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A Radical-induced Extrusion Reaction of 2-(Benzylsulfonyl)tropones to 2- and 4-Benzyltropones

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Synopsis. Several 2-(benzylsulfonyl)tropones were thermolized to give 2- and 4-benzyltropones. The radical mechanism for the thermolysis was elucidated by a deuterium-labelling experiment.

Upon thermolysis, 2-(benzyloxy)tropones (**1**) can be transformed to the 3- (**2**) and 5-benzyltropolones (**3**) in good yields *via* a radical chain reaction.[1] This behavior in the thermal reaction was unexpected, so we have undertaken the study with some other derivatives; the findings obtained from the sulfonyl derivatives will be described here.

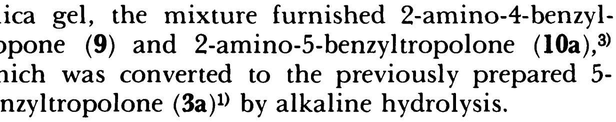
The substrates, 2-(benzylsulfonyl)tropones (**4**), with some amounts of 2-(benzylsulfinyl)tropones (**5**), were prepared by the *m*-chloroperbenzoic acid (MCPBA)-oxidation of the crresponding 2-(benzylthio)tropones (**6**).

These **6** were thermally unreactive up to 195°C, where **1** caused a rearrangement to **2** and **3**, but the corresponding sulfones, **4**, have caused a new type of thermally-induced elimination: by heating at 180°C to 225°C in tetralin, 2-(benzylsulfonyl)tropone (**4a**) yielded 2-benzyltropone (**7a**), 23%, a pale yellow oil,[2] and 4-benzyltropone (**8a**), 7.5%, a pale yellow oil. The structure of **8a** was determined by chemical correlation. After a brief treatment with hydrazine hydrate in ethanol, **8a** yielded a 3:2-mixture of 2-aminotropones. By preparative thin-layer chromatography (PTLC) on silica gel, the mixture furnished 2-amino-4-benzyltropone (**9**) and 2-amino-5-benzyltropolone (**10a**),[3] which was converted to the previously prepared 5-benzyltropolone (**3a**)[1] by alkaline hydrolysis.

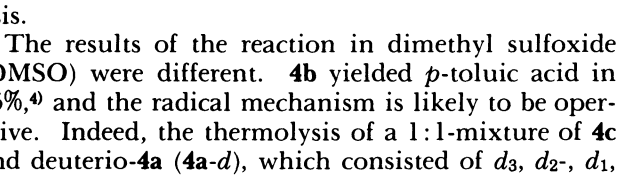
Two other sulfones, *p*-methyl (**4b**) and *p*-bromo (**4c**) derivatives, gave similar products upon the thermolysis.

The results of the reaction in dimethyl sulfoxide (DMSO) were different. **4b** yielded *p*-toluic acid in 65%,[4] and the radical mechanism is likely to be operative. Indeed, the thermolysis of a 1:1-mixture of **4c** and deuterio-**4a** (**4a**-*d*), which consisted of d_3, d_2-, d_1, and d_0-derivatives (19:58:20:3), in dioxane revealed an extensive cross-over recombination of two components in the mass spectra (Table 1) of the thermolysates (**7a**, **7c**, **8a**, and **8c**), to leave no ambiguity for the intermolecular path.

Consequently, the present reaction is another example of the radical substitution of benzyl group onto the tropone ring initiated by a homolysis of X–C bond of the C-2 position to form the delocalized species.



Scheme 1.



Scheme 2.

Experimental

*Preparation of 2-(Benzylthio)tropone (**6a**).* To an EtOH solution (3 cm³) of 2-mercaptotropone (200 mg) and NaOMe (100 mg), benzyl chloride (230 mg) was added and refluxed for 2 h on an oil bath. The mixture was evaporated, and the residue was chromatographed on a silica-gel column to give yellow needles, mp 98—99°C (**6a**). 237 mg (70%) [Found: C, 73.89; H, 5.38%. Calcd for $C_{14}H_{12}OS$: C, 73.65; H, 5.30%. δ[5]=4.00 (2H, s) and 6.7—7.4 (10H, m). δ(C)=36.7, 127.5 (2C), 128.6 (2C), 128.9 (2C), 129.9, 132.6, 134.7 (2C), 136.1, 158.7, and 183.2. ν: 1615, 1555, 1460, 1385, 985, 915, 840, and 765 cm⁻¹].

*2-(*p*-Methylbenzylthio)tropone (**6b**).* This was prepared as colorless needles, mp 98—100.5°C [Found: C, 74.20; H, 5.79%. Calcd for $C_{15}H_{14}OS$: C, 74.35; H, 5.82%. δ=2.29 (3H, s), 3.98 (2H, s), and 6.7—7.3 (9H, m)], in 87% yield.

