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CHEMISTRY

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1960

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Abstract

Full Text

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ACETYLATION AND DEUTERIUM-EXCHANGE REACTIONS IN THE SYDNONE SERIES

(Presented by Academician M. I. Kabachnik, August 3, 1959)

Among the reactions determining the chemical behavior of sydnones, reactions of electrophilic substitution directed at the carbon atom in position 4 of the sydnone ring are of substantial importance. Sydnones having a hydrogen atom in position 4 quite readily replace it by halogen ([1], [2]), nitro ([2]) and sulfo groups ([3]), and mercury ([3], [4]). In order to study further electrophilic substitution in the sydnone series, we investigated acylation and deuterium-exchange reactions.

Using 3-phenylsydnone as an example, it was found that, under the action of acetic anhydride or benzoyl chloride in the presence of various condensing agents (aluminum chloride, zinc chloride, tin tetrachloride, and phosphoric acid) at various temperatures, acylation does not occur.

Fig. 1. IR transmission spectra: **1** —3-ethylsydnone, **2** —3-ethyl-4-acetylsydnone

It proved possible to introduce an acetyl group into 3-phenylsydnone by heating with acetic anhydride and boron trifluoride etherate. The resulting 4-acetyl-3-phenylsydnone was identical with that recently synthesized by the Grignard method from 4-bromo-3-phenylsydnone ([5]). Under these conditions, acetylation of 3-ethylsydnone proceeded more readily.

In the IR spectrum of 4-acetyl-3-ethylsydnone (Fig. 1), along with the usual carbonyl absorption band observed in the spectra of sydnones (1740 cm^{-1}), a second carbonyl band appears at 1635 cm^{-1}, evidently belonging to the carbonyl group of the acetyl residue. The considerable shift of this band toward lower frequencies (in comparison not only with the bands of aliphatic ketones (1710 cm^{-1}), but also with those of aliphatic-aromatic ketones (1690 cm^{-1})) indicates strongly pronounced electron-donor properties of the sydnone system with respect to substituents in position 4.

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Fig. 2. IR transmission spectra: 1—deuterated ethylene-bis-3-sydnone, 2—ethylene-bis-3-sydnone, 3—deuterated 3-phenylsydnone, 4—3-phenylsydnone.

Figure 2: Fig. 2. IR transmission spectra: 1—deuterated ethylene-bis-3-sydnone, 2—ethylene-bis-3-sydnone, 3—deuterated 3-phenylsydnone, 4—3-phenylsydnone.

To study the deuterium-exchange reaction, we chose ethylene-bis-3-sydnone and 3-phenylsydnone: the former as a representative of sydnones with aliphatic substituents, the latter with aromatic substituents.

Both compounds are sparingly soluble in cold water and alcohol and therefore could readily be isolated after treatment with deuterated water or aqueous alcohol. Ethylene-bis-3-sydnone, m.p. 171° (decomp.), obtained by the known method···

starting from ethylenediaminediacetic acid (6), was heated in a sealed ampoule on a boiling water bath in a mixture of $D_2O—C_2H_5OD$ (ratio 1 : 1) in the presence of D_2SO_4 (pH 1-2) for 10 h. The precipitate that separated after cooling was filtered off, dried, and analyzed for deuterium content.

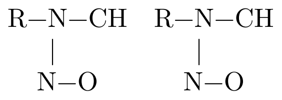
It was found that, under these conditions, exchange of hydrogen for deuterium had proceeded to 33% (the deuterium enrichment of the combustion water was 11100 γ, or 11.1%; two of the six hydrogen atoms in the molecule are capable of exchange).

The results of the deuterium exchange were also confirmed by the IR spectrum of the deuterated sydnone (Fig. 2), which shows appreciable changes in comparison with the completely coincident spectra of the starting sydnone and of sydnone treated under the above conditions with ordinary aqueous alcohol with addition of H_2SO_4.

