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"EXTENDED DEAMINATIONS"-- REACTIONS OF ALKANE DIAZOTATES WITH THIONYL CHLORIDE[1]

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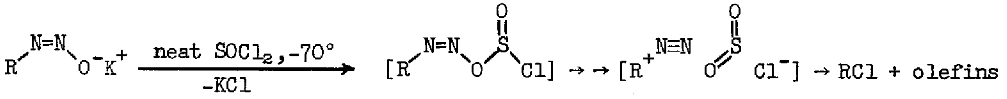
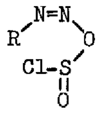
We examined the title reactions [eq. (1)] because of the possibility that the anticipated alkyldiazo chlorosulfites, II, might directly lose two gas molecules, thus affording products via doubly gas-separated ion pairs III, without the intermediacy of alkyl chlorosulfites, IV.[4] We

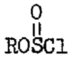


(1)

I II III

A series, R = $C_6H_5CHCH_3$; B series, R = n-$C_6H_{13}CHCH_3$


IIA'


$RO\overset{O}{\overset{\|}{S}}Cl$

IV

call this comparatively rare type of reaction an "extended deamination" because of the loss of two gas molecules from II.[5]

Slow addition of HMPA solutions of diazotates IA[6] or IB[7] to excess, neat $SOCl_2$ (-70°) gave "instantaneous" quantitative nitrogen evolution. When the reaction was done at 0°, near quantitative (98%) evolution of SO_2 (bp, -10°) was also observed.[8] Reaction mixtures were quenched with ice-cold Na_2CO_3 solution. Organic products were then obtained by ethereal extraction, drying, concentration, and gc[9] analysis and isolation. Identities were established by comparison with authentic samples. The reactions were also run with diazotates derived from optically active precursor amides.[6,7] The products, yields, optical activities of the alkyl chlorides obtained, and the stereochemical courses of the I → RCl transformations are summarized in Table I.

In crucial experiments, chlorosulfite IVB[16a,b] was added to the $SOCl_2$ before addition of diazotate IB. Nmr integrations of IVB's carbinyl proton sextet at δ 5.2 (vs. an internal benzene standard), before and after the decomposition of IB, demonstrated the quantitative stability of IVB under the reaction conditions. Nmr also revealed the absence of IVB ($<$1%) in freshly prepared (-70°) crude reaction mixtures from IB and $SOCl_2$. These experiments exclude IVB as an intermediate and establish an extended deamination sequence for the reaction of IB and $SOCl_2$, eq. (1). The instability[16c] of IVA prevented parallel controls in the A series of reactions, but it seems quite unlikely, in view of the 2-octyl results, that the unstable IVA[16d] would be an intermediate in the 1-phenylethyl (A) reaction series. Here, additionally, the potential cation is more stable.

TABLE I. Reactions of $R-N=N-O^-$ with $SOCl_2$

Run	Diazotate[a]	Temp (°C)	Products (Yield, %)[b]	α_D of RCl[c]	Net Stereochemistry[d,e]
1	IA	0	styrene (19), RCl (9)[f]	-1.109° (22)	11.0 [30.9] % retn
2	IA	-40	styrene (15), RCl (22)	-1.090° (21)	10.8 [30.3] % retn
3	IA	-70	styrene (23), RCl (26)	-1.177° (27)	11.7 [32.9] % retn
4	IB	-70	octenes (11), RCl (5.3)[g]	+0.275° (21)	9.2% inv
5	IB	-70	octenes (16), RCl (1.1)	+0.352° (21)	11.8% inv
6	IB[h]	-70	octenes (7.5), RCl (2.4)[i]	+0.365° (29)	12.2% inv
7	IB[j]	-70	octenes (15), RCl (4.5)[k]		
8	IB[l]	-70	octenes (7.7), RCl (1.0)		

