

A New Bis-Sydnone

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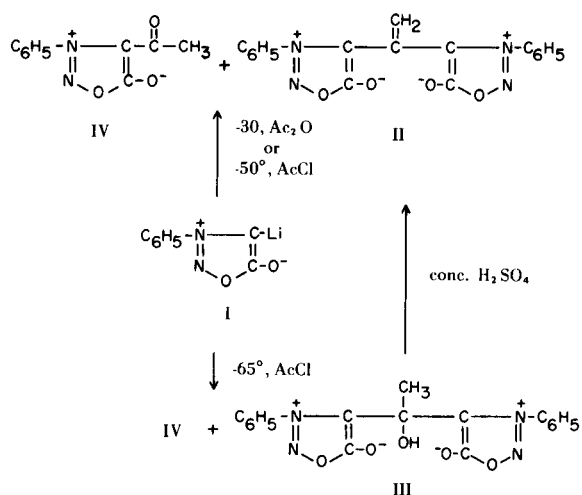
As a result of the ease of the direct lithiation procedure (1) for preparing 4-(3-phenylsydnonyl)lithium (I) and the paucity of reports (2a-d) utilizing this intermediate, we have been applying some of the more common chemistry of organolithium compounds to I. A recent report by Suciú and Mihai (3) on the reactions of I with a variety of acid and non-metallic chlorides, prompts this report on the synthesis and properties of a new bis-sydnone, *unsym*-4,4'-bis-(3-phenylsydnonyl)ethylene (II) and our findings on the formation of the known alcohol (3), methyl-4,4'-bis-(3-phenylsydnonyl)carbinol (III).

The reaction of I with acetic anhydride at -30° , expected to yield III, surprisingly afforded compound II and some methyl-4-(3-phenylsydnonyl) ketone (IV) (4).

Structure II was supported by (a) its mass spectrum (5) which showed a fragmentation pattern consistent with the ethylenic structure and the parent radical ion at m/e 348; (b) the absence of hydroxyl group absorption in the infrared spectrum but the presence of a sydnone carbonyl at 5.75μ ; (c) an ultraviolet absorption maximum at $330 m\mu$ (ϵ , 18,000), a bathochromic shift of $20 m\mu$ from the absorption of 3-phenylsydnone ($310 m\mu$). This shift in absorption was similar to that produced by the extended conjugation in IV ($324 m\mu$) (4). Finally the dehydration of the bis-sydnone III afforded II.

The carbinol III for the dehydration was obtained in low yield by allowing the 3-phenylsydnone in ether, after treatment with *n*-butyllithium at -20° , to react with acetyl chloride at -65° . Under slightly different conditions (same molar quantities of reactants) none of the carbinol was isolated. Thus, addition of acetyl chloride at -50° and maintenance of the reaction at that temperature for 45 minutes or at -20° and warming to room temperature (or refluxing) gave II and IV. Comparison of this product II with those secured from the acetic anhydride reaction and the dehydration of III, showed them to be identical.

It is surprising that Suciú and Mihai (3) did not find similar products in their reactions. They did mention, however, that III gave a stable carbonium ion when dissolved in concentrated sulfuric acid. Our continuing



studies in this area should afford an explanation of this difference in results. In the absence of sufficient experimental results, it is not possible to speculate (6) on the causative factors for this alkene formation.

EXPERIMENTAL (7)

Reaction of 3-Phenylsydnonyllithium With Acetic Anhydride.

To a suspension of 3-phenylsydnone (8) (2.0 g.; 0.012 mole) in 45 ml. of ether at -20° was added 10 ml. of *n*-butyllithium (9). After stirring 55 minutes at -20° , 1.8 g. (0.018 mole) of acetic anhydride was added at -30° . After 2 hours stirring at -30° , the yellow solution was hydrolyzed with aqueous sodium phosphate which formed a precipitate in the water layer. The mixture was filtered and the residue recrystallized twice from ethanol to afford 0.20 g. (16%) (10) of yellow crystalline *unsym*-4,4'-bis-(3-phenylsydnonyl)ethylene (II), m.p. $176-177^{\circ}$.

Anal. Calcd. for C₁₈H₁₂N₄O₄: C, 62.06; H, 3.45; N, 16.09. mol. wt. 348. Found: C, 62.10; H, 3.65; N, 15.99; mol. wt. 374 (Rast) and 348 (mass spectral).

