TABLE I

Physical Properties of Isomeric Bis(trimethylsilyl)-xylylenes

| Isomer | M.P., °C. | B.P., °C./mm. | $d_4^t$ | $n_D^{20}$ |
|---|---|---|---|---|
| *ortho* | 2–3 | 75–6/0.55 | $0.8686^{25}$ | 1.4950 |
| *meta* | 4.0 | 73–4/0.6 | $0.8595^{24.7}$ | 1.4919 |
| *para* | 61–3 | 73–4/0.3 | ... | ... |

## EXPERIMENTAL

*Bis(trimethylsilyl)-o-xylylene.* This compound was prepared according to the procedure described in a previous article[1] from 0.75 mol. of *o*-xylylene dibromide, 6.0 mol. of trimethylchlorosilane and 1.64 mol. of magnesium. The material collected at 75–6° (0.55 mm.) was identified as bis(trimethylsilyl)-*o*-xylylene, m.p., 2–3; $d_4^{25}$ 0.8686 and $n_D^{20}$ 1.4950.

*Anal.* Calcd. for $C_{14}H_{26}Si_2$: C, 67.13; H, 10.46; Si, 22.40. Found: C, 67.28, 67.22; H, 10.02, 10.13; Si, 22.45, 22.40.

*Bis(dimethylchlorosilyl)-p-xylylene.* This compound was also prepared by the same procedure[1] from 70.0 g. (0.40 mol.) of *p*-xylylene dichloride, 113.8 g. (1.05 mol.) of dimethyldichlorosilane and 23.5 g. (0.97 g.-atom) of magnesium in tetrahydrofuran. Distillation yielded 35.8 g. (33% yield) of bis(dimethylchlorosilyl)-*p*-xylylene, m.p. 74–77°; b.p. 110–112° (0.47 mm.).

*Anal.* Calcd. for $C_{12}H_{20}Si_2Cl_2$: C, 49.47; H, 6.92; Si, 19.26; Cl, 24.34. Found: C, 49.35, 49.47; H, 7.07; 7.11; Si, 19.26, 19.34; Cl, 24.41, 24.32.

Chemistry Department
Ford Motor Co.
20000 Rotunda Drive
P. O. Box 2053
Dearborn, Mich.

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# Reactions of Sulfoxides with Organic Halides. Preparation of Aldehydes and Ketones

Harold R. Nace[1] and John J. Monagle

*Received May 11, 1959*

The increasing interest[2–5] in the unusual behavior of organic halides in the presence of dimethyl sulfoxide prompts us to publish preliminary results of an investigation being carried out in this laboratory.[6]

In striking contrast to the reaction of arene- and alkane-sulfonates of secondary alcohols with dimethyl sulfoxide to yield olefins,[7] the sulfonates of primary alcohols react with dimethyl sulfoxide to yield, instead of the expected olefin, a mixture of aldehyde, acetal, and the alcohol derived from the starting ester. For example, hexyl tosylate gave hexanal, the methyl hexyl acetal of hexanal, and 1-hexanol. The corresponding aldehydes were also identified as products from the reaction of butyl and octyl benzenesulfonates in dimethyl sulfoxide. Heating the alcohol or aldehyde with or without the sulfonic acid did not give the same reaction products.

The reaction was then extended to the production of aldehydes from primary alkyl or aralkyl halides and dimethyl sulfoxide or other sulfoxides. It was also found that ketones could be obtained in fair yield in certain cases, *e.g.*, benzophenone from diphenylmethyl chloride. Representative examples are given in Table I. During the course of this investigation the preparation of *p*-nitrobenzaldehyde by reaction of *p*-nitrobenzyl chloride with dimethyl sulfoxide was reported.[2]

The reaction of sulfonates and halides with sulfoxides can be carried out conveniently at temperatures in the range 100–160° in an excess of the sulfoxide as solvent, with or without an acid acceptor such as sodium bicarbonate. With dimethyl sulfoxide, low-boiling products are formed which

TABLE I

Preparation of Aldehydes and Ketones[a]

$$R_1R_2CHX + R_3\overset{\overset{\large O}{\uparrow}}{S}R_3 \longrightarrow R_1R_2CO$$

| R₁ | R₂ | R₃ | X | Reaction Temp. | Reaction Time-hr. | % Yield |
|---|---|---|---|---|---|---|
| $n$-$C_3H_7$ | H | $CH_3$ | $—OSO_2C_6H_5$ | 100 | 2.0 | .. |
| $n$-$C_5H_{11}$ | H | $CH_3$ | $—OSO_2C_6H_5$ | 100 | 2.0 | Approx. 20 |
| $C_6H_5$ | H | $CH_3$ | —Cl | 100 | 10.0 | 58 |
| $C_6H_5$ | H | $C_6H_5$ | —Cl | 114–125 | 6.0 | 66 |
| $p$-$CH_3—C_6H_4$ | H | $CH_3$ | —Br | 90–161 | 3.5 | 63 |
| $C_6H_5$ | $C_6H_5$ | $CH_3$ | —Cl | 100 | 2.25 | 44 |

[a] Slight excess of sodium bicarbonate (based on halide) used as acid acceptor.

