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"NORMAL" AND "CINE" SUBSTITUTION IN THE THIOALKOXY-DEHALOGENATION OF HALOGENOBENZOFURANZANS—II

SENSIBILITY OF EACH PATHWAY TO THE CHANGE OF ALKANETHIOLATE ION

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Abstract—Thioalkoxy-dehalogenation of 4-halogenobenzofurazans affording "normal" and "cine" substitution products has been more extensively investigated. Evidence for a partial intervention of AEa-type mechanism in NS product formation is now available. The competition of this pathway increases with the bulkiness of thiolate ion. Kinetic data for different thiolates are reported indicating a sensitivity to steric effects not only in the "normal" substitution but also in the "cine" substitution pathway.

Halogenobenzofurazans (excepted 4-fluorobenzofurazan) react with sodium thiometoxide in methanol affording, together with the normal substitution (=NS) products (i.e. those with structure corresponding to the starting halogeno-derivatives), also "cine" substitution (=CS) products in which thiomethoxy-group occupies the position adjacent to that vacated by the halogen.[1] On the basis of results obtained in deuterio-methanol, NS products have been attributed to an SNAr-like mechanism,[2] while CS products have been attributed to a competitive addition-elimination "anomalous-type" mechanism (AEa).[3] No evidence was found for intervention of such an "anomalous type" mechanism in the formation of NS product from 4-halogenobenzofurans (i.e. by nucleophilic addition involving the positions 4–7[AEa_{4-7}] instead of 4–5[AEa_{4-5}]: see also Scheme 1). By this mechanism NS product deuteriated in the position 7 would be obtained in deuterio methanol as solvent. NMR spectrum of NS product, obtained in deuterio-methanol, revealed no incorporation of deuterium in any position, within the experimental error, while CS product (i.e. 5-methylthiobenzofurazan) contained deuterium in the only position previously occupied by the halogen in an amount corresponding to deuteriation percentage of the medium (*ca.* 85%). However a considerable decrease of the CS/NS products ratios was also observed in going from light to deuterio-methanol, indicating an unfavourable kinetic solvent effect for AEa_{4-5} mechanism (involving proton abstraction by the medium) as compared with SNAr mechanism. A similar unfavourable solvent effect would also be operative for the hypothetical AEa_{4-7} pathway. This, if involved to a lower extent than AEa_{4-5} mechanism, could practically be suppressed in deuterio-methanol.

In the light of these considerations, we have now performed the thioalkoxy-dehalogenation in "inverted" conditions, i.e. with 4-halogeno-7-deuteriobenzofurazans in light methanol. In these conditions evidences for some competition of AEa mechanism also in the formation of NS product (i.e. 4-methylthiobenzofurazan) have been found.

Furthermore, since a different sensibility to the bulkiness of the nucleophile was expected for each mechanism of the reaction, we have examined the reaction also with sodium thio-iso-propoxide and thio-tert-butoxide. Finally, in order to obtain indications on the sensibility to the electronic effects, the reactivities of 4-chloro- and 4-bromobenzofurazan with sodium thioethoxide, thio-n-propoxide and thio-n-butoxide have been measured.

RESULTS AND DISCUSSION

^{1}H NMR investigation of 4-methylthiobenzofurazan obtained as NS product from the reaction of 4-fluoro-, 4-chloro- and 4-bromo-7-deuteriobenzofurazan with sodium thiomethoxide in the range 25–45° has been carried out. Some amount of hydrogen incorporation in the position 7 (previously occupied by deuterium) has been detected in all cases, excepted in 4-methylthiobenzofurazan obtained from 4-fluoro-7-deuteriobenzofurazan. The observed exchange D–H can reasonably be related to the particular mechanism of the thioalkoxy-dehalogenation. In fact no appreciable D–H exchange has been detected in the unreacted 4-halogeno-7-deuteriobenzofurazan nor in the

