.05 [b]	Aq	Imidazole	0.05	23	62	15
0.05	0.05 [a]	Aq	Isoquinoline	0.05	53	16	23
0.05	0.05 [a]	Aq	4-Cyanopy	0.05	51	26	18
0.05	0.05 [b]	Aq	4-Cyanopy	0.05	38	47	15
0.05	0.05 [a]	Aq	2-Meimidazole	0.05	50	26	19
0.30	0.30 [a]	Aq	2-Meimidazole	0.30	43	39	12
0.05	0.05 [b]	Aq	2-Meimidazole	0.05	24	65	11
0.05	0.05 [a]	Aq	1-Meimidazole	0.05	50 [e]	19	12
0.05	0.05 [a]	Aq	1,4-Thioxan	0.05	41	48	9
0.05	0.05 [b]	Aq	1,4-Thioxan	0.05	33	67	Trace
0.05	0.05 [a]	Aq	PBu_3	0.05	36	46	18
0.05	0.05 [b]	Aq	PBu_3	0.05	20	57	23
0.05	0.05 [a]	$P(OMe)_3$			35	43	22
0.05	0.05 [a]	$P(OPh)_3$			13	75	13
0.05	0.05 [b]	$P(OPh)_3$			14	68	18
0.05	0.05 [a]	Aq	PhSSPh	0.05	13	80	7
0.05	0.05 [a]	PPh_3			8	85	8
0.05	0.05 [b]	Aq	PPh_3	0.05	0	100	Trace
0.05	0.05 [a]	Aq			0	91	9
0.05	0.05 [a]	Aq	$AsPh_3$	0.05	0	40	60
0.05	0.05 [a]	Aq	$SbPh_3$	0.05	0	50	50

[a] Photochemical reaction. [b] Thermal reaction. [c] Some (≤10%) $PhCH_2SOCl$ formed. [d] Includes some PhCHO when O_2 was present. [e] 19% $PhCH_2SO_2Cl$ also formed.

the presence as intermediates of benzyl radicals, which are known to react readily with bromotrichloromethane to give benzyl bromide and trichloromethyl radicals (equation 9) [10]. However, little of the trichloroethylbenzene can have been formed by combination of benzyl and trichloromethyl radicals, because despite the formation of hexachloroethane, the yield of the other radical recombination product, dibenzyl (equation 10), is negligible. Indeed, in none of the several studies of the free radical halogenation of toluene and of other alkylbenzenes with bromotrichloromethane has there been any report of the formation of trichloroethylbenzene or its derivatives [10]. The relatively high yields of trichloroethylbenzene formed in the absence of imidazole, and especially the very high yields of trichloroethylbenzene formed when imidazole is present, are therefore consistent with a direct reaction between the trichloromethyl radical and the benzylcobaloxime (equation 11). A similar significant increase in the yield of a product of displacement from an organocobaloxime by trichloromethyl radicals was previously noted in the reaction of propadienylcobaloximes with bromotrichloromethane [2]. Since imidazole is known to coordinate more strongly to cobalt(III) than the other ligands described in this work [11], this is a firm indication that it is the six-coordinate benzylcobaloxime which is the reactive species in the displacement reaction leading to trichloroethylbenzene.

$$\mathrm{Ph\dot{C}H_2 + BrCCl_3 \rightarrow PhCH_2Br + \dot{C}Cl_3} \qquad (9)$$

$$\mathrm{Cl_3\dot{C} + Ph\dot{C}H_2 \rightarrow C_2Cl_6 + PhCH_2CCl_3 + (PhCH_2)_2} \qquad (10)$$

$$\mathrm{Cl_3\dot{C} + PhCH_2Co^{III}(dmgH)_2L \rightarrow PhCH_2CCl_3 + Co^{II}(dmgH)_2L} \qquad (11)$$

Both the rate of the reaction and the yield of trichloroethylbenzene are influenced by the nature of the substituents in the aromatic ring in the order: polymethyl $\geqslant$ methyl $>$ H $>$ 4-chloro $>$ 4-nitro. This order of reactivity is a result of a complicated function of the rates of initiation and propagation, but the higher yields in the case of the methyl-substituted benzylcobaloximes are consistent with a direct displacement process at the α-carbon of the benzyl group.

The reactions of trichloromethanesulphonyl chloride, which is a known precursor of trichloromethyl radicals [12], were studied initially in an attempt to maximise the yield of trichloroethylbenzene, and subsequently in order to investigate the role of the sixth (axial) ligand on the character of the reaction. Though reasonable yields of trichloroethylbenzene were obtained under mild conditions and in very dilute solution, this reaction did not match that of bromotrichloromethane for simplicity and yield in the large scale preparations. Two features of the study of axial ligands stand out: first that the yield of trichloroethylbenzene is highest when strongly coordinating ligands, such as heteroaromatic nitrogen bases, are present, and is negligible when only weakly coordinating ligands, such as water, triphenylarsine [13], and triphenylstibine, are present. Secondly, the yield of trichloroethylbenzene decreased slightly as the concentration of trichloromethanesulphonyl chloride increased. We ascribe this in part to competing heterolytic reactions between the reagent and either the equatorial dioximato ligands or the axial base ligand, which change the character of the complex and retard the rate of or change the course of the homolytic displacement process.