*2-(*p*-Brmobenzylthio)tropone (**6c**).* This was prepared as yellow needles, mp 133—135°C [Found: 54.46; H, 3.64%. Calcd for $C_{14}H_{11}OSBr$: C, 54.74; H, 3.61%. δ=4.02 (2H, s) and 6.8—7.5 (9H, m)], in 73% yield.

*MCPBA-oxidatin of **6a**.* *a)*: To a $CHCl_3$ solution (8 cm³) containing **6a** (455 mg, 2 mmol), MCPBA (740 mg, 3.4 mmol) dissolved in $CHCl_3$ (16 cm³) was added drop by drop for 4 h, and kept for an additional 24 h at 15—25°C. Then the separated crystals, MCBA, were filtered off, and the filtrate was washed with aqueous $NaHSO_3$, $NaHCO_3$, and NaCl, and dried on $MgSO_4$. Silica gel column chromatography of the organic solution afforded **4a**, 347 mg (67%), colorless needles, mp 113—114°C [Found; C, 64.83; H, 4.71%. Calcd for $C_{14}H_{12}O_3S$: C, 64.60; H, 4.65%. δ=4.90 (2H, s), 7.0—7.5 (9H, m), and 7.8—9.0 (1H, m). δ(C)=60.9, 127.6, 128.5 (2C), 128.7, 130.7 (2C), 131.5, 136.0, 139.5, 140.4, 143.7, 146.0, and 182.4. ν: 1635, 1585, 1305, 1270, 1215, 1145, 1125, and 780 cm⁻¹], and **5a**, 107 mg (22%), a colorless oil [Found: M⁺, 244.0544. Calcd for $C_{14}H_{12}O_2S$: M⁺, 244.0558. δ=3.95 (1H, d, J=12 Hz), 4.40 (1H, d, J=12 Hz), and 6.8—7.6 (10H, m). δ(C)=57.6, 128.0 (2C), 129.6, 130.3 (2C), 132.7, 135.5, 135.9, 137.3, 140.9, 155.9, and 183.6. ν: 1620, 1590, 1555, 1260, 1070, 1050, 875, 860, and 760 cm⁻¹].

TABLE 1. THE DEUTERIUM CONTENTS (%) IN THE PRODUCTS OF THE CROSS-OVER THERMOLYSIS OF **4a**-*d* AND **4c** DETERMINED BY MASS SPECTROMETRY

Products	d_0	d_1	d_2	d_3
7a	43.8	28.6	20.8	6.8
7c	48.9	35.8	10.4	4.9
8a	32.3	30.0	24.5	13.2
8c	35.4	26.7	22.8	15.0

b): Similarly, the oxidation of **6a** (115 mg, 0.5 mmol) in $CHCl_3$ (8 cm^3) with MCPBA (216 mg, 1.0 mmol) at 15—25°C for 24 h yielded 118 mg (91%) of **4a**.

*2-(*p*-Methylbenzylsulfonyl)tropone (**4b**).* This was prepared as colorless needles, mp 173—175°C [Found: C, 65.38; H, 5.12%. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14%. δ= 2.26 (3H, s), 4.76 (2H, s), 6.8—7.3 (8H, m), and 7.83 (1H, dd, J=8, 2 Hz)], in 80% yield.

*2-(*p*-Bromobenzylsulfonyl)tropone (**4c**).* This was prepared as yellow needles, mp 135—137°C [Found: M^+, 337.9598 and 339.9590. Calcd for $C_{14}H_{11}O_3SBr$: M^+, 337.9612 and 339.9592. δ=4.77 (2H, s), 6.8—7.7 (8H, m), and 7.84 (1H, m)], in 99% yield.

*Thermolysis of **4a**.* A tetralin solution (2 cm^3) of **4a** (136 mg) was heated at 215°C for 1.5 h on an oil bath under N_2 atmosphere. During the reaction, an intermittent evolution of SO_2 occurred. The mixture was then fractionated with a short silica-gel column and with PTLC to furnish **7a**, a colorless oil [Found: M^+, 196.0877. Calcd for $C_{14}H_{12}O$: M^+, 196.0888. δ=3.94 (2H, s), 6.8—7.3 (5H, m), and 7.21 (5H, s). δ(C)=40.5, 126.4, 128.5 (2C), 129.5 (2C), 132.6, 133.6, 135.4 (2C), 139.0, 140.6, 154.7, and 186.6], 24 mg (23%), which was identical with the sample prepared by the Nozoe's method,[2] and **8a**, a colorless oil [Found: M^+ 196.0889. δ=3.82 (2H, s) and 6.7—7.4 (10H, m). δ(C)=45.7, 126.9, 128.8 (2C), 128.9 (2C), 133.0, 136.2 (2C), 138.9, 140.3, 141.3, 148.2, and 187.6], 8 mg (7.5%).