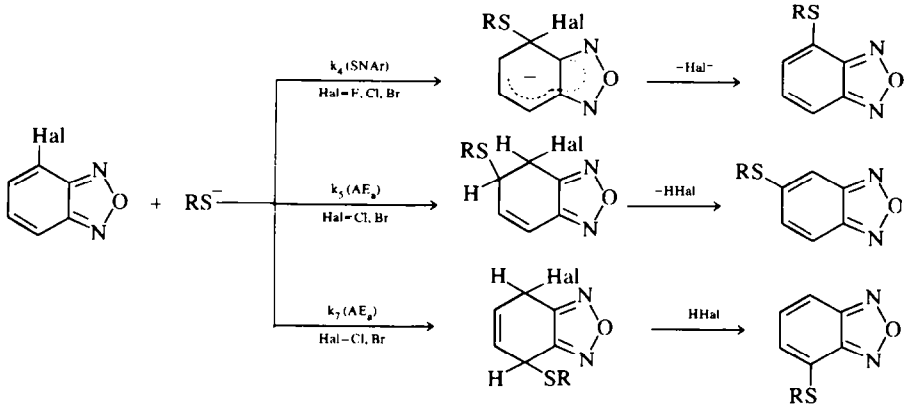
Table 1. Relative percentages of NS (SNAr and AEa) and CS (AEa) products obtained from reactions between 4-halogenobenzofurazans and CH_3S^- in MeOH

Halogen	°C	NS (SNAr)	NS (AEa)	CS AEa
4-Chloro	25	45.6	19.6	34.8
	35	54.6	13.7	31.7
	45	63.4	11.2	25.4
4-Bromo	25	48	16	36
	35	52.3	14.7	33
	45	61	11	28

Relative % of NS(Total) and CS products were determined by VPC. Relative % of NS(SNAr) and NS (AEa) were measured by percentage of H incorporated (NMR) in the position 7 of 4-MeS-benzofurazan starting from 4-halogeno-7-deuteriobenzofurazans. The experimental error in the latter case is higher, since it is subjected both to VPC and NMR error. (ca. 10%)

5-methylthiobenzofurazan obtained from it. These findings resemble those observed for the CS product obtained in MeOD, for which AEa mechanism was proposed, as above reported.[1] Therefore it is likely that a similar mechanism is partly involved also in the formation of NS product, to a percentage (Table 1) exactly corresponding to the observed D–H exchange.

In the light of there considerations the overall scheme of the alkylthio-dehalogenation of 4-halogenobenzofurazans can be completed as below.



Scheme 1.

On the basis of the reported scheme and Table 1, rate constants corresponding to overall NS products formation[1] can be further dissected in those corresponding to each mechanism of reaction (i.e. NS_{SNAr} and NS_{AEa}) as reported in Table 2.

On the other hand an interesting investigation can be made by changing the thioalkoxide ion in order to ascertain the sensibility of each pathway to the bulkiness of the nucleophile. For this aim we have carried out experiments both on 4-halogeno- and 4-halogeno-7-deuteriobenzofurazans (halogen=F, Cl, Br) with sodium thio-isopropoxide and thio-tert-butoxide in methanol. The percentage of 4- and 5-alkylthiobenzofurazans obtained by each pathway are reported in Table 3, while the overall rate constants and those obtained by their dissection on the basis of the cited percentages are in Table 4. The experimental error for the rate constants $k_{NS(SNAr)}$ and $k_{NS(AEa)}$ are rather considerable (as for thiomethoxy-dehalogenation: see experimental). However, the inspection of the reported data allows some interesting considerations to be made:

(i) In all cases, when the nucleophile changes from MeS^- to iso-propyl-S^- and t-butyl-S^-, a corresponding decrease of reactivity is observed, in contrast with the enhanced electron availability on the sulphur and according the increase of the bulkiness on going in the same order;

(ii) The decrease of reactivity (measured by the ratios $k_{MeS^-}/k_{isopropS^-}$ and $k_{MeS^-}/k_{t\text{-}ButS^-}$: Table 5) is highly dependent on the site of the reaction. In fact, if the carbon directly linked with the halogen is attacked, the decrease in reactivity reaches a maximum, being greater in the case of chloro- and bromo- than for the fluoro-derivative.

