TABLE II

MELTING POINTS OF SUBSTITUTED BENZYL DERIVATIVES OF BARBITURATES

	Melting point, °C., derivatives					
	p-Nitrobenzyl		p-Chlorobenzyl		p-Bromobenzyl	
Barbiturate[c]	Block	Tube	Block	Tube	Block	Tube
Amytal[10]	172	169	102	102–105	134	133
Barbital[8]	193	192	144	142	147	146
Cyclopal	181.5 dec.	185 dec.	110.5	122[b]	116	119
Delvinal	131.5	132.5	71	72.5	75.5	77
Dial[10]	192	191.5	134	134	133	132.5
Dormin[9]		196.3				
Evipan[9]		114.5				
Idobutal[9]		127.5				
Ipral[10]	157	157	146	145	153	151
Isonal[9]		192				
Neonal[10]	149	147.5	96	95	98	99
Noctal[9]		200.5				
Nostal[10]	206	203.5	142	141	147	146
Pentobarbital[10]	152[a]	154[a]	111	111	114	114
Pernocton[9]		191.5				
Phanodorn[9]		196				
Phenobarbital[8]	184	182.5	114	113	118	117
Prominal[9]		114.5				
Proponal[9]		182.3				
Rutonal[9]		197				
Sandoptal[10]	180	178	122	122	128	127
Seconal	158	163	102	103	110	111.5
Sigmodal	172	178	91	92	92	95
5-Allyl-5-phenylbarbituric acid[9]		152				

[a] Softens at 148°. [b] Shrinks from the tube but does not melt at 110.5°. Melts sharply at 122°. [c] The superior number after the barbiturate refers to its source in the literature.

seconal, and sigmodal have been prepared and their melting points determined.

2. The p-nitrobenzyl derivatives have been found to be most suitable for the purpose of identification.

BOULDER, COLO. RECEIVED MAY 12, 1944

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

The Catalytic Reduction of Nitrocinnamic Acids and Esters

BY ELKAN R. BLOUT AND DOROTHY C. SILVERMAN

The preparation of aminocinnamic acids and esters is generally carried out by the reduction of the corresponding nitro compounds. Alkaline ferrous hydroxide is the reagent usually preferred by previous workers,[1,2] but we have found that it gives low yields of impure material. Other methods described include electrolytic reduction,[3] the use of tin and hydrochloric acid,[4] zinc dust and, acetic acid,[5] iron powder,[6] and sodium sulfide in sodium hydroxide solution.[7] Adams, Cohen and Rees[8] have noted that ethyl m-nitrocinnamate may be reduced to the corresponding amine using a small amount of platinum-oxide platinum black as the catalyst. Adkins[9] has suggested that a nickel catalyst might selectively reduce nitro compounds in the presence of carbon–carbon double bonds.

In this communication, it is shown that Raney nickel does effectively catalyze the hydrogenation of aromatic nitro groups in preference to aliphatic double bonds conjugated with a benzenoid ring, and it is possible to prepare in good yields aminocinnamic acids and esters from the corresponding nitro compounds.

Nitrocinnamic acids and esters are not easily soluble at room temperature in organic solvents, but we have found that an ethyl alcoholic *sus-*

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(1) *Cf.* Tiemann and Opperman, *Ber.*, **13**, 2056 (1880).

(2) Gabriel, *ibid.*, **15**, 2291 (1882); Gabriel and Herzberg, *ibid.*, **16**, 2036 (1883); E. Fischer and Kuzel, *Ann.*, **221**, 261 (1884); Friedlander and Lazarus, *ibid.*, **229**. 233 (1885).

(3) Marie, *Compt. rend.*, **140**, 1248 (1905).

(4) Bender, *Ber.*, **14**, 2359 (1881); Miller and Kinkelin, *ibid.*, **18**, 3234 (1885); Underwood and Kochmann, THIS JOURNAL, **48**, 254 (1926).

(5) Heller, *Ber.*, **43**, 1907 (1910).

(6) McCluskey and Sber, THIS JOURNAL, **49**, 452 (1927).

(7) Slotta and Szyszka, *Ber.*, **68**, 184 (1935).

