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ACTIVATION OF CS_2 IN REACTION WITH BUTADIENE CATALYZED BY PALLADIUM COMPLEXES

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Recently we realized the catalytic activation of elemental sulfur using metal complex catalysts in reactions with 1,3-dienes. This allowed us to produce, in a single stage, unsaturated linear and cyclic sulfides [1-3].

Continuing our investigations of catalytic reactions taking place with the participation of small molecules and aiming at the preparation of difficult to obtain organic sulfur compounds, we carried out for the first time the heterocyclization of CS_2 with butadiene, a reaction catalyzed by palladium phosphine complexes. These complexes are widely used to activate CO_2, NH_3, H_2O, S, and SO_2 [1-10]. To prepare the catalyst, we used the $Pd(acac)_2$—PPh_3—$AlEt_3$ system.

We established that butadiene and CS_2, taken in a ratio 1:1 in toluene at 130°C, in the presence of the indicated catalytic system were converted to 1,3E,7Z-octatriene and $Ph_3P{=}S$. When this reaction was carried out in DMF, we obtained dicrotyl sulfide, whose yield was over 8% [10]. All our attempts to increase the yield by varying the reaction conditions as well as by using different activating ligands proved futile.

When we introduced into the reaction mass simultaneously CO_2 and NH_3 and when we substituted 1,2-bis(diphenylphosphino)ethane for Ph_3P (molar ratio $Pd:diphos:CO_2:NH_3 = 1:1:300:500$), we were able to obtain a mixture of saturated, six-membered 1,4-bis-sulfides and 1,4-bis-sulfoxides (I)-(IV) with an overall yield of 93% (DMF; 150°C; 20 h). In addition to (I)-(IV), whose ^{13}C NMR spectra are given in Table 1, we observed the formation of linear saturated sulfides (V)-(VI). The ratio (I)-(III):(IV):(V):(VI) = 25:67:1.5:6.5.

As can be seen, only three (Ia-c) of the theoretically possible eight stereoisomers of 2,3,5,6-tetramethyl-1,4-dithiocyclohexane were obtained in the conditions of our experiments. As concerns 2-ethyl-5,6-dimethyl-1,4-dithiocyclohexanes, they were represented by all four possible stereoisomers (IIa-d), and 2,5-diethyl-1,4-dithiocyclohexanes were identified as cis and trans isomers (IIIa) and (IIIb).

What attracted our attention was the circumstance that in all our experiments we observed the formation of saturated 1,4-dithianes, sulfides, and 1,4-bis-sulfoxides from butadiene and CS_2. Apparently, the NH_3 used in the reaction under heterocyclization conditions acted as a source of hydrogen atoms, and the formed unsaturated sulfides were reduced to the corresponding saturated compounds (I)-(VI) in the presence of palladium complexes. Concerning the formation of sulfoxides, it can be assumed that an oxidation reaction of 1,4-bis-sulfides (I) by CO_2 took place in our experiments under the influence of Pd complexes. These results can be explained if we take into consideration publications [10, 11], where it was shown that under mild conditions, CO_2 oxidized quantitatively Ph_3P to $Ph_3P{=}O$ in the presence of Pd complexes.

One question still remained unclear: it related to an increase in the catalytic activity of Pd complexes in the heterocyclization reaction when CO_2 and NH_3 were introduced simul-

