BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2944—2945 (1972)

Acylation of Sydnones

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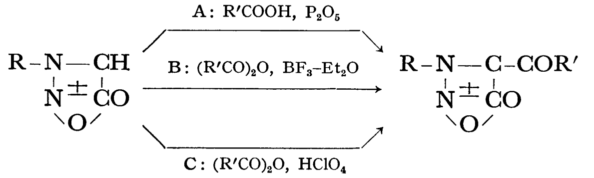
(Received March 31, 1972)

4-Acetyl-3-phenylsydnone was prepared by the reaction of the Grignard reagent obtained from 4-bromo-3-phenylsydnone, with acetic anhydride.[1] Acylation of sydnone is an electrophilic reaction which shows the aromaticity of sydnone ring. Successful results were obtained by using aliphatic carboxylic acid in the presence of phosphorus pentoxide[2] (method A) and acetic anhydride in the presence of boron trifluoride etherate[3] (method B). Formylation of sydnone by the Vilsmeier reaction was also reported.[4] However, only a few 4-acylsydnones were obtained by these methods.

In this note we report on some attempts at acylation by methods A and B, and present a new mode of acylation of sydnones with acid anhydride and perchloric acid (method C).

Acylation of 3-phenylsydnone with phenylacetic acid, cyclohexanecarboxylic acid, or *trans*-cinnamic acid in the presence of phosphorus pentoxide afforded the corresponding 4-acyl derivatives. However, acylation with chloroacetic acid, α-bromopropionic acid or crotonic acid was unsuccessful, resulting in the recovery of 3-phenylsydnone or the formation of benzene-insoluble tarry product. 3-Phenylsydnone also was not acylated by either the action of carboxylic acid in the presence of dicyclohexylcarbodiimide in benzene solution or that of acid anhydride in the presence of sulfuric acid. Benzoylation of 3-phenylsydnone by benzoyl perchlorate in benzene was also unsuccessful. Acylation of 3-benzylsydnone by method A or B afforded 4-acetyl-3-benzylsydnone.



We found that acylation of sydnones with acid anhydrides in the presence of perchloric acid took place easily at room temperature with good yields. However, there is a limit in the effectiveness of acid anhydride, and acylation with acid anhydrides having electron-withdrawing groups such as monochloroacetic anhydride, trichloroacetic anhydride, trifluoroacetic anhydride, or benzoic anhydride was unsuccessful.

The 4-acyl derivatives obtained are given in the following Table.

Experimental

4-Acetyl-3-phenylsydnone (1). A typical procedure for the preparation of 4-acyl-3-substituted sydnones is as follows. To a suspension of 3-phenylsydnone (3.2 g) in 15 m*l* of acetic anhydride, 1 m*l* of perchloric acid (60%) was added drop by drop with stirring in an ice-salt bath. After stirring and cooling for 0.5 hr, the cooling bath was removed and stirring was continued for 12 hr at room temperature. The reaction mixture was poured into cold water, stirred to decompose the excess acetic anhydride and neutralized with sodium carbonate. The product, a viscous oil at first, solidified gradually on standing overnight. Recrystallization from ethanol gave 2.5 g (61%) of **1**, colorless plates, mp 143°C. IR: 1795, 1778, 1667 cm^{-1}.

3-Phenyl-4-propionylsydnone (2). The reaction of 3-phenylsydnone (1.6 g) with propionic anhydride (15 g) in the presence of perchloric acid (0.5 m*l*) afforded 1.5 g of crude product (mp 87—88°C), which was recrystallized from ethanol to give 1.1 g (50%) of **2**, colorless thin needles, mp 90—91°C. IR: 1798, 1666 cm^{-1}.

4-Acetyl-3-cyclohexylsydnone (3). The reaction of 3-cyclohexylsydnone (0.42 g) with acetic anhydride (5 m*l*) in the

TABLE 1.

