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HOMOLYTIC DISPLACEMENT AT CARBON

VII *. REGIOSPECIFIC SYNTHESIS OF *S*-ALLYL-*N*,*N*-DIMETHYLSULPHONAMIDES FROM ALLYLCOBALOXIMES AND THE ADDITION OF *N*,*N*-DIMETHYLSULPHONYL CHLORIDE TO TERMINAL OLEFINS

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Summary

Unsymmetrical allylcobaloximes, e.g. 3-methylbut-3-enylbis(dimethylglyoximato)pyridinecobalt(III), react regiospecifically with *N*,*N*-dimethylsulphamoyl chloride to give good yields of the rearranged product *S*-allyl-*N*,*N*-dimethylsulphonamide, e.g. 1,1,*N*,*N*-tetramethylallylsulphonamide. Symmetrical allylcobaloximes react similarly to give the expected single allylsulphonamides. Buta-1,2-dienylbis(dimethylglyoximato)pyridinecobalt(III) also reacts regiospecifically with *N*,*N*-dimethylsulphamoyl chloride to give 1,*N*,*N*-trimethylpropynylsulphonamide. It is proposed that the organic product-forming step of the reaction involves the homolytic displacement of cobaloxime(II) by regiospecific attack of the *N*,*N*-dimethylsulphamoyl radical on the γ-carbon of the allyl or propadienyl ligand. This is supported by the observation that *N*,*N*-dimethylsulphamoyl chloride adds to terminal olefins under free radical conditions.

We have demonstrated that several trichloromethyl radical precursors, such as carbon tetrachloride, bromotrichloromethane, and trichloromethanesulphonyl chloride, react readily with allyl- and substituted allyl-cobaloximes, without the need for added initiators even at ambient temperature and in the dark, to give single trichlorobut-3-ene products [2]. We proposed that each of these processes proceed by a chain mechanism in which a trichloromethyl radical is first generated by reaction of adventitious cobaloxime(II), or of cobaloxime(II) formed by decomposition of some of the allylcobaloxime(III), with the precursor, and that the trichloromethyl radical then reacts directly with the

* For part VI see ref. 1.

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TABLE I

PRODUCTS ($R'SO_2NMe_2$) OF REACTION OF ORGANOCOBALOXIMES ($RCo(dmgH)_2Py$) WITH *N,N*-DIMETHYLSULPHAMOYL CHLORIDE IN $CDCl_3$ OR CH_2Cl_2 AT AMBIENT TEMPERATURE

R	R'	Analysis Found (calcd.)				^{13}C NMR (δ ppm)					^1H NMR (δ ppm)					
		C	H	N	S	C-1	C-2	C-3	NMe_2	C—Me	H-1 *cis*	H-1 *trans*	H-2	H-3	C—Me	NME_2
$Me_2C:CH\cdot CH_2$	$CH_2:CH\cdot CMe_2$	47.4 (47.5)	8.2 (8.5)	7.7 (7.9)	17.1 (18.1)	117.3	138.3	66.2	39.5	22.8	5.29	5.29	6.12	—	1.47	2.91 [a]
$Ph\cdot CH:CH\cdot CH_2$	$CH_2:CH\cdot CHPh$	58.8 (58.7)	6.7 (6.7)	6.3 (6.2)	13.6 (14.2)	121.7	128.8	71.4	38.1	[b]	5.40	5.38	6.33	4.80	—	2.66 [c]
$MeCH:CH\cdot CH_2$	$CH_2:CH\cdot CHMe$	44.2 (44.2)	8.0 (8.0)	8.8 (8.6)	18.0 (19.6)	120.3	133.1	61.1	38.3	14.8	5.30	5.35	5.90	3.80	1.45	2.90 [c]
$CH_2:CH\cdot CH_2$	$CH_2:CH\cdot CH_2$	40.3 (40.3)	7.8 (7.4)	9.25 (9.4)	21.35 (21.5)	123.4	125.9	53.7	38.0	—	5.38	5.39	5.91	3.72	—	2.82 [e]
$CH_2:CMe\cdot CH_2$	$CH_2:CMe\cdot CH_2$	43.8 (44.2)	7.8 (8.0)	8.3 (8.6)	18.7 (19.6)	119.7	134.7	56.9	37.9	22.6	5.14	5.04	—	3.64	1.98	2.94
$CH_2:CPh\cdot CH_2$	$CH_2:CPh\cdot CH_2$	59.0 (58.7)	6.8 (6.7)	6.2 (6.2)	13.8 (14.2)	121.6	125.3	55.1	37.5	[f]	5.65	5.46	—	4.09	—	2.67 [g]
$MeCH:C:CH$	$HC\equiv C\cdot CHMe$					49.0	78.4	74.8	38.8	16.4	2.40	—	—	3.95	1.64	3.01 [h]

