

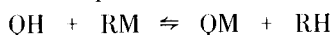
Mesoionic Compounds VI. (1a)
Metallation of Sydnones. An Estimation of Acidity.

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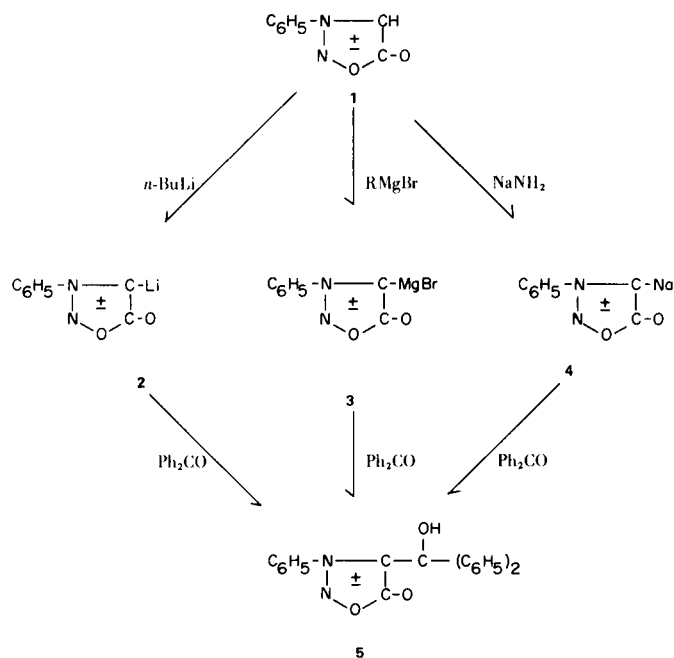
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Contrary to the earlier report of Baker *et al.* (2), Ohta and Kato (3) were able to convert 4-halo-3-phenylsydnones into their respective Grignard reagents. A previous communication in this series (4) reported that treatment of 3-phenylsydnone (1) directly with *n*-butyllithium produced the organometallic derivative 2. We now report that 1 can be converted directly into 3-phenylsydnonylmagnesium bromide (3) by treatment with any of a variety of Grignard reagents (*cf.* Table I). We also describe here the preparation of 3-phenylsydnonylsodium (4) by reacting 1 with sodium amide in tetrahydrofuran. The amide anion in this reaction was apparently detrimental to the sydnone structure. An organosodium reagent would be a more suitable reagent for this direct conversion to 4.

The ease with which 1 was directly metallated led us to qualitatively examine the relative acidity of this sydnone, which was previously assumed only from theoretical data (4). The organometallic compounds (RM) listed in Table I, were added to a solution of 1 (QH) in tetrahydrofuran which produced the equilibrium,



the metallated sydnone (QM) being removed by treatment with benzophenone to afford the stable, readily isolable crystalline, diphenyl-4-(3-phenylsydnonyl)carbinol (5).



Correlation of the pK_a values (5) for the conjugate acids (RH) of the metallic salts employed with the yield of carbinol 5 is shown in Table I. Allowing for the nature of

TABLE I

pK_a Values of Conjugate Acids With Yields of Carbinol

Base (RM)	Conjugate Acid (RH)	Approximate pK_a	Percent Yield of Carbinol	
			Crude	Pure
<i>n</i> -BuLi	<i>n</i> -BuH	43	84	60
<i>n</i> -BuMgBr			73	71
PhLi	PhH	37	74	69
PhMgBr			65	60
PhCH ₂ Li	PhCH ₃	35	63	58
NaNH ₂	NH ₃	34	44	23
HC≡CMgBr	HC≡CH	25	64	56
C ₁₃ H ₉ MgBr	Fluorene	23	63	60
C ₉ H ₇ MgBr	Indene	20	31	28
PhC≡CMgBr	PhC≡CH	18.5	52	32

these determinations, the results clearly show the acidity of **1** to be greater than expected for the trigonally hybridized carbon at the four-position of the sydnone ring. Our estimate of a pK_a between 18-20 for 3-phenylsydnone supports the mesoionic structure attributed to these compounds.

