to be 2-(4'-chlorophenyldithio)-2-methylpropanoic acid contaminated with a small amount of 2,2'-dithiodiisobutyric acid.

**Registry No.**—4-$ClC_4H_4SSCMe_2CO_2H$, 30247-81-5; 4-chlorophenyl disulfide, 1142-19-4.

**Acknowledgment.**—We are grateful to the National Science Foundation for the support of C. P. E. and to the Toni Company, Chicago, Ill., for the support of J. S. during the summers of 1968 and 1969.

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# *Notes*

## Lithium Aluminum Hydride Reduction of Bridged Bicyclic Nitroso Chloride Dimers

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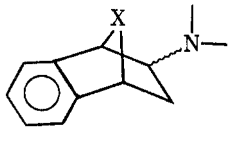
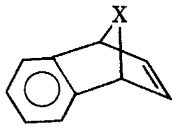
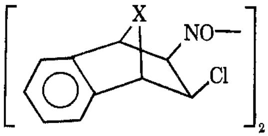
*Received December 7, 1970*



**1a**, X = $CH_2$
**b**, X = O

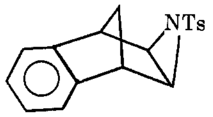


**2a**, X = $CH_2$
**b**, X = O

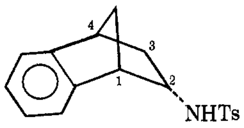


**3a**, X = $CH_2$
**b**, X = O

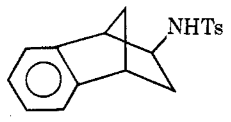
In connection with synthetic routes to amino compounds of type **1**, we have examined the $LiAlH_4$ reduction of the nitrosyl chloride adducts **3** derived from the olefins **2**. Thus, treatment of **2a** with nitrosyl chloride in chloroform followed by dilution with methanol afforded the white dimer **3a**[1] in 68% yield. Reaction of **3a** with $LiAlH_4$ in dioxane (heterogeneous mixture) followed by acylation with *p*-toluenesulfonyl chloride in pyridine provided a mixture from which two compounds could be isolated. The major product (*ca.* 45%), mp 153–154°, was shown to be the *exo*-aziridine **4** by comparison with authentic material prepared from **2a** and tosyl azide.[2] The minor product (*ca.* 5%), mp 142–144°, is assigned the endo structure **5** on the basis of its composition and the following nmr (100 MHz, $C_6D_6$) evidence: $\delta$ 1.82 (doublet of quartets, $J$ = 12.3, 9.8, 4.0 Hz, $H_3$ exo), 2.73 (broad singlet, $H_4$), 3.11 (doublet of triplets, $J$ = 1.0, 1.0, 4.0 Hz, $H_1$), 3.59 (broad doublet, $J$ = 9.8, 4.0, and *ca.* 0.9 Hz, $H_3$ endo). The presence of a 4-Hz coupling between $H_1$ and $H_2$ dictates the exo configuration for $H_2$ (and thus the endo configuration for the *N*-tosyl group) since it is well established that coupling of significant magnitude between such protons in bicyclic systems is observed only when $H_2$ is exo.[3] Further, **5** is isomeric with **6**, mp 123–125°, which was prepared by treatment of **2a** with sodium azide–mercuric acetate–sodium borohydride in THF–$H_2O$,[4] followed by $LiAlH_4$ reduction of the azide and tosylation (60% overall yield). This sequence would be expected to lead to the exo product **6**; that this is indeed the case is supported by the apparent absence of coupling between $H_1$ and $H_2$ in the nmr spectrum (100 MHz, $C_6D_6$) of **6**. Careful comparison of the nmr spectra of **4**, **5**, and **6** with the spectrum of the mixture from reduction of **3a** showed the composition to be 60% **4**, 25% **5**, and 15% **6**.



