References and Notes

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Deamination of 2-Phenyl-2-(2-methoxyphenyl)-ethylamine

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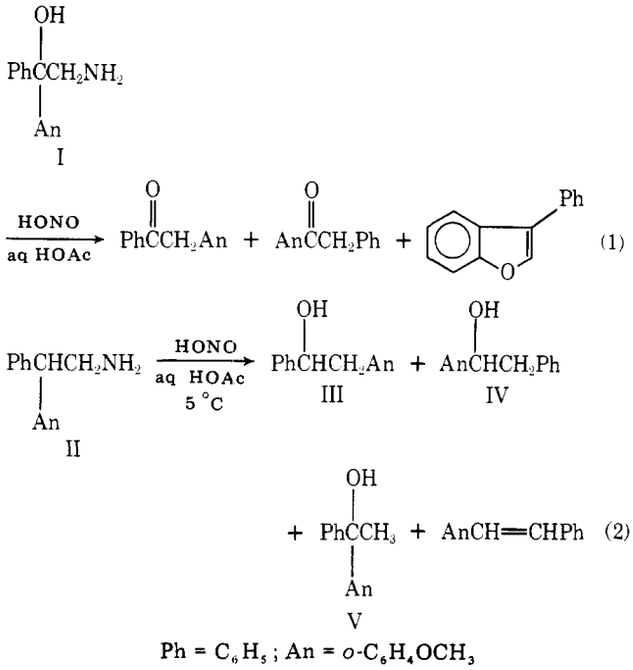
Received February 28, 1977

Previously we reported[1] the results of deamination of amino alcohol I, which demonstrated the first example of *o*-MeO-5 participation[2] in such rearrangements (eq 1). We now report the deamination of the related amine II (eq 2).



Ph = C_6H_5; An = *o*-$C_6H_4OCH_3$

Treatment of the hydrochloride of II with sodium nitrite in aqueous acetic acid at 5 °C produced (after treatment of the reaction mixture with lithium aluminum hydride to cleave any acetates) alcohols III,[3,4] IV,[3,5,6] a minor amount (<5%) of V,[7] and an alkene fraction consisting of *o*-methoxystilbenes.[5,8,9] There is no indication of *o*-MeO-5 participation in the present case, in direct contrast to the deamination of I.

Typical migratory aptitudes of aryl groups in such reactions of diarylethylamines (Ph = 1.00) are *p*-tolyl, 1.18,[10] and *p*-anisyl, 1.44.[11] Such results have been interpreted in terms of ground-state conformational control in both amino alcohol and amine cases.[12,13] The migratory ability of the *o*-anisyl group in various rearrangements has been shown to be <1.[1,14,15,16] In the present case, the migratory ratio for the *o*-anisyl group (III/IV by ^1H NMR analysis) is 2.67. This appears to be substantially the highest migratory aptitude observed for any aryl group in reactions of this kind, for reasons about which we can only speculate at this time. Furthermore, we find no evidence of *o*-MeO-5 participation in the present case. We are attempting experiments designed to provide information about ground-state conformations in diarylethylamines and diarylethyl amino alcohols and thus yield some insight into the reasons for the observed migration tendencies.

Experimental Section

2-Methoxybenzophenone. Addition of phenylmagnesium bromide to *o*-methoxybenzaldehyde (Aldrich Chemical Co., Inc.), followed by oxidation of the crude product with Jones reagent in benzene (48 h reflux), provided 2-methoxybenzophenone: mp 36–37 °C (lit.[17] mp 39 °C).

2-Phenyl-2-(2-methoxyphenyl)ethanal (VI). 1-Phenyl-1-(2-methoxyphenyl)ethene[18] was prepared by treatment of 2-methoxybenzophenone with methylmagnesium iodide in tetrahydrofuran, followed by dehydration of the alcohol product (V[7]) with H_2SO_4 (pH 1) during workup: yield 89%; bp 120–125 °C (2 Torr). H_2O_2 (30%, 21 mL) was added dropwise to formic acid (97%, 100 mL) and the solution was allowed to stand for 1 h. Then a solution of the alkene[18] (31.0 g) in benzene (100 mL) was added dropwise and the mixture was stirred overnight. The layers were separated and the benzene layer was extracted with water, saturated $NaHCO_3$, and water, and dried. The benzene was removed at reduced pressure and the aldehyde was distilled: yield 23.7 g (71%); bp 135 °C (~1 Torr) [lit.[19] bp 198–200 °C (16 Torr)]; IR (neat) 2715, 1723 cm^{-1}; NMR ($CDCl_3$) δ 3.62 (3 H, s, OCH_3), 5.05 (1 H, d, J = 3 Hz, CH), 7.19 (9 H, m, ArH), 9.83 (1 H, d, J = 3 Hz, CHO).