*The Reaction of **8a** with Hydrazine Hydrate.* An EtOH solution (10 cm^3) of **8a** (28 mg) was refluxed with 80% N_2H_4 hydrate (30 mg) for 2 h. Then, the mixture was fractionated with $CHCl_3$ and water, and the organic extract was purified by PTLC on silica gel to yield a yellow oil, **9**, 12 mg [Found: M^+, 211.0998. Calcd for $C_{14}H_{13}ON$: M^+, 211.0997. δ=3.88 (2H, s), 5.86 (2H, m), 6.70 (1H, br. s), and 7.0—7.4 (8H, m)], and **10**, 9 mg [Found: M^+, 211.0998. δ=3.88 (2H, s), 5.82 (2H, br. s), 6.76 (1H, d, J=10 Hz), and 6.9—7.3 (8H, m)].

*Hydrolysis of **10** to **3a**.* An EtOH solution (2 cm^3) of **10** (5 mg) and KOH (5 mg) was refluxed for 2 h. The mixture was then evaporated to dryness, acidified with dil HCl, and extracted with $CHCl_3$. Colorless needles, mp 119—120°C, 5 mg, thus obtained were identical in every respect to the previously prepared sample of **3a**.[1]

*Thermolysis of **4b**.* A tetralin solution (5 cm^3) of **4b** (90 mg) was heated at 200°C for 1.7 h. The products isolated by PTLC were **7b**, a colorless oil, 19 mg (28%) [Found: M^+, 210.1047. Calcd for $C_{15}H_{14}O$: M^+ 210.1045. δ=2.30, 3.90 (2H, s), and 6.7—7.3 (9H, m)], and **8b**, a colorless oil, 5.5 mg (8%) [Found: M^+, 210.1043. δ=2.32 (3H, s), 3.78 (2H, s), and 6.7—7.4 (9H, m)].

*Thermolysis of **4b** in DMSO.* A DMSO solution (0.3 cm^3) of **4b** (50 mg) was heated at 180°C for 1.5 h. The mixture was diluted with ether, and extracted with aqueous KOH to give 16 mg (65%) of colorless crystals, mp 178—179°C, which were identical with *p*-toluic acid.

*Thermolysis of **4c**.* A tetralin solution (5 cm^3) of **4c** (170 mg) was heated at 225°C for 2 h. The products isolated by PTLC were **7c**, a colorless oil, 27 mg (20%) [Found: M^+, 274.0001 and 275.9958. Calcd for $C_{14}H_{11}OBr$: M^+, 273.9993 and 275.9973. δ=3.90 (2H, s) and 6.8—7.4 (9H, m)], and **8c**, a colorless oil, 1 mg (0.7%) [Found: M^+, 274.0009 and 275.9971. δ=3.78 (2H, s) and 6.7—7.5 (9H, m)].

*Thermolysis of a 1:1-Mixture of **4a**-d and **4c**.* A decalin solution (4 cm^3) of **4a**-*d* (123 mg) and **4c** (150 mg) was refluxed for 1.5 h on an oil bath under an N_2 stream. The mixture was then fractionated on a silica-gel column to give the thermolysates; their isotope distributions are given in Table 1.

References

1) H. Takeshita, H. Mametsuka, A. Chisaka, and N. Matsuo, *Chem. Lett.*, **1981**, 73.

2) T. Nozoe, T. Mukai, and I. Murata, *Proc. Jpn. Acad.*, **29**, 169 (1953).

3) In comparing the ^{13}C-NMR of these 2-aminobenzyltropones with the parent 2-aminotropone (**11**), the following chemical shift differences, $\Delta\delta$(C-*n*)=δ(**11**)−δ(**9** or **10**), were obtained; for **9**, $\Delta\delta$(C-3)=−2.2, $\Delta\delta$(C-4)=−20.2, $\Delta\delta$(C-5)= −1.4, and $\Delta\delta$(C-6)=−0.7, and for **10**, $\Delta\delta$(C-3)=1.8, $\Delta\delta$(C-4)= 0.1, $\Delta\delta$(C-5)=−13.5, and $\Delta\delta$(C-6)=−2.9.

4) H. Takeshita, H. Mametsuka, and N. Matsuo, *Bull. Chem. Soc. Jpn.*, **55**, 1137 (1982).

5) The NMR spectra were measured in $CDCl_3$ solutions, and the chemical shifts were expressed in δ scale from the internal Me_4Si.