reduced pressure on a hot water bath, and the residue was taken up in 300 ml. of ether. The ether solution was washed with 150 ml. of saturated sodium bicarbonate solution, treated with decolorizing charcoal, and dried over anhydrous magnesium sulfate. The ether was evaporated under reduced pressure to leave 14.0 g. (76%) of ethyl 5-cyano-2-oximino-valerate, m.p. 73°.

(d) *From 2,6-diacetoximinocyclohexanone and n-butylamine in ethanol.* With vigorous stirring 14.6 g. (0.20 mole) of *n*-butylamine was added to a slurry of 24.0 g. (0.10 mole) of 2,6-diacetoximinocyclohexanone in 200 ml. of absolute ethanol. The temperature rose rapidly from 25 to 55° during the addition of the first few ml. of the amine, then dropped off slowly as the rest was added. After addition was complete, the resulting clear solution was evaporated under reduced pressure on a hot water bath. The residue was taken up in 500 ml. of ether, and the ether solution was washed with dilute hydrochloric acid and saturated sodium bicarbonate solution. It was then treated with decolorizing charcoal and dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure left 14.5 g. (79%) of ethyl 5-cyano-2-oximinovalerate, m.p. 70°. The infrared spectrum of this material showed that it contained a trace of amide.

Methyl 2-acetoximino-5-cyanovalerate. A mixture of 800 ml. of dry benzene, 120 g. (0.5 mole) of 2,6-diacetoximinocyclo-hexanone, and 27 g. (0.5 mole) of sodium methoxide was stirred vigorously. In 1 hr. the temperature rose from 27 to 65°. The mixture was cooled to 45°, and the temperature rose in 15 min. to 51°. The mixture was cooled to 40°, and no further increase in temperature occurred. A test with *p*H paper showed that the mixture was neutral, and it was cooled to room temperature and filtered. After drying the filter cake weighed 40 g. (theory for sodium acetate, 41 g.). The benzene was evaporated at reduced pressure at 50°, and the residue was held under vacuum for 24 hr. to insure removal of all volatile material. There remained 66 g. (62%) of methyl 2-acetoximino-5-cyanovalerate, a brown oil. After standing for several days the oil partially crystallized. The mixture of liquid and solid was recrystallized from a mixture of equal volumes of ethyl acetate and cyclohexane to give 33 g. (31%) of white crystalline methyl 2-acetoximino-5-

cyanovalerate, m.p. 48°. The infrared spectrum of this solid was essentially identical to that of the oil.

Anal. Calcd. for $C_9H_{12}O_4N_2$: C, 50.94; H, 5.70; N, 13.20. Found: C, 50.80; H, 5.73; N, 13.50.

Action of sodium acetate in ethanol on 2,6-diacetoximino-cyclohexanone. With vigorous stirring 5.0 g. (0.0610 mole) of anhydrous sodium acetate was added to a slurry of 10.0 g. (0.0416 mole) of 2,6-diacetoximinocyclohexanone in 30 ml. of absolute ethanol. The temperature rose rapidly to 80°, then dropped slowly. After standing an hour the mixture was heated to 60° under reduced pressure to evaporate the ethanol. The residue was taken up in 100 ml. of ether, and the solid which failed to dissolve was removed by filtration. The filtrate was washed with saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The ether was evaporated under reduced pressure to leave 7.8 g. of white solid, m.p. 50–56°. Comparison of the infrared spectrum of this material with those of ethyl 5-cyano-2-oximinovalerate and methyl 2-acetoximino-5-cyanovalerate indicated that this material was composed of about equal amounts of ethyl 5-cyano-2-oximinovalerate (theory, 7.7 g.) and ethyl 2-acetoximino-2-cyanovalerate (theory, 9.4 g.).

Isopropyl 5-cyano-2-oximinovalerate from 2,6-diacetox-iminocyclohexanone and n-butylamine in isopropanol. The procedure described for the analogous reaction in ethanol was followed using an equal volume of isopropanol. There was obtained 16.5 g. (83%) of isopropyl 5-cyano-2-oximino-valerate, a brownish oil. After standing several days the oil crystallized. A portion of the solid was recrystallized from a 5:1 cyclohexane–ethyl acetate mixture to give white crystals of isopropyl 5-cyano-2-oximinovalerate, m.p. 55–56°.

Anal. Calcd. for $C_9H_{14}O_3N_2$: C, 54.53; H, 7.12; N, 14.14. Found: C, 54.43; H, 7.24; N, 14.09.