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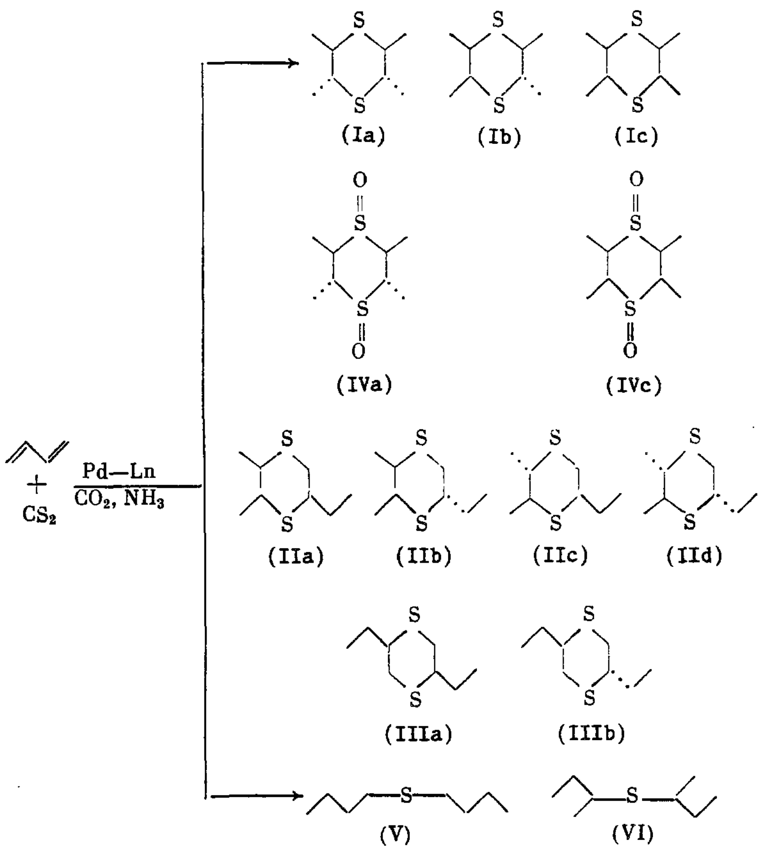

taneously into the reaction mass. We should point out that a decrease in the concentration of CO_2 from 300 to 100 mmoles per 1 g-atom of Pd did not produce any noticeable effect on the yield and the composition of the heterocyclization products.

When CO_2 or NH_3 were introduced into the reaction environment separately, we did not observe their promoting effect, and only when these molecules were used together, was it possible to produce the heterocyclization of CS_2 with butadiene to obtain (I)-(VI).

A structural analysis of the obtained 1,4-bis-sulfoxides (IVa,b) showed that these latter could be obtained only by oxidizing 1,4-bis-sulfides (Ia) and (Ic). At the same time, in a reaction mass containing 1,4-bis-sulfoxides, we did not discover even traces of the oxidation products of other 1,4-dithianes (IIa-d), (IIIa, b), (V), and (VI) to their corresponding 1,4-bis-sulfoxides. Apparently, the bulkier ethyl substituents of 1,4-bis-sulfides (IIa-d), (IIIa, b), (V) and (VI), as compared to the methyl groups of (Ia-d), presented steric hindrances to the approach of the oxidant to the reactive center, that is, to sulfur atoms, preventing their conversion to sulfoxide groups. To confirm the above hypothesis, we conducted special experiments oxidizing separately 1,4-bis-sulfides (Ia-c) ,(IIa-d) and (IIIa, b) with CO_2 in the presence of catalyst $Pd(acac)_2Ph_2P(CH_2)_2PPh_2$ in a DMF solution (150°C; 20 h) and in the presence of NH_3. We discovered that in these conditions, only 1,4-dithianes (Ia) and (Ic) underwent oxidation to (IVa, c), while compounds (IIa-d) and (IIIa, b) remained completely unchanged in this reaction.

Moreover, this method was found also unsuitable to oxidize dimethylsulfide, thiophene, and thiocyclohexane. It seems that during the heterocyclization of CS_2 with butadiene, the produced tetramethyl-1,4-dithiocyclohexanes displaced 1,2-bis(diphenylphosphino)ethane in the coordination sphere of the central atom of the catalyst, became activated, and reacted with CO_2 molecules, producing the corresponding sulfoxides.

We cannot exclude the possibility that in our heterocyclization experiments in the presence of CO_2, CS_2, and palladium complexes, active sulfur monoxide (SO) particles were being generated, and that precisely these reacted with butadiene, following a strict regioselectivity, producing (IVa) and (IVc).

The highest yields of 1,4-dithianes (I)-(III) and sulfides (V) and (VI) were obtained in polar aprotic solvents (DMF, HMPTA, and N-methylpyrrolidone) at a ratio Pd:diphos = 1:1.

