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Formic Acid Reduction. IV.[1] Barbituric Acid Derivatives. Reduction of 5-Arylmethylenebarbituric Acids and Some Analogous Barbituric Acid Derivatives

Minoru Sekiya and Chizuko Yanaihara

Shizuoka College of Pharmacy[2]

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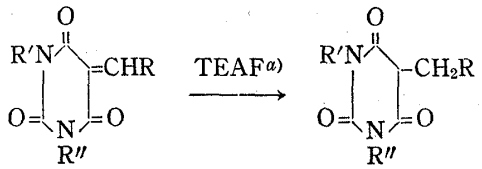
By means of heating in triethylammonium formate given by $5HCO_2H \cdot 2N(C_2H_5)_3$, hydrogenation of 5-methylidene bond attached to barbituric acids was effected in general. The method was found to be convenient for preparation of 5-arylmethylbarbituric acids and some other 5-alkylbarbituric acids with certain advantages: good yield of the products and selectivity at the double bond of 5-position.

In the preceding paper[1] we have mentioned the finding that 5-benzylidenebarbituric acid undergoes reduction with triethylammonium formate TEAF[3] to give 5-benzylbarbituric acid. The reaction takes place readily and nearly quantitatively by heating with the reagent, and the same reaction is also brought about by the use of a mixture of barbituric acid and benzaldehyde instead of 5-benzylidenebarbituric acid.

Table I.



R	R′	R″	Reaction temp., °C	Form[b] of the product	Yield, % Method A	Method B
C_6H_5	H	H	65—70	S	91[c]	89[c]
o-$NO_2C_6H_4$	H	H	85—90	S	90	
m-$NO_2C_6H_4$	H	H	60—65	S	95	
p-$NO_2C_6H_4$	H	H	60—65	S	94	89
o-$CH_3OC_6H_4$	H	H	70—75	S	89	
p-$CH_3OC_6H_4$	H	H	85—90	S	91	84
p-$(CH_3)_2NC_6H_4$	H	H	120—125	S	86	70
$C_6H_5CH_2$	H	H	95—100	S	86	
C_6H_5CH=CH	H	H	95—100	S	81	68
C_6H_5	CH_3	H	75—80	A	89	
$C_6H_5CH_2$	CH_3	H	115—120	A	83	
C_6H_5CH=CH	CH_3	H	110—115	A	86	
C_6H_5	CH_3	CH_3	70—75	A	92	
$C_6H_5CH_2$	CH_3	CH_3	115—120	A	84	
C_6H_5CH=CH	CH_3	CH_3	105—110	A	87	

a) The general procedures are given in experimental.
b) Form of the product isolated from the reaction mixture. The following abbreviations are used: S=triethylammonium salt, A=free acid.
c) These are quoted from the previously reported paper (ref. 1).

1) Part III: M. Sekiya and C. Yanaihara, *Chem. Pharm. Bull.* (Tokyo), **17**, 738 (1969).
2) Location: *Oshika, Shizuoka.*
3) Liquid, bp 95° (15 mmHg), given by $5HCO_2H \cdot 2N(C_2H_5)_3$. (K. Ito, *Yakugaku Zasshi*, **86**, 1166 (1966)).

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This reaction is evidently one involving reduction of carbon–carbon double bond, which is referred to as a new type of reaction caused by formic acid, so we were tempted to extend such a type of the reaction. The present paper deals with extension to a variety of other 5-arylmethylenebarbituric acids and some analogous barbituric acid derivatives. The substrate compounds including four new compounds are listed in Table I. On referring to the previous report,[4] all these compounds were easily obtained in good yields from barbituric acids generally by means of dropwise addition of the corresponding aldehyde to their warm solutions.

The TEAF reductions of all these compounds were successfully carried out by the general procedure (Method A) in which a mixture of the substrate and TEAF in 1/12 (as HCO_2H) molar proportion was heated at a temperature range within a limit of 5° so as to effect considerable evolution of carbon dioxide. Treatment of the reaction mixture gave, as shown in Table I, the corresponding 5-alkylbarbituric acid derivatives generally in excellent yield. With the exception of four compounds, 5-benzyl-, 5-phenethyl-, 5-benzyl-1,3-dimethyl- and 5-benzyl-1-methyl-substituted barbituric acid, these barbituric acid derivatives have not been described previously.

