

melting point 88–90°. Thus, it is apparent that the solvent used is important in determining the final products of reaction. We found, indeed, that the derivative of methyl vinyl ketone can also be obtained if tetrahydrofuran and *tert*-butyl alcohol are used as solvents. In the latter case the derivative precipitates quickly and addition of the alcohol to the double bond does not take place. In the former case, as in the diglyme solutions, the solvent cannot react with the ketone or its derivative. Our work with methyl vinyl ketone has led us to begin investigating in some detail the products that are formed from the derivative of methyl vinyl ketone and of the alkoxybutanones in acidic solutions. We shall report on this investigation at a later date. It is quite apparent to us at this stage that attempts to make the derivatives of these ketones by conventional methods very often lead to products that are not the expected derivatives.

EXPERIMENTAL

Diacetone alcohol 2,4-dinitrophenylhydrazone. One milliliter of vacuum distilled diacetone alcohol was added to 20 ml. of a diglyme solution containing 0.8 g. of 2,4-dinitrophenylhydrazine. To this was added 3 ml. of acetic acid. The solution was allowed to stand at room temperature for 2 hr. and was then placed in the refrigerator for 24 hr. Water was added to the cold solution until it became turbid and the solution was again refrigerated until crystallization occurred. The orange product, m.p. 137–147°, was recrystallized twice from ethanol and then twice from benzene, giving glistening orange plates, m.p. 157–9°; λ_{\max} (CHCl₃): 370 mm μ ; λ_{\max} (ligroin): 351 mm μ ; ϵ_{\max} (CHCl₃): 23,250.

Anal. Calcd. for C₁₂H₁₆N₄O₅: C, 48.65; H, 5.44; N, 18.9. Found³: C, 48.59; H, 5.36; N, 18.69.

A small amount of the derivative was dissolved in ethanol and acidified with concentrated hydrochloric acid. A red precipitate formed overnight. Crystallization from diglyme gave m.p. 203°. The melting point of the derivative of mesityl oxide was 203°.

Methyl vinyl ketone 2,4-dinitrophenylhydrazone. To a solution of 0.2 ml. of methyl vinyl ketone (Matheson, Coleman and Bell, technical, used without purification) in 10 ml. of the diglyme reagent solution was added 3 drops of concentrated hydrochloric acid. The solution stood overnight at room temperature. Addition of water gave an orange product, m.p. 137–8°. Several recrystallizations from ethanol gave long orange needles, m.p. 139.5–140.5°; λ_{\max} (CHCl₃): 370 mm μ ; λ_{\max} (ligroin): 352 mm μ ; ϵ_{\max} (CHCl₃): 24,670.

Anal. Calcd. for C₁₀H₁₀N₄O₄: C, 48.00; H, 4.03; N, 22.38. Found³: C, 48.07; H, 4.24; N, 22.62.

4-Ethoxybutanone-2 2,4-dinitrophenylhydrazone. This was obtained first when attempting to make the 217° product from methyl vinyl ketone by the described² procedure. A solution was made by boiling 1 g. of 2,4-dinitrophenylhydrazine in a mixture of 45 ml. of ethanol, 5 ml. of dioxane (freshly purified) and 1 ml. of concentrated hydrochloric acid. The cool solution was filtered from solid that had crystallized and was added to a solution of 1 ml. of methyl vinyl ketone in 2 ml. of ethanol. A small amount of an orange yellow solid precipitated, m.p. 202–8°. Dilution of the filtrate with water gave a flocculent yellow precipitate, m.p. 84–87°. Several crystallizations from ethanol gave light

orange crystals, m.p. 92–3°; (literature: 89–90°⁴; 100–1°⁵); λ_{\max} (CHCl₃): 362 mm μ ; λ_{\max} (ligroin): 344 mm μ ; ϵ_{\max} (CHCl₃): 21,570.

Anal. Calcd. for C₁₂H₁₆N₄O₅: C, 48.65; H, 5.44; N, 18.90. Found⁶: C, 48.38; H, 5.30; N, 18.80.

4-Methoxybutanone-2 2,4-dinitrophenylhydrazone. The procedure described above was used. Again, the solution precipitated a yellow orange solid, m.p. 208–210°. Treatment of the filtrate as above gave a yellow product, m.p. 97–100°. Several crystallizations from methanol gave blunt, dark yellow needles, m.p. 88–90°; (literature⁶: 85–86°) λ_{\max} (CHCl₃): 364 mm μ ; λ_{\max} (ligroin): 345 mm μ ; ϵ_{\max} (CHCl₃): 21,520.

