product by rapid distillation at low pressure. When all products boiling below 104° at 8 mm. had been collected, the high-boiling residue was fractionated at 33 mm. through a 100-plate Podbielniak HeliGrid column. The results obtained are given in Fig. 1.

Analysis of the distillation curve (Fig. 1) indicates the following products: fractions (3) and (4), *t*-butylbenzene (88 g. = 0.66 mole), $n^{20}D$ 1.4968, b. p. 74.8° (35 mm.); fractions (8) and (9), isobutylbenzene (45 g. = 0.34 mole), $n^{20}D$ 1.4880, b. p. 77.5° (33 mm.); fraction (11), 2-methyl-3-phenylpropene-1 (27 g. = 0.204 mole), $n^{20}D$ 1.5080, b. p. 78.5–79.5° (33 mm.); fraction (14), β,β-dimethylstyrene (8 g. = 0.065 mole), $n^{20}D$ 1.5367, b. p. 92–93° (33 mm.); fraction (16) to (19), recovered neophyl chloride (56 g. = 0.33 mole), $n^{20}D$ 1.5250, b. p. 119.4° (33 mm.).

The high-boiling residue was steam distilled to remove the biphenyl (223 g., 1.45 mole, m. p. 69–70°). The residual oil (130 g.) was subjected to molecular distillation. The analysis and molecular weight (262) of the distillate indicate that this material consists of dimers (calcd. mol. wt. 266) of two neophyl radicals; it is not a single substance, but a mixture. From this mixture one solid dimer (m. p. 128–129°) was isolated. The residual oil could not be crystallized.

Identification of the Reaction Products.—The *t*-butylbenzene was identified by the melting point (169–170°, uncor.) of its *p*-acetamido derivative.[7] The melting point of a mixture with an authentic sample of *p*-acetamido-*t*-butylbenzene showed no depression.

The structures of 2-methyl-2-phenylpropene-1 and of β,β-dimethylstyrene have recently been proven by ozonolysis.[4] The physical constants of the 2-methyl-3-phenylpropene-1 (Fraction 11) here obtained are identical with those found by Whitmore. The refractive index here observed for β,β-dimethylstyrene (fraction 14) is a little lower than his figure; but this fraction is small and probably slightly impure. As corroborative evidence for the identity of these compounds, their molecular weights were determined by bromide–bromate titration[8]: 2-methyl-3-phenylpropene-1: calcd. mol. wt., 132; found, 127. β,β-Dimethylstyrene: calcd. mol. wt., 132; found, 131. The absorption spectra of these two substances and that of *t*-butylbenzene (Fig. 2) were determined on a Beckman photoelectric quartz spectrophotometer. Isooctane was used as solvent. The spectrum of β,β-dimethylstyrene is similar to that of styrene, with an absorption maximum at 2450 Å. On the other hand, Fraction (3) has an absorption spectrum corresponding closely to that of *t*-butylbenzene, as would be expected if the fraction is 2-methyl-3-phenylpropene-1.

To prove the identity of the carbon skeleton in the compounds composing fractions (9), (11), and (14), the latter two fractions were hydrogenated at 2000 pounds pressure and at 80°; ether was used as the solvent and Raney nickel as the catalyst. The two hydrogenation products and the isobutylbenzene (fraction 9) were converted to the *p*-acetamido derivatives. The melting points are listed in Table I.

TABLE I

MELTING POINTS (UNCOR.) OF SOME *p*-ACETAMIDO DERIVATIVES OF BENZENE

	Hydrocarbon	M. p. of *p*-acetamido derivative, °C.	M. p. of *p*-acetamido isobutylbenzene, °C.	M. p. of mixture, °C.
1	Fraction 9	129–130	129–130	129–130
2	Fraction 11 (hydrogenated)	129–130	129–130	129–130
3	Fraction 14	129–130	129–130	129–130
4	*s*-Butylbenzene	123–124	129–130	110–112

These results are compatible with the previous assumption that fraction (9) is isobutylbenzene; fraction (11) is 2-methyl-3-phenylpropene-1; fraction (14) is β,β-dimethylstyrene.