Using 5-benzylidenebarbituric acid, attempts to carry out the reaction with formic acid instead of TEAF[5] were unsuccessful even at higher temperature, resulting in recovery of the starting material. Therefore, TEAF seems a distinguished reagent effective for the reduction, or the triethylamine containing in the reagent appears to act as basic catalyst in the reduction.

As previously exemplified[1] in the formation of 5-benzylbarbituric acid, ease of the formation of 5-arylmethylenebarbituric acids from barbituric acids and aldehydes made it possible to effect the same formation directly by heating in TEAF a mixture of barbituric acid and aldehyde. This modified method (method B) was performed with some representative substrates as shown in Table I.

As can be seen from the reductions of nitro-substituted 5-benzylidene- and 5-cinnamylidene-barbituric acids in Table I, the attacking position was shown to be limited at the double bonds of the 5-positions, their nitro groups and the double bonds adjacent to their phenyls did not suffer the reduction. The retention of the nitro group in the products was confirmed by the elemental analyses and on the basis of the infrared spectra, where absorption maxima for NO_2 appeared at 1528—1535 cm^{-1} and 1350—1360 cm^{-1}.

With a representative product, 5-cinnamylbarbituric acid, its cinnamyl group was clearly confirmed as in the following. Hydrogenation of the product with palladium–on–charcoal catalyst under ordinary pressure gave γ-phenylpropylbarbituric acid after uptake of one mole equivalent of hydrogen, this product, unknown previously, was identified with an authentic specimen, which was obtained from the 5-cinnamylidenebarbituric acid by hydrogenation procedure using palladium–on–charcoal catalyst, in which uptake of two mole equivalent of hydrogen was observed. The assignment of the cinnamyl group in the structure was substantiated by nuclear magnetic resonance (NMR) spectrum, which showed methylene protons at τ 6.87 (triplet), methylidyne proton of barbituric acid nucleus at τ 6.11 (triplet), and vinylene protons at τ 3.42 (doublet) and at τ 3.55—4.16 (multiplet). Also an infrared spectrum of the product gave a band at 961 cm^{-1} suggesting *trans* relationship of the double bond, and an ultraviolet spectrum of that gave the absorbance at 256 mμ which was distinguished from that at 320 mμ shown by 5-phenethylidenebarbituric acid. As for the other analogous 5-cinnamyl products their infrared and ultraviolet spectra were also in accord with the above observations.

4) *Organic Syntheses*, **21**, 5 (1941).
5) TEAF was used as a handy reagent, as formates composed of other aliphatic tertiary amines appear also effective for the reduction.

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In summary, the TEAF reduction of 5-methylidyne bond attached to barbituric acid analog is a convenient, general method for the preparation of 5-arylmethyl or some 5-alkyl substituted barbituric acids. Advantages of the method are high yield of the product and selectivity at 5-methylidyne bond, which are otherwise not easely accessible.

Experimental

Preparation of 5-Arylmethylenebarbituric Acids and Some Analogous Compounds——Among the fourteen compounds shown in Table I, 5-(*p*-nitrobenzylidene)-, 5-(*o*-methoxybenzylidene)-, 5-phenethylidene-, 1-methyl-5-phenethylidene- and 1,3-dimethyl-5-phenethylidene-barbituric acid have not been described previously. On referring to the previous paper[4] all these unknown and known compounds were prepared from barbituric acid analogs and aldehydes by the following general procedure. A solution of 0.05 mole each of barbituric acids (70 ml of H_2O for barbituric acid and of 50% aqueous ethanol for N-methyl and N,N'-dimethylbarbituric acid was used for solution) was heated on a boiling water bath with vigorous stirring and to the solution a solution of 0.06 mole each of the aldehydes dissolved in 20 ml of ethanol was added dropwise, whereupon the product immediately precipitated. After the addition, the heating and the stirring were continued for further 1.5 hr. On cool, the precipitate was collected by filtration, washed with H_2O, then with ethanol and dried. Usually, the material obtained was shown to be nearly pure by noting the exact correspondence of the infrared spectrum and the melting point with those of another specimen which was purified by recrystallization. The materials thus prepared are 5-*o*-nitrobenzylidene-[mp 250—251° (decomp.), lit.,[6] mp 250—252° (decomp.)], 5-*m*-nitrobenzylidene-[mp 253—255° (decomp.), lit.,[7] mp 254—255° (decomp.)], 5-*p*-methoxybenzylidene- (mp 277—279°, lit.,[8] mp 279—280°), 1-methyl-5-benzylidene- (mp 216—218°, lit.,[9] mp 218°), 1,3-dimethyl-5-benzylidene- (mp 159—160°, lit.,[10] mp 159—159.5°) and 1,3-dimethyl-5-cinnamylidene-substituted barbituric acid (mp 197—200°, lit.,[10] mp 196—197°), and the compounds, described in the following, which have not been known previously or the melting points of which are different from those reported.