**4**



**5**



**6**

Prior thermal isomerization of **3a** followed by $LiAlH_4$ reduction and tosylation, as before, led to a mixture of **4**, **5**, and **6** in approximately the same ratio. It thus seems reasonable to suppose that the reduction of **3a** occurs *via* a prior isomerization to a chloro oxime (which could not be isolated). Recent work has shown that $LiAlH_4$ reduction of bridged oximes gives predominantly aziridines.[5]

The 7-oxa analog **3b** behaved differently. Treatment of **2b** with nitrosyl chloride provided **3b** (61%).[1] Reduction of **3b** with $LiAlH_4$ (either directly or after thermal isomerization) followed by tosylation afforded a mixture from which two isomeric, chlorine-containing tosyl amides could be isolated by fractional crystallization from 2-propanol. The less soluble isomer, mp 185–187° (*ca.* 20% yield), is assigned the exo-cis structure **9**; the more soluble isomer, mp 196–198° (*ca.* 20% yield), was assigned the endo-trans structure **9**. Careful examination of the nmr spectrum of the crude mix-

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(1) Exo–cis stereochemistry is based on analogy with other NOCl additions [*e.g.*, J. B. Miller, *J. Org. Chem.*, **26**, 4905 (1961); J. Meinwald, Y. C. Meinwald, and T. N. Baker, III, *J. Amer. Chem. Soc.*, **86**, 4074 (1964)] and subsequent transformations.

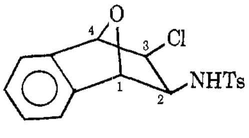
(2) M. M. Martin and R. A. Koster, *J. Org. Chem.*, **33**, 3428 (1968).

(3) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

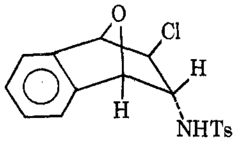
(4) C. H. Heathcock, *Angew. Chem., Int. Ed. Engl.*, **8**, 134 (1969).

(5) For a recent summary, see K. Kotera and K. Kitahonoki, *Org. Prep. Proced.*, **1**, 305 (1969).

ture showed that **8** and **9** accounted for at least 80% of the products.



**8**



**9**

The configurational assignments for **8** and **9** rest on nmr (100 MHz) arguments analogous to those presented for **5** and **6**. Thus in **9**, $H_1$ and $H_2$ are coupled by *ca.* 2.1 Hz as shown by double resonance. Irradiation of the doublet at $\delta$ 3.36 ($H_1$) causes collapse of the $H_2$ quartet at $\delta$ 4.22 to a doublet (values at 100 MHz, $CdCl_3$). No such coupling exists between $H_1$ and $H_2$ in **8**. Further nmr shift values are presented in Table I.

TABLE I

| Compd | $H_1$ | $H_2$ | $H_3$ | $H_4$ | NH |
|---|---|---|---|---|---|
| **5** | 3.18 | 3.59 | 4.10 | 3.18 | |
| **6** | 3.25 | 3.25 | 1.8 | 3.25 | 5.85 |
| **9** | 3.36 | 4.22 | 5.21 | 5.26 | 3.91 |
| **8** | 5.12 | 3.76 | 4.06 | 5.28 | 5.38 |

The most conspicuous distinguishing feature between the endo pairs (**5** and **9**) and the exo pairs (**6** and **8**), which further supports our configurational assignments made on the basis of coupling constants, is the very low field resonance position for the $H_3$ endo protons in **5** and **9**. This is obviously a result of the more proximal location of these protons in the endo orientation to the highly anisotropic sulfonamide and/or aromatic moieties of the *N*-tosyl function. The considerably smaller shift for $H_1$ on proceeding from **5** to **6** than from **9** to **8** is, however, troubling. This anomalous observation could possibly be rationalized if, in the exo compound **8**, the tosyl NH proton is intramolecularly hydrogen bonded to the bridge oxygen. This would have the effect of fixing the tosyl amide in close proximity to $H_1$, thereby exerting a deshielding influence upon this proton *via* a syn-diaxial mechanism.[6] In support of this explanation are two observations: (a) the lower field resonance position for the tosyl NH in **8** ($\delta$ 5.38) relative to **9** ($\delta$ 3.91) is strongly indicative of hydrogen bonding,[7] and (b) the presence of a 1.0-Hz coupling between $H_1$ and $H_4$ in **8** but not in **9** suggests some modification of the bridgehead molecular orbitals through which spin information is transmitted from $H_1$ to $H_4$. However, we see no evidence for hydrogen bonding in the ir spectrum of **8**.