The Five Monocarboxylic Acids of Phenanthrene[1,2]

JOSEPH A. DIXON AND D. D. NEISWENDER, JR.[3]

The syntheses, melting points, ultraviolet and infrared spectra of the five monocarboxylic acids of phenanthrene are reported.

During a study of the synthesis and properties of alkylphenanthrenes it was found that many of the best synthetic routes to these hydrocarbons involve substitution reactions on phenanthrene or a partially hydrogenated phenanthrene. Such reactions frequently produce mixtures of isomers and it is necessary for identification to convert the substitution products to known structures. The monocarboxylic acids of phenanthrenes are a logical set of reference structures, as many functional groups can be converted readily to the carboxylic acid group.

Although syntheses and melting points of the five isomeric phenanthrene monocarboxylic acids have been reported,[4–18] examination of the literature

(1) Taken in part from the dissertation submitted by D. D. Neiswender in partial fulfillment of the requirements for the Ph.D. degree at The Pennsylvania State University.

(2) Presented in part before the Division of Organic Chemistry at the 133rd National Meeting of the American Chemical Society, San Francisco, California, April, 1958.

(3) American Petroleum Institute Fellow, 1955–1957. Present address: Research and Development Laboratories, Socony Mobil Oil Co., Inc. Paulsboro, New Jersey.

(4) L. F. Fieser, *J. Am. Chem. Soc.* **54**, 4110 (1932).

(5) J. R. Dice and P. A. Smith, *J. Org. Chem.* **14**, 179 (1949).

reveals the following: The structural assignments of the 2- and 3- acids depend on the validity of the separation and identification of the mixture of acids obtained upon sulfonation of phenanthrene by Werner in 1902;[19] the reported melting points of a given monocarboxylic acid may differ as much as 11°; the 2- and 3- and 9- acids all melt in the range 250° to 270°; and the infrared and ultraviolet spectra have not been reported.

Because of this, the acids have been synthesized by unambiguous routes and their melting points, and infrared and ultraviolet spectra determined.

Each of the acids was purified by fractional distillation of the methyl ester, crystallization of the fractions, saponification of the purified ester, and crystallization of the acid.
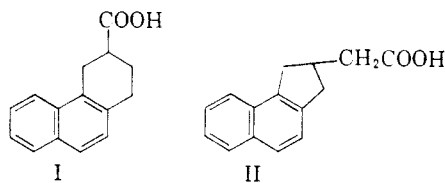
Phenanthrene-1-carboxylic acid[4–7] and phenanthrene-4-carboxylic acid[10–12] were prepared from 4-(α-naphthyl)butanoic acid and 4-(β-naphthyl)-butanoic acid respectively by an excellent synthetic route designed by Rutherford and Newman.[20] When the naphthylbutanoic acids were prepared by Friedel-Crafts acylation of naphthalene, only the *beta* acid could be separated from the mixture of isomers. Fractional crystallization, fractional neutralization of the acids, and fractional acidification of the sodium salts failed to yield the *alpha* acid free of the *beta* acid.[21] Therefore, the 4-(α-naphthyl)butanoic acid was prepared by Wolff-Kishner reduction of the keto acid obtained from the reaction of α-naphthylmagnesium bromide with succinic anhydride.

The 2-phenanthrene carboxylic acid[8,9] was the only isomer prepared by a substitution reaction on phenanthrene. Acetylation of 9,10-dihydrophenanthrene,[6] dehydrogenation with sulfur and haloform

oxidation yielded this acid. As treatment of 2-acetyl-9,10-dihydrophenanthrene with hypochlorite led to diphenyl-2,2′,3-tricarboxylic acid,[22] the dehydrogenation was performed prior to the oxidation.

3-Phenanthrene carboxylic acid[8,9] was synthesized from 1-keto-1,2,3,4-tetrahydrophenanthrene carboxylic acid[23] (I). Clemmensen reduction, conversion to the methyl ester, dehydrogenation with sulfur and saponification yielded the 3-acid.

The cyclization of (1-naphthylmethyl)succinic acid may lead to either I or II.[23] In the present work, catalysis by hydrogen fluoride or by sulfuric acid led to the formation of I, but the yield was significantly higher from the reaction in which hydrogen fluoride was used. The structure of the product was established by the infrared spectrum[24] and by reduction and dehydrogenation of the keto-acid to the phenanthrene acid.