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[1] Present address: Department of Chemistry, Brown University.

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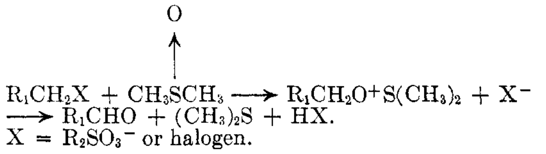
include dimethyl sulfide, methyl mercaptan and dimethyl disulfide. If an acid acceptor is not used, large amounts of formaldehyde are also formed. With diphenyl sulfoxide, a high-boiling residue, presumably diphenyl sulfide, is formed.

The formation of aldehyde can be conveniently accommodated by the following scheme:



$$R_1CH_2X + CH_3\overset{\overset{O}{\uparrow}}{S}CH_3 \longrightarrow R_1CH_2O^+S(CH_3)_2 + X^- \longrightarrow R_1CHO + (CH_3)_2S + HX.$$

$X = R_2SO_3^-$ or halogen.

Evidence for the existence of the intermediate salt has already been presented,[5] and Hunsberger and Tien have proposed a similar mechanism for ethyl bromoacetate with dimethyl sulfoxide.[4]

Complete details, including a study of reaction variables and experiments with other halides and sulfonates, will be reported later.

E. I. DU PONT DE NEMOURS & CO., INC.
WILMINGTON 99, DEL.

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## *meso*- and *dl*-9,10-Octadecanediols[1]

A. N. WRIGLEY, F. D. SMITH, AND A. J. STIRTON[2]

*Received May 15, 1959*

The 9,10-octadecanediols were desired as examples of secondary glycols. Stereochemically definitive syntheses of the *meso*- and *dl*-9,10-octadecanediols, by performic acid treatment of the corresponding *trans*- and *cis*-octadecenes, have been reported by Criegee and co-workers.[3]

Other workers[4,5] had reported the preparation of the "high-melting" forms of such glycols by catalytic hydrogenation of acyloins, but had experienced difficulty in isolating the "low-melting" forms in a pure state. Our own experience with platinum oxide hydrogenation of nonyloin was similar.

A more convenient method of preparation was found to be the reduction of nonyloin with sodium borohydride, which proceeded almost quantitatively to a mixture of the two forms. Separation by crystallization from aqueous ethanol gave yields of 42% of the *meso* and 56% of the *dl* modification. Identities were confirmed by independent preparation of the *meso* form by *cis*-hydroxylation[6] of *cis*-octadecene[7] with hydrogen peroxide–osmium tetroxide and of the *dl* form by ring opening, with Walden inversion,[8] performed on *cis*-9,10-epoxyoctadecane.[7]

Since greater solubility has been correlated with lower melting point and *dl* or *threo* configuration in the case of stilbene dibromide[9] and various esters of the isomeric 9,10-dihydroxystearic acids,[10,11] it was interesting to make solubility measurements (Table I) on the present diols and two related compounds.

TABLE I

SOLUBILITY OF 9,10-DISUBSTITUTED OCTADECANES, STEARIC ACIDS AND OCTADECANOLS

| Compound | M.P. | Solvent | Solubility, g./l. of Soln. at 25° |
|---|---|---|---|
| *meso*-Octadecanediol | 130° | 95% EtOH | 11.9 |
| *dl*-Octadecanediol | 78° | 95% EtOH | 30.2 |
| *meso*-Octadecanediol | 130° | Benzene | 2.6 |
| *dl*-Octadecanediol | 78° | Benzene | 13.7 |
| *erythro*-Dihydroxystearic acid[a] | 131° | 95% EtOH | 8.8 |
| *threo*-Dihydroxystearic acid[a] | 95° | 95% EtOH | 69.8 |
| Dichlorooctadecanol[b] | 31° | 95% EtOH | 19.0[d] |
| Dichlorooctadecanol[c] | 12° | 95% EtOH | 843.[d] |

[a] Ref. (8). [b] Presumably *erythro* since made by chlorination of elaidyl alcohol.[12] [c] Presumably *threo* since made by chlorination of oleyl alcohol.[12] [d] Measurements made at 0°.

In each case the *dl* or *threo* modification is considerably more soluble, as well as lower melting.

### EXPERIMENTAL

*meso-9,10-Octadecanediol by hydrogenation of nonyloin.* Hydrogenation at room temperature of 10 g. of nonyloin over $PtO_2$, gave a 30% yield of 9,10-octadecanediol, m.p. 130.0–130.4° (reported[5] 127°,[3] 127.5–128°). On admixture this substance did not change the melting point of *meso*-9,10-octadecanediol reference compound. Its infrared spectrum measured on a KBr disk was superimposable on that of the reference compound.

*meso- and dl-Octadecanediols by sodium borohydride reduction of nonyloin.* In 235 ml. of 95% alcohol 18.7 g. of nonyloin was reduced by treatment with 1.24 g. of sodium boro-

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[1] Presented at the 135th National Meeting of the American Chemical Society, Boston, Massachusetts, April 6, 1959.

[2] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Eastern Regional Research Laboratory, Philadelphia 18, Pa.

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