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## The Direct Lithiation of 3-Phenylsydnone

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Sir:

The conversion of 3-phenyl-4-bromosydnone (II) to 3-phenylsydnone-4-carboxylic acid (IV) by a halogen-metal interconversion with *n*-butyl lithium (*i. e.*, I-II-III-IV) has been reported (2a). Recently, two additional publications (3) reported employing this method to prepare 4-lithium sydnones.

As part of our study on the synthesis and reactivity of mesoionic compounds, it was decided to explore reactions of the organometallic derivatives of sydnones (4). Molecular orbital calculations (5) revealed an electronic charge distribution shown in VII. The ring bears an aggregate positive charge of the order 0.7-0.9 balanced by a negative charge on the exocyclic oxygen. This information coupled with other physical data (6a) led Baker and Ollis (6b) to propose structure VIII as an adequate representation of sydnones. We assumed, based on this MO representation, that the hydrogen at the 4-position on the sydnone ring might be sufficiently acidic for the direct replacement by *n*-butyl lithium. Additional indirect support for this assumption was Kato and Ohta's (2b) mention of reactions where II showed indications of behaving as a positive bromine compound. As expected, 3-phenylsydnone (I) was directly converted into 3-phenyl-4-lithium sydnone (III) in 60% yield, assayed as the carboxylic acid IV.

A solution of 10 ml. of *n*-butyl lithium (7) (15% in hexane; approximately 1.46 M) was added dropwise to a suspension of 3-phenylsydnone (8) (2.0 g., 0.012 mole) in 50 ml. of ether at  $-20^{\circ}$  in a nitrogen atmosphere. After stirring 55 minutes, gaseous carbon dioxide was bubbled through the solution for 45 minutes. The temperature was allowed to rise to  $0^{\circ}$  at which it was maintained during the carbonation. The mixture was decomposed with water, the ether layer separated and discarded. The water layer was washed three times with ether and then acidified to pH 2 with concentrated hydrochloric acid. The crude product (1.61 g.) was recrystallized three times from ethanol to yield 1.52 g. (59.9%) of pure acid, m.p.  $190-191^{\circ}$  (9). Using powdered dry ice for the carbonation gave a yield of 55.5% of pure acid after three recrystallizations from ethanol, m.p.  $190-191^{\circ}$ .

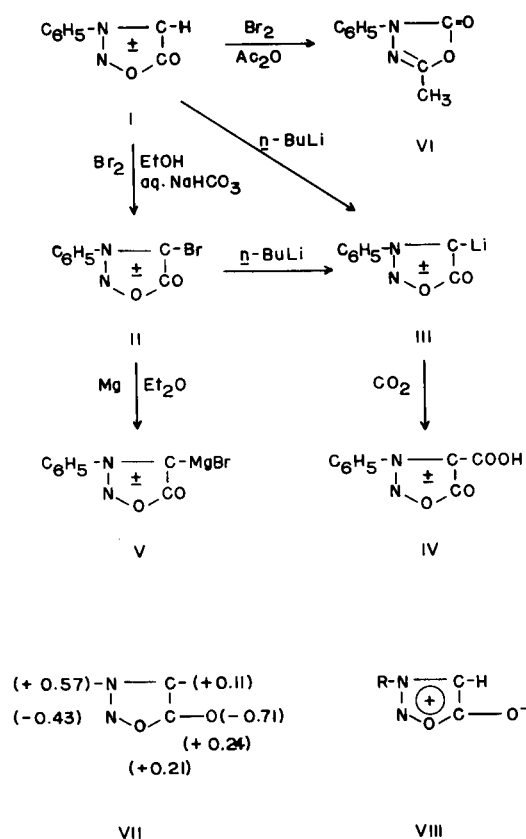
*Anal.* (10) Calcd. for  $C_9H_8N_2O_4$ : C, 52.43; H, 2.91; N, 13.59. Found: C, 52.33; H, 3.12; N, 13.65.

Infrared spectrum (11):  $3077-2857\text{ cm}^{-1}$  (broad OH),  $1818\text{ cm}^{-1}$  (sydnone C=O),  $1681\text{ cm}^{-1}$  (carboxyl C=O).

The reported yield for the halogen-metal interconversion method (2a) increased by *ca.* 10% when the procedure was modified by the use of gaseous carbon dioxide. The reaction temperature for the direct lithiation was  $-20^{\circ}$  while the halogen-metal interconversion was performed at  $-50^{\circ}$ . If the direct method was run at  $-50^{\circ}$  the yield of acid decreased while above  $-20^{\circ}$  decomposition occurred. Thus,  $-20^{\circ}$  gave the optimum conversion of I to III.

A comparison of the direct and halogen-metal interconversion methods revealed the overall yields based on I are about identical. Naturally, the direct method is facilitated by not requiring the preparation of II.

We initially began our study of 4-lithium sydnones utilizing the halogen-metal interconversion method (2a). The precursor, II, had been obtained by



treatment of I with bromine in acetic anhydride at 0° or *N*-bromosuccinimide in boiling chloroform (12); with bromine in acetic acid in the presence of sodium acetate (2a) and also bromine in aqueous potassium bromide (13,14). All attempts to obtain II in this laboratory by the bromine in acetic anhydride method (12) confirmed Stansfield's (15) finding of the conversion of I into 2-methyl-4-phenyl-1,3,4-oxadiazol-5-one (VI), m.p. 78-82°. Kato and Ohta (2b) reported obtaining a 78% yield of II employing an ether suspension of I with bromine in the presence of solid sodium bicarbonate. While this method is relatively more efficient than any procedure previously reported, its success depends on the presence of water in the ether solvent. We have found sodium dried ether results in decomposition of I (or II) when bromine is added to the ether-sydnone-sodium bicarbonate suspension. The electrophilic bromination should be favored and the acidity of the hydrogen at the 4-position enhanced in a highly polar and basic medium. Thus, utilizing an aqueous sodium bicarbonate-ethanol solvent system, the 3-phenylsydnone readily dissolved and the bromination occurred in yields of 80-84%.

At room temperature, sodium bicarbonate (2.0 g., 0.024 mole) in 30 ml. of water was added to a suspension of I (1.0 g., 0.006 mole) in 50 ml. of ethanol. The resultant cloudy solution clarified to an orange colored solution on the addition of bromine (1.0 g., 0.006 mole) in 25 ml. of ethanol. After 15-30 minutes stirring, 30 ml. of water was added and the ethanol removed at reduced pressure. The precipitate which deposited was filtered, washed repeatedly with water and recrystallized three times from benzene-petroleum ether (30-60°), m.p. 139-140° (dec.). A mixture melting point with an authentic sample (2b) showed no depression. The yields for six preparations were 80-84%.

*Anal.* Calcd. for  $C_8H_5BrN_2O_2$ : C, 39.83; H, 2.07; N, 11.62; Br, 33.15. Found: C, 39.85; H, 2.21; N, 11.70; Br, 33.00.

The Grignard reagent V has been prepared from

II (16). In view of our success with the direct lithiation of I we are presently studying the reactions of a variety of 4-lithium sydnones and also investigating the scope and utility of the acidic character of the hydrogen at the 4-position of sydnones, particularly in the preparation of V and other reactive organometallic intermediates.

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