(8) Adams, Cohen and Rees, THIS JOURNAL, **49**, 1093 (1927).

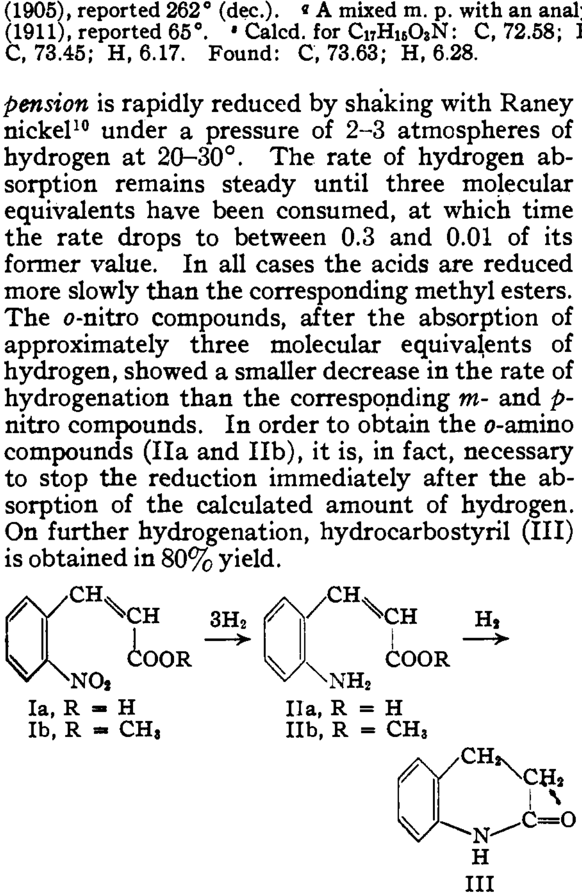
(9) Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, Wis., 1937, p. 126.

TABLE OF RESULTS

Substance reduced	Moles of hydrogen absorbed	Time in hours	Product	Yield,[a] %	M. p., °C.[b]	M. p., °C.,[b] of benzoylamino derivative
p-Nitrocinnamic acid	2.8	6	*p*-Aminocinnamic acid	73	175 –176 (dec.)[c]	279 –280 (dec.)[d]
Methyl-*p*-nitrocinnamate	3.0	3	Methyl-*p*-aminocinnamate	76	125 –127[e]	187.5–188[f]
α-Methyl-*p*-nitrocinnamic acid	2.8	6	α-Methyl-*p*-aminocinnamic acid	84	197 –198 (dec.)[g]	239 –240[h]
m-Nitrocinnamic acid	3.0	12	*m*-Aminocinnamic acid	76	181.5–183[i]	232 –234[j]
Methyl *m*-nitrocinnamate	3.0	4.5	Methyl *m*-aminocinnamate	81	77 – 79[k]	144 –146[m]
o-Nitrocinnamic acid	3.1	5	*o*-Aminocinnamic acid	37	157 –159 (dec.)[n]	266 –269[p]
o-Nitrocinnamic acid	4.0	16	Hydrocarbostyril	90	165 –166.5[q]	
Methyl *o*-nitrocinnamate	3.0	1.5	Methyl *o*-aminocinnamate	74	65 – 67[r]	176 –177[s]
Methyl *o*-nitrocinnamate	3.9	4.5	Hydrocarbostyril	79	165 –166.5[t]	

[a] Yields are based on pure product of m. p. given. [b] All m. p.'s are corrected. [c] Reported[1] 175–176°. [d] Heller, *Ber.*, **46**, 3974 (1913), reported 274° (dec.). [e] Einhorn and Oppenheimer, *Ann.*, **311**, 154 (1900), reported 128–129°. [f] Calcd. for $C_{17}H_{15}O_3N$: C, 72.58; H, 5.38. Found: C, 72.51; H, 5.45. [g] Calcd. for $C_{10}H_{11}O_2N$: C, 67.78; H, 6.26. Found: C, 67.52; H, 6.04. [h] Calcd. for $C_{17}H_{15}O_3N$: C, 72.58; H, 6.38. Found: C, 72.55; H, 5.35. [i] Reported[1] 180–181°. [j] Reported[d] 229°. [k] German Patent 101,685, *Chem. Zentr.*, **70**, I, 1174 (1899), reported 84°. [m] Calcd. for $C_{17}H_{15}O_3N$: C, 72.58; H, 5.38. Found: C, 72.28; H, 5.10. [n] Reported[1] 158–159° (dec.). [p] Reissert, *Ber.*, **38**, 3423 (1905), reported 262° (dec.). [q] A mixed m. p. with an analytical sample showed no depression. [r] Mayer, *Ber.*, **44**, 2298 (1911), reported 65°. [s] Calcd. for $C_{17}H_{15}O_3N$: C, 72.58; H, 5.38. Found: C, 72.45; H, 5.19. [t] Calcd. for C_9H_9ON: C, 73.45; H, 6.17. Found: C, 73.63; H, 6.28.