[a] IA was derived[6] from 1-phenylethylamine, α_D^{22} -3.546° (neat, 0.1 dm), 92.6% optically pure.[10] The diazotate is taken to have the same optical purity. IB was derived[7] from 2-aminooctane, α_D^{24} -2.51° (neat, 0.5 dm), 94.4% optically pure.[11] The diazotate is known to be formed with complete retention.[12] [b] A series yields were by nmr, CH_3OH standard; B series yields were by gc, toluene standard. [c] All readings (neat, 0.1 dm) were taken on a Perkin-Elmer Model 141 spectropolarimeter; temperatures are reported in (°C). [d] Optically pure 1-phenylethyl chloride has α_D^{25} 109° (neat, 1 dm, minimum value).[13] This chloride was optically unstable to the gc conditions required for its isolation. Duplicate gc control experiments with optically pure chloride indicated the loss of 64 ± 5% of optical rotation. The stereochemical results for Runs 1-3, based upon isolated 1-phenylethyl chloride, have been corrected (÷ 0.356) to approximate the true stereochemical courses of the reactions. Corrected values appear in brackets. Optically pure 2-chlorooctane has α_D^{20} 31.6° (neat, 1 dm).[14] 2-Chlorooctane was optically stable to the reaction and work-up conditions. [e] Alkyl amines and halides of the same rotational sign belong to the same optical series.[15] Halide rotations have been corrected for the optical purities of the initial diazotates (amines). [f] No 1-phenylethanol was detected, but this alcohol would have been converted to RCl under the reaction conditions. Based on the IB reactions (see below), 3-4% of ROH might have been expected. [g] 2-Octanol (3-4%) formed in these reactions. Controls showed that RCl is not substantially hydrolyzed (1%) to ROH on work-up, and that ROH is not substantially converted (1.5%) to RCl by $SOCl_2$ under the reaction conditions. Both RCl and ROH are therefore primary products of (IB + $SOCl_2$). The alcohol could arise from reaction of IB with HCl liberated during the formation of octenes from IIB. [h] 2.6 mole-% of HCl was added to the $SOCl_2$ solvent. [i] About 3% of 2-octanol was formed. [j] 75 vol-% of CH_2Cl_2 was added to the $SOCl_2$ solvent. [k] 4% of 2-octanol was formed. [l] 3.3 equiv. (based on IB) of $(n\text{-}C_4H_9)_4N^+Cl^-$ was added to the $SOCl_2$ solvent.

Although the title reactions, eq. (1), appear to be extended deaminations, the timing of C-N, N-O, and S-Cl bond fissions in II is unclear. Covalent II could be concertedly converted to III, or could reach III by at least three alternative cascades of ion pair intermediates. (a) Initial S-Cl cleavage[16b] to $[RN{=}NOSO^+Cl^-]$ could be followed by either stepwise or concerted loss of SO_2 and N_2. (b) Initial N-O cleavage to $[RN_2^{+-}OSOCl]$[17] could be followed by independent, rapid fragmentations at C-N and S-Cl bonds (order uncertain). (c) Concerted fission could take place at C-N and N-O, affording $[R^+N{\equiv}N^-OSOCl]$, in which the anion could fragment further to (SO_2, Cl^-) before diffusion destroyed the initial cage. The complexity is enhanced by the likely dependence of pathway on the identity of R.

Because IIA can yield the relatively stable 1-phenylethyl cation, the ultimate formation of ion pair IIIA is reasonable, and can occur either concertedly or by path (c). Conversion of (*syn*[18]) diazotate IA to 1-phenylethyl chloride accords with the intervention of such an ion pair in that the stereochemical results (Table I, runs 1-3) are similar to the 39% net retention attributed to the decomposition via an ion pair of $[C_6H_5CH(CH_3)N{=}NCl]$ in dioxane,[19] and differ from the 31% net inversion observed upon capture of $[C_6H_5CH(CH_3)N{=}NOH]$ by external chloride ion in liquid ammonia.[20] Decomposition of IIA from cyclic conformation IIA' could have given RCl with high net retention, but, evidently, this does not occur.[21] The observed stereochemical result is more in accord with an "extended" ion pair intermediate (IIIA), formed with a geometry related to that of its precursor (II) in the pictured "zig-zag" conformation.