Table 3. Relative percentages of NS(SNAr, and AEa) and CS products obtained from reactions between 4-halogenobenzofurazans and RS^- in methanol at 45°

Halogen	RS	NS SNAr	NS AEa	CS AEa
4-Fluoro	$(CH_3)_2CHS^-$	100	—	—
	$(CH_3)_3CS^-$	100	—	—
4-Chloro	$(CH_3)_2CHS^-$	44.7	36.8	18.5
	$(CH_3)_3CS^-$	21	49	30
4-Bromo	$(CH_3)_2CHS^-$	48.5	32	19.5
	$(CH_3)_3CS^-$	22	52	26

Table 2. Second order kinetic constants (sec^{-1} mol^{-1} l) for the reactions between 4-halogenobenzofurazans and CH_3S^- in CH_3OH. k_4, k_5, k_7 refer to NS(SNAr), CS (AEa) and NS (AEa) mechanism respectively

Halogen	°C	$k_{NS_{tot}}$†	k_4	k_7	k_5†	E_a(kcal/mol) NS (SNAr)	NS (AEa)	CS† (AEa)	$\Delta s^{\neq}$(cal mol^{-1} K^{-1}) NS (SNAr)	NS (AEa)	CS (AEa)
4-Fluoro	25	9.1×10^{-4}	9.1×10^{-4}			16.2			−20		
	35	2.2×10^{-3}	2.2×10^{-3}								
	45	5.2×10^{-3}	5.2×10^{-3}								
4-Chloro	25	1.8×10^{-5}	1.3×10^{-5}	5.4×10^{-6}	9.5×10^{-6}	20.4	12	14.4	−14.4	−44.5	−35.3
	35	5.5×10^{-5}	4.4×10^{-5}	1.1×10^{-5}	2.5×10^{-5}						
	45	1.3×10^{-4}	1.1×10^{-4}	1.9×10^{-5}	4.4×10^{-5}						
4-Bromo	25	8.5×10^{-5}	6.4×10^{-5}	2.1×10^{-5}	4.8×10^{-5}	17.8	12	13	−20.1	−41.7	−36.6
	35	2.4×10^{-4}	1.9×10^{-4}	5.3×10^{-5}	1.2×10^{-4}						
	45	5.0×10^{-4}	4.2×10^{-4}	7.5×10^{-5}	1.9×10^{-4}						

†Data from Ref. 1.

Table 4. Second order kinetic constants (sec $^{-1}$ mol $^{-1}$ l) for reactions between 4-halogenobenzofurazans and RS^-Na^+ in MeOH at 45°

Halogen	RS	k_4	k_7	k_5
4-Fluoro	$(CH_3)_2CHS$	1.4×10^{-3}	—	—
	$(CH_3)_3CS^-$	1.3×10^{-4}	—	—
4-Chloro	$(CH_3)_2CHS$	1.4×10^{-5}	1.2×10^{-5}	5.9×10^{-6}
	$(CH_3)_3CS^-$	1.1×10^{-6}	2.7×10^{-6}	1.6×10^{-6}
4-Bromo	$(CH_3)_2CHS$	5.3×10^{-5}	3.6×10^{-5}	2.2×10^{-5}
	$(CH_3)_3CS$	4.3×10^{-6}	1.0×10^{-5}	5.1×10^{-6}

and f referring to the expected on the basis of electronic effects and the found values respectively).

Plotting kinetic data (Table 6: k_4) corresponding to sodium thioethoxide, thio-n-propoxide, and thio-n-butoxide (for which the steric hindrance would practically be constant because of the unchanged α-branching)[5] against σ^* (Taft),[6] a high sensibility to electronic effects (ρ values *ca.* −4) is observed for both 4-chloro- and 4-bromobenzofurazan. Therefore $(k_{isopropS^-})_e$ and $(k_{tButS^-})_e$ would be much higher than k_{MeS^-} and hence the actual steric effects considerably larger than those indicated by the ratios in Table 5.

Analogous considerations can be made for the steric effects related to the cine-substitution.

