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SYDNONES

REACTION OF LITHIUM PHENYLSYDNONE WITH PHOSGENE

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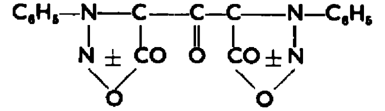
Abstract—The reaction of lithium phenylsydnone with phosgene yields two new compounds, 4-bis(3-phenylsydnonyl)-ketone, and 4-bis(3-phenylsydnonyl)-carbinol.

Lithium phenylsydnone reacts with phosgene, producing three substances. One is a yellow crystalline compound, m.p. 230°, and analyses for $C_{17}H_{10}N_4O_5$ (I) corresponding to 4-bis(3-phenylsydnonyl)-ketone, with the following structure:



I

This structure is supported by the IR spectrum (Fig. 1). In addition to the carbonyl sydnone bands at 1770–1800 cm^{-1},[1] the compound exhibits a high-intensity band at about 1660 cm^{-1}, which is in good agreement with a carbonyl group conjugated with two aromatic residues of the sydnone-type.

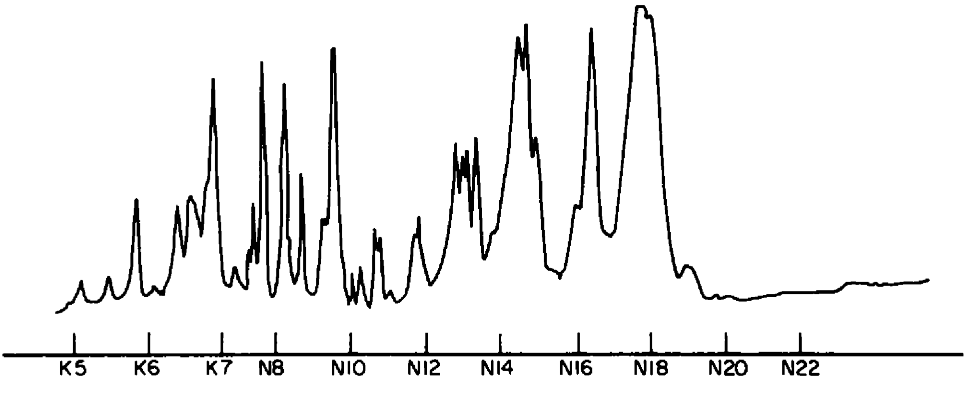


Fig. 1

The UV spectrum shows a λ_{max} in tetrahydrofuran at 225 mμ, with $\varepsilon = 9700$, which agrees with the data in the literature for substances in the same class.[2] A shoulder is present at 315 mμ.

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[1] J. C. Earl, R. C. W. Le Fèvre, A. G. Pulford and A. Walsh, *J. Chem. Soc.* 2207 (1951).

[2] D. P. Hammick and D. J. Voaden, *J. Chem. Soc.* 3303 (1961).

The other two substances (IIA, IIB) obtained in this reaction are both white and crystalline, and the analytical data agree with the formula $C_{17}H_{12}N_4O_5$, but IIA, has a m.p. at 185°, while IIB has a m.p. at 210°. The mixed m.p. of IIA and IIB is not depressed, being 210°. This may indicate that the two substances represent two different crystalline forms of the same compound.

The agreement in the IR spectra of IIA and IIB measured in pellet form, and nujol indicates that no change is brought about by the pressure effect in the potassium bromide pellets. Moreover, the IR spectra are consistent with the structure 4-bis(3-phenylsydnonyl) carbinol and exhibit a γ_{OH} band at about 3360 cm^{-1} (in both the KBr pellet, and nujol), a γ_{C-H} band at 2975 cm^{-1} (KBr pellet), and very weak bands at 2900 and 2930 cm^{-1}. As shown in Fig. 2, the spectrum of II exhibits only sydnone carbonyl bands.