[a] $J_{1,2}$ = 10.5 and 17.3 Hz. [b] Phenyl resonances at δ 133.6, 131.3, 129.4, 128.8 ppm. [c] Phenyl proton resonance at δ 7.37, ppm $J_{1,2}$ = 10.3 and 17.4 Hz, $J_{2,3}$ = 7.0 Hz. [d] $J_{1,2}$ = 9.0 and 18.0 Hz, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 6.1 Hz. [e] $J_{1,2}$ = 9.1 and 17.4 Hz, $J_{2,3}$ = 7.0 Hz. [f] Phenyl resonances at δ 139.3, 137.2, 128.6, 126.3 ppm. [g] Phenyl proton resonance at δ 7.32 ppm. [h] $J_{3,4}$ = 7.0 Hz.

allylcobaloxime(III) through a completely regiospecific attack at the γ-carbon of the allyl ligand, with synchronous or subsequent loss of cobaloxime(II) (equations 1 and 2).

$$Cl_3CX + Co^{II}(dmgH)_2L \rightarrow Cl_3\dot{C} + XCo^{III}(dmgH)_2L \quad (1)$$

$$Cl_3\dot{C} + R^1R^2C : CR^3CH_2Co^{III}(dmgH)_2L \rightarrow$$

$$Cl_3C \cdot CR^1R^2 \cdot CR^3 : CH_2 + Co^{II}(dmgH)_2L \quad (2)$$

Such reactions are not confined to trichloromethyl radicals, but have also been observed with other carbon radicals derived from halogeno-, cyano-, and carbethoxy-substituted methyl halides [2,3] and with sulphonyl radicals [4] derived from a series of arene-, alkane-, and substituted alkane-sulphonyl halides. (e.g. equations 3 and 4).

$$RSO_2Cl + Co^{II}(dmgH)_2L \rightarrow R\dot{S}O_2 + ClCo^{III}(dmgH)_2L \quad (3)$$

$$R\dot{S}O_2 + R^1R^2C : CR^3 \cdot CH_2Co^{III}(dmgH)_2L \rightarrow$$

$$RSO_2CR^1R^2 \cdot CR^3 : CH_2 + Co^{II}(dmgH)_2L \quad (4)$$

We now describe further extension of these reactions to the synthesis of allylsulphonamides from dimethylsulphamoyl chloride and to the use of organocobaloximes in the initiation of some novel additions of dimethylsulphamoyl chloride to terminal olefins.

Results and discussion

On mixing a slight excess of *N,N*-dimethylsulphamoyl chloride (1) with 3-methylbut-2-enylbis(dimethylglyoximato)pyridinecobalt(III) (2; ca 0.3 mol dm^{-3}) in $CDCl_3$ at ambient temperature, a smooth reaction takes place over about 1 h to give predominantly 1,1-dimethylallyl-*N,N*-dimethylsulphonamide (3) and chlorobis(dimethylglyoximato)pyridinecobalt(III) (4; equation 5). Separation of the organic products from the inorganic products was readily achieved by column chromatography, but separation of the last traces of the reagent 1 from the organic product 3 was achieved only after hydrolysis of the former. No trace of the other product isomer (3-methylbut-2-enyl-*N,N*-dimethylsulphonamide) could be detected in the product mixture. The course of the reaction was monitored several times by ^1H NMR spectroscopy, but the behaviour was not sufficiently uniform and reproducible to allow a particular kinetic order to be ascribed. The characteristics of the product 4 are shown in Table 1.

