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CARBON SUBOXIDE AND SOME OF ITS REACTIONS

XXIII. Reaction of Carbon Suboxide With Oxazolidines

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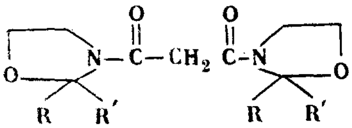
The reaction of carbon suboxide with a number of oxazolidines is investigated, and a number of previously undescribed oxazolidines malonated at the nitrogen atom are obtained. A structure for them is proposed.

In line with the plan of previous investigations of the reaction of carbon suboxide with cyclic imines [1], it was of interest to react it with oxazolidines. It is known that oxazolidines are quite labile substances, prone to ring closure, and to conversion into acyclic compounds of the Schiff's base type [2-4]. It has previously been shown that oxazolidines substituted at the nitrogen atom, retain their cyclic structure [5].

The reaction of carbon suboxide with oxazolidines can proceed in three directions: 1) the oxazolidines react with the C_3O_2 to give bis(oxazolidines-3) of malonic acid (i.e., according to the equation which applies to other heterocyclic imines [1]), 2) the hydroxyl of the acyclic form reacts with carbon monoxide, 3) the Schiff's base group > C=N– reacts with the C_3O_2.

It has now been shown that freshly distilled oxazolidines (heating leads to shift of equilibrium in the direction of formation of the cyclic form) react with carbon suboxide to give satisfactory yields of compounds having the following structure:



	I	II	III	IV	V	VI	VII
R	H	CH_3	CH_3	$-CH_2-CH_2$ CH_2	H	H	C_6H_5
R′	CH_3	CH_3	C_2H_5	$-CH_2-CH_2$	C_6H_5	p-$CH_3OC_6H_4$	$C_6H_5CH=CH$

The IR spectra of the compounds synthesized showed a sharp absorption band in the 1665-1640 cm^{-1} region, characteristic of the carbonyl group of amides of carboxylic acids, and not of esters (a band in the 1750 cm^{-1} region is characteristic of the latter, and it was absent). This and the analytical data lead to the conclusion that the compounds here synthesized have the structure given above (table).

Properties of Synthesized Bis(oxazolidines-3) of Malonic Acid

Compound No.	Mp, °C	Formula	Found		Calculated		Yield, %
			N, %	mol. wt.	N, %	mol. wt.	
I	94—95	$C_{11}H_{18}O_4N_2$	11.58	249	11.57	242	60
II	113—114	$C_{13}H_{22}O_4N_2$	10.60	263	10.35	270	75
III	66—67	$C_{15}H_{26}O_4N_2$	9.58	286	9.40	298	48
IV	137—138	$C_{19}H_{30}O_4N_2$	8.25	354	8.0	350	80
V	82 (decomp)	$C_{21}H_{22}O_4N_2$	7.43	378	7.65	366	78
VI	70 (decomp)	$C_{23}H_{26}O_6N_2$	6.46	440	6.57	426	64
VII	147—148	$C_{37}H_{34}O_4N_2$	5.18	553	4.92	570	65

Experimental

The carbon suboxide was prepared by high temperature pyrolysis of diacetyltartaric acid [7], and passed directly into the reaction mixture from the pyrolysis furnace.

The oxazolidines were prepared by a modified Cope method [8, 9]. The following were synthesized: 2-methyloxazolidine bp 28-29° (21-22 mm), 2, 2-dimethyloxazolidine bp 29-30° (9-10 mm), 2-methyl-2-ethyloxazolidine bp 48° (14 mm), 2-cyclohexanooxazolidine bp 81-82° (10-11 mm), 2-phenyloxazolidine bp 126-127° (8 mm), 2-(p-methoxyphenyl) oxazolidine mp 34-35° (from benzene), and 2-ω-styryl-2-phenyloxazolidine mp 109-110° (from benzene) and 2-ω-styryl-2-phenyloxazolidine mp 109-110° (from benzene).

Preparation of compound I. 2.0 g (23 mmole) 2-methoxyoxazolidine was dissolved in 30-40 ml dry diethyl ether, and dry carbon suboxide gas was passed into the solution at room temperature to neutral reaction. After standing for 3-4 days the yellowish crystals were filtered off with suction, and recrystallized from hot ether, using active charcoal. A further quantity of the product was obtained by evaporating the mother liquors. Mp 94-95° (from ether). Compound I was soluble in benzene, ethanol, chloroform, acetone, water, less soluble in ether.

Compounds II-VII were similarly obtained, with but little change in the method. Compounds II, III were prepared using a reaction temperature of −10° to −15°, IV-VII at room temperature. In preparing V the reaction medium was xylene + ether (2 : 1), and for all the other compounds it was ether. Compounds II-VII had low solubilities in water and most organic solvents.

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