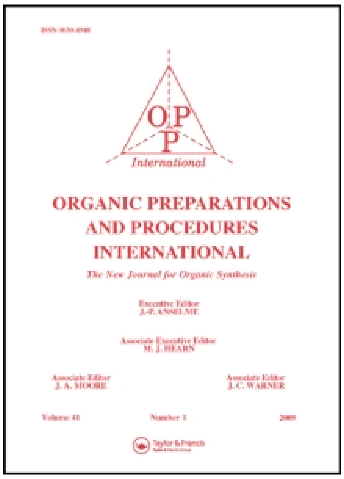

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DIPHENYLACETYLENE. THE NUCLEOPHILIC RING CLEAVAGE OF 1,2,3-THIADIAZOLES

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DIPHENYLACETYLENE.

THE NUCLEOPHILIC RING CLEAVAGE OF 1,2,3-THIADIAZOLES

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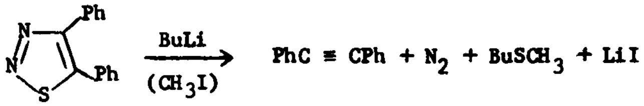

$PhC \equiv CPh + N_2 + BuSCH_3 + LiI$

I II

Heterocyclic compounds containing sulfur in the ring undergo ring cleavage with *n*-butyllithium[1-4] and this reaction is facilitated when the ring contains an -N=S- grouping.[5] We have already described the base cleavage of 4-substituted 1,2,3-thiadiazoles as a convenient route to 1-alkynyl thioethers[6], and have commented upon the cleavage of 4-methyl-5-phenyl-1,2,3-thiadiazole by *n*-butyllithium.[5]

Although certain 1,2,3-thiadiazoles have been reported to evolve nitrogen on treatment with base, the nature of this decomposition has not been further investigated.[7] We have found that when 4,5-diphenyl-1,2,3-thiadiazole,[8] I is treated with *n*-butyllithium at -60°C, nitrogen is evolved and diphenylacetylene II is obtained in 78% yield.[a]

The closely related benzo-1,2,3-thiadiazole[9] III, evolves nitrogen with a catalytic amount of *n*-butyllithium to form compound IV, m.p.

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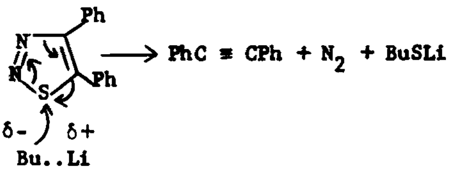
[a] Nucleophilic attack at the sulfur of I results in ring opening.

I



$PhC \equiv CPh + N_2 + BuSLi$

230-240° dec.[b]

Experimental

4,5-Diphenyl-1,2,3-thiadiazole I. A mixture of deoxybenzoin (98 g., 0.5 mole) carbethoxyhydrazine (54 g., 0.6 mole) acetic acid (1 ml.) and methanol (400 ml.) was stirred and heated under reflux on an oil bath at 100°C. After 1 hour, the methanol was removed completely by distillation under reduced pressure from the same bath (*ca.* 3 hrs). Thionyl chloride (238 g., 2 moles) was added to the cold crude carbethoxyhydrazone and after the reaction was complete (no further gas evolution), the reaction mixture was heated in an oil bath at 60°C for one hour and then concentrated under reduced pressure. Ice water (300 ml.) was added and the resulting yellow solid filtered, washed with ice water and dried. Recrystallisation from methanol gave 103.5 g. (87%) of I as a pale yellow solid m.p. 92-93°, lit.[8] m.p. 93-94°.

Benzo-1,2,3-thiadiazole III A solution of sodium nitrite (40 g., 0.55 mole) in water (100 ml.) was added slowly to a stirred ice-cold mixture of *o*-aminobenzenethiol (62 g., 0.5 mole) in conc. hydrochloric acid (500 ml.). After stirring overnight at ambient temperature, the mixture was diluted

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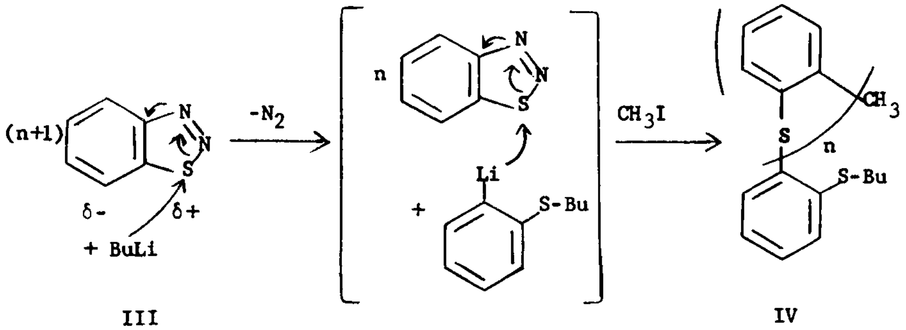
[b] A tentative structural assignment for IV is made based on the following reaction mechanism.



with water (1.2 l.) and continuously extracted with ether for 24 hours. The ethereal extract was dried ($MgSO_4$), filtered and concentrated. Distillation of the residue gave 54.4 g. (80%) of III as a faint yellow oil, b.p. 120°/10 mm., m.p. 34°, lit.[9] m.p. 35°.

<u>Diphenylacetylene</u> II <u>n</u>-Butyllithium in hexane (22 ml. of a 2-molar soln., 0.044 mole) was added slowly to the pale yellow, cold (-60°C) solution of 4,5-diphenyl-1,2,3-thiadiazole (9.2 g., 0.04 mole) in dry THF (80 ml.) in a nitrogen atmosphere. There was an immediate exothermic reaction with copious gas evolution and the colour of the solution became reddish brown. The temperature of the reaction mixture was maintained below -50°C. After the addition was complete the mixture was kept at this temperature for an additional 1/2 hour, methyl iodide (4 ml.) added in one lot, and the mixture allowed to come to room temperature and concentrated under reduced pressure. Water (30 ml.) was added and the mixture extracted with ether (3 X 30 ml). The combined ethereal extracts were dried ($MgSO_4$), filtered and the solvent removed. The pale yellow oily solid was recrystallised twice from hexane to give 5.5 g., (78%) of diphenylacetylene as white needles m.p. 59-60°, identical (m.p. mixed m.p. and IR spectrum) with an authentic sample.

<u>Polymer</u> IV Slow addition of <u>n</u>-butyllithium in hexane (26 ml. of a 2-molar soln., 0.051 mole) to a cold (-70°C) solution of benzo-1,2,3-thiadiazole (6.8 g., 0.05 mole) in dry THF (100 ml.), resulted in an immediate exothermic reaction with vigorous gas evolution which ceased after <u>ca</u>. 1/5 the butyllithium was added. During the addition a solid began to separate. After the addition was complete the mixture was left at -70°C for 1/2 hour, methyl iodide (10 g.) added and the mixture concentrated under reduced pressure. Water (50 ml.) was added and the faint yellow solid filtered, washed with water and dried. The solid weighed 10.3 g. and melted at 230-240° with darkening. The solid was almost insoluble in ether, THF,

ethyl acetate and methanol.

n-Butyllithium in hexane was obtained from Raylo Chemicals Limited, Edmonton, Alberta, Canada and diphenylacetylene from Farchan Acetylenic Chemicals, Willoughby, Ohio 44094, U. S. A.

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