TABLE 1. ^{13}C NMR Spectra of Compounds (I)-(IV) (δ, ppm)

Compound	CH_2CH_3	CH_3	CH_2	CH
2,6-cis-3,5-trans-Tetramethyl-1,4-Dithiocyclohexane (Ia)	–	20.69q	–	39.88d
2,3,5-cis-6-trans-Tetramethyl-1,4-Dithiocyclohexane (Ib)	–	14.56q 18.15q 19.0q 19.84q	–	36.82d 40.54d 44.85d 45.95d
2,3,5,6-cis-Tetramethyl-1,4-Dithiocyclohexane (Ic)	–	16.84q	–	37.73d
2-cis-Ethyl 5,6- cis-Dimethyl-1,4-Dithiocyclohexane (IIa)	11.42q 27.81t	15.60q 18.80q	35.45t	38.06d 39.17d 41.52d
2-trans-Ethyl-5,6-cis-Dimethyl-1,4-Dithiocyclohexane (IIb)	11.16q 28.40t	13.77q 19.39q	28.98t	36.75d 44.06d 47.13d
2-cis-Ethyl-5-trans-6-cis-Dimethyl-1,4-Dithiocyclohexane (IIc)	11.81q 26.96	20.04q 20.37q	33.23t	39.30d 40.73d 41.58d
2-cis-Ethyl-5-cis-6-trans-Dimethyl-1,4-Dithiocyclohexane (IId)	11.36q 28.66t	18.47q 19.19q	32.27t	43.28d 45.17d 47.26d
2,5-cis-Diethyl-1,4-Dithiocyclohexane (IIIa)	11.70q 27.44t	–	34.18t	40.03d
2,5-trans-Diethyl-1,4-Dithiocyclohexane (IIIb)	11.68q 27.09t	–	32.51	41.59d
2,6-cis-3,5-trans-Tetramethyl-1,4-di(thioxo)-cyclohexane (IVa)	–	18.54q	–	61.30d
2,3,5,6-cis-Tetramethyl-1,4-di(thioxo)cyclohexane (IVc)	–	14.39q	–	58.32d

TABLE 2. Effect of the Solvent Nature on the Product Composition in the Reaction between CS_2 and Butadiene* (150°C; 20 h; molar ratio Pd: diphos:CS_2:  :CO_2:NH_3 = 1:1:300:300:300:500)

Solvent	Aggregate,* yield, %	Composition of the reaction products, %		
		(I)—(III)	(IV)	(V), (VI)
DMF	93	25	67	8
HMPTA	78	34	53	13
N-Methylpyrrolidone	50	40	59	1
Toluene	7	–	71	19
Sulfolane	–	–	–	–

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*The yields of the isolated products are given.

The substitution of toluene for the indicated solvents leads to an increased selectivity for 1,4-bis-sulfoxides to 71%; however, the aggregate yield of the heterocyclization products dropped to 7% (Table 2).

Analogous results were obtained when the concentration of the palladium catalyst was decreased twofold. The selectivity towards 1,4-bis-sulfoxides increased in this case to 83%.

Thus, despite the complex character of the investigated reaction, it presents, without doubt, a great interest in obtaining in a single stage the difficult to obtain substituted 1,4-dithiocyclohexanes and disulfoxides starting from butadiene and CS_2.

EXPERIMENTAL

We used in our work freshly redistilled CS_2, recondensed NH_3, 98% pure butadiene, and absolute DMF. The mixture of products (I)-(III) was analyzed with a Chrom-47 chromatograph (2.4 m column; Carbowax 6000 [PEG-6000]; carrier gas, helium).

The individual products (I)-(III) were isolated by GLC using a Chrom-31 chromatograph (5 m column; Carbowax 6000 [PEG-6000] or 5% SE-30 on Chromatron N-AW; carrier gas, helium).

The PMR spectra were obtained with Tesla BS-487B and Tesla BS-467B instruments in $CDCl_3$ with respect to TMS. The NMR ^{13}C spectra were registered on a Jeol-FOQ spectrometer with wide-band attenuation of protons in a homoresonance regime, with respect to TMS. The IR spectra were taken with a UR-20 spectrometer (film). The mass spectra were obtained with an MX-1306 instrument at 70 eV and an ionization chamber temperature of 200°C.