The 2-octyl cation is less stable than the 1-phenylethyl cation, suggesting that decomposition of IIB should prefer paths (a) or (b). In either case, chloride could be available within an ion pair *before* the 2-octyl cation was formed. Depending on the mutual rotations within this ion pair, an excess of chloride could react at the rear-side of the octyl moiety, as opposed to the predominant front-side capture evident in the IIA decompositions. This would account for the marginal excess of inversion observed in formation of the 2-chlorooctane (Table I, runs 4-6).[22] 2-Chlorooctane does not appear to form by S_N2 capture of "external" chloride because neither the yield nor the stereochemical inversion are enhanced when chloride sources HCl,[23] CH_2Cl_2,[24] or $(\underline{n}\text{-}C_4H_9)_4N^+Cl^-$ are added to the $SOCl_2$ used to decompose IB.[25] It is interesting that the principal reaction of the ion pair(s) produced from IIB is elimination. This has also been observed during certain 2-octyl chlorosulfite decompositions.[16b] In both cases, chloride counterion could be the effective base.[26]

Despite the low yields of products,[27] reactions (1) are of much mechanistic interest. Other extended deaminations can be readily designed and are to be investigated.

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References and Notes

(1) Alkane Diazotates, XXII; for Part XXI, see R. A. Moss and E. R. Grover, *J. Org. Chem.*, in press.

(2) Fellow of the A. P. Sloan Foundation.

(3) Postdoctoral Research Associate on leave from Sumitomo Chemical Co., Osaka, Japan.

(4) Ion pairs are commonly intermediates in deaminations, but only a single gas molecule (nitrogen) is usually involved. See (a) E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Interscience, New York, N.Y., 1968, pp. 440-483; (b) R. A. Moss, *Acc. Chem. Research*, **7**, 421 (1974).

(5) Examples of other extended deaminations include the reactions of alkyl azides with NO^+: M. P. Doyle, J. L. Whitefleet, and M. A. Zaleta, *Tetrahedron Lett.*, 4201 (1975); M. P. Doyle, D. M. Hedestrand, S. C. Busman, and D. Alexander, *J. Amer. Chem. Soc.*, **97**, 5554 (1975); and earlier papers in this series; and the reactions of alkyl sulfinylamines and isocyanates with NO^+, G. A. Olah, N. Friedman, J. M. Bollinger, and J. Lukas, *ibid.*, **88**, 5328 (1966). The former reaction has been largely restricted to triphenylmethyl, benzhydryl, or benzyl azides. In neither case have there been any stereochemical studies of the ensuing transformations. Consequently, until our present report, detailed analysis of the fate of species such as II or III has not been possible.

(6) R. A. Moss and C. E. Powell, *J. Org. Chem.*, **40**, 1213 (1975).

(7) R. A. Moss and S. M. Lane, *J. Amer. Chem. Soc.*, **89**, 5655 (1967).

(8) SO_2 was absorbed in 0.1 *N* NaOH solution; sulfite was oxidized to sulfate with 30% H_2O_2; and consumed base was determined by back-titration with 0.1 *N* HCl. In a duplicate experiment,

the evolved gasses were collected and examined in the mass spectrometer. SO_2 and N_2 were readily identified (M^+); HCl was absent.

(9) A series: 8' x 0.25", 8% SF-96 on a 60/70 Anakrom ABS Teflon column, 100°. B series: 18' x 0.25", 15% Carbowax 20M on a 60/80 Gas-Chrom R column, 115°.

(10) Based upon α_D^{22} -38.30° (neat, 1 dm) for the optically pure amine: W. Theilacker and H.-G. Winkler, *Chem. Ber.*, **87**, 690 (1954).

(11) Based upon α_D^{19} -2.66° (neat, 0.5 dm) for the optically pure amine: F. G. Mann and J. W. G. Porter, *J. Chem. Soc.*, 3384 (1950).

(12) R. A. Moss and G. M. Love, *J. Amer. Chem. Soc.*, **95**, 3070 (1973).

(13) R. L. Burwell, A. D. Shields, and H. Hart, *ibid.*, **76**, 908 (1954). The reported values for retention in IA → RCl are therefore maxima. They could be too high by as much as 16%.

