UDC 547.541'234 : 542.941.7[546.74]

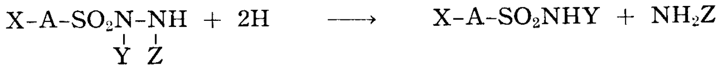
14. **Takeo Ueda and Tadakazu Tsuji** : Reduction of Arylsulfonylhydrazine with Activated Raney Nickel.

(*Rharmaceutical Institute, Keio-Gijuku University**1)

Regarding the reduction of arylsulfonylhydrazine, Curtius and Lorensene1) reported that the compound was resistant to various reducing agents and exclusively afforded arylsulfonic acid with zinc powder in acetic acid. In connection with the above work, it was found that benzenesulfonylhydrazine was indifferent to catalytic reduction over palladium-carbon catalyst, but afforded benzenesulfonamide and ammonia with activated Raney nickel W-2.2) This finding is of interest in respect to application of this new reaction to the synthesis of special kinds of arylsulfonamide derivatives and amido compounds. This reaction is shown by the following equation, the mechanisms of which will be reported in the near future.

Arylsulfonylhydrazines having various substituent groups were also subjected to the reduction with Raney nickel W-2 and it was found that cleavage of N-N bond took place to afford the corresponding sulfonamide, just as in the case of benzenesulfonylhydrazine. The results obtained with these hydrazines are shown in Table I. This reduction, in general, was carried out by heating under reflux the methanolic solution of arylsulfonylhydrazine with excess of activated Raney nickel W-2 prepared from Raney nickel alloy. Arylsulfonamide thus obtained was identified with an authentic sample by the mixed melting point test.

It was thereby made clear that arylsulfonylhydrazine was converted into the corresponding arylsulfonamide by reduction with Raney nickel as shown by the following equation:



$$\text{X-A-SO}_2\underset{\text{Y}}{\text{N}}\text{-}\underset{\text{Z}}{\text{NH}} + 2\text{H} \longrightarrow \text{X-A-SO}_2\text{NHY} + \text{NH}_2\text{Z}$$

where, X stands for a substituent group in the aromatic ring, Y for substituent group in N, Z for a substituent group in N, and A for aromatic ring residue.

The detailed scope and limit of this new reaction will be reported in the future.

Experimental

General Procedure for Reduction of Arylsulfonylhydrazine—To a solution of 0.014 mole of arylsulfonylhydrazine in 60 cc. of 50% MeOH, Raney Ni W-2 (prepared from 15 g. of Raney Ni alloy) was added and the mixture was heated under reflux for 2 hr. After removal of Raney Ni by filtration, the filtrate was acidified with dil. HCl, concentrated on a water bath, and the residual solution was chilled. Arylsulfonamide obtained was recrystallized from hydr. EtOH. Admixture of this material with an authentic sample of arylsulfonamide was undepressed.

The mother liquid, left after arylsulfonamide was removed was evaporated to dryness. The residue, which was positive to carbylamine test, was dissolved in water, neutralized, followed by successive take-up with Et_2O and HCl, and the HCl extract was evaporated to dryness. The residue was identified with an authentic sample of the amine by admixture.

Summary

Reduction of benzenesulfonylhydrazine over activated Raney nickel W-2 afforded benzenesulfonamide and ammonia by cleavage of N-N bond. By application of this reduction with Raney nickel, arylsulfonylhydrazines having various substituent groups yielded corresponding arylsulfonamides and an amine.

(Received November 14, 1960)

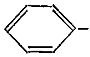
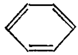
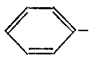
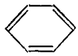
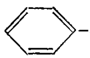
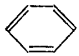
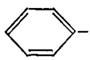
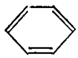
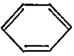
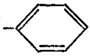
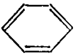
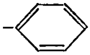
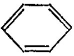
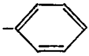
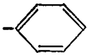
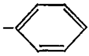
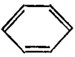
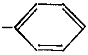
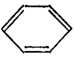
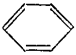
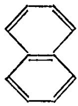
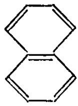
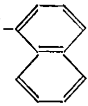
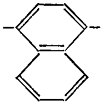
---

*1 Shinano-machi, Shinjuku-ku, Tokyo (上田武雄, 辻 忠和).