$$Me_2NSO_2Cl + R^1R^2C : CR^3 \cdot CH_2Co(dmgH)_2py \rightarrow$$

(1) (2, $R^1 = R^2 = Me$, $R^3 = H$;
5, $R^1 = Me$, $R^2 = R^3 = H$;
6, $R^1 = Ph$, $R^2 = R^3 = H$;
11, $R^1 = R^2 = R^3 = H$;
12, $R^1 = R^2 = H$, $R^3 = Me$;
13, $R^1 = R^2 = H$, $R^3 = Ph$)

$$Me_2NSO_2CR^1R^2 \cdot CR^3 : CH_2 + Co(dmgH)_2py \qquad (5)$$

(4, $R^1 = R^2 = Me$, $R^3 = H$; (3)
8, $R^1 = Me$, $R^2 = R^3 = H$;
9, $R^1 = Ph$, $R^2 = R^3 = H$;
14, $R^1 = R^2 = R^3 = H$;
15, $R^1 = R^2 = H$, $R^3 = Me$;
16, $R^1 = R^2 = H$, $R^3 = Ph$)

$$Me_2NSO_2Cl + MeCH : C : CHCo(dmgH)_2py \rightarrow$$

(7)

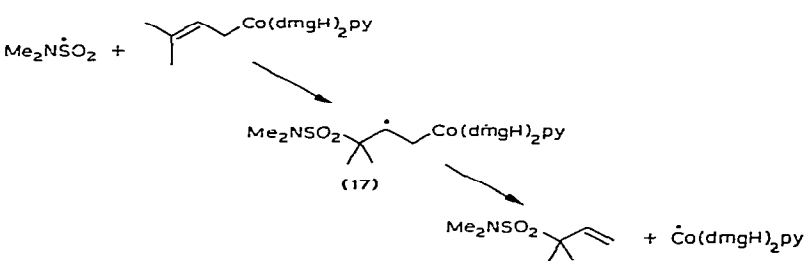
$$Me_2NSO_2CHMe \cdot C \vdots CH + ClCo(dmgH)_2py \qquad (6)$$

(10)

Similar regiospecific reactions were also observed between **1** and but-3-enyl-, 3-phenylallyl-, and buta-1,2-dienyl-bis(dimethylglyoximato)pyridinecobalt(III) (**5**—**7**, respectively), in each case giving a single 1-substituted allyl or a single 1-substituted propynyl-*N*,*N*-dimethylsulphonamide (**8**—**10**, respectively). No trace of the isomeric 3-substituted allylsulphonamide or the isomeric butadienylsulphonamide could be detected. The yield of the propynylsulphonamide **10** was greatly increased by carrying out the reaction at 10°C under irradiation with tungsten lamps through pyrex apparatus.

The expected sulphonamides **14**—**16** were also obtained from the corresponding reactions of **1** with the allyl-, 2-methylallyl-, and 2-phenylallyl-cobaloximes (**11**—**13**, respectively, equation 5) [3].

The regiospecific character of these reactions, their acceleration on irradiation with tungsten light through pyrex, and the non-uniformity of reaction rates, all parallel the results found with the arene- and alkane-sulphonyl halides [3]. We therefore propose that they proceed by a similar mechanism, in which the *N*,*N*-dimethylsulphamoyl radical attacks the γ-carbon of the allyl or butadienyl ligand, displacing the cobaloxime(II) radical via an intermediate adduct radical **17**, and generating the observed product sulphonamide (equation 7). The cobaloxime(II) then reacts with *N*,*N*-dimethylsulphamoyl chloride to regenerate the sulphamoyl radical (equation 8). As in the other reactions, the presence and ready formation of traces of cobaloxime(II) in these solutions (equation 9) [5] results in erratic initiation of the chain sequence and creates difficulties in the detailed studies of the mechanism of these processes.



(7)

$$Me_2NSO_2Cl + Co(dmgH)_2py \longrightarrow Me_2N\dot{S}O_2 + ClCo(dmgH)_2py \qquad (8)$$

The reaction of the *N,N*-dimethylsulphamoyl radical with unsaturated organic molecules has not previously been described, though they have been implicated in the chlorination of some hydrocarbons. However, the apparent ready attack of these radicals at the terminal unsaturated carbon of the allyl ligands suggested to us that it might also be possible to add *N,N*-dimethylsulphamoyl chloride to terminal olefins under appropriate conditions of initiation. Accordingly, when a mixture of oct-1-ene and *N,N*-dimethylsulphamoyl chloride was irradiated in methylene chloride with tungsten lamps in the presence of 5 mol% of sec-butylbis(dimethylglyoximato)pyridinecobalt(III), the main organic product was *N,N*-dimethyl-2-chlorooctylsulphonamide **18**. Similar treatment of dec-1-ene and hex-1-ene gave the addition products **19** and **20** (equation 9).

