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SYDNONES—III

SOME REACTIONS OF LITHIUM PHENYLSYDNONE WITH ACID AND NON-METALLIC CHLORIDES

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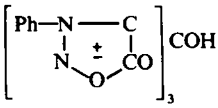
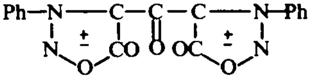
Abstract—The reactions of lithium phenylsydnone with the acid chloride of 3-phenylsydnonyl 4-carboxylic acid, as well as with acetyl, valerianyl, benzoyl, oxalyl chlorides and with phosphorous trichloride, phosphorous oxychloride, sulphur monochloride and thionyl chloride, are described.

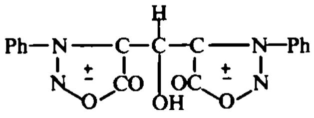
THE reaction of lithium phenylsydnone (I) with phosgene yields 4-bis(3-phenylsydnonyl) ketone (III) and 4-bis(3-phenylsydnonyl) carbinol (IV)[1] and not the triphenylsydnonyl carbinol (II) as expected.[2]



II

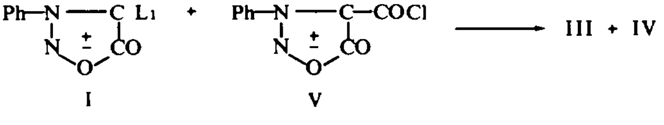


III



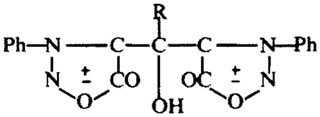
IV

The intermediate formation of the acid chloride of 3-phenylsydnonyl 4-carboxylic acid (V) was proved by reaction of the latter with lithium phenylsydnone (I) under the conditions for the reaction of I with phosgene[1] and production of the ketone III and the carbinol IV.

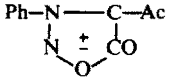


The relationship between III and IV suggests that the carbinol may be obtained by the reduction of the ketone (being analogous to the reduction of carbonylic compounds by action of organometallic derivatives[3]) or less probably *vice versa*. Both these possibilities were checked by treating III as well as IV with butyl lithium (in the case of III also with lithium phenylsydnone I) but as only the starting materials were recovered the carbinol III is not formed from the ketone II or *vice versa*, hence the reduction occurs prior to their formation. As no addition product of the organometallic compound to the carbonyl group of the ketone III, i.e. II or VIb is formed, the final products result from the reaction between the acid chloride V and the lithium derivative I.

In order to clarify this stage, the reaction of I with other acid chlorides and also with some non-metallic chlorides was investigated. The reactions between I and acetyl, valerianyl, and benzoyl chlorides. proceed normally giving the tertiary carbinols VI.



VIa $R = Me^-$
VIb $R = Bu^-$
VIc $R = Ph^-$



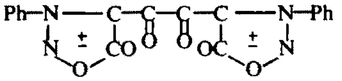
VI

VII

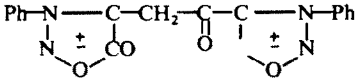
The ketones formed as intermediates during these reactions, in the presence of the lithium derivative must be converted into tertiary carbinols VI. In the case of acetyl chloride small amounts of 3-phenyl 4-acetylsydnone (VII) could be isolated and this compound gave the carbinol VIa when treated with I. This fact proves that generally the carbonyl group bound to a sydnone ring reacts with nucleophilic reagents.

It seems therefore that the lack of reactivity on the carbonyl group is characteristic only of compounds containing two sydnonyl radicals bound to the keto group. This lack of reactivity is difficult to explain since it could be electronic or steric in origin.

The reaction of I with oxalyl chloride yields in addition to 4,4′-bis(3-phenylsydnonyl) α-diketone (VIII), 4-phenylsydnonyl methyl-4′ phenylsydnonyl ketone (IX).

