In each case the mixture of the two forms melted at the melting point of the higher melting form.

3(α)-12(β)-Diacetoxy-*ter-nor*-diphenylethylene prepared by this method had a melting point of 127–129°, while the reported melting point was 158–160°.[3] The high negative rotation (−138° in chloroform) left no doubt that it was the desired substance.

3(α)-12(β)-Diacetoxy-*nor*-cholanic acid,[4] high melting form, 209–210°; low melting form, 164–66°.

Anal. Calcd. for $C_{27}H_{42}O_6$: C, 70.1; H, 9.2. Found: high melting form, C, 69.9; H, 9.4; low melting form, C, 69.6; H, 9.5.

3(α)-12(β)-diacetoxy-*bis-nor*-cholanic acid, high melting form, 167.8°; low melting form, 99.5–100°.

Anal. Calcd. for $C_{26}H_{40}O_6$: C, 69.6; H, 9.0. Found: high melting form, C, 69.4; H, 9.2; low melting form, C, 69.2; H, 8.9.

Two new compounds were prepared, the above 3(α)-12(β)-diacetoxy-*bis-nor*-cholanic acid and ethyl 3(α)-acetoxy-12-ketocholanate (m. p. 123–124°).

Anal. Calcd. for $C_{28}H_{44}O_5$: C, 73.0; H, 9.6. Found: C, 73.0; H, 9.9.

(3) Hoehn and Mason, THIS JOURNAL, **60**, 1493 (1938).

(4) Brink, Clark and Wallis, *J. Biol. Chem.*, **162**, 701 (1946), found a melting point of 205–6°.

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The Catalytic Reduction of α-Nitrostilbenes to α, β-Diphenylethylamines

BY WARREN D. MCPHEE, ERNST S. ERICKSON, JR.,[1] AND U. JOSEPH SALVADOR

In a recent publication[2] from these Laboratories it was reported that the methods of the literature did not afford practicable procedures for the catalytic reduction of α-nitrostilbenes to α,β-diphenylethylamines.

$$Ar—CH=\underset{\displaystyle NO_2}{\overset{|}{C}}—C_6H_5 \longrightarrow Ar—CH_2—\underset{\displaystyle NH_2}{\overset{|}{CH}}—C_6H_5$$

Subsequent to our previous work we have found that α-nitrostilbenes may be conveniently reduced in methanol in the presence of a readily prepared palladium-on-charcoal catalyst. The amines are easily isolated as their hydrochlorides in a state of purity. In one instance, α-nitro-4′-methoxystilbene gave rise to a small amount of the corresponding oxime when the hydrogen uptake was less than theoretical.

The diphenylethylamine hydrochlorides described herein are being studied pharmacologically by Dr. T. J. Becker and his associates in these Laboratories.

TABLE I

SUBSTITUTED α-NITROSTILBENES, Ar—CH=C(NO)$_2$—C_6H_5

Substituent	Reaction temp., °C.	Yield, %	M. p., °C.	N, % Calcd.	N, % Found
2′-Methoxy	3	85	117.5–119	5.49	5.75
2′-Benzyloxy	3	74	131–132	4.23	4.56
4′-Methoxy	22	64	152–153[a]		
4′-Benzyloxy	22	61	113–114.5	4.23	4.74
3′-Methoxy-4′-benzyloxy	22	49	132–132.5	3.88	3.83

[a] Knoevenagel and Walter [*Ber.*, **37**, 4502 (1904)] report m. p. 151.

Experimental[3]

Substituted α-nitrostilbenes were prepared by condensing a substituted benzaldehyde with an equivalent of phenylnitromethane in the presence of methanolic methylamine, either at room temperature (22°) or in the refrigerator (3°). Analytical samples were recrystallized from alcohol.

The following experiment is typical: **α-nitro-2′-methoxystilbene** was prepared by shaking 6.85 g. (0.05 mole) of phenylnitromethane, 6.80 g. (0.05 mole) of *o*-methoxybenzaldehyde and 2.5 cc. of methanolic methylamine (10 g. of methylamine in 70 cc. of methanol) until solution occurred. The solution was placed in the refrigerator for fifteen hours. The resultant bright yellow crystals were admixed with ether to dissolve the oily impurities, filtered and dried in the air. This material (10.8 g.) was pure enough for reduction, melting at 113–115°. Recrystallization from alcohol gave yellow needles of m. p. 117.5–119°. The same reaction carried out at room temperature gave approximately the same yield of material of equal purity.

Substituted α,β-diphenylethylamine hydrochlorides were prepared by the following general method: 10 g. of the substituted nitrostilbene was dissolved in 150 cc. of boiling methanol. One gram of Darco G-60 and 0.2 g. of palladium chloride were added and the hot mixture was hydrogenated immediately at 55° and 50–60 lb. initial pressure. Reductions were generally complete in one to three hours. The catalyst was then removed by filtration and 10 cc. of saturated ethereal hydrogen chloride was added to the cooled filtrate. The resulting solution was evaporated to dryness *in vacuo* and white crystals formed immediately. These were washed with acetone and recrystallized.

TABLE II

SUBSTITUTED α,β-DIPHENYLETHYLAMINE HYDROCHLORIDES, Ar—CH_2—$CH(NH_2)$—C_6H_5·HCl

Substituted β-phenyl	Reduction time, hr.	Yield, %	M. p., °C.	Recryst. solvent	N, % Calcd.	N, % Found
2-Methoxy	16	52	249–250.5	Dil. HCl	5.31	5.36
2-Hydroxy	3	86	223–224.5	Dil. HCl	5.61	5.54
4-Methoxy[a,b]	3	67	212–213	MeOH-EtOAc		
4-Hydroxy[a]	3	75	255–256	MeOH-EtOAc		
3-Methoxy-4-hydroxy[a]	1	87	220–221	MeOH-EtOAc		

[a] Ref. 1. [b] Phenyl *p*-methoxybenzyl ketoxime, m. p. 130–131°, was isolated in small amount. *Anal.* Calcd. for $C_{15}H_{15}NO_2$: N, 5.82. Found: N, 5.92. Buck and Ide [THIS JOURNAL, **53**, 1536 (1931)] report m. p. 133°.

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(1) At present, Lieutenant (j.g.), U. S. N. R.

(2) McPhee and Erickson, THIS JOURNAL, **68**, 624 (1946).

(3) Microanalyses by the Misses Alice Rainey and Patricia Curran.