EXPERIMENTAL

The *n*-butyllithium was purchased from Foote Mineral Co., Easton, Pa. and assayed as 1.47 *M* by double titration (6). *n*-Butylmagnesium bromide, phenyllithium and phenylmagnesium bromide were prepared as described (7) and the molarity of ether solutions assayed as 2.00, 0.892 and 2.10 *M*, respectively, on direct titration with hydrochloric acid. The benzylithium, prepared according to Gilman and Schwebke (8), assayed as 0.956 *M*. Ethynylmagnesium bromide was prepared as reported (9) and assayed for 0.73 *M*. The Grignards of fluorene, indene and phenylacetylene were prepared as described below for fluorene.

All reactions were performed in a nitrogen atmosphere. The following procedures illustrate the experimental methods employed.

Diphenyl-4-(3-Phenylsydnonyl)carbinol (**5**).

A. Using *n*-Butyllithium.

A solution of 30 ml. (0.044 mole) of *n*-butyllithium was added to a solution of 3-phenylsydnone (6.48 g., 0.040 mole) in 120 ml. of tetrahydrofuran (THF) at -20° . After stirring one hour, 10.9 g. (0.060 mole) of benzophenone in 10 ml. of THF was added at -30° . After two hours stirring at -30° , the reaction was poured into 400 ml. of water containing 3.0 g. (0.050 mole) of acetic acid. The mixture was extracted with three 100 ml. portions of benzene and the combined organic extracts were washed with water three times, dried (magnesium sulfate), filtered and the filtrate was evaporated at reduced pressure to give orange solids. After one recrystallization from benzene, the carbinol (11.55 g., 83.9%) melted at $153-158^\circ$. Three recrystallizations from benzene gave pure carbinol, m.p. $157-159^\circ$ (uncorrected), 8.29 g. (60.3%); ir (potassium bromide) 3.0μ (OH) and 5.76μ (sydnone carbonyl); uv λ max (ethanol) ($\log \epsilon$) 214 (4.41) and 309 (4.28) nm; nmr (dimethylsulfoxide, 60 MHz, TMS internal reference) 7.32 (s, 15H, three phenyl rings), and 6.78 δ (s, 1H, hydroxyl).

Anal. (10) Calcd. for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found: C, 73.50; H, 4.73; N, 7.85.

B. Using *n*-Butylmagnesium Bromide.

A solution of 25 ml. (0.050 mole) of the Grignard was added to a solution of **1** (3.24 g., 0.020 mole) in 70 ml. of THF at $2-3^\circ$. After one hour stirring, 10.9 g. (0.061 mole) of benzophenone in 10 ml. of THF was added at 5° . After two hours stirring at $5-10^\circ$, the reaction was poured into 400 ml. of water containing 3 g. (0.050 mole) of acetic acid. The red oily solids were isolated as

described in procedure A above. One recrystallization from benzene-hexane gave 5.0 g. (72.8%) of **5**, m.p. $156-158^\circ$. A second recrystallization (benzene-hexane) afforded a pure product (4.90 g., 71.3%), m.p. $157-159^\circ$.

C. Using Fluorylmagnesium Bromide.

To a solution of fluorene (9.96 g., 0.060 mole) in 70 ml. of THF at 5° was added 25.8 ml. (0.050 mole) of ethylmagnesium bromide and the solution was stirred at 25° for two hours. A solution of **1** (3.24 g., 0.020 mole) in 70 ml. of THF was added to the above fluorylmagnesium bromide solution at 5° . After stirring one hour at 5° , 10.96 g. (0.060 mole) of benzophenone in THF was added at 5° . After stirring three hours at that temperature the solution was poured into 400 ml. of water containing 4.20 g. (0.070 mole) of acetic acid. The dark red oily solid was isolated as described in procedure A. Two recrystallizations from benzene-hexane gave 4.13 g. (60.1%) of the carbinol, m.p. $159-160^\circ$.

D. Using Sodium Amide.

To a solution of **1** (3.24 g., 0.020 mole) in 70 ml. of THF at 5° was added 1.0 g. (0.025 mole) of sodium amide. After one hour stirring at 5° , 5.50 g. (0.030 mole) of benzophenone in 10 ml. of THF was added dropwise at $2-3^\circ$. After stirring three hours at 5° , the slurry was poured into 400 ml. of water containing 3.0 g. (0.050 mole) of acetic acid. The dark red oil was isolated as described in procedure A. After one recrystallization from benzene and two recrystallizations from methanol the pure carbinol (1.55 g., 22.6%) melted at $157-160^\circ$.

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