Interaction of CS_2 with Butadiene. A mixture of 0.31 g $Pd(acac)_2$ and 0.4 g of $Ph_2P(CH_2)_2PPh_2$ was dissolved in 25 ml of DMF and stirred under argon for 10 min. The catalyst was then transferred into a steel autoclave (100 ml) and cooled to −50°C, 0.3 mole of CS_2, 0.5 mole of NH_3, and 0.3 mole butadiene were added, and the autoclave was filled with CO_2 (50 atm). The reaction mass was heated for 20 h at 150°C, then cooled, diluted with 100 ml of benzene, washed with water, and dried over Na_2SO_4. After removing the solvent, 18.4 g (93%) of (I)-(VI) was obtained; they were separated by vacuum distillation into (I)-(III), (V), (VI), and (IV). (I)-(III), bp 42-55°C (1 mm), n_D^{20} 1.5286. Mass spectrum, m/z: 176. PMR spectrum (δ, ppm): (Ia), 1.42 d (CH_3, J = 7.0 Hz), 2.8 m (SCH); (Ib), 1.17 m and 1.46 d (CH_3, J = 7.0 Hz), 2.88 m (SCH); (Ic) + (IId), 1.00 t (CH_3, J = 9 Hz), 1.22 d (CH_3, J = 7 Hz), 1.29 d (CH_3, J = 7 Hz), 2.79 m ($\underline{CH_2}-CH_3$), 3.03-3.23 m (SCH); (IIa) + (IIb), 0.98 t (CH_3, J = 7.7 Hz), 1.16 d (CH_3, J = 7 Hz), 1.12-1.61 m ($\underline{CH_2}-CH_3$), 2.82 m (SCH); (IIc), 0.98 t (CH_3, J = 7.3 Hz), 1.37 d (CH_3, J = 6 Hz), 1.39 d (CH_3, J = 7 Hz), 1.8 m ($\underline{CH_2}-CH_3$), 2.65-3.11 m (SCH); (IIIa), 0.99 t (CH_3, J = 7.3 Hz), 1.23-1.46 m ($\underline{CH_2}-CH_3$), 2.83 m (SCH); (IIIb), 1.01 t (CH_3, J = 6 Hz), 1.30-1.76 m ($\underline{CH_2}-CH_3$), 2.74-2.92 m (SCH).

(IV), bp 85-90°C (1 mm), n_D^{20} 1.5629. Mass spectrum, m/z 208. PMR (δ, ppm): (IVa), 1.59 d (CH_3, J = 6.9 Hz), 4.15 m (S[O]CH); (IVb), 1.52 d (CH_3, J = 6.9 Hz), 4.46 m (S[O]·CH).

(V), (VI), bp 30°C (1 mm). Mass spectrum, m/z 144, n_D^{20} 1.5053. PMR spectrum (δ, ppm): (V), 1.00 t (6H, CH_3, J = 7.0 Hz), 1.37 m (8H, CH_2), 2.67 m (2H, SCH); (VI), 0.98t (6H, CH_3, J = 7.0 Hz), 1.28d (6H, CH_3, J = 6.0 Hz), 1.61 m (4H, CH_2), 2.73 m (2H, SCH).

CONCLUSIONS

1. We have shown the feasibility of catalytic activation of CS_2 in the reaction with butadiene in the presence of the $Pd(acac)_2-PPh_3-AlEt_3$ system, 1,2-bis(diphenylphosphino)ethane, and promoters (a mixture of CO_2 and NH_3), to obtain in single stage substituted 1,4-dithio- and 1,4-di(thioxo)cyclohexanes with high yields.

2. We discovered that the heterocyclization of CS_2 with butadiene is accompanied by a selective oxidation of the produced tetramethyl-1,4-dithiocyclohexanes to the corresponding 1,4-bis-sulfoxides with the aid of CO_2, under the action of palladium complexes.

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