The difference in behavior between **3a** and **3b** can be rationalized if it is assumed that in **3b** the organometallic reagent complexes on the bridgehead oxygen (and the nitroso group) rather than displacing chloride ion.

## Experimental Section

**Benzonorbornadiene Nitroso Chloride Dimer 3a.**—A stirred solution of 2.84 g (0.020 mol) of benzonorbornadiene in 30 ml of chloroform was cooled to 0° and purged with nitrosyl chloride for 5 min. After an additional 30 min at 0°, the green solution (containing some white solid) was diluted with 30 ml of methanol and filtered to afford 2.82 g (68.2%) of **3a** as fine white needles, mp 167–169° dec. Attempted recrystallization of this material led to extensive decomposition.

*Anal.* Calcd for $(C_{11}H_{10}ClNO)_2$: C, 63.62; H, 4.85; Cl, 17.07; N, 6.75. Found: C, 63.42; H, 5.03; Cl, 17.28; N, 6.83.

**7-Oxabenzonorbornadiene Nitroso Chloride Dimer 3b.**—The procedure described for **3a** afforded **3b** as a white powder, mp 153–154° dec, in 73% yield.

*Anal.* Calcd for $(C_{10}H_8ClNO)_2$: C, 57.29; H, 3.84; Cl, 16.91; N, 6.68. Found: C, 57.09; H, 3.97; Cl, 16.63; N, 6.82.

**Reduction of 3a.**—A stirred mixture of 2.07 g (0.010 mol) of **3a**, 3.8 g of $LiAlH_4$, and 100 ml of dioxane was cautiously heated to *ca.* 70° when a vigorously exothermic reaction set in. The source of heat was removed and the reaction allowed to subside. The mixture was then refluxed 1 hr and let stand overnight. Excess $LiAlH_4$ was destroyed by dropwise addition of 4 ml of $H_2O$, 3 ml of 20% NaOH, and 14 ml of $H_2O$. The mixture was extracted with ether and the ether solution washed with cold $H_2O$. Removal of solvent *in vacuo* from the dried ($K_2CO_3$) solution afforded a pale yellow oil (1.58 g) which rapidly darkened on exposure to air. An ice cold solution of this oil in 20 ml of ether was treated with 5 ml of pyridine and then, in one portion, with 1.90 g (0.010 mol) of *p*-toluenesulfonyl chloride. The resulting yellow-green mixture was stirred at 0° for 2 hr and then at room temperature overnight. The mixture was diluted with $H_2O$ (100 ml) and extracted with ether. The ether layer was washed with 50-ml portions of cold $H_2O$, cold 5% $NaHCO_3$, cold $H_2O$, cold 0.5 *N* HCl, and cold $H_2O$ and dried ($Na_2SO_4$). Removal of the solvent *in vacuo* provided 2.50 g of a yellow-green gum, a portion of which was reserved for the nmr spectrum. The remainder was dissolved in 15 ml of hot 2-propanol and the solution allowed to cool. The solid which precipitated was removed and the mother liquor concentrated portionwise, each crop of solid being collected separately. The less soluble product amounted to 1.40 g (45%) and, after recrystallization from 2-propanol, had mp 153–154°. Its spectra were superimposible on those of authentic exo-aziridine **4**. The more soluble product **5** amounted to 0.16 g (5%) of white needles and had mp 142–144° after recrystallization from 2-propanol.

*Anal.* Calcd for $C_{18}H_{19}NO_2S$: C, 68.99; H, 6.11; N, 4.47; S, 10.23. Found: C, 68.84; H, 6.01; N, 4.65; S, 10.51.