5-(*p*-Nitrobenzylidene)barbituric Acid——Yield, 84%. Pale yellow needles (from AcOH), mp 287—288° (decomp.). UV λ_{max}^{MeOH} mμ: 264, 310. *Anal.* Calcd. for $C_{11}H_7O_5N_3$: C, 50.58; H, 2.70; N, 16.09. Found: C, 50.58; H, 2.79; N, 16.00.

5-(*o*-Methoxybenzylidene)barbituric Acid——Yield, 90%. Yellow needles (from AcOH), mp 264—266°. UV λ_{max}^{MeOH} mμ: 245 (shoulder), 320 (shoulder), 378. *Anal.* Calcd. for $C_{12}H_{10}O_4N_2$: C, 58.53; H, 4.09; N, 11.38. Found: C, 58.52; H, 4.11; N, 11.17.

5-Phenethylidenebarbituric Acid——Yield, 88%. Pale yellow needles (from AcOH), mp 210—212°. UV λ_{max}^{MeOH} mμ: 320. *Anal.* Calcd. for $C_{12}H_{10}O_3N_2$: C, 62.60; H, 4.38; N, 12.17. Found: C, 62.15; H, 4.63; N, 11.89.

1-Methyl-5-phenethylidenebarbituric Acid——Yield, 91%. Colorless prisms (from acetone), mp 201—203°. UV λ_{max}^{MeOH} mμ: 260, 320 (shoulder). *Anal.* Calcd. for $C_{13}H_{12}O_3N_2$: C, 63.92; H, 4.95; N, 11.47. Found: C, 63.59; H, 5.14; N, 11.00.

1,3-Dimethyl-5-phenethylidenebarbituric Acid——Yield, 86%. Colorless prisms (from acetone), mp 193—195°. UV λ_{max}^{MeOH} mμ: 234 (shoulder), 336. *Anal.* Calcd. for $C_{14}H_{14}O_3N_2$: C, 65.10; H, 5.46;N, 10.85. Found: C, 64.97; H, 5.82; N, 10.49.

1-Methyl-5-cinnamylidenebarbituric Acid——Yield, 94%. Orange plates (from acetone), mp 257—259°. This compound was previously reported as a material of mp 245—248°. UV λ_{max}^{MeOH} mμ: 250, 370. *Anal.* Calcd. for $C_{14}H_{12}O_3N_2$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.89; H, 4.78; N, 10.74.

5-*p*-Dimethylaminobenzylidenebarbituric Acid——Yield, 90%. Red needles (from AcOH), mp 275—277° (decomp.), lit.,[11] mp 262—263°. UV λ_{max}^{MeOH} mμ: 247, 270 (shoulder), 463. *Anal.* Calcd. for $C_{13}H_{13}O_3N_3$: C, 60.22; H, 5.05; N, 16.21. Found: C, 59.98; H, 5.15; N, 16.23.

5-Cinnamylidenebarbituric Acid——Yield, 97%. Yellow needles (from ethanol), mp 260—262° (decomp.), lit.,[6] mp 226—228°. UV λ_{max}^{MeOH} mμ: 244 (shoulder), 250, 373. *Anal.* Calcd. for $C_{13}H_{10}O_3N_2$: C, 64.46; H, 4.16; N, 11.57. Found: C, 64.74; H, 4.23; N, 11.82.

