

A CONVENIENT METHOD FOR THE PREPARATION OF UNSYMMETRICAL  
DISULFIDES BY THE USE OF DIETHYL AZODICARBOXYLATE

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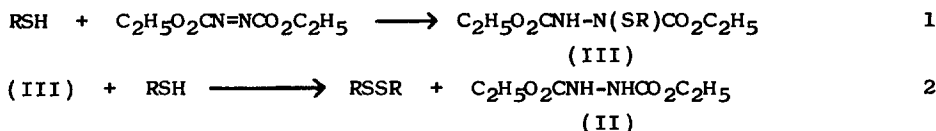
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It is well known that diethyl azodicarboxylate (I) is used as a strong hydrogen acceptor (1). For instance, (I) is capable of dehydrogenating a wide variety of primary or secondary alcohols, mercaptans, and hydrazobenzenes and converting them into aldehydes or ketones, disulfides and azobenzenes. In this process, (I) is reduced to diethyl hydrazodicarboxylate (II). In connection with this reaction of mercaptans with (I), Diels and Wulff (2) reported that dimethyl azodicarboxylate reacts with ethyl mercaptan to give a (1:1) adduct.

In the present study, the oxidative coupling of two different mercaptans, with the formation of unsymmetrical disulfide, has been brought about by the use of diethyl azodicarboxylate (I). When (I) was allowed to react with an equimolar amount of n-amyl mercaptan in ether at room temperature for 2 hr, the reaction mixture changed in color from orange red, characteristic color of (I), to pale yellow and an adduct of n-amyl mercaptan and (I) [ bp 123-5°/0.1mmHg;  $n_D^{25}$  1.4621; Anal. Calcd. for  $C_{11}H_{22}N_2O_4S$ : C, 47.46; H, 7.97; N, 10.06; S, 11.52; Found: C, 47.91; H, 8.04; N, 10.52; S, 11.10 ] was obtained in an 80% yield.

It was found that the adduct reacted with n-amyl mercaptan by refluxing in benzene for 5 hr to give n-amyl disulfide (82%) and (II) (86%). From these results, it is noted that mercaptans are dehydrogenated with (I) to disulfides by two step processes. In the first step, mercaptans add to (I) giving the adduct, diethyl N-alkanesulfonylhydrazodicarboxylates (III) (eq. 1). In the second step, the adduct thus formed reacts with mercaptans cleaving nitrogen-sulfur bond of (III) to give disulfide and (II) (eq. 2).



The completion of the initial reaction forming intermediate (III) can be easily checked by a change in color, so it would be expected that the unsymmetrical disulfide can be prepared by the successive addition of a second mercaptan to the resulted solution. In fact, various unsymmetrical disulfides (IV) can be prepared along with diethyl hydrazodicarboxylate in good yields according to the equation 3. The results are showed in Table I.

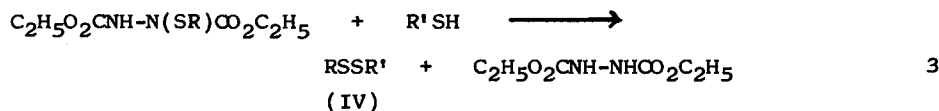


TABLE I  
Unsymmetrical Disulfides\*\* Prepared via Diethyl N-Alkanesulfonyldicarboxylates

R	R'	Reaction Conditions*		Yields (%)			B.P. /Mm. or [M.P.]
		eq. 1	eq. 3	II	IV	$n_D^{25}$	
n-C <sub>5</sub> H <sub>11</sub>	C <sub>6</sub> H <sub>5</sub>	E, RT, 2 hr	E, RT, 24 hr	82	90	1.5652	91°/0.5
C <sub>6</sub> H <sub>5</sub>	n-C <sub>5</sub> H <sub>11</sub>	E, RT, 0.5 hr	E, RT, 24 hr	75	86	"	"
C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	B, 60-70, 2 hr	B, RF, 5 hr	74	86	1.5853	69°/0.5
C <sub>6</sub> H <sub>5</sub>	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	E, RT, 0.5 hr	E, RT, 5 hr	60	75		[58-9°]
n-C <sub>5</sub> H <sub>11</sub>	CH <sub>2</sub> CO <sub>2</sub> Et	B, RT, 2 hr	B, RF, 15 hr	85	81	1.4918	98-9°/0.5
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	CH <sub>2</sub> CO <sub>2</sub> Et	W, RT, 24 hr	B, RF, 5 hr	50	78	1.5688	138-9°/0.5

E: Ether, B: Benzene, W: Without solvent, RT: Room temperature, RF: Reflux.

\* All experiments described in this paper were carried under an atmosphere of nitrogen. \*\* The disulfides were also characterized as single pure substances by the elemental analysis.

It is noted that the present method for the preparation of unsymmetrical disulfides using diethyl azodicarboxylate as dehydrogenating agent possesses a potential synthetic utility, because the reaction proceeds under mild and neutral conditions giving unsymmetrical disulfides in good yields.

#### REFERENCES

1. F. Yoneda, K. Suzuki and Y. Nitta, J. Org. Chem., **32**, 727 (1967).
2. O. Diels and C. Wulff, Ann., **437**, 309 (1924).