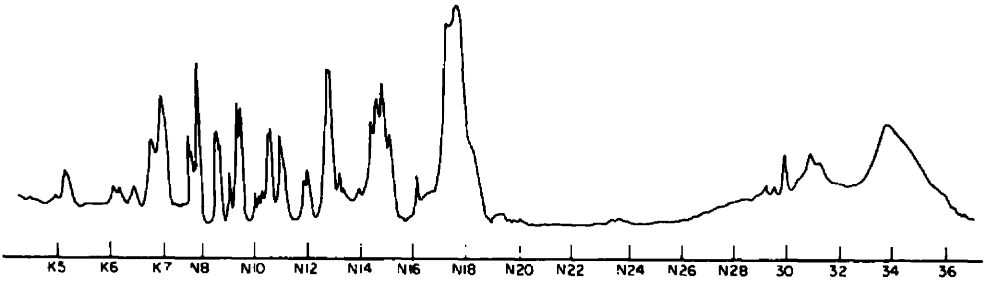
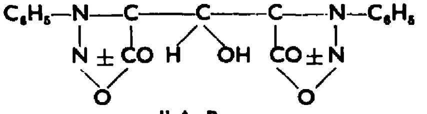


Fig. 2

The UV spectra of IIa, b are also identical in either pellet form or in solution: $\lambda_{\max}^{\mathrm{THF}} = 245$ mμ, and 325 mμ, $\varepsilon = 13{,}000$, a value which is somewhat greater than the average value for substances in the same class.[2]

Owing to the limited solubility of the substances in acetone and in other solvents, the NMR measurements do not reveal an OH group.

The physical measurements support the structure for 4-bis(3-phenylsydnonyl)-carbinol (IIA + B), which has two different crystalline forms:



II A, B.

It is surprising that both these are obtained during fractional crystallization of the crude product from the same solvent.

The formation of carbinol II together with ketone I is accounted for by the reducing action of the reaction medium on 4-bis(3-phenylsydnonyl)-ketone, which might be the primary reaction product.

Both carbinol forms, IIa, IIb, on exposure to day-light, acquire a mustard yellow colour. The resulting substance III, m.p. 210°, analyses for $C_{17}H_{12}N_4O_5$, and a mixed m.p. with either IIa, or b, is not depressed, being 210°.

Since irradiation of the solid phase produces no change, IIa or b was irradiated in a solution of EtOH–Me_2CO. After about 2 weeks, the initial substance was partially recovered, together with an undefined resin-like brown-coloured product. The study of these compounds is in progress.

EXPERIMENTAL

A solution of Buli in ether was prepared in an inert atmosphere, utilizing wire-drawn metallic Li (1 g–0·142 M), 20 ml dry ether, 10 g (0·0730 M) BuBr in 15 ml dry ether.[3] The mixture filtered in a current of inert gas was added drop-wise to 10 g (0·0415 M) of sydnone bromine suspension in 20 ml dry ether, at the temp of −50°, under vigorous stirring. The stirring was continued for about 30 min at −50°.[4]

To this lithium sydnone solution, 2·1 g (0·0212 M) of phosgene in 15 ml benzene was added drop-wise, with efficient stirring for 5–10 min. After precipitation of lithium bromide, stirring was continued for about 30 min at −50°.

Finally, the mixture was poured into cold water, and the product, 5·5 g (38%), m.p. 180°, was partially extracted by trituration with 200 ml boiling EtOH. After concentration *in vacuo* of the red-coloured alcoholic solution, and cooling to −10°, yellow crystals, m.p. 223–224°, were obtained.

After repeated recrystallization (2–3 times) from EtOH–Me_2CO, 1·5–2 g of ketone I were obtained, m.p. 230°. (Found C, 58·25; H, 2·67; N, 15·94; $C_{17}H_{10}N_4O_5$ mol. wt. 350·28 requires: C, 58·29; H, 2·88; N, 15·99%.)

The fraction of product insoluble in the alcohol (≃1·5 g) was fractionally recrystallized from a mixture of EtOH–Me_2CO, and the two components IIA, and IIB separated. The two fractions were separately recrystallized (1–2 times) from the same solvent mixture yielding IIA (≃0·2–0·3 g), m.p. = 186°. (Found C, 57·86; H, 4·03; N, 16·13; $C_{17}H_{12}N_4O_5$, mol. wt. 352·30 requires: C, 57·95; H, 3·44; N, 15·90%), and IIB (0·7–0·8 g), m.p. = 210°. (Found C, 58·07; H, 3·93; N, 15·96; $C_{17}H_{12}N_4O_5$ mol. wt. 352·30 requires: C, 57·95; H, 3·44; N, 15·90%).

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[3] R. G. Jones and H. Gilman, *Org. Reactions* Vol. VI, p. 352. Wiley, New York (1951).

[4] H. Kato and M. Ohta, *Bull. Chem. Soc. Japan* 32, 282 (1959).