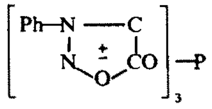


VIII

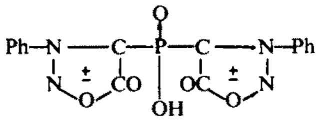


IX

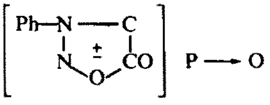
The reaction of lithium phenylsydnone (I) with phosphorous trichloride, yields 4,4′,4″-tris(3-phenylsydnonyl)phosphine (X) a compound containing three sydnone rings bound to the same central atom. In the case of phosphorous oxychloride only two halogen atoms react with I, giving the 4,4′-bis(3-phenylsydnonyl) phosphinic acid (XI) and not the expected, tris-phenylsydnonyl phosphine oxide (XII).



X

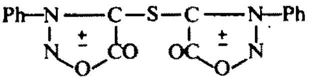


XI

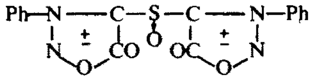


XII

Sulphur monochloride and the thionyl chloride react with I yielding 4,4′-bis(3-phenylsydnonyl) sulphide (XIII) and 4,4′-bis(3-phenylsydnonyl) sulphoxide (XIV) respectively.



XIII



XIV

TABLE 1

B.P.S.	BuLi	Acid chloride	Crude prod. washed with:	Recryst. from: washed product/ residue from filtrate	Crystalline product/ colour/m.p.	Yield based on B.P.S. %	Obs
1 g (4·4 mM)	0·33 g (4·7 mM)	V[4 6] (without solvent) 1 g (4·7 mM)	EtOH	EtOH—CH_2Cl_2/	IV[1]/white/210°	21	When using BuLi in excess, only IV is obtained
				EtOH—CH_3COCH_3	III[1]/yellow/230°	4	
3·7 g (15 mM)	1·13 g (17 mM)	(a) $CdCl_2$ 2·8 g (15 mM)	Benzene Et_2O	H_2O · EtOH/	VI a/white/212°	14	
		(b) CH_3COCl 1·2 g (15 mM)		H_2O—EtOH Et_2O—Benzene H_2O	VII[7]/white/142°	10	no depression with VII[7]
3·2 g (13 mM)	0·85 g (13 mM)	Bu-COCl[8] 0·8 g (6·6 mM)		EtOH	VI b/ white/158–60°	10	
5 g (20 mM)	1·33 g (20·8 mM)	PhCOCl 2·37 g (17 mM)	Trituration with H_2O	H_2O—EtOH	VI c/ white/203–205°	23	
4 g (17 mM)	1·1 g (17 mM)	$(COCl)_2$[9] 1·09 g (8·3 mM)		H_2O—CH_3COCH_3	VIII/ yellow/238–240°	10	
				EtOH	IX/yellow/205°	2	
5·5 g (23 mM)	1·46 g (23 mM)	PCl_3 0·9 g (6·56 mM)		MeOH—CH_3COCH_3	X/white/250°	23	
5·5 g (23 mM)	1·46 g (23 mM)	$POCl_3$ 1 g (6·65 mM)	Trituration with EtOH	H_2O	XI/white/280°	12	
5 g (20·8 mM)	1·33 g (20·8 mM)	S_2Cl_2 2·8 g (20·8 mM)		EtOH—CH_3COCH_3	XIII[10]/yellow/ 158°	34	
(6·5 g (27 mM)	1·73 g (27 mM)	$SOCl_2$ 1·62 g (13·6 mM)		EtOH—CH_3COCH_3	XIV/white/164°	20	