The ether layer from the above reaction mixture was separated and the water layer extracted with ether until colorless. The combined ether solutions were dried (magnesium sulfate), filtered and the filtrate evaporated. The resultant residue was recrystallized three times from absolute ethanol to yield 0.30 g. (20.4%) of methyl-4-(3-phenylsydnonyl) ketone (IV), m.p. $137-138^{\circ}$. The

infrared spectrum of this product was identical to that of an authentic sample of the ketone (4).

Reaction of 3-Phenylsydnonyllithium With Acetyl Chloride.

Procedure A.

A solution of 10 ml. of *n*-butyllithium was added dropwise to a suspension of 2.0 g. (0.012 mole) of 3-phenylsydnone in 40 ml. of ether at -20° . After 15 minutes stirring at -20° , acetyl chloride (2.0 g., 0.026 mole) was added dropwise at -65° at which temperature the reaction was maintained for an additional 2.5 hours after addition was completed. On pouring the reaction solution into aqueous sodium phosphate, a brown gum formed at the ether-water interface which was filtered and recrystallized twice from absolute ethanol to afford 0.10 g. (7.9%) of light yellow crystalline methyl-4,4'-bis-(3-phenylsydnonyl) carbinol (III), m.p. $217-218^{\circ}$ (lit. (3) m.p. 212°).

The infrared spectrum (5% potassium bromide) showed a hydroxyl band at 3.05μ and the sydnone carbonyl at 5.75μ . The u.v. maximum was at $310 m\mu$ (ϵ , 15,700).

Anal. Calcd. for $C_{18}H_{14}N_4O_5$: C, 59.02; H, 3.83; N, 15.30; mol. wt. 350. Found: C, 58.87; H, 3.93; N, 15.55; mol. wt. 337 (Rast).

The ether layer from the above reaction filtrate was separated and the water layer handled as described in the preparation of II. The combined ether solutions yielded 0.33 g. (22.5%) of the ketone IV, m.p. $137-138^{\circ}$ after three recrystallizations from absolute ethanol.

Procedure B.

This procedure was identical to Procedure A except the acetyl chloride was added at -50° and the reaction maintained at this temperature for 45 minutes. The reaction solution was worked up in the same manner, forming a precipitate in the water layer. The isolated solid was twice recrystallized from absolute ethanol to yield 0.30 g. (24.0%) of II, m.p. $176-177^{\circ}$. The remaining ether layer was combined with the ether extracts of the water layer as in Procedure A to afford 0.42 g. (28.6%) of pure ketone IV.

Dehydration of III.

To a solution of III (0.30 g., 0.00086 mole) in 20 ml. of hexane was added 0.5 ml. of concentrated sulfuric acid. To the red gum formed was added 15 ml. of water and the white solid which resulted on trituration was filtered. One recrystallization from absolute ethanol afforded 0.22 g. (73.7%) of alkene II, m.p. $176-177^{\circ}$. The infrared spectrum of this product was identical to the spectrum of products secured from the procedures described above.

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- (4) C. V. Greco, J. Tobias and L. B. Kier, *J. Heterocyclic Chem.*, **4**, 160 (1967). *Cf.* also, V. G. Yashunskii and V. F. Vasil'eva *Dok. Akad. Nauk SSSR*, **130**, 350 (1960).
- (5) Mass spectral analysis performed by Morgan-Schaeffer, Canada, on a Hitachi Perkin Elmer Model RMU-6D, ionizing energy 70 ev.
- (6) It has been our experience in such reactions that the temperature is critical. At such low temperatures, small changes result in production of different products. It is not likely that the acetic anhydride is responsible for the probable dehydration of carbinol III since the same result was achieved with acetyl chloride. What is more likely is a base catalyzed dehydration of III analogous to the dehydration of aldols produced from sterically hindered or aromatic aldehydes which occurs under the reaction conditions employed for the condensation.
- (7) All melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were measured on a Perkin Elmer Infracord 137 and ultraviolet spectra on a Bausch and Lomb Spectronic 505, all samples dissolved in methanol. All reagents were used without further purification. The anhydrous ethyl ether was further dried over sodium ribbon. All reactions involving *n*-butyllithium were performed in a nitrogen atmosphere.
- (8) J. C. Earl and A. W. Mackney, *J. Chem. Soc.*, 899 (1935).
- (9) Purchased from Foote Mineral Company, Exton, Pa. as a 15% hexane solution and assayed as 1.46 *M* by the procedure of H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944).
- (10) All yields involving compound I are based on 60% conversion of 3-phenylsydnone to I. *Cf.* reference 1.

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