Summary

1. Neophyl chloride does not react with pure phenylmagnesium bromide, but, in the presence of cobaltous chloride, it reacts vigorously to give *t*-butylbenzene, isobutylbenzene, 2-methyl-3-phenylpropene-1, β,β-dimethylstyrene, a mixture of dimers and biphenyl.

2. A free-radical mechanism, involving rearrangement of the neophyl free radical to the β,β-dimethylphenethyl free radical is shown to be consistent with the products isolated.

CHICAGO, ILLINOIS RECEIVED APRIL 7, 1944

(7) Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937).

(8) "Scott's Standard Methods of Chemical Analysis," Vol. II, p. 2253. Van Nostrand and Company, New York, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Identification of Some Barbiturates

BY RAYMOND N. CASTLE AND CHARLES F. POE

The investigation reported in this communication was undertaken with the object of studying the possibilities of differentiating among some of the more recent barbituric acid derivatives placed on the market.

The numerous color tests[1,2,3,4,5] for barbiturates reported in the literature are usually not sufficiently specific. It was therefore decided to seek a more reliable identification among derivatives prepared by use of certain reagents. A search of the literature revealed that substituted benzyl halides have already proved their worth in such identifications.[6,7,8,9,10] We have, therefore undertaken the preparation and study of the substituted benzyl derivatives of four new barbituric acids[11] recently introduced into medicine, namely,

(1) Zwikker, *Pharm. Weekblad*, **68**, 975 (1931).

(2) Koppanyi, Dille, Murphy and Krop, *J. Am. Pharm. Assoc.*, **23**, 1074 (1934).

(3) Dille and Koppanyi, *ibid.*, **23**, 1079 (1934).

(4) Pesez, *J. pharm. chim.*, **25**, 508 (1937).

(5) Pesez, *ibid.*, **28**, 379 (1938).

(6) Lyons and Dox, THIS JOURNAL, **51**, 288 (1929).

(7) Hargreaves and Nixon, *J. Am. Pharm. Assoc.*, **22**, 1250 (1933).

(8) Hultquist and Poe, *Ind. Eng. Chem., Anal. Ed.*, **7**, 398 (1935).

(9) Jespersen and Larsen, *Arch. Pharm.*, **275**, 28 (1937).

(10) Hultquist, Poe and Witt, *Ind. Eng. Chem., Anal. Ed.*, **14**, 219 (1942).

(11) The authors wish to express appreciation to Eli Lilly and Company, Riedel de Haen, Inc., Sharpe and Dohme, and the Upjohn Company for furnishing, respectively, the samples of seconal, sigmodal, delvinal, and cyclopal.

cyclopal (5-cyclopentenyl-5-allyl-barbituric acid); delvinal (5-ethyl-5-(1-methyl-1-butenyl)-barbituric acid); seconal (5-allyl-5-α-methylpropylcarbinylbarbituric); and sigmodal (5-*s*-amyl-5-β-bromallyl-barbituric acid), as listed in Table I.

TABLE I

SUBSTITUTED BENZYL DERIVATIVES OF CYCLOPAL, DELVINAL, SECONAL AND SIGMODAL

Derivatives	Melting point cor., °C. Block	Tube	Analyses, % halogen or nitrogen Calcd.	Found
p-Chlorobenzyl				
cyclopal	110.5	122[a]	14.67	14.59
delvinal	71	72.5	14.97	14.85
seconal	102	103	14.55	14.63
sigmodal	91	92	26.63	26.72
o-Chlorobenzyl				
cyclopal	101.5	103	14.67	14.73
delvinal	101.5	103	14.97	14.80
sigmodal	103	105	26.63	26.80
p-Bromobenzyl				
cyclopal	116	119	27.93	27.84
delvinal	75.5	77	28.41	28.64
seconal	110	111.5	27.73	27.84
sigmodal	92	95	36.59	36.45
o-Bromobenzyl				
cyclopal	108.5	110	27.93	27.91
delvinal	100.5	102	28.41	28.27
seconal	94	98	27.73	27.70
sigmodal	108	115	36.59	36.59
p-Nitrobenzyl				
cyclopal	181.5 dec.	185 dec.	11.11	11.00
delvinal	131.5	132.5	11.33	11.21
seconal	158	163	11.02	10.79
sigmodal	172	178	9.54	9.34

[a] Shrinks from the tube but does not melt at 110.5°. Melts sharply at 122°.