I   II

9-Phenanthrene carboxylic acid was prepared by carbonation of the Grignard reagent from 9-bromophenanthrene.[15,16] In addition the Diels-Alder adduct of acrylic acid and 1,1′-bicyclohexenyl was dehydrogenated with sulfur at 150–210° to produce the same acid. This established that almost completely hydrogenated phenanthrene carboxylic acids could be dehydrogenated easily and in good yield without migration or loss of the carboxylic group.

The melting points of the five phenanthrene carboxylic acids and the corresponding methyl esters are listed in Table I. In Figs. 1 and 2 are shown the infrared and ultraviolet spectra respectively.

The melting points of the esters agree well with previously reported values. However, the melting points observed in this laboratory of four of the acids were significantly higher than the literature values. For each acid, the melting point was determined both on a Nalge-Axelrod hot stage and in a capillary tube immersed in a stirred oil bath. The thermometers were checked against one calibrated by the National Bureau of Standards.

Examination of the infrared spectrum in the 6–15 micron region appears to be the best procedure for identification of an unknown phenanthrene acid.

(6) W. E. Bachmann and C. H. Boatner, *J. Am. Chem. Soc.* **58**, 2097 (1936).

(7) W. E. Bachmann and N. C. Deno, *J. Am. Chem. Soc.* **71**, 3062 (1949).

(8) H. Gilman and T. H. Cook, *J. Am. Chem. Soc.* **62**, 2813 (1940).

(9) E. Mosettig and J. van de Kamp, *J. Am. Chem. Soc.* **52**, 3704 (1930).

(10) O. Kruber, *Ber.* **67B**, 1000 (1934).

(11) L. F. Fieser, M. F. Fieser, and E. B. Hershberg, *J. Am. Chem. Soc.* **58**, 2322 (1936).

(12) M. F. Ansell and D. H. Hey, *J. Chem. Soc.* 2874 (1950).

(13) A. F. McKay and H. F. Brownell, *J. Org. Chem.* **15**, 648 (1950).

(14) M. A. Goldberg, E. P. Ordas, and G. Carsch, *J. Am. Chem. Soc.* **69**, 260 (1947).

(15) E. W. Shoppee, *J. Chem. Soc.* 37 (1933).

(16) W. E. Bachmann, *J. Am. Chem. Soc.* **56**, 1363 (1934).

(17) D. H. Hey and J. M. Osbond, *J. Chem. Soc.* 3164 (1949).

(18) T. A. Beissman and R. W. Tess, *J. Am. Chem. Soc.* **62**, 514 (1940).

(19) A. Werner, *Ann.* **321**, 248 (1902).

(20) K. G. Rutherford and M. S. Newman, *J. Am. Chem. Soc.* **79**, 213 (1957).

(21) M. S. Newman, R. B. Taylor, T. Hodgson, and A. B. Garrett, *J. Am. Chem. Soc.* **69**, 1784 (1947) and references therein.

EXPERIMENTAL

Infrared spectra. The spectra of the acids were obtained with a Perkin-Elmer Recording Infrared Spectrophotometer,

(22) D. D. Neiswender, W. B. Moniz, and J. A. Dixon, to be published.

(23) J. C. Bardahn, D. Nasipuri, and R. N. Adhya, *J. Chem. Soc.* 355 (1956).

(24) L. F. Fieser and M. F. Fieser, *Natural Products Related to Phenanthrene*, Reinhard Publ. Corp., New York, 1949, p. 202.

Model 21. Pellets containing 200.0 mg. of anhydrous, high purity potassium bromide and 1.0 mg. of the acid were used in obtaining the spectra. A pellet containing 200.0 mg. of potassium bromide was placed in the reference beam.

Ultraviolet spectra. These spectra were obtained using a Beckman Model DU Spectrophotometer equipped with a Spectracord. The solubility of the acids in *n*-hexane was too low ($<1 \times 10^{-6} M$); therefore absolute ethanol was used as a solvent. Concentrations in the range of $10^{-5} M$ were used.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.1; H, 4.5; neut. equiv. 222. Found: C, 80.8; H, 4.4; neut. equiv. 221.

2-Acetyl-9,10-dihydrophenanthrene. This ketone was prepared by the method of Burger and Mosettig[25] and was purified by fractional distillation through a 36″ spinning band column (obtained from Nester and Faust, Exton, Pa.). Yield 58%, b.p. 152° (0.21 mm.), $n_D^{25} = 1.6581$.

2-Acetylphenanthrene. Powdered sulfur (8.9 g., 0.28 mole) and 2-acetyl-9,10-dihydrophenanthrene (61.6 g., 0.28 mole)