pension is rapidly reduced by shaking with Raney nickel[10] under a pressure of 2–3 atmospheres of hydrogen at 20–30°. The rate of hydrogen absorption remains steady until three molecular equivalents have been consumed, at which time the rate drops to between 0.3 and 0.01 of its former value. In all cases the acids are reduced more slowly than the corresponding methyl esters. The *o*-nitro compounds, after the absorption of approximately three molecular equivalents of hydrogen, showed a smaller decrease in the rate of hydrogenation than the corresponding *m*- and *p*-nitro compounds. In order to obtain the *o*-amino compounds (IIa and IIb), it is, in fact, necessary to stop the reduction immediately after the absorption of the calculated amount of hydrogen. On further hydrogenation, hydrocarbostyril (III) is obtained in 80% yield.



Ia, R = H
Ib, R = CH₃

IIa, R = H
IIb, R = CH₃

III

In no case when hydrogenation was stopped after the absorption of three molecular equivalents of hydrogen did we isolate any of the corresponding aminohydrocinnamic acid or ester.

It is possible to reduce an aqueous alkaline solution of the nitrocinnamic acids by shaking with hydrogen in the presence of Raney nickel using a procedure analogous to that Stevinson and Hamilton[11] reported for the preparation of aminoarylarsonic acids from the corresponding nitro acids. This method, however, gives smaller yields of less pure material than the procedure described in this communication.

Experimental

Materials.—The *p*-nitrocinnamic acid, methyl *p*-nitrocinnamate, methyl *m*-nitrocinnamate, and the methyl *o*-nitrocinnamate were obtained from Eastman Kodak Company and used without further purification since their melting points corresponded within 1° to those recorded in the literature. We are indebted to Mr. B. E. Ostberg for the preparation of the α-methyl-*p*-nitrocinnamic acid. The *m*-nitrocinnamic acid was obtained by condensation of *m*-nitrobenzaldehyde with malonic acid in the presence of pyridine. The *o*-nitrocinnamic acid was obtained by the alkaline hydrolysis of methyl *o*-nitrocinnamate.

General Method.—Five grams of the nitrocinnamic acid (or ester) was suspended in 50 cc. of absolute ethyl alcohol in a pressure bottle, and 2–3 g. (wet weight) of Raney nickel was added. The bottle was successively evacuated and flushed three times with hydrogen and then shaken until either the rate of hydrogen uptake had decreased at least tenfold or the calculated amount of hydrogen had been absorbed. The initial pressure was approximately 30 pounds, and the temperature varied between 20–30°. When reduction was complete, the solution was filtered free of Raney nickel, heating if necessary to dissolve any precipitated compound. The main portion of the product was obtained by the addition of sufficient cold water to cause crystallization, a further fraction being obtained by concentration of the mother liquor *in vacuo* under nitrogen. In every case the first fraction was pure as shown by melting point determinations and amounted to at least 85% of the total yield.

Summary

A method is described for the selective catalytic hydrogenation of aromatic nitro groups in preference to aliphatic double bonds conjugated with a benzenoid ring. This method has been applied to the preparation in good yields of aminocinnamic acids and esters.

CAMBRIDGE 39, MASS. RECEIVED JUNE 2, 1944

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[10] Raney, U. S. Patent 1,628,190 (1927); Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).

[11] Stevinson and Hamilton, *ibid.*, **57**, 1298 (1935).