TABLE 2

Sub-stance	Formula/mol.weight	Analysis %					Spectral data	
			C	H	N	P	IR	UV
VI a	$C_{18}H_{14}N_4O_5$/366·32	Found : Requires :	58·79; 59·01;	4·04; 3·85;	15·28; 15·30;	— —	$\gamma_{C=O}$ = 1750 cm^{-1}; γ_{OH} = 3330 cm^{-1};	λ_{max}^{MeOH} = 308 mμ ε = 18,700
VII	$C_{10}H_8N_2O_3$/204·18	Found : Requires :	59·16; 58·83;	4·28; 3·95;	13·71; 13·73;	— —	—	—
VI b	$C_{21}H_{20}N_4O_5$/408·43	Found : Requires :	61·71; 61·75;	5·13; 4·93;	13·84; 13·72;	— —	$\gamma_{C=O}$ = 1750 cm^{-1}; γ_{OH} = 3290 cm^{-1}; γ_{CH^2} = 2660, 2930 cm^{-1}	λ_{max}^{EtOH} = 312 mμ
VI c	$C_{23}H_{16}N_4O_5$/428·39	Found : Requires :	64·26; 64·48;	3·73; 3·77;	12·94; 13·08;	— —	$\nu_{C=O}$ = 1750 cm^{-1}; γ_{OH} = 3220 cm^{-1};	λ_{max}^{MeOH} = 311 mμ ε = 15,500
VIII	$C_{18}H_{10}N_4O_6$/378·29	Found : Requires :	57·18; 57·15;	2·84; 2·66;	15·01; 14·88;	— —	$\gamma_{C=O\ cyclic}$ = 1790 cm^{-1}; $\gamma_{C=O\ exocyclic}$ = 1660–1680 cm^{-1};	$\lambda_{max}^{CH_3COCH_3}$ = 340 mμ ε = 9000
IX	$C_{18}H_{12}N_4O_5$/364·31	Found : Requires :	59·01; 59·34;	3·49; 3·32;	15·44; 15·38;	— —	$\gamma_{C=O\ cyclic}$ = 1780–1800 cm^{-1}; $\gamma_{C=O\ exocyclic}$ = 1640 cm^{-1}; γ_{CH_2} = 2850, 2920 cm^{-1};	$\lambda_{max_1}^{EtOH}$ = 290 mμ $\lambda_{max_2}^{EtOH}$ = 350 mμ

TABLE 2—*continued*

X	$C_{24}H_{15}N_6O_6P$/514·385	Found : 55·81; Requires : 56·03;	3·26; 2·94;	16·48; 16·34;	— —	$\gamma_{C=O}$ = 1770 cm^{-1};	$\lambda_{max\,1}^{CHCl_3}$ = 242 mμ ε_1 = 12,600 $\lambda_{max\,2}^{CHCl_3}$ = 343 mμ ε_2 = 16,000
XI	$C_{16}H_{11}N_4O_6P$/386·225	Found : 48·03;* Requires : 49·75;	2·92; 2·87;	14·54; 14·51;	7·65; 8·01;	$\gamma_{C=O}$ = 1770 cm^{-1}; $\gamma_{P\to O}$ = 1280 cm^{-1};	λ_{max}^{MeOH} = 313 mμ ε = 2670
				S			
XIII	$C_{16}H_{10}N_4O_4S$/354·33	Found : 54·29; Requires : 54·23;	3·11; 2·84;	16·01; 15·82;	9·65; 9·04;	$\gamma_{C=O}$ = 1770 cm^{-1};	$\lambda_{max\,1}^{CHCl_3}$ = 242 mμ ε_1 = 1390 $\lambda_{max\,2}^{CHCl_3}$ = 342 mμ ε_2 = 1580
XIV	$C_{16}H_{10}N_4O_5S$/370·336	Found : 51·78; Requires : 51·89;	2·81; 2·72;	15·18; 15·13;	— —	$\gamma_{C=O}$ = 1770 cm^{-1}; $\gamma_{S\to O}$ = 1090 cm^{-1};	$\lambda_{max\,1}^{CHCl_3}$ = 241 mμ ε_1 = 8790 $\lambda_{max\,2}^{CHCl_3}$ = 320 mμ ε_2 = 9200

* The low analysis found are probably due to incomplete combustion of the phosphinic acid[11]

No reaction products could be obtained by treating $SiCl_4$ or $SnCl_4$ with I under similar conditions. Further none of the carbinols react under normal conditions with $SOCl_2$, $POCl_3$ or PCl_5 to give the respective chlorides, thus proving decreased reactivity of a central carbon atom to which two sydnone rings are bound.