2-Phenyl-2-(2-methoxyphenyl)ethanal Oxime (VII). A mixture of aldehyde VI (8 g), hydroxylamine hydrochloride (8 g), sodium hydroxide (8 g), water (160 mL), and ethanol (150 mL) was heated at reflux for 1 h. Standard workup yielded 3.4 g of the oxime: mp 112–114 °C; IR ($CHCl_3$) 3200, 1245, 1039 cm^{-1}; NMR ($CDCl_3$) δ 3.69 (3 H, s, OCH_3), 5.25 (1 H, d, J = 8 Hz, CH), 7.2 (9 H, m, ArH), 7.83 (1 H, d, J = 8 Hz, CHN), 8.70 (1 H, s, OH).

2-Phenyl-2-(2-methoxyphenyl)ethylamine Hydrochloride (II HCl). Oxime VII was reduced with lithium aluminum hydride in refluxing diethyl ether for 24 h. Saturated Na_2SO_4 was added dropwise to quench the reaction. The ether layer was dried ($MgSO_4$) and then saturated with anhydrous HCl. The crystals of II HCl which formed were recrystallized from ethanol–acetone: mp 215–217 °C; IR (KBr) 3400, 1245, 1030, 908 cm^{-1}; NMR (free base, $CDCl_3$) δ 3.25 (2 H, d, J = 8 Hz, CH_2), 3.74 (3 H, s, OCH_3), ~3.74 (2 H, br s, NH_2), 4.50 (1 H, t, J = 8 Hz, CH), 7.25 (9 H, m, ArH).

Anal. Calcd for $C_{15}H_{18}ClNO$: C, 68.30; H, 6.78; N, 5.31; Cl, 13.44. Found: C, 68.60; H, 7.04; N, 4.93; Cl, 13.44.

Deamination Reactions. In a typical run 40 mg of amine hydrochloride II HCl and 40 mg of $NaNO_2$ were dissolved in 10 mL of 50% acetic acid and allowed to stand for 4 h at 5 °C. Then 1 mL of saturated NH_2SO_3H was added, followed by 15 mL of 6 N NaOH. The reaction mixture was extracted with CH_2Cl_2 (three 10-mL portions) and the combined extracts were dried ($MgSO_4$). Solvent was removed at reduced pressure and 30 mL of anhydrous ether was added. Then ~50 mg of lithium aluminum hydride was added to cleave any acetates. The reaction was quenched with saturated Na_2SO_4, and the aqueous layer was extracted with CH_2Cl_2 (three 10-mL portions). The combined organic layers were dried and solvent was removed at reduced pressure to leave an oil, which was diluted with 1 mL of diethyl ether and chromatographed on thick-layer silica gel plates with acetone–benzene (1:99). The alcohol fraction was removed and analyzed by ^1H NMR using the methoxyl singlets (solvent $CDCl_3$, δ 3.70 for III, 3.65 for IV, 3.42 for V) at expanded sweep width for quantification. Duplicate runs gave the same results.

A similar run with 328 mg of II HCl (1.24 mmol) and 390 mg of $NaNO_2$ but without the $LiAlH_4$ treatment allowed isolation of 113 mg (0.497 mmol) of mixed alcohols, 46.2 mg (0.143 mmol) of mixed acetates, and 61.4 mg (0.290 mmol) of an alkene fraction which appeared by ^1H NMR to be a mixture of *o*-methoxystilbenes;[5,8,9] net recovery, 75%.

The alkene fraction isolated above was subjected to the deamination conditions and shown to be unchanged; the alcohols were also shown to be stable to the reaction conditions, as judged by TLC and ^1H NMR.

Acknowledgment. We wish to thank Dr. Edward Rosenberg for helpful discussions and suggestions.

Registry No.—II, 63059-14-3; II HCl, 51431-51-7; III, 30314-63-7; IV, 22817-10-3; V, 32250-84-3; VI, 63059-15-4; VII, 63059-16-5; 1-phenyl-1-(2-methoxyphenyl)ethene, 24892-80-6; 2-methoxybenzophenone, 2553-04-0.