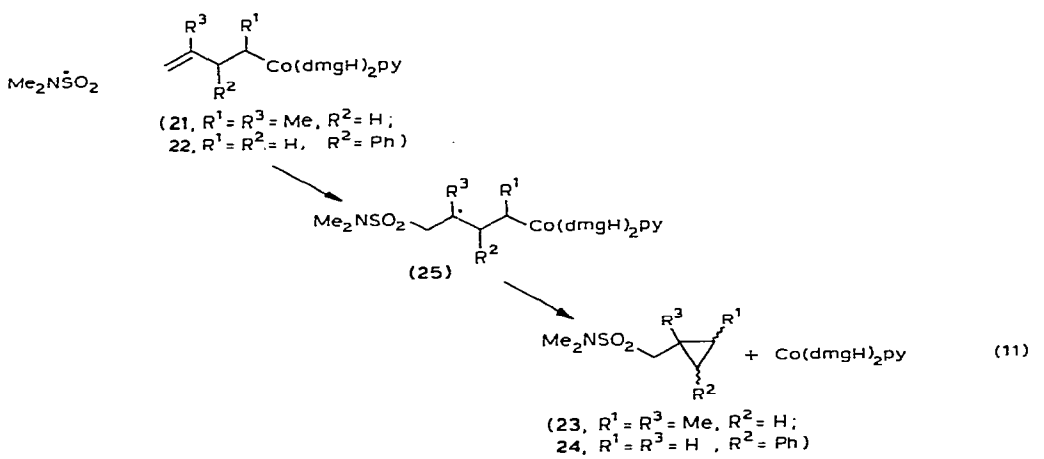
$$Me_2NSO_2Cl + CH_2{=}CH \cdot R \xrightarrow{s\text{-}BuCo(dmgH)_2py} Me_2NSO_2CH_2CHCl \cdot R \qquad (9)$$

(**18**, R = n-C_6H_{13};
19, R = n-C_8H_{17};
20, R = n-C_4H_9)

Clearly, these additions proceed by a combination of reaction 8 and reaction 10, initiation being provided by the homolytic cleavage of the sec-butylcobaloxime [6].

$$Me_2N\dot{S}O_2 + CH_2 : CHR \rightarrow Me_2NSO_2CH_2\dot{C}HR \qquad (10)$$

Further confirmation of the attack of *N,N*-dimethylsulphamoyl radicals on unsaturated carbon comes from the formation, in lower yield, of several substituted cyclopropylsulphonamides (**23** and **24**, equation 11) from the irradiation with tungsten lamps of mixtures of *N,N*-dimethylsulphamoyl chloride and the but-3-enylbis(dimethylglyoximato)pyridinecobalt(III) complexes **21** and **22**. These reactions probably proceed through the intermediate radical **25**, a major competition path being the homolytic cleavage of the carbon—cobalt bond prior to attack at the terminal olefinic carbon. The products were therefore appreciably less pure than those from the allylcobaloximes and we were unable to purify them completely. They were therefore characterised by mass spectrometry and ^1H NMR spectoscopy.



(11)

Experimental

The allylcobaloximes [5], buta-1,2-dienylcobaloxime [5], 2-phenylbut-3-enylcobaloxime [4] and 4-methylpent-4-en-2-ylcobaloxime [7] were prepared as described earlier from the appropriate organic halide or tosylate and cobaloxime(I). The cobaloxime(I) was prepared by anaerobic alkaline disproportionation of cobaloxime(II) in methanol.

Reactions of allyl and dienylcobaloximes with N,N-dimethylsulphamoyl chloride.

In a typical reaction, 3-methylbut-2-enylbis(dimethylglyoximato)pyridinecobalt(III) (1 g, 2.0 mmol) and *N,N*-dimethylsulphamoyl chloride (0.3 g, 2.2 mmol) in methylene chloride (4 cm^3) were warmed to 40°C for a few seconds and maintained at ambient temperature overnight. The mixture was chromatographed on silica gel (Mallinkrodt CC4 special), eluting the organic products with methylene chloride and chlorobis(dimethylglyoximato)pyridinecobalt(III) with ethyl acetate. The organic products were re-chromatographed to give 1,1,*N,N*-tetramethylallylsulphonamide (0.20 g, 1.1 mmol; 55%). Similar reactions of other allylcobaloximes gave *N,N*-dimethylallylsulphonamide (58%), 1,*N,N*-trimethylallylsulphonamide (47%), 2,*N,N*-trimethylallylsulphonamide (77%), *N,N*-dimethyl-2-phenylallylsulphonamide (49%) and *N,N*-dimethyl-1-phenylsulphonamide (yield not estimated due to impure cobaloxime reagent).