Table 5. Ratios $k_{CH_3S^-}/k_{iso\ propyls^-}$ and $K_{CH_3S}/k_{tert\text{-}butylS}$ for reactions between halogenobenzofurazans and RS^- in methanol at 45°

Halogen	$k_{CH_3S^-}/k_{iso\text{-}propS^-}$ NS(SNAr)	NS(AEa)	CS(AEa)	$k_{CH_3S^-}/k_{tert\text{-}butS^-}$ NS(SNAr)	NS(AEa)	CS(AEa)
4-Fluoro	3.7	—	—	40	—	—
4-Chloro	7.8	16	7.5	96	7.2	27.5
4-Bromo	8	2.1	8.8	98	7.5	37

When a C–H is attacked, the ratios $k_{MeS^-}/k_{isopropS^-}$ and $k_{MeS^-}/k_{t\text{-}ButS^-}$ are smaller and are also different for the attack on the carbon adjacent to C–X (i.e. C_5) and C_7. Thus when the carbon 5 is involved, a relatively larger decrease of reactivity is observed, which indicates that some repulsive interactions with the halogen are operative also in this case. This is consistent with the suggestion previously made by us on the synchronous character of the addition (postulated rate-determining step) in CS mechanism, in which a trans addition is expected.[4] In fact in this case the RS-group and the halogen would be in a relative *cis* position and hence with some possibility of a mutual repulsive interaction. From another point of view it may be noted that the reactivity on C_7 is lower than on C_5 in the case of MeS^-, while the situation is inverted in the case of isopropS$^-$ and t-butS$^-$. This indicates that when the steric hindrance is relatively unimportant, the position 5 is more reactive with respect to the position 7, which would reflect the different activation of the two positions.[1] When the bulkiness of the nucleophile increases, the situation is reversed, once more indicating a higher sensitivity to steric effects when the position 5 is involved, probably because of the steric repulsion between the nucleophile and the halogen linked on the adjacent carbon 4.

(iii) Finally, the decrease of reactivity is also dependent on the size of the halogen. This is more clearly observed for the SNAr pathway for which data for fluoro-, chloro- and bromo-derivative are available (AEa pathway do not occur with fluoro-derivative). In fact when the nucleophilic attack occurs directly on C_4-Hal, both the ratios $k_{MeS^-}/k_{isopropS^-}$ and $k_{MeS^-}/k_{t\text{-}ButS^-}$ are considerably higher for chloro- and bromo- than for fluoro-derivative, according the smaller radius of the fluoro. However the steric effects are not very different for chloro- and bromo-derivative (within the experimental error). This could partly be due to a balance between the bulkiness and the polarizability of the two halogens. It may be considered that the above reported ratios are obviously not the exact measure of the steric effects, which would be given by the ratios $(k_{isopropS^-})_e/(k_{isopropS^-})_f$ and $(k_{t\text{-}ButS^-})_e/(k_{t\text{-}ButS^-})_f$ (subscripts e

Table 6. Second order kinetic constants (sec $^{-1}$ mol^{-1} l) for reactions between 4-halogenobenzofurazans and RS^- in MeOH at 45°

Halogen	RS	k_4	k_7	k_5
4-Chloro	EtS	5.3×10^{-5}	1.2×10^{-5}	2.0×10^{-5}
	n-propS$^-$	6.9×10^{-5}	1.8×10^{-5}	2.3×10^{-5}
	n-butS$^-$	6.8×10^{-5}	1.8×10^{-5}	2.4×10^{-5}
4-Bromo	EtS	1.9×10^{-4}	5.0×10^{-5}	6.8×10^{-5}
	n-propS	2.5×10^{-4}	6.2×10^{-5}	8.2×10^{-5}
	n-butS	2.5×10^{-4}	6.2×10^{-5}	8.2×10^{-5}

From the above considerations we can conclude that in the thioalkoxy-dehalogenation of halogenobenzofurazans the steric effects are rather important for both SNAr and CS pathways. These findings which well agree with the proposed mechanism of the reaction, seem also interesting in the general question of the steric effects in nucleophilic reactions at unsaturated carbons.[5,7]

EXPERIMENTAL

M.ps were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were recorded in CCl_4 on Varian HA-100 (when indicated) and JEOL MINIMAR JNM-60II instruments. Microanalyses were made on a Hewlett-Packard C, H, N, analyser.