(14) H. R. Hudson, *Synthesis*, **1**, 112 (1969), Table 5, footnote *c*; H. M. R. Hoffmann, *J. Chem. Soc.*, 1249 (1964).

(15) J. A. Mills and W. Klyne, *Prog. Stereochem.*, **1**, 194-195 (1954).

(16) (a) E. S. Lewis and C. E. Boozer, *J. Amer. Chem. Soc.*, **74**, 308 (1952); (b) C. E. Boozer and E. S. Lewis, *ibid.*, **75**, 3182 (1953); (c) K. B. Wiberg and T. M. Shryne, *ibid.*, **77**, 2774 (1954). (d) We were unable to detect IVA by nmr in 30 min. old (-70°) solutions of 1-phenylethanol in $SOCl_2$, only RCl was present. IVB is quite stable under these conditions.

(17) D. J. Cram, *J. Amer. Chem. Soc.*, **75**, 332 (1953) suggests that ROSOCl fragments to R^{+-}OSOCl. See, also, A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 379 (1957).

(18) For a discussion and leading references, see reference 4b.

(19) H. Felkin, *Compt. Rend. Acad. Sci. (Paris)*, **236**, 298 (1953).

(20) R. A. Moss, P. E. Schueler, and T. B. K. Lee, *Tetrahedron Lett.*, 2509 (1973).

(21) We discount radical mechanisms for decomposition of IIA. The addition of IA to $SOCl_2$ containing 25 vol-% of cumene gave neither ethylbenzene nor 2,3-diphenylbutane, both of which would have been expected had the 1-phenylethyl radical intervened.

(22) A similar idea was used to explain the formation of inverted RCl during certain thermolyses of IVB.[16b]

(23) The failure of added HCl to increase the yield of the 2-chlorooctane product weighs against formation of the latter by reaction of IB with HCl released in octene formation. Moreover, the lack of enhanced racemization in the presence of added HCl (Table I, run 6) weighs against chloride formation by addition of HCl to the octene byproduct. Although a parallel control was not carried out with IA, it is unlikely that 1-phenylethyl chloride was substantially formed by the addition of HCl to styrene. Thus, over runs 1-3 (Table I), the absolute yield of chloride nearly tripled, and the product ratio styrene/chloride varied from 2.1 to 0.68, yet the stereochemistry of formation of the chloride was essentially unchanged. These results are inconsistent with significant chloride formation by the extraneous, racemizing styrene + HCl pathway.

(24) CH_2Cl_2 intercepts deaminatively generated bridgehead cations: E. H. White, R. H. McGirk, C. A. Aufdermarsh, Jr., H. P. Tiwari, and M. J. Todd, *J. Amer. Chem. Soc.*, **95**, 8107 (1973).

(25) In contrast, essentially racemic 2-chlorooctane is formed from IB and $(CH_3)_3SiCl$ in HMPA, presumably via $RN{=}NOSi(CH_3)_3$, but yield (11 → 23%) and net inversion (0.1 → 27%) respond to the addition of LiCl: R. A. Moss and P. E. Schueler, *J. Amer. Chem. Soc.*, **96**, 5792 (1974).

(26) For examples of counter-ion induced elimination in deaminative processes see: E. H. White, *J. Amer. Chem. Soc.*, **77**, 6014 (1955); T. Cohen, A. R. Daniewski, G. M. Deeb, and C. K. Shaw, *ibid.*, **94**, 1786 (1972); and R. A. Moss and K. M. Luchter, *J. Org. Chem.*, **37**, 1155 (1972).

(27) The decomposition of IB, in particular, produces much tar. A referee has asked whether "the cause of the predominant inversion in reactions of IB with $SOCl_2$ (could) be displacement of HMPA from a solvent separated ion pair?" We believe the answer is no. If HMPA trapped anything, it would trap IIB, or [$RN{=}NOSO^+Cl^-$], or [RN_2^{+-}OSOCl], or even IIIB with *inversion*. Subsequent attack of Cl^- would produce RCl with net *retention* as a consequence of "double inversion".