Preparation.—These new derivatives were prepared by the general method[12,13] for the preparation of *p*-nitrobenzyl esters of an acid. The following procedure is typical of the procedure used.

***p*-Nitrobenzyl-delvinal.**—0.04 mole of sodium carbonate and 0.02 mole of delvinal are dissolved in just sufficient boiling water to dissolve the barbituric acid and the alkali. To this solution is added 0.04 mole of *p*-nitrobenzyl bromide dissolved in ethyl alcohol. The volume of alcohol used is twice as great as the volume of water so that a 65% alcohol mixture is obtained. The mixture is then refluxed for about one-half hour.[14] After ten minutes crystals begin to separate.[15] The product is filtered and washed well with water to remove any unreacted barbituric acid salts, alkali carbonate, alkali halide, or any mono-substituted benzyl derivative that may be formed. After three recrystallizations from chloroform the product crystallizes as thick, pale yellow prisms; m. p. 132.5°.

Anal. Calcd. for $C_{25}H_{26}N_4O_7$: N, 11.33. Found: N, 11.22, 11.20.

Halogen was determined by the sodium–absolute alcohol method recommended by Kamm.[16] Nitrogen was determined by a modified Kjeldahl procedure. Margosches and Kristen[17] dissolve the sample in alcohol and reduce the nitro group with zinc and hydrochloric acid, prior to the usual digestion. In our hands this method yielded consistently low results. However, using the Elek and Sobotka[18] modification, in which dextrose is added to the digestion mixture after the zinc–hydrochloric acid reduction, good results were obtained.

The melting points were taken on the block Maquenne apparatus as well as in the usual capillary tubing immersed in a mechanically stirred bath. The rate of heating was 0.5° per minute. The melting point taken was that temperature at which the last crystal disappeared. The melting points are corrected. Each analysis is an average of two or more determinations.

Table I lists the melting points and analyses. Table II gives the melting points listed in Table I, together with the melting points of similarly substituted benzyl derivatives of other barbiturates listed in the literature.

Discussion

From Table I it becomes evident that the *o*-bromobenzyl and the *o*-chlorobenzyl derivatives would not be satisfactory for the characterization of the barbituric acids here studied, since those which crystallized melted within a rather narrow range. The *o*-chlorobenzyl seconal derivative could not be induced to crystallize.

From Table II it is seen that the *p*-nitrobenzyl derivatives have melting points far enough apart to make them valuable as a means of identification.

Due to the fact that there is some duplication of melting points it seems advisable to make two or even three derivatives of the unknown compound. Because of the ease of preparation and purification of the resulting derivatives, the *p*-nitrobenzyl bromide is the reagent of choice.

Summary

1. The *o*-bromobenzyl, the *o*-chlorobenzyl, the *p*-bromobenzyl, the *p*-chlorobenzyl and the *p*-nitrobenzyl derivatives of cyclopal, delvinal,

(12) Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1932, p. 179.

(13) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., second edition, 1940, p. 132.

(14) The *p*-chlorobenzyl- and the *p*-bromobenzyl- derivatives are refluxed about one and one-half hours. The *o*-chlorobenzyl- and the *o*-bromobenzyl- derivatives are refluxed about three hours.

(15) In some instances the *o*-chlorobenzyl- and the *o*-bromobenzyl- derivatives separate as oils which crystallize only on standing in the refrigerator.

(16) Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1932, p. 199.

(17) Margosches and Kristen, *Z. ges. Schiess-Sprengstoffen*, **18**, 39 (1923); see *C. A.*, **17**, 3656 (1923).

(18) Elek and Sobotka, THIS JOURNAL, **48**, 501 (1926).

TABLE II

MELTING POINTS OF SUBSTITUTED BENZYL DERIVATIVES OF BARBITURATES

Barbiturate[c]	Melting point, °C., derivatives: *p*-Nitrobenzyl Block	*p*-Nitrobenzyl Tube	*p*-Chlorobenzyl Block	*p*-Chlorobenzyl Tube	*p*-Bromobenzyl Block	*p*-Bromobenzyl 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-*

(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 Sher, 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.