1) Th. Curtius, F. Lorenzene : J. prakt. Chem. [2], **58**, 160 (1898).

2) Org. Syntheses, **21**, 15 (1941).

TABLE I.

No.	Reactant	Product	Yield (%)		m.p. (°C)		Analysis of Arylsulfonamide N (%)	
			Arylsulfonamide	Amine	Arylsulfonamide	Amine	Calcd.	Found
1	-SO_2NHNH_2	-SO_2NH_2, NH_3	50.8	43.9[a]	151~152	—	8.92	8.88
2	-$SO_2NHN=C(CH_3)_2$	-SO_2NH_2, $NH_2-CH(CH_3)_2$	37.5	35.6	150~152	150~152[c]	8.92	8.95
3	-$SO_2NHN=CHC_6H_5$	-SO_2NH_2, $NH_2-CH_2C_6H_5$	26.8	27.3	150~152	246~248[c,d]	8.92	9.23
4	-$SO_2NHNHC_6H_5$	-SO_2NH_2, $NH_2-C_6H_5$	14.4	15.1	150~151	197~198[e,c]	8.92	8.76
5	CH_3CONH--SO_2NHNH_2	CH_3CONH--SO_2NH_2, NH_3	51.2	48.4[a]	219~220	—	13.08	13.05
6	CH_3CONH--$SO_2NHN=C(CH_3)_2$	CH_3CONH--SO_2NH_2, $NH_2-CH(CH_3)_2$	48.6	47.3	219~220	150~152[c]	13.08	13.12
7	CH_3CONH--$SO_2\underset{CH_3}{\underset{\vert}{N}}-NH_2$	CH_3CONH--SO_2NHCH_3, NH_3	7.1	5.2[a]	182~183[b]	—	12.28	12.13
8	CH_3CONH--$SO_2\underset{CH_3}{\underset{\vert}{N}}-N=C(CH_3)_2$	CH_3CONH--SO_2NHCH_3, $NH_2-CH(CH_3)_2$	74.5	73.8	182~183	150~152[c]	12.28	12.43
9	NH_2--SO_2NHNH_2	NH_2--SO_2NH_2, NH_3	72.5	71.0[a]	163~165	—	16.28	16.40
10	NH_2--$SO_2NHNHCOC_9H_{19}$	NH_2--SO_2NH_2, $NH_2COC_9H_{19}$	9.9	10.6	163~164	98~99[f]	16.28	16.39
11	-SO_2NHNH_2	-SO_2NH_2, NH_3	32.3	29.2[a]	211~212	—	6.76	6.66
12	CH_3CONH--SO_2NHNH_2	CH_3CONH--SO_2NH_2, NH_3	44.1	39.3[a]	263~264	—	10.66	10.53

[a] NH_3 evolved from the reaction mixture during the whole process was collected in 0.2*N* H_2SO_4 and excess H_2SO_4 was titrated.
[b] Mangiti: Atti accad. nazl. Lincei. Rend., Classe sci. fis. mat. e. nat., [7], **1**, 452 (1940).
[c] Hydrochloride.
[d] Analysis of chloroplatinate. Calcd. for $C_7H_{11}NCl_6Pt$: Pt, 37.73. Found: 37.82.
[e] Identified as acetanilide, m.p. 113~114°, mixed m.p. 114°.
[f] For isolation of caprinamide, the reaction mixture was extracted with Et_2O and Et_2O residue was recrystallized from hydr. EtOH. Mixed m.p. with authentic sample, 98~99°.