Comp no.	Comp		Method	Mp °C	Yield%	Found (Calcd)		
	R	R′				C%	H%	N%
1	C_6H_5	CH_3	C	143[a)]	61	—	—	—
2	C_6H_5	C_2H_5	C	90—91[b)]	50	—	—	—
3	C_6H_{11}	CH_3	C	42—43	74	57.25 (57.13)	6.60 (6.71)	13.16 (13.33)
4	$C_6H_5CH_2$	CH_3	A	61—62	29	—	—	—
			B	62—63	45	—	—	—
			C	60—62	73	60.40 (60.54)	4.63 (4.62)	13.04 (12.84)
5	C_6H_5	C_6H_{11}	A	101—102	59	66.42 (66.16)	6.03 (5.92)	10.56 (10.29)
6	C_6H_5	$C_6H_5CH_2$	A	96—97	19	68.38 (68.56)	4.35 (4.32)	10.08 (10.00)
7	C_6H_5	$C_6H_5CH{=}CH$	A	142	34	69.67 (69.85)	4.00 (4.14)	9.81 (9.59)

a) Lit,[2] 141.5—142.5°C. b) Lit,[2] 92.5—94°C.

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1) H. Kato and M. Ohta, *Nippon Kagaku Zasshi*, **78**, 1653 (1957).

2) C. V. Greco, J. Tobias, and L. B. Kier, *J. Heterocyclic Chem.* **4**, 160 (1967).

3) V. G. Yashunskii and V. F. Vasil'eva, *Dokl. Akad. Nauk SSSR*, **130**, 350 (1960).

4) C. J. Thoman, D. J. Voaden, and I. M. Hunsberger, *J. Org. Chem.*, **29**, 2044 (1964).

presence of perchloric acid (3 drops) afforded 0.49 g of crude product (mp 38°C), which was recrystallized from ethanol to give 0.39 g (74%) of **3**, colorless plates, mp 42—43°C. IR: 1771, 1658 cm^{-1}.

4-Acetyl-3-benzylsydnone (4). Method A. 4.4 g of 3-benzylsydnone, 2 m*l* of glacial acetic acid and 12 g of phosphorus pentoxide afforded 1.6 g (29%) of **4**, colorless needles, mp 61—62°C.

Method B. 0.88 g of 3-benzylsydnone, 2.0 g of acetic anhydride and three drops of boron trifluoride-etherate afforded 0.49 g (45%) of **4**, mp 62—63°C (from ether–petroleum ether).

Method C. 3.52 g of 3-benzylsydnone, 15 m*l* of acetic anhydride and 1 m*l* of perchloric acid afforded 4 g of the crude product (mp 56—59°C) which was recrystallized from ether–petroleum ether to give 3.2 g (73%) of **4**, colorless needles, mp 60—62°C. IR: 1780, 1662 cm^{-1}. The IR spectra of the three product obtained above are superimposable.

4-Cychohexylcarbonyl-3-phenylsydnone (5). Method A. 4 g of 3-phenylsydnone, 3.5 g of cyclohexanecarboxylic acid and 12 g of phosphorus pentoxide afforded 4 g (59%) of **5**, mp 101—102°C (from ethanol). IR: 1785, 1665 cm^{-1}.

3-Phenyl-4-phenylacetylsydnone (6). Method A. 4 g of 3-phenylsydnone, 4.3 g of phenylacetic acid and 12 g of phosphorus pentoxide afforded 1.34 g (19%) of **6**, colorless needles, mp 96—97°C. IR: 1790, 1655 cm^{-1}.

4-Cinnamoyl-3-phenylsydnone (7). Method A. 4 g of 3-phenylsydnone, 4.5 g of cinnamic acid (*trans*) and 12 g of phosphorus pentoxide afforded the crude product containing cinnamic acid anhydride and was recrystallized from methanol to give 2.5 g (34%) of **7**, colorless needles, mp 142°C. IR: 1786, 1650 cm^{-1}.