Materials. MeOH for kinetic experiments was purified by standard procedures. CCl_4 for NMR measurements was a good commercial product (RP Carlo Erba). D_2O and D_2SO_4 for hydrogen-deuterium exchange were good commercial products (Merck). 4-Fluorobenzofurazan, b.p. 83° at 12 mm; 4-chlorobenzofurazan m.p. 83–84°C; and 4-bromobenzofurazan m.p. 107°, were synthesized as previously described.[8] 4-Fluoro-7-deuterio-, 4-chloro-7-deuterio- and 4-bromo-7-deuterio-benzofurazan were prepared from the corresponding light products by H–D exchange with D_2SO_4 (96–98%) in D_2O at 100° for 24 hr *ca.* The deuteriated halogenobenzofurazans (m.m.ps with light products undepressed) showed at least 90% deuterium incorporation in the position 7 (NMR signals of protons 5 and 6 as reference). Methylmercaptan was synthesized according to the method described by Backer and Stienstra.[9] All the other alkylmercaptans were good commercial products (Schelling).

Reaction products. Excepted 4-fluorobenzofurazan (which affords only NS derivative) in the other cases both NS and CS alkylthioderivatives were obtained and relative percentages measured by VPC. The NS (overall) and CS products were separated each from the other by cromatography on silica gel (hexane-ether 7:3 as eluent). The percentages of NS (via SNAr) and NS (via AEa) products were determined by hydrogen incorporation in the position 7, starting from 4-halogeno-7-deuteriobenzofurazans and after separation of the overall NS from CS product as above described. Since the deuteriation on the position 7 was generally not complete (≥90%) the hydrogen percentage present in the cited position of starting 4-halogeno-7-deuteriobenzofurazans was obviously taken into account in the evaluation of the hydrogen incorporated during the alkylthiodehalogenation.

Analytical data. Those referring to 4-methylthio- (m.p. 77–78°) and 5-methylthiobenzofurazan (m.p. 101–102°) have been reported previously.[1]

4-Ethylthio-benzofurazan (m.p. 43–44°), Found: C, 53.60; H, 4.57; N, 15.80; S, 17.70%. 5-Ethylthio-benzofurazan (m.p. 74–75°), Found: C, 53.68; H, 4.85; N, 15.68; S, 17.60; required for $C_8H_8N_2OS$: C, 53.13; H, 4.77; N, 15.55; S, 17.63%. 4-n-Propylthio-benzofurazan (oil), Found: C, 55.70; H, 5.40; N, 14.40; S, 16.46%. 5-n-Propylthio-benzofurazan (oil), Found: C, 55.50; H, 5.45; N, 14.40; S, 16.65%. 4-Isopropylthio-benzofurazan (oil), Found: C, 54.94; H, 5.07; N, 14.51; S, 16.57%. 5-Iso-propylthio-benzofurazan (oil) Found: C, 55.57; H, 5.12; N, 14.20; S, 16.20; required for $C_9H_{10}N_2OS$: C, 55.60; H, 5.20; N, 14.50; S, 16.47%).

4-n-Butylthio-benzofurazan (oil), Found: C, 57.29; H, 5.85; N, 12.87; S, 14.81%. 5-n-Butylthio-benzofurazan (oil), Found: C, 57.40; H, 5.90; N, 13.12; S, 15.42%. 4-t-Butylthio-benzofurazan (m.p. 46–47°), Found: C, 58.0; H, 5.82; N, 13.65; S, 15.25%. 5-t-Butylthio-benzofurazan (oil), Found: C, 56.37; H, 5.67; N, 13.21; S, 15.50; required for $C_{10}H_{12}N_2OS$: C, 57.64; H, 5.81; N, 13.46; S, 15.38%).