In the reaction of buta-1,2-dienylbis(dimethylglyoximato)pyridinecobalt(III), the reaction mixture was irradiated in a pyrex water-cooled cell for 2 h using 4 × 150 watt tungsten spot-lamps at a distance of about 10 cm. The product sulphonamide decomposed during repeated attempts at purification and was therefore identified by ^1H NMR spectroscopy and mass spectrometry (Table 1). Estimated yield 54%.

Reaction of but-3-enylcobaloximes

In a typical reaction, 2-phenylbut-3-enylbis(dimethylglyoximato)pyridinecobalt(III) (1 g, 2.0 mmol) and *N,N*-dimethylsulphamoyl chloride (0.3 g, 2.2 mmol) in methylene chloride (10 cm^3) were irradiated as above for 2 h. The organic product was separated as above, but likewise decomposed during repeated attemps at purification, and was identified by ^1H NMR spectroscopy as at least one isomer of *N,N*-dimethyl-2-phenylcyclopropylcarbinylsulphonamide {^1H NMR: δ 0.91, 1.15, 1.26 (multiplets cyclopropane), 3.42 (doublet CH_2SO_2), 2.95 (singlet NMe_2), 7.3 ppm (multiplet Ph); mass spectrum: *m/e* 175 (*M* − 64)}. Similarly prepared was a mixture of isomers of 1,2,*N,N*-tetramethylcyclopropylcarbinylsulphonamide {^1H NMR: δ 0.8—1.1 (multiplet cyclopropane), 3.4 (singlet CH_2SO_2), 3.0 (singlet NMe_2), 1.1—1.2 ppm (multiplet Me); mass spectrum: *m/e* 128 (*M* − 64)}.

Reactions of terminal olefins

Oct-1-ene (0.14 cm^3, 0.88 mmol) *N,N*-dimethylsulphamoyl chloride (0.13 g, 0.88 mmol) and sec-butylbis(dimethylglyoximato)pyridinecobalt(III) (0.018 g, 42 μmol) in methylene chloride (0.5 cm^3) were irradiated as above for 4 h. The product was chromatographed as above and the organic product was pumped

at 0.01 torr for 5 h. The remaining material was shown by NMR and mass spectrometry to be 2-chloro-*N*,*N*-dimethyl-n-octylsulphonamide {^{1}H NMR: δ 4.34 (multiplet H_2), 3.34 (quartet H_1), 3.31 (quartet H_1'), 2.91 (singlet NMe_2), 0.8—0.9 and 1.2—1.4 ppm (C_6H_{13}); $J_{1,1'}$ 14.60, $J_{1,2}$ 6.35, and $J_{1',2}$ 6.10 Hz; mass spectrum: *m/e* 257 and 255 in ratio 3 : 1; ^{13}C NMR: δ 56.7 and 56.2 (C_1 and C_2), 38.6 (NMe_2), 14.5, 23.2, 26.5, 29.1, 32.2 ppm}. Similarly prepared were 2-chloro-*N*,*N*-dimethyl-n-decylsulphonamide {^{1}H NMR: δ 4.32 (multiplet H_2), 3.34 (quartet H_1), 3.31 (quartet H_1') 2.91 (singlet NMe_2), 0.8—1.0 and 1.2—1.4 ppm (multiplet C_8H_{17}); $J_{1,1'}$ 14.45, $J_{1,2}$ 6.32, $J_{1',2}$ 6.26 Hz; mass spectrum: *m/e* 285 and 283 in ratio 3 : 1}, and 2-chloro-*N*,*N*-dimethyl-n-hexylsulphonamide {^{1}H NMR: δ 4.33 (multiplet H_2), 3.35 (quartet H_1), 3.35 (quartet H_1'), 2.91 (singlet MNe_2), 09—1.0 and 1.2—2.1 ppm (multiplets C_4H_9); $J_{1,1'}$ 14.40, $J_{1,2}$ 6.34, $J_{1',2}$ 6.27 Hz; mass spectrum: *m/e* 229 and 227 in ratio 3 : 1}.

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