absorption for pure prodigiosin in isopropyl alcohol occurs at 466 mμ (ε 4.3 × 10^4). Moreover, a mixture of the magenta solid with prodigiosin hydrochloride, m.p. 148.5–150.0° (dec.), prepared from prodigiosin, showed no depression of the melting point and the infrared spectra for the two hydrochlorides are identical.

We attribute the presence of the hydrochloride in our chromatogram to an artifact arising from the introduction of traces of hydrogen chloride, or hydrochloric acid, during working up the mixture derived from the perchlorate. We were able to isolate 33.3 mg. of pure hydrochloride from the reaction of 2.00 g. of prodigiosin perchlorate with sodium hydroxide. Aside from operational losses, this corresponds to a yield of 2% and the combination of prodigiosin with 3.4 mg. of hydrogen chloride.

The compound described by the Russian workers is apparently identical with ours, as far as a comparison can be made. However, it should be pointed out that their product was derived by way of a process wherein the bacterial pigment was treated in one step with sodium hydroxide. We have observed an immediate change in color from that for the acid derivative (red) to that for the free base (orange) when sodium hydroxide is added to an isopropyl alcohol solution of the salt. Therefore, it cannot be unequivocally concluded from the earlier work that prodigiosin hydrochloride is a bacterial product. While it is possible that the conditions employed in the earlier study may have permitted incomplete reaction of any hydrochloride present, it would seem that another explanation, such as used to explain our results, should be considered.

EXPERIMENTAL

Magenta solid derived from prodigiosin perchlorate. The solid was isolated and purified as has already been described.[5]

Anal. Calcd. for $C_{20}H_{26}ON_3Cl$: C, 66.74; H, 7.28; N, 11.68; Cl, 9.86. Found: C, 66.90; H, 7.51; N, 11.56; Cl, 9.68.

The ultraviolet-visible absorption spectra were determined with a Beckman Model DU spectrophotometer. The spectrum for the magenta solid was measured using a solution containing 0.928 mg. of the compound per 100 ml. of isopropyl alcohol solution. The spectrum for the free base derived from the magenta solid was measured using the mixture obtained by adding 0.20 ml. of 0.507*N* aqueous sodium hydroxide to 9.80 ml. of a solution having 1.240 mg. of the magenta colored solid per 100 ml. of isopropyl alcohol solution.

Prodigiosin hydrochloride. One hundred milligrams of prodigiosin, m.p. 152.0–153.0° (dec.) was dissolved in about 15 ml. of petroleum ether and dry hydrogen chloride was added to the resulting solution until precipitation of the hydrochloride was complete. The mixture was stored in a refrigerator for an hour and the solid removed by filtration. After one recrystallization from a mixture of benzene and petroleum ether 65 mg. of magenta colored hydrochloride, m.p. 148.5-150.0° (dec.) was obtained.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF SANTA CLARA
SANTA CLARA, CALIF.

Preparation of 1-Methylsulfonyl-4-phenyl-1,3-butadiene

V. BALIAH AND SP. SHANMUGANATHAN

Received March 11, 1958

In connection with a study of conjugated sulfones, we required 1-methylsulfonyl-4-phenyl-1,3-butadiene. It was prepared by the following sequence:

$$CH_3SO_2CH_3 \xrightarrow{C_2H_5MgBr} CH_3SO_2CH_2MgBr$$

$$\xrightarrow[(2)\ HCl]{(1)\ C_6H_5CH{=}CHCHO} CH_3SO_2CH_2CHOHCH{=}CHC_6H_5$$

$$\longrightarrow CH_3SO_2CH{=}CHCH{=}CHC_6H_5$$

EXPERIMENTAL

3-Hydroxy-4-methylsulfonyl-1-phenyl-1-butene. A solution of ethylmagnesium bromide (prepared from 4.5 g. of magnesium, 20.8 g. of ethyl bromide and 100 ml. of ether) was added to 16.5 g. (0.18 mole) of dimethyl sulfone in 750 ml. dry anisole. A bulky white precipitate separated. The mixture was stirred by means of a liquid-sealed mechanical stirrer and heated on a water bath for 3 hr. and then stirred at room temperature for a further 2 hr. A solution of 16.5 g. (0.125 mole) of freshly distilled cinnamaldehyde in 50 ml. dry anisole was then added rapidly and stirring continued at room temperature for 16 hr. The reaction product was hydrolyzed with hydrochloric acid (2.5*N*, 100 ml.). The aqueous layer was separated and extracted with two 25-ml. portions of benzene. The benzene extract together with the anisole layer was washed thrice with 50-ml. portions of a saturated solution of sodium chloride and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure, the solid residue collected and washed with a few ml. of light petroleum (b.p. 70–80°). The yield of the crude product was 25.2 g. (90%). It crystallized as colorless plates from benzene and melted at 111–112°.

Anal. Calcd. for $C_{11}H_{14}O_3S$: C, 58.4; H, 6.2; S, 14.2. Found: C, 58.4; H, 5.9; S, 14.4.

The *acetate*, prepared with acetic anhydride and pyridine, crystallized from ethanol as needles, m.p. 85–86°.

Anal. Calcd. for $C_{13}H_{16}O_4S$: C, 58.2; H, 6.0. Found: C, 58.8; H, 6.2.

The *benzoate*, prepared in the usual manner, crystallized from ethanol as needles, m.p. 146–147°.

Anal. Calcd. for $C_{18}H_{18}O_4S$: C, 65.4; H, 5.5. Found: C, 65.7; H, 5.7.

1-Methylsulfonyl-4-phenyl-1,3-butadiene. A suspension of 2 g. of the foregoing hydroxy unsaturated sulfone in 4 ml. of 85% phosphoric acid was heated under reflux for 15 min., cooled, and diluted with water. A pasty mass was thrown out. It was dissolved in 50 ml. of hot benzene and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a yellow pasty mass which solidified after several days. The yield was 0.6 g. (32%). Recrystallization from ethanol gave colorless needles, m.p. 89–90.5°.

Anal. Calcd. for $C_{11}H_{12}O_2S$: C, 63.4; H, 5.8. Found: C, 63.1; H, 5.6.

DEPARTMENT OF CHEMISTRY
ANNAMALAI UNIVERSITY
ANNAMALAINAGAR, INDIA