Anal. Calcd. for C₁₁H₁₄N₄O₅: C, 46.81; H, 5.00; N, 19.84. Found⁴: C, 46.64; H, 4.89; N, 19.70.

Ultraviolet spectra. A Beckman DK-2 instrument was used. The ligroin used was Eastman Kodak's permanganate purified, b.p. 66–75°. Because of the unexpectedly high values of λ_{\max} of the diacetone alcohol derivative the corresponding λ_{\max} of mesityl oxide were determined. They were 383 mm μ (CHCl₃) and 365 mm μ (ligroin). The λ_{\max} (isooctane) given² for mesityl oxide was 364 mm μ ; while the λ_{\max} (isooctane) calculated² for methyl vinyl ketone was 354 mm μ .

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Isomeric Bis(trimethylsilyl)xylylenes

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In a recent article¹ we described the synthesis of *m*- and *p*-bis(trimethylsilyl)xylylenes from coupling the respective xylylene dihalides and trimethylchlorosilane with magnesium in tetrahydrofuran. We wish to report the successful preparation of the remaining isomer, bis(trimethylsilyl)-*o*-xylylene, to complete the series and an additional dichloro-derivative of the *p*-isomer, bis(dimethylchlorosilyl)-*p*-xylylene. The physical properties of the three isomeric compounds are summarized in Table I and the infrared absorption spectrum of the *o*-isomer is reproduced in Fig. 1.

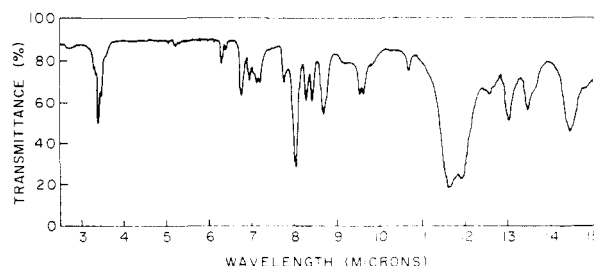


Fig. 1. Bis(trimethylsilyl)-*o*-xylylene

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TABLE I
PHYSICAL PROPERTIES OF ISOMERIC BIS(TRIMETHYLSILYL)-
XYLYLENES

Isomer	M.P., °C.	B.P., °C./mm.	d_4^{25}	n_D^{20}
<i>ortho</i>	2-3	75-6/0.55	0.8686 ²⁶	1.4950
<i>meta</i>	4.0	73-4/0.6	0.8595 ^{24,7}	1.4919
<i>para</i>	61-3	73-4/0.3

EXPERIMENTAL

Bis(trimethylsilyl)-o-xylene. This compound was prepared according to the procedure described in a previous article¹ from 0.75 mol. of *o*-xylene 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*-xylene, m.p., 2-3; d_4^{25} 0.8686 and n_D^{20} 1.4950.

Anal. Calcd. for $C_{14}H_{20}Si_2$: 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-xylene. This compound was also prepared by the same procedure¹ from 70.0 g. (0.40 mol.) of *p*-xylene dichloride, 113.8 g. (1.05 mol.) of dimethylchlorosilane and 23.5 g. (0.97 g.-atom) of magnesium in tetrahydrofuran. Distillation yielded 35.8 g. (33% yield) of bis(dimethylchlorosilyl)-*p*-xylene, 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.

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

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The increasing interest²⁻⁵ 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

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TABLE I
PREPARATION OF ALDEHYDES AND KETONES^a

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

R ₁	R ₂	R ₃	X	Reaction Temp.	Reaction Time-hr.	% Yield
<i>n</i> -C ₃ H ₇	H	CH ₃	—OSO ₂ C ₆ H ₅	100	2.0	..
<i>n</i> -C ₅ H ₁₁	H	CH ₃	—OSO ₂ C ₆ H ₅	100	2.0	Approx. 20
C ₆ H ₅	H	CH ₃	—Cl	100	10.0	58
C ₆ H ₅	H	C ₆ H ₅	—Cl	114-125	6.0	66
<i>p</i> -CH ₃ —C ₆ H ₄	H	CH ₃	—Br	90-161	3.5	63
C ₆ H ₅	C ₆ H ₅	CH ₃	—Cl	100	2.25	44

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