Deuteration of 3-phenylsydnone was also carried out by heating on a boiling water bath in an ampoule with heavy water in the presence of deuterosulfuric acid (pH $\sim$ 1, time 13 h). Comparison of the IR spectrum of the deuterated sydnone with the spectra of the starting sydnone and of sydnone from the control experiment shows that, in this case as well, exchange of the hydrogen atom in position 4 for deuterium occurs. Participation in this reaction of hydrogen atoms of the phenyl radical can be excluded, since it was shown (1) that substitution reactions (halogenation, nitration) do not affect the benzene ring in 3-phenylsydnone. Attempts to carry out deuteration of both sydnones under milder conditions did not lead to noticeable exchange of hydrogen atoms.

Fig. 2. IR transmission spectra: **1**—deuterated ethylene-bis-3-sydnone, **2**—ethylene-bis-3-sydnone, **3**—deuterated 3-phenylsydnone, **4**—3-phenylsydnone.

Both the acylation and deuterium-exchange reactions carried out by us confirm the ability of sydnones to undergo electrophilic substitution reactions at the fourth carbon atom of the ring. In this connection it should be noted that the formula of sydnones I presently accepted by a number of chemists is not consistent with the experimental data, since reactions characteristic of it should be not electrophilic but nucleophilic substitution reactions.



$$\begin{array}{c} R{-}N{-}CH \\ | \\ N{-}O \end{array} \qquad \begin{array}{c} R{-}N{-}CH \\ | \\ N{-}O \end{array}$$

(I) (II)

Moreover, as we indicated earlier (3), this mode of representation is also contradicted by the fact that the IR spectra of sydnones show the presence of a "true" carbonyl group. This is revealed still more clearly

exocyclic double bond at position 5 in sydnonimines. The IR spectrum that we recorded for the exoacetyl derivative of 3,4-diphenylsydnonimine (7) contains an absorption band (1632 cm^{-1}) characterizing the presence of a carbonylimine grouping $\backslash C = N - CO-$ (8).

In our opinion, the structural features of sydnones are most correctly reflected by the formulas proposed by Earl (9); however, for the sake of simplification it is advisable to use the mesoionic formula (II).

Experimental Part

Acetylation of 3-phenylsydnone. To a mixture of 3 g (0.0185 mole) of 3-phenylsydnone and 2.75 g (0.027 mole) of acetic anhydride, 1 ml of boron trifluoride etherate was added at once, and the mixture was stirred for 3 hours at 100-110°. The reaction mass was decomposed with water; the resinous product was dissolved in alcohol, purified with charcoal, and, after evaporation of the alcohol, extracted with ether, giving 3-acetyl-4-phenylsydnone, m.p. 142.5-143° (from absolute alcohol). According to the literature (5), m.p. 139°.

$C_{10}H_8N_2O_3$.	Found %:	C 58.77; H 3.99; N 13.67
	Calculated %:	C 58.82; H 3.95; N 13.72.

Acetylation of 3-ethylsydnone. To a mixture of 1.5 g (0.013 mole) of 3-ethylsydnone and 1.84 g (0.018 mole) of acetic anhydride, with stirring, 0.8 ml of boron trifluoride etherate was added in one portion; slight warming was observed. After heating at 100-110° for 2 hours, the reaction mixture was treated with water while cooling and neutralized with sodium bicarbonate. The separated oil was combined with the ether extract of the aqueous layer. The ether solution was dried over ignited magnesium sulfate, the ether was distilled off, and 0.9 g of 3-ethyl-4-acetylsydnone was obtained, b.p. 102-104° at 0.8 mm; n_D^{20} 1.5190; d_4^{20} 1.2383.

$C_6H_8N_2O_3$.	Found %:	C 46.43; H 5.34; N 18.14
	Calculated %:	C 46.15; H 5.16; N 17.94.

Semicarbazone, m.p. 217.5-218° (decomp., from alcohol).

$C_7H_{11}N_5O_3$.	Found %:	C 39.19; H 5.21; N 32.76
	Calculated %:	C 39.43; H 5.20; N 32.85.

We express our sincere gratitude to Yu. N. Sheinker for the spectral studies performed by him and to M. N. Shchukina for constant attention to the work and useful advice.

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Received
15 VII 1959

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Note: Figure translations are in progress. See original paper for figures.

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