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RANEY NICKEL DESULPHURISATION OF SOME ORGANO-SULPHUR COMPOUNDS

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Compounds like thiolesters (1) and diacylsulphides (2) are known to yield the corresponding aldehydes on treatment with Raney nickel. Under similar conditions, Baddiley (3) obtained ethylbenzene from methylphenyldithioacetate and Cline, Campaigne and Spies (4) obtained trans-α,β-dimethylstilbene from thioacetophenone. We report here the Raney nickel desulphurisation of compounds of the type Ar-CO-SS-CO-Ar (I), Ar-CS-SS-CS-Ar (II), $(Ar\text{-}CHS)_3$ (III), and Ar-CS-SH as their lead salts (IV).

Two types of the catalyst Raney nickel W_2 (5) have been used: (a) The catalyst as prepared, was stored under water, but before use, was washed with alcohol and then used in presence of alcohol (let it be designated W_{2A}); (b) the catalyst was stored under water, but before use, water was completely removed by azeotropic distillation in presence of benzene, cyclohexane or methylcyclohexane, and experiments were carried out in presence of the same dry solvent (catalyst designated W_{2B}).

The reactions have been carried out by heating the sulphur compound in presence of the catalyst for 2 hours in the refluxing solvent. After filtering out the catalyst and distilling off the solvent, either the products have been obtained as such or subsequent purification has been done by chromatographing through alumina column.

The results have been summarised in the next page (6).

$$\underset{\text{I}}{\text{Ar-CO-SS-CO-Ar}} \xrightarrow{W_{2A}} \underset{63\%}{\text{Ar-CHO}} + \underset{2\%}{\text{Ar-CO-OH}} \qquad \text{(Ar = Phenyl)}$$

$$\underset{\text{I}}{\text{Ar-CO-SS-CO-Ar}} \xrightarrow{W_{2B}} \underset{40\text{-}55\%}{\text{Ar-CHO}} + \underset{6\text{-}23\%}{\text{Ar-CO-OH}} \qquad \text{(Ar = Phenyl, p-tolyl and anisyl)}$$

$$\underset{\text{II}}{\text{Ar-CS-SS-CS-Ar}} \xrightarrow{W_{2A}} \underset{66\%}{\text{Ar-CH}_2\text{-CH}_2\text{-Ar}} \qquad \text{(Ar = Anisyl)}$$

$$\underset{\text{II}}{\text{Ar-CS-SS-CS-Ar}} \xrightarrow{W_{2B}} \underset{48\text{-}65\%}{\text{Ar-C}\equiv\text{C-Ar}} \qquad \text{(Ar = Anisyl, p-tolyl and p-chlorophenyl)}$$

$$\underset{\text{III}}{(\text{Ar-CHS})_3} \xrightarrow{W_{2A}} \underset{45\%}{\text{Ar-CH=CH-Ar}} + \underset{34\%}{\text{Ar-CH}_2\text{-CH}_2\text{-Ar}} \qquad \text{(Ar = Anisyl)}$$

$$\underset{\text{III}}{(\text{Ar-CHS})_3} \xrightarrow{W_{2B}} \underset{73\text{-}83\%}{\text{Ar-CH=CH-Ar}} \qquad \text{(Ar = Phenyl, p-tolyl and anisyl)}$$

$$\underset{\text{IV}}{(\text{Ar-CS-S-})_2\text{Pb}} \xrightarrow{W_{2B}} \underset{60\%}{\text{Ar-C}\equiv\text{C-Ar}} \qquad \text{(Ar = Anisyl)}$$

Compounds of the type I yielded both the aldehydes and the corresponding acids with either type of the catalyst. But the amount of the acid depended on the type of catalyst and its age (Table I)

The acid has always been found adsorbed in the catalyst and has to be extracted with $NaHCO_3$. Although benzaldehyde itself has been found to produce some benzoic acid under identical conditions, it appears that the acid is not formed entirely via the aldehyde, because when benzaldehyde itself was treated with 4 months old Raney nickel W_{2B}, the yield of the acid did not exceed 7%. Carrying out the reaction under nitrogen atmosphere did not substantially alter the yield of the acid. Further, no detectable amount of benzyl alcohol was produced even when benzoic acid was obtained to the extent of 23%. All these observations are possibly indicative of the fact that the acid is formed as a result of a competitive nucleophilic reaction of the adsorbed alkali on the disulphide itself.