Reduction with TEAF

General Procedure (Method A)——To 25.9 g (0.3 mole as HCO_2H) of TEAF 0.025 mole each of the prepared 5-arylmethylenebarbituric acid or the analogous compounds was added. The mixture was heated with constant stirring and a constant stream of air free from CO_2 was passed in order to check

6) M. Radi and P. Papini, *Gazz. Chim. Ital.*, **76**, 369 (1946); *C.A.*, **42**, 1284 (1948).
7) H. Zenno, *Yakugaku Zasshi*, **74**, 199 (1954).
8) R. Wizinger and P. Kolliker, *Helv. Chim. Acta*, **38**, 372 (1955).
9) T. Ukita, K. Kato, M. Hori, and H. Nishikawa, *Chem. Pharm. Bull.* (Tokyo), **8**, 1021 (1960).
10) S. Akahori, *Nippon Kagaku Zasshi*, **52**, 601 (1931).
11) R.E. Heckert, U.S. Patent 2803640 (1957) [*C.A.*, **52**, 3353 (1958)].

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transfer of evolving CO_2 by $Ba(OH)_2$ solution. The temperature was raised so as to effect considerable evolution of CO_2 which was roughly determined by checking $Ba(OH)_2$ solution. The temperature was kept within a limit of about 5°. Until ceasing of CO_2 evolution, it took about 20 min and the heating and the stirring were continued for further 10 min. In most cases, the major part of reduction product was deposited as its triethylammonium salt in the reaction mixture and on cool was collected by filtration and followed by washing with acetone. Further crystals were also obtained by concentration of the filtrate of the reaction mixture. Free acid was liberated from the salt product by treatment with aqueous HCl. In contrast to the above, in the cases forming the products of 1-methyl- and 1,3-dimethylbarbituric acid derivatives, the reaction gave clear reaction solution and by concentration of the solution the product was obtained as free acid.

Improved Procedure (Method B)——Formation of the same reduction products as obtained in the above was directly effected by using barbituric acids and aldehydes instead of the 5-substituted barbituric acids. When a mixture of 0.025 mole of barbituric acid, 0.05 mole of aldehyde and 25.9 g (0.3 mole as HCO_2H) of TEAF was heated, the reaction took place in the same way as in Method A and processed by the same procedures to give the corresponding 5-arylmethylbarbituric acid analog.

Assignment and Identification of the Reduction Products——Assignment and identification of the products, triethylammonium salts and free acid, obtained by the TEAF reduction are indicated in the following.

5-(*o*-Nitrobenzyl)barbituric Acid——Triethylammonium Salt: Yellow needles (from ethanol–H_2O), mp 209—210° (decomp.). UV λ_{max}^{MeOH} mμ: 265. IR ν_{max}^{KBr} cm^{-1}: 1530, 1350 (NO_2). *Anal.* Calcd. for $C_{17}H_{24}O_5N_4$: C, 56.03; H, 6.64; N, 15.38. Found: C, 55.77; H, 6.59; N, 15.47. Free acid: Colorless needles (from ethanol), mp 204—205° (decomp.). *Anal.* Calcd. for $C_{11}H_9O_5N_3$: C, 50.19; H, 3.45; N, 15.97. Found: C, 50.32; H, 3.69; N, 15.80.

5-(*m*-Nitrobenzyl)barbituric Acid——Triethylammonium Salt: Yellow prisms (from ethanol–H_2O), mp 222—223° (decomp.). UV λ_{max}^{MeOH} mμ: 265. IR ν_{max}^{KBr} cm^{-1}: 1535, 1358 (NO_2). *Anal.* Calcd. for $C_{17}H_{24}O_5N_4$: C, 56.03; H, 6.64; N, 15.38. Found: C, 55.85; H, 6.83; N, 15.43. Free acid: Colorless needles (from ethanol), mp 205—206°. *Anal.* Calcd. for $C_{11}H_9O_5N_3$: C, 50.19; H, 3.45; N, 15.97. Found: C, 49.82; H, 3.63; N, 16.00

5-(*p*-Nitrobenzyl)barbituric Acid——Triethylammonium Salt: Yellow needles (from H_2O), mp 231—232° (decomp.). UV λ_{max}^{MeOH} mμ: 266. IR ν_{max}^{KBr} cm^{-1}: 1528, 1360 (NO_2). *Anal.* Calcd. for $C_{17}H_{24}O_5N_4$: C, 56.03; H, 6.64; N, 15.38. Found: C, 55.64; H, 6.66; N, 15.64. Free acid: Colorless needles (from ethanol), mp 257—258° (decomp.). *Anal.* Calcd. for $C_{11}H_9O_5N_3$: C, 50.19; H, 3.45; N, 15.97. Found: C, 50.19; H, 3.57; N, 16.06.