**Thermal Isomerization and Reduction of 3a.**—A stirred mixture of 2.07 g (0.010 mol) of **3a**, 50 ml of dioxane, and 1 drop of triethylamine was heated to reflux. Within 5 min all of the solid dissolved forming a pale green solution. After an additional 10 min the color faded. No precipitate formed when the solution was cooled. This solution was added dropwise to a slurry of 3.8 g (0.10 mol) of $LiAlH_4$ and 50 ml of THF (exothermic reaction). After the addition was complete, the mixture was stirred at reflux 1 hr and then at room temperature overnight. Work-up and tosylation were as described for **3a**. Nmr examination of the crude product showed approximately 65% **4**, 20% **5**, and 15% **6**.

**Reduction of 3b.**—The procedure described for **3a** afforded from 2.10 g (0.010 mol) of **3b**, 2.32 g of a mixture of **8** and **9**. Fractional crystallization from small volumes of 2-propanol provided the less soluble **8** as white needles, mp 185–187°, after further recrystallizations from 2-propanol (20% isolated yield).

*Anal.* Calcd for $C_{17}H_{16}ClNO_3S$: C, 58.36; H, 4.61; N, 4.00; S, 9.17; Cl, 10.14. Found: C, 58.21; H, 4.59; N, 3.95; S, 8.92; Cl, 10.23.

The more soluble **9** was isolated from the mother liquors in *ca.* 20% yield. Recrystallization from 2-propanol afforded white needles of **9**, mp 196–198°.

*Anal.* Found: C, 58.20; H, 4.52; N, 4.17; S, 9.07; Cl, 10.30.

***exo*-1,2,3,4-Tetrahydro-2-(*p*-tolylsulfonamido)1,4-methanonaphthalene (6).**—A stirred solution of 6.36 g (0.020 mol) of mercuric acetate in 20 ml of $H_2O$ was treated, in order, with 20 ml of THF, 3.72 g (0.060 mol) of $NaN_3$, and 2.84 g (0.020 mol) of **2a**. The resulting curdy white mixture was heated to 50–55° for 18 hr, cooled, and treated with 20 ml of 15% aqueous KOH followed by a solution of 0.40 g $NaBH_4$ in 20 ml of 15% aqueous KOH. The resulting black mixture was stirred in an ice bath, treated with excess solid NaCl, and extracted with several portions of ether. The combined ether extracts were quickly washed with three 30-ml portions of ice–$H_2O$ and dried ($Na_2SO_4$, 0°). The resulting pale yellow solution was added dropwise to a stirred mixture of 3.8 g of $LiAlH_4$ and 100 ml of ether (exothermic

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[6] K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *Chem. Commun.*, 759 (1966); P. B. Sollman, R. Nagarajan, and R. M. Dodson, *ibid.*, 552 (1967).

[7] G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, Chapter 4.

reaction). After the addition was complete, the mixture was stirred at reflux 1 hr and at room temperature overnight. Work-up and tosylation as described for **3a** afforded 3.77 g (60%) of **6** as a chalky solid, mp 119–124°. Several recrystallizations from 2-propanol afforded pure **6** as white needles, mp 123–125°.

*Anal.* Calcd for $C_{18}H_{19}NO_2S$: C, 68.99; H, 6.11; N, 4.47; S, 10.23. Found: C, 68.74; H, 6.32; N, 4.73; S, 10.50.

**Registry No.**—**3a**, 30135-80-9; **3b**, 30135-81-0; **5**, 30166-89-3; **6**, 30166-90-6; **8**, 30166-91-7; **9**, 30166-92-8.

**Acknowledgment.**—We are grateful to Professors J. E. Baldwin (MIT) and E. Wenkert (Indiana) for helpful discussions.

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## *trans*-1-Aryl-2-(arenesulfonyl)ethenes. Copper-Catalyzed Addition of Sulfonyl Chlorides to Substituted Styrenes[1]

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*Received January 21, 1971*

*trans*-1-Phenyl-2-(benzenesulfonyl)ethene (**2**, R = R′ = $C_6H_5$) has been prepared by (a) the condensation of benzenesulfonylacetic acid with benzaldehyde,[3] (b) the addition of benzenethiol to phenylacetylene followed by oxidation of the resulting *trans*-1-phenyl-2-(phenylmercapto)ethene with hydrogen peroxide,[4] and (c) the copper-catalyzed addition of benzenesulfonyl chloride to styrene followed by dehydrohalogenation of the resulting 1-chloro-1-phenyl-2-(benzenesulfonyl)ethane (**1**, R = R′ = $C_6H_5$) with triethylamine.[5] In this paper we would like to describe our studies on the synthetic utility of method c.