TABLE I

Amount of Benzoic acid obtained from Benzoyldisulphide.

Catalyst	Age	Medium	% yield of aldehyde	% yield of acid
W_{2A}	Fresh	95% EtOH	63.0	2.0
	4 months	Abs. EtOH	62.2	2.5
W_{2B}	Fresh	Cyclohexane	55.0	6.0
	1 month	"	54.2	7.8
	4 months	"	40.0	20.1
	"	Benzene	41.4	23.0

When compounds of the type (II) were treated with Raney nickel W_{2A}, the products were exclusively of the type Ar-CH_2-CH_2-Ar (7). With W_{2B} catalyst, however, the results were quite interesting. Bis-(p-methoxythiobenzoyl)disulphide yielded two white crystalline products, A (50%) and B (14%), m.p. 145°C and 122°C respectively. On refluxing A with either neutral or alkaline $KMnO_4$, or with chromic acid in acetic acid, small amount of anisic acid, and another yellowish crystalline product A_1, m.p. 130°C, were obtained. A_1 was identified to be anisil by comparison with a known sample of the same. The I.R. spectrum of A did not show any characteristic band for olefinic bond, but with sodium and alcohol, A was converted into p,p'-dimethoxystilbene (confirmed by comparison with a known sample). On passing hydrogen bromide in the cold in acetic acid medium, A yielded a white crystalline product A_2, m.p. 180-81°C. All these observations indicated that A may be dianisylacetylene, and this was corroborated by the analytical data (8). (Calc. for A, $C_{16}H_{14}O_2$, C: 80.64; H: 5.93; mol. wt. 238. Found C: 80.41; H: 6.26; mol. wt. 241. Calc. for A_2, $C_{16}H_{16}O_2Br_2$, Br: 40.0; found Br: 40.9). Final confirmation was made through independent synthesis of dianisylacetylene by oxidising the dihydrazone of anisil with HgO (9) and comparing the I.R. spectra.

B also yielded anisil on oxidation with $KMnO_4$. The I.R. spectrum of B was compared with those of A and dianisylacetylene, and they were found to be exactly identical. Therefore, A and B must be two forms of the same compound, an observation which was in line with that by Kunimoto (10) who reported the existence of di-p-tolyl acetylene in two forms. His observations were confirmed by us when two forms of di-p-tolylacetylene, m.p. 134°C and 131°C respectively were obtained on desulphurisation of bis-(p-tolylthiobenzoyl)disulphide with Raney nickel W_{2B}. However, only one form of di-p-chlorophenylacetylene, m.p. 172°C, was obtained and the corresponding diphenylacetylene could not be obtained in pure form.

The thioacids (as their lead salts) when desulphurised with W_{2B} catalyst, corresponding disubstituted acetylenes were also obtained in fairly good yield.

The thioaldehydes yielded both stilbenes and bibenzyls with W_{2A} catalyst,but only stilbenes with W_{2B} catalyst.

It appears that desulphurisation of dithioacids or dithiodisulphides using relatively hydrogen-poor Raney nickel W_{2B} may be conveniently employed for preparation of corresponding disubstituted acetylenes.

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(6) These data represent results from experiments carried out with catalysts which were either fresh or one month old. In case of benzoyldisulphide, the catalyst W_{2B} was upto 4 months old.

(7) When this paper was almost ready, report about some data by W. A. Bonner on the action of ordinary Raney nickel on similar compounds came to our notice (Chemistry of Organic Sulphur Compounds, Vol II, p.42, Pergamon Press, London, 1966). Our findings agree with those by Bonner.

(8) Microanalyses were carried out by Dr. F. Pascher, Mikroanalytische Laboratorium, 53 Bonn, Buschstrasse 54, West Germany.

(9) This was the method used by A. C. Cope, D. S. Smith and R. J. Cotter for the preparation of diphenylacetylene (Org. Synth., Coll. Vol IV, p.377 John Wiley, New York, 1963).

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