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Mass Spectrometry of Alkenyl and Aryl Thiolacetates

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Received March 15, 1977

The mass spectra of alkenyl and aryl thiol acetates were studied in connection with our investigations of the photochemistry of these compounds.[1,2,3] The three important fragmentation mechanisms involve cleavage of the sulfur carbonyl carbon bond as shown by paths a, b, and c in Schemes I and II. Homolysis of this bond is also the primary photochemical reaction.

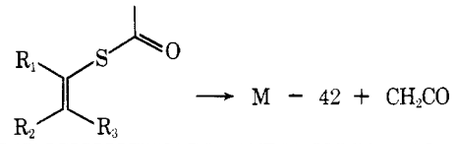
Path a, which involves the simultaneous dissociation of the sulfur–carbonyl carbon bond and the transfer to the sulfur fragment of the α-hydrogen atom, may occur by a four-centered mechanism to form ketene and the vinyl thiol radical cations or by a six-centered mechanism to form ketene and thioaldehyde radical cations (Scheme III).

For alkyl vinyl thioethers, the six-centered hydrogen-atom transfer is highly favored over the four-centered mechanism as ion cyclotron resonance spectroscopy has been used to show that deuterium is transferred from the β carbon of the alkyl side chain to the sulfur fragment to form thioaldehyde radical cations in preference to vinyl thiol radical cations by a 9:1 ratio.[4]

In the mass spectra of four saturated alkyl thioacetates, namely methyl, ethyl, propyl, and isobutyl thiolacetate, we observed no M − 42 ions. In contrast, the seven alkenyl thiolacetates which we studied formed the M − 42 ion in relative abundances ranging from 5 to 100% as shown in Table I.

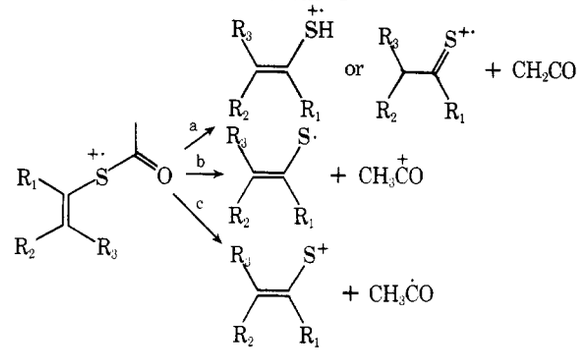
In saturated esters the six-centered hydrogen-atom transfer is structurally precluded, but the four-centered mechanism is possible. Thus, the absence of the M − 42 ions for the saturated alkyl thiolacetates coupled with the ICR work on alkyl vinyl thiol ethers indicates the six-centered mechanism is probably responsible for the formation of the M − 42 ions from the alkenyl thiolacetates.

Table I

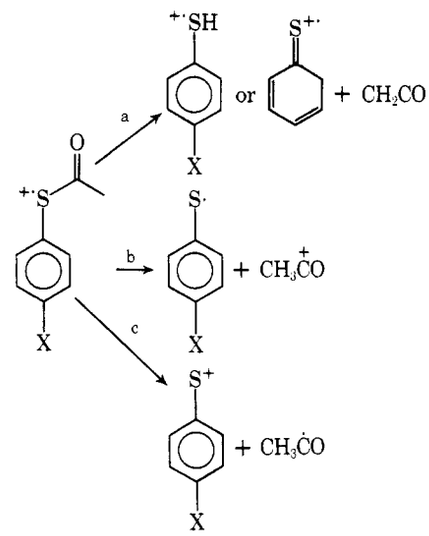


R_1	R_2	R_3	Registry no.	Rel abundance M − 42, %
H	H	H	10340-63-3	5
H	CH_3	CH_3	63059-17-6	70
H	$(CH_3)_3C$	H	63059-18-7	17
H	C_6H_5	H	52214-53-6	78
H	CH_3	H	63059-19-8	10
	$(CH_2)_3$	H	16214-69-0	38
	$(CH_2)_4$	H	15786-82-0	100

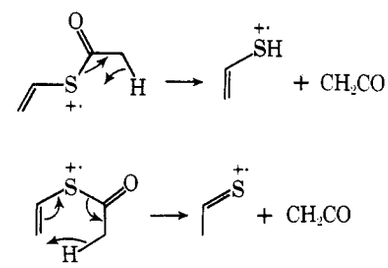
Scheme I



Scheme II



Scheme III



The two cyclic enethiolacetates, cyclopentenyl thiolacetate (1) and cyclohexenyl thiolacetate (2), display relative abundances of the M − 42 ion of 38 and 100%, respectively. If the transition state for the formation of these M − 42 ions were four centered, then the relative abundances of the ions should