Arenesulfonyl chlorides can be added to styrenes to give 1-chloro-1-aryl-2-(arenesulfonyl)ethanes [**1**, R,R′ = aryl (eq 1)] in good to excellent yields (see Table I).

$$RCH{=}CH_2 + R'SO_2Cl \xrightarrow[Et_3N\cdot HCl,\ CH_3CN]{CuCl_2} \underset{\underset{\textbf{1}}{Cl}}{RCHCH_2SO_2R'} \quad (1)$$

The reaction appears to be little affected by substituent electronic effects or by steric effects of substituents in the 2 and 6 positions of either the sulfonyl chloride or the styrene. Treatment of the 1-chloro-1-aryl-2-(arenesulfonyl)ethanes (**1**) with triethylamine in benzene afforded the corresponding *trans*-1-aryl-2-(arenesulfonyl)ethenes [**2**, R, R′ = aryl (eq 2)] in excellent yield (see Table II).[6]

Table I.—Sulfonyl Chloride Adducts 1

| Registry no. | R | R′ | Mp, °C | Yield, % | Calcd, % C | H | Cl | S | Found, % C | H | Cl | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 6461-58-1 | $C_6H_5$ | $C_6H_5$ | 88–90[a] | 75 | | | | | | | | |
| 30158-41-9 | $C_6H_5$ | 2,4,6-$[CH(CH_3)_2]_3C_6H_2$ | 119–120 | 89 | 67.87 | 7.68 | 8.71 | 7.88 | 68.02 | 7.86 | 8.90 | 8.13 |
| 30158-42-0 | $C_6H_5$ | 2,4,6-$(CH_3)_3C_6H_2$ | 98–99 | 84 | 63.24 | 5.93 | 10.98 | 9.93 | 63.15 | 6.15 | 11.08 | 9.96 |
| 30158-43-1 | $C_6H_5$ | 2-$C_{10}H_7$ | 124.5–125 | 89 | 65.34 | 4.57 | 10.72 | 9.69 | 65.16 | 4.55 | 10.95 | 9.45 |
| 30158-44-2 | $C_6H_5$ | 4-$FC_6H_4$[b] | 88–90 | 82 | 56.28 | 4.05 | 11.87 | 10.73 | 56.28 | 3.84 | 11.70 | 10.95 |
| 30158-45-3 | $C_6H_5$ | 4-$BrC_6H_4$[c] | 90.5–91 | 96 | 46.75 | 3.36 | 9.86 | 8.91 | 47.02 | 3.55 | 9.90 | 9.01 |
| 30158-46-4 | $C_6H_5$ | 4-$O_2NC_6H_4$[d] | 136–137 | 78 | 51.61 | 3.72 | 10.88 | 9.84 | 51.85 | 3.93 | 10.76 | 9.80 |
| 30158-47-5 | $C_6H_5$ | 2-$O_2NC_6H_4$[e] | 106–107 | 82 | 51.61 | 3.72 | 10.88 | 9.84 | 51.38 | 3.86 | 11.00 | 9.73 |
| 30158-48-6 | $C_6H_5$ | 2-$O_2N$-4-$ClC_6H_3$[f] | 135–137 | 82 | 46.69 | 3.05 | 19.69 | 8.90 | 46.85 | 3.26 | 19.44 | 8.97 |
| 30158-49-7 | 4-$CH_3C_6H_4$ | $C_6H_5$ | 91–93 | 65 | 61.11 | 5.13 | 12.03 | 10.88 | 61.35 | 5.06 | 12.01 | 10.68 |
| 30158-50-0 | 4-$C_6H_5C_6H_4$ | $C_6H_5$ | 130–132 | 46[g] | 67.31 | 4.80 | 9.94 | 8.98 | 67.58 | 4.68 | 9.66 | 9.09 |
| 30158-51-1 | 2,6-$(CH_3)_2C_6H_3$ | $C_6H_5$ | 75–77 | 78 | 62.24 | 5.51 | 11.49 | 10.37 | 62.35 | 5.57 | 11.69 | 10.49 |
| 30158-52-2 | 4-$ClC_6H_4$ | $C_6H_5$ | 80.5–82 | 68 | 53.34 | 3.84 | 22.50 | 10.17 | 53.56 | 4.09 | 22.63 | 10.39 |
| 30158-53-3 | 3-$O_2NC_6H_4$[h] | $C_6H_5$ | 86–88 | 74 | 51.61 | 3.72 | 10.88 | 9.84 | 51.53 | 3.70 | 11.00 | 9.75 |
| 6038-47-7 | $C_6H_5$ | $CH_3$ | 70.5–72 | 66 | 49.42 | 5.07 | 16.22 | 14.66 | 49.53 | 5.11 | 15.94 | 14.43 |
| 30158-39-5 | $C_6H_5$ | $C_6H_5CH_2$ | 121–122 | 6[i] | 61.11 | 5.13 | 12.03 | 10.88 | 61.23 | 5.10 | 11.76 | 10.87 |
| 30158-56-6 | $C_6H_5$ | $BrCH_2$[j] | 101–102 | 80 | 36.32 | 3.39 | 11.91 | 10.77 | 36.21 | 3.15 | 11.99 | 10.72 |