The carbinols IV, VIa and VIc, are discoloured when submitted to UV radiation and the radicals formed are readily detected by electronic paramagnetic spin resonance. Free radicals are also obtained by γ-radiation (5×10^6 rad). Under identical conditions the carbinol IV forms the greatest concentrations of free radicals. Compounds IV, VIa, b, c, VIII and IX also give stable carbonium ions when dissolved in conc H_2SO_4 and are being investigated.

EXPERIMENTAL

Condensation of lithium phenylsydnone (I) *with acid chlorides.* The reaction between bromophenylsydnone[4] (B.P.S.) and BuLi[5] was carried out in inert gas atmosphere, by adding dropwise with stirring, the latter to the former (both in ethereal soln containing about 0·25 and 0·1 g substance per ml respectively) while stirring. During this and the subsequent stages the temp was maintained at -50 to $-60°$. The mixture was stirred for 0·5 hr[4] after which an ethereal soln containing about 0·3 g/ml of freshly distilled acid chloride was added. After stirring 0·5 hr, the mixture was poured into water* and the ppt (sometimes a sticking mass) together with that obtained by evaporation of the organic layer was purified. (Tables 1 and 2).

Formation of III, IV, VIa, VII, VIII and IX. The slightly coloured crude product obtained above, was washed with solvents and filtered. The filtrate was evaporated and the residue recrystallized to yield III or VII (IX was obtained from the mother liquors from the recrystallization of VIII). The washed crystals after recrystallization yielded IV, VIa, or VIII.

4,4′ *Bis*(*3-phenylsydnonyl*) *methyl carbinol* (VIa). To a suspension of I[4] (obtained as above from B.P.S.[4] 0·36 g or 1·49 mM in 2 ml dry ether and 1·1 ml ethereal soln of BuLi[5] 0·1 g 1·56 mM) VII (0·3 g; 1·47 mM) were added at $-60°$ with stirring which was continued for 0·5 hr. The mixture was then poured into water acidified with HCl. The product VIa (m.p. 160°, after washing with ether and benzene was recrystallized from ether–alcohol as white crystals m.p. 212° (45 mg 10% based on VII) was identical with VIa, giving no depression in a mixed m.p. and having the same IR spectra.

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REFERENCES

[1] N. Suciu, Gh. Mihai, M. Elian and E. Stroescue, *Tetrahedron* **21**, 1379 (1965).
[2] F. Glaser, W. Shäfer, *Angew. Chem.* **71**, 372 (1959).
[3] M. S. Kharasch and O. Reinmuth, *Grignard Reactions of non-metallic substances* p. 730. Constable, London (1954).
[4] H. Kato and M. Ohta, *Bull. Chem. Soc. Japan* **32**, 282 (1959).
[5] R. G. Jones and H. Gilman, *Organic Reactions* Vol. VII; p. 352. Wiley, New York (1951).
[6] K. Kishimoto and M. Ohta, *Nippon Kagaku Zasshi* **83**, 833 (1962).
[7] V. G. Yashunski, *Dokl. Akad. Nauk. SSSR* **130**, 350 (1960).
[8] H. E. Fierz-David and W. Kuster, *Helv. Chim. Acta* **22**, 82 (1939).
[9] S. David, *Preparation of Organic intermediates* p. 242. Wiley, New York (1951).
[10] H. Kato and M. Ohta, *Bull. Chem. Soc. Japan* **30**, 210 (1957).
[11] P. A. Chopard, R. F. Hudson and G. Klopman, *J. Chem. Soc.* 1379 (1965).

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* Acidified water (HCl) was used in the case of III, IV and VIII, IX.