NMR data (in CCl_4, Internal standard TMS). Data for 4-methylthio- and 5-methylthio-benzofurazan have been reported.[1]

4-Ethylthio-benzofurazan: three benzofurazan protons in the range 2.1–2.9 τ, two methylene protons (qu) at 6.7 τ and three methyl protons (tri) at 8.6 τ, JH_{CH_2}–$H_{CH_3} \simeq 7.5$ c/s;

5-Ethylthio-benzofurazan: three benzofurazan protons ($H_4 \simeq 2.43\ \tau$; $H_6 \simeq 2.68\ \tau$; $H_7 \simeq 2.10\tau$; $J_{4-6} = 1.5$ c/s; $J_{4-7} \simeq 0.9$ c/s; $J_{6-7} \simeq 9.6$ c/s), two methylene protons (qu) at 6.85 τ and three methyl protons (tri) at 8.5 τ, JH_{CH_2}–$H_{CH_3} \simeq 7.5$ c/s; 4-n-propylthio-benzofurazan: three benzofurazan protons in the range 2.2–2.9 τ and seven alkyl protons in the range 6.5–9.1 τ; 5-n-propylthio-benzofurazan: three benzofurazan protons ($H_4 \simeq 2.5\ \tau$; $H_6 \simeq 2.7\ \tau$; $H_7 \simeq 2.15\ \tau$; $J_{4-6} \simeq 1.5$ c/s; $J_{4-7} \simeq 0.9$ c/s; $J_{6-7} \simeq 9.6$ c/s) and seven alkyl protons in the range 6.70–9.10 τ; 4-iso-propylthio-benzofurazan: three benzofurazan protons in the range 2.2–2.8 τ, one methynyl proton (m) at 6 τ and six Me protons (d) at 8.6 τ, JH_{CH}–$H_{CH_3} \simeq 6.5$ c/s;

5-Iso-propylthio-benzofurazan: three benzofurazan protons ($H_4 \simeq 2.4\ \tau$; $H_6 \simeq 2.7\ \tau$, $H_7 \simeq 2.1\ \tau$; $J_{4-6} \simeq 1.5$ c/s; $J_{4-7} \simeq 0.7$ c/s; $J_{6-7} \simeq 9$ c/s), one methynyl proton (m) at 6.3 τ and six Me protons (d) at 8.5 τ, JH_{CH}–$H_{CH_3} \simeq 6.5$ c/s; 4-n-butylthio-benzofurazan: three benzofurazan protons in the range 2.1–3.0 τ and nine alkyl protons in the range 6.5–9.3 τ; 5-n-butylthio-benzofurazan: three benzofurazan protons ($H_4 \simeq 2.5\ \tau$; $H_6 \simeq 2.7\ \tau$; $H_7 \simeq 2.15\ \tau$; $J_{4-6} \simeq 1.5$ c/s; $J_{4-7} \simeq 0.7$ c/s; $J_{6-7} \simeq 9$ c/s) and nine alkyl protons in the range 6.7–9.2 τ; 4-t-butylthio-benzofurazan: three benzofurazan protons in the range 2.15–2.8 τ and nine equivalent alkyl protons (s) at 8.62 τ (Varian HA-100); 5-t-butylthio-benzofurazan: three benzofurazan protons ($H_4 = 2.05\ \tau$; $H_6 = 2.64\ \tau$; $H_7 = 2.30\ \tau$; $J_{4-6} \simeq 1.4$ c/S; $J_{4-7} \simeq 1.0$ c/s; $J_{6-7} = 9.3$ c/s) and nine equivalent alkyl protons at 8.60 τ (Varian HA-100).

Rate measurement. Kinetic experiments were carried out in methanol (pseudo-first order conditions) in thermostatted apparatus, following the appearance of halide ion (Volhard), or disappearance of the base (thioalkoxide) for the reactions of 4-fluorobenzofurazan. The used conditions were those previously reported for thiomethoxy-dehalogenation.[1] The pseudofirst order kinetic constants so obtained were dissected in those corresponding to each pathway and divided for the concentration of RS (in excess), giving the second order rate costants. The experimental error for $k_{C\text{-}S}$ and $k_{NS(overall)}$ is ±3%, while for k values obtained by further dissection of $k_{NS(overall)}$ (i.e. $k_{NS(SNAr)}$ and $k_{NS(AEa)}$) it is more higher, depending on NMR error (*ca.* 10%).

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