[a] M. Asscher and D. Vofsi [*J. Chem. Soc.*, 4962 (1964)] report mp 89–90°. [b] *Anal.* Calcd for $C_{14}H_{12}ClFO_2S$: F, 6.36. Found: F, 6.45. [c] *Anal.* Calcd for $C_{14}H_{12}BrClO_2S$: Br, 22.22. Found: Br, 22.30. [d] *Anal.* Calcd for $C_{14}H_{12}ClNO_4S$: N, 4.30. Found: N, 4.58. [e] *Anal.* Calcd for $C_{14}H_{12}ClNO_4S$: N, 4.30. Found: N, 4.28. [f] *Anal.* Calcd for $C_{14}H_{11}Cl_2NO_4S$: N, 3.86. Found: N, 3.87. [g] A large amount of polymerization of 4-vinylbiphenyl occurred. [h] *Anal.* Calcd for $C_{14}H_{12}ClNO_4S$: N, 4.30. Found N, 4.35. [i] Most of the α-toluenesulfonyl chloride decomposed to benzyl chloride and sulfur dioxide (see text and Experimental Section) resulting in a low yield of 1:1 adduct. [j] *Anal.* Calcd for $C_9H_{10}BrClO_2S$: Br, 26.85. Found: Br, 26.70.

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[1] Unsaturated Sulfones and Suitable Precursors. III. For previous papers in this series, see W. E. Truce, C. T. Goralski, L. W. Christensen, and R. H. Bavry, *J. Org. Chem.*, **35**, 4217 (1970); W. E. Truce and C. T. Goralski, *ibid.*, **35**, 4220 (1970).

[2] Halogens Research Laboratory, The Dow Chemical Co., Midland, Mich. 48640.

[3] V. Baliah and M. Seshapathirao, *J. Org. Chem.*, **24**, 867 (1959).

[4] H. G. Klein, Ph.D. Thesis, Purdue University, 1961.

[5] M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964).

[6] The vinyl sulfones **2** were identified as the trans isomers by their nmr ($J_{vinyl}$ = 14–16 cps) and infrared ($\omega_{vinyl}$ = 10.2–10.5 μ) spectra which are typical of trans 1,2-disubstituted olefins. We earlier described the reaction of these vinyl sulfones (Table II) with dimethylsulfonium methylide to give the corresponding *trans*-1-(arenesulfonyl)-2-arylcyclopropanes: W. E. Truce and C. T. Goralski, *J. Org. Chem.*, **34**, 3324 (1969).