The three other main products, dibenzyl, benzyl chloride and α-toluenesulphonyl chloride can all be ascribed to reactions of the intermediate benzyl radicals. The latter can react with trichloromethanesulphonyl chloride (equation 12) to give benzyl chloride, with free sulphur dioxide [14] and subsequently with trichloromethanesulphonyl chloride to give α-toluenesulphonyl chloride (equation 13), and can dimerise to give dibenzyl. The proportions of these three products will thus be a function of the exact concentrations of sulphur dioxide and trichloromethanesulphonyl chloride in solution. Whilst the latter can be controlled, the former will be a function of the course of the overall reaction and of the reaction conditions, and cannot be readily controlled. Moreover, the isolated yields of α-toluenesulphonyl chloride are an unreliable guide because it is subject to further reaction with some of the ligands present in solution. Further studies of the formation of sulphonyl chlorides will be reported later [15].

$$\mathrm{Ph\dot{C}H_2 + Cl_3C\cdot SO_2Cl \rightarrow PhCH_2Cl + Cl_3C\cdot \dot{S}O_2 \rightarrow Cl_3\dot{C} + SO_2} \tag{12}$$

$$\mathrm{Ph\dot{C}H_2 + SO_2 \rightarrow Ph\dot{S}O_2 \xleftrightarrow{Cl_3C\cdot SO_2Cl} PhSO_2Cl + Cl_3C\cdot \dot{S}O_2} \tag{13}$$

In view of the case of preparation of a wide range of substituted benzylcobaloximes in high yield from the corresponding benzyl halides and the bis(dimethylglyoximato)cobaltate(I) ion [16], their straightforward reaction with bromotrichloromethane in the presence of imidazole at elevated temperature provides the most convenient route for the preparation [17] of trichloroethylarenes, which may also be applicable to other 2,2,2-trisubstituted ethylarenes derived from the more stable trisubstituted methyl radicals.

Experimental

Materials

Benzyl- and substituted benzyl-bis(dimethylglyoximato)pyridinecobalt(III) complexes were prepared as described earlier [16] from the corresponding benzyl halide and the bis(dimethylglyoximato)pyridinecobaltate(I) ion prepared by disproportionation of bis(dimethylglyoximato)pyridinecobalt(II) in alkaline aqueous solution under N_2.

Benzylbis(dimethylglyoximato)aquocobalt(III) was similarly prepared from benzyl chloride and the bis(dimethylglyoximato)aquocobaltate(I) ion in aqueous methanol. The methanol was removed in vacuo, water was added to the resultant slurry and the benzylbis(dimethylglyoximato)aquocobalt(III) was filtered off, washed with ice-cold water, and dried in vacuo.

Several benzylbis(dimethylglyoximato)ligandcobalt(III) complexes were prepared by shaking a slurry of benzylbis(dimethylglyoximato)aquocobalt(III) (1 mmol) with a solution of the appropriate ligand (1 mmol) in methylene chloride or in methanol. The resulting solution was evaporated to dryness and the residue was recrystallised from methanol or methylene chloride pentane mixtures.

Photochemical reactions with trichloromethanesulphonyl chloride

In a typical reaction, benzylbis(dimethylglyoximato)pyridinecobalt(III) (1.0 g, 2.1 mmol) and trichloromethanesulphonyl chloride (0.45 g, 2.1 mmol) in methylene chloride (10 cm^3) were stirred and photolysed with tungsten lamps (4 × 150 watt) at about 10 cm from the water-cooled all-pyrex apparatus at about 8°C for 1.5 h. Some of the methylene chloride was distilled off and pentane (ca. 5 cm^3) was added. The mixture was washed, filtered, and the filtrate was partially evaporated and re-extracted with pentane, which was dried (Na_2SO_4) and the excess of pentane was distilled off. The proportions of benzylic products in the residue were determined by ^{1}H NMR and the relative yields of hexachloroethane and trichloroethylbenzene were determined by GLC of the original extract. The yields of hexachloroethane were erratic, but never exceeded that of the trichloroethylbenzene. Similar reactions were carried out with other benzylbis(dimethylglyoximato)ligandcobalt(III) complexes, in some cases after addition of an equimolar amount of another monodentate ligand, allowing time for the solution to become homogeneous before addition of the trichloromethanesulphonyl chloride.

Photochemical reactions with bromotrichloromethane

In a typical reaction benzylbis(dimethylglyoximato)trimethylphosphitecobalt(III) (0.5 mmol) and bromotrichloromethane (0.5 mmol) in methylene chloride (10 cm^3) were irradiated and worked up as described above.

Thermal reactions with bromotrichloromethane

In a typical reaction, benzylbis(dimethylglyoximato)ligandcobalt(III) [ligand = pyridine, triphenylphosphine, or trimethylphosphite] (2.5 mmol) and bromotrichloromethane (25 mmol) in chloroform (5 cm^3) were sealed in a glass tube and heated to 55°C for 5 h. The product was worked up as described above. In several cases, imidazole (10 mmol) was added before reaction, and in one case imidazole was added after reaction and the mixture was heated and worked up as described above. Trichloroethylbenzene was prepared as follows: Benzylbis(dimethylglyoximato)pyridinecobalt(III) (9.8 g, 20 mmol) and bromotrichloromethane (8.9 g, 40 mmol) were heated with chloroform (60 cm^3) in a sealed tube to 70°C for 5 h. The product was extracted with pentane as described above and fractionally distilled to give trichloroethylbenzene (3.0 g, 75%).

Thermal reactions of trichloromethanesulphonyl chloride

In a typical reaction, benzylbis(dimethylglyoximato)aquocobalt(III) (1.0 g, 2.1 mmol) and trichloromethanesulphonyl chloride (0.45 g, 2.1 mmol), with or without an additional ligand (4-methylpyridine, 4-cyanopyridine, 2-methylimidazole, 1,4-thioxan, tributylphosphine, or triphenylphosphine; 2.1 mmol) and methylene chloride (40 cm^3) were heated in a sealed tube at 50°C for 4.5 h, and the products were worked up as above.

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