5-(*o*-Methoxybenzyl)barbituric Acid——Triethylammonium Salt: Colorless needles (from ethanol–H_2O), mp 227—229° (decomp.). UV λ_{max}^{MeOH} mμ: 224, 268. *Anal.* Calcd. for $C_{18}H_{24}O_4N_3$: C, 61.87; H, 7.79; N, 12.03. Found: C, 61.37; H, 8.00; N, 11.96. Free acid. Colorless needles (from ethanol), mp 210—212°. *Anal.* Calcd. for $C_{12}H_{12}O_4N_2$: C, 58.06; H, 4.87; N, 11.29. Found: C, 57.79; H, 4.98; N, 11.31.

5-(*p*-Methoxybenzyl)barbituric Acid——Triethylammonium Salt: Pale yellow needles (from ethanol–H_2O), mp 211—213° (decomp.). UV λ_{max}^{MeOH} mμ: 226, 268. *Anal.* Calcd. for $C_{18}H_{27}O_4N_3$: C, 61.87; H, 7.79; N, 12.03. Found: C, 61.62; H, 7.84; N, 12.19. Free acid: Colorless needles (from ethanol), mp 198—200°. *Anal.* Calcd. for $C_{12}H_{12}O_4N_2$: C, 58.06; H, 4.87; N, 11.29. Found: C, 57.56; H, 4.87; N, 11.34.

5-(*p*-Dimethylaminobenzyl)barbituric Acid——Triethylammonium Salt: Rosy prisms (from ethanol–H_2O), mp 196—198° (decomp.). UV λ_{max}^{MeOH} mμ: 265, 300 (shoulder). *Anal.* Calcd. for $C_{19}H_{30}O_3N_4$: C, 62.96; H, 8.34; N, 15.46. Found: C, 62.61; H, 8.26; N, 15.62. Free acid: Rosy needles (from ethanol), mp 201—202° (decomp.). *Anal.* Calcd. for $C_{13}H_{15}O_3N_3$: C, 59.76; H, 5.76; N, 16.08. Found: C, 59.40; H, 6.04; N, 15.59.

5-Phenethylbarbituric Acid——Triethylammonium Salt: Colorless plates (from ethanol), mp 194—196° (decomp.). UV λ_{max}^{EtOH} mμ: 264. *Anal.* Calcd. for $C_{18}H_{27}O_3N_3$: C, 64.84, H, 8.16; N, 16.60. Found: C, 64.34; H, 8.34; N, 12.48. Free acid: Colorless needles (from ethanol), mp 211—213°, lit.,[12] mp 212—213°. *Anal.* Calcd. for $C_{12}H_{12}O_3N_2$: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.34; H, 5.34; N, 12.33.

5-Cinnamylbarbituric Acid——Triethylammonium Salt: Pale yellow prisms (from ethanol), mp 178—179° (decomp.). UV λ_{max}^{EtOH} mμ: 256. *Anal.* Calcd. for $C_{19}H_{27}O_3N_3$: C, 66.06; H, 7.88; N, 12.17. Found: C, 65.58; H, 7.95; N, 12.30. Free acid: Pale yellow needles (from ethanol), mp 215—217°. UV λ_{max}^{EtOH} mμ: 256. IR ν_{max}^{KBr} cm^{-1}: 961 (trans $-CH=CH-$). NMR (in CF_3COOH): doublet (1H) at 3.42 τ ($C_6H_5C\underline{H}=CH-$), multiplet (1H) at 3.55—4.16 τ ($-CH=C\underline{H}-CH_2-$), triplet (1H) at 6.11 τ ($-COC\underline{H}-CO-$), triplet (2H) at 6.87 τ ($=CH-C\underline{H}_2-CH\langle$). *Anal.* Calcd. for $C_{13}H_{12}O_3N_2$: C, 63.92; H, 4.95; N, 11.47. Found: C, 63.89; H, 4.99; N, 11.95.

5-Benzyl-1,3-dimethylbarbituric Acid——Colorless prisms (from acetone), mp 115—117°, lit.,[13] mp 116.5—117.5°. UV λ_{max}^{MeOH} mμ: 268. *Anal.* Calcd. for $C_{13}H_{14}O_3N_2$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.00; H, 6.01; N, 11.44.

12) A.W. Dox, *J. Am. Chem. Soc.*, **46**, 2843 (1924).
13) A.C. Cope, D. Heyl, D. Peck, C. Eide, and A. Arroyo, *J. Am. Chem. Soc.*, **63**, 356 (1941).

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5-Penethyl-1,3-dimethylbarbituric Acid——Colorless plates (from acetone–H_2O), mp 96—97°. UV λ_{max}^{MeOH} mμ: 270. *Anal.* Calcd. for $C_{14}H_{16}O_3N_2$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.39; H, 6.12; N, 10.96.

5-Cinnamyl-1,3-dimethylbarbituric Acid——Colorless needles (from ethanol), mp 230–231°. UV λ_{max}^{MeOH} mμ: 261. IR ν_{max}^{KBr} cm^{-1}: 963 (trans -CH=CH-). *Anal.* Calcd. for $C_{15}H_{16}O_3N_2$: C, 66.16; H, 5.92; N, 10.29. Found: C, 66.08; H, 5.85; N, 10.45.

5-Benzyl-1-methylbarbituric Acid——Colorless needles (from acetone–H_2O), mp 123—125°, lit.,[14] mp 123—125°. UV λ_{max}^{MeOH} mμ: 266. *Anal.* Calcd. for $C_{12}H_{12}O_3N_2$: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.33; H, 5.64; N, 12.31.

5-Phenethyl-1-methylbarbituric Acid——Colorless needles (from ethanol), mp 101—102°. UV λ_{max}^{MeOH} mμ: 269. *Anal.* Calcd. for $C_{13}H_{14}O_3N_2$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.36; H, 5.76; N, 11.20.

5-Cinnamyl-1-methylbarbituric Acid——Colorless needles (from ethanol), mp 212—214° (decomp.). UV λ_{max}^{MeOH} mμ: 265. IR ν_{max}^{KBr} cm^{-1}: 962 (-CH=CH-). *Anal.* Calcd. for $C_{14}H_{14}O_3N_2$: C, 65.10; H, 5.46; N, 10.85. Found: C, 64.72; H, 5.60; N, 10.75.

Preparation of 5-(γ-Phenylpropyl)barbituric Acid——a) A solution of 3.5 g of triethylammonium 5-cinnamylbarbiturate dissolved in 70 ml of H_2O was mixed with palladium–on–charcoal freshly prepared from 0.04 g of $PdCl_2$ and 0.4 g of charcoal and hydrogenated under ordinary pressure at ordinary temperature by usual method. Absorption was nearly ceased after uptake of one mole equiv. of hydrogen in about 30 min. After removal of catalyst by filtration, the filtrate was acidified with aqueous HCl. The resulting precipitate was collected by filtration, washed with H_2O and dried. Yield, 2.4 g (91%). Recrystallization from ethanol-H_2O gave colorless fine plates, mp 185—187°. UV λ_{max}^{EtOH} mμ: 264. *Anal.* Calcd. for $C_{13}H_{14}O_3N_2$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.18; H, 5.74; N, 11.53.

b) A suspension of 0.6 g of 5-cinnamylidenebarbituric acid in 150 ml of ethanol was catalytically hydrogenated over palladium–on–charcoal catalyst fleshly prepared from 0.01 g of $PdCl_2$ and 0.1 g of charcoal by the same manner as in a). Absorption was nearly ceased after uptake of 2 mole equiv. of hydrogen in about 100 min. After removal of catalyst by filtration, concentration of the filtrate gave crystals, which were collected by filtration and washed with H_2O. Yield, 0.05 g. (89%). Recrystallization from ethanol-H_2O gave fine plates, mp 185—186°; undepressed by admixture with the specimen obtained in a).

Acknowledgement The authors are indebted to the Members of the Central Analysis Room of this college for elementary analyses.

14) H. Aspelund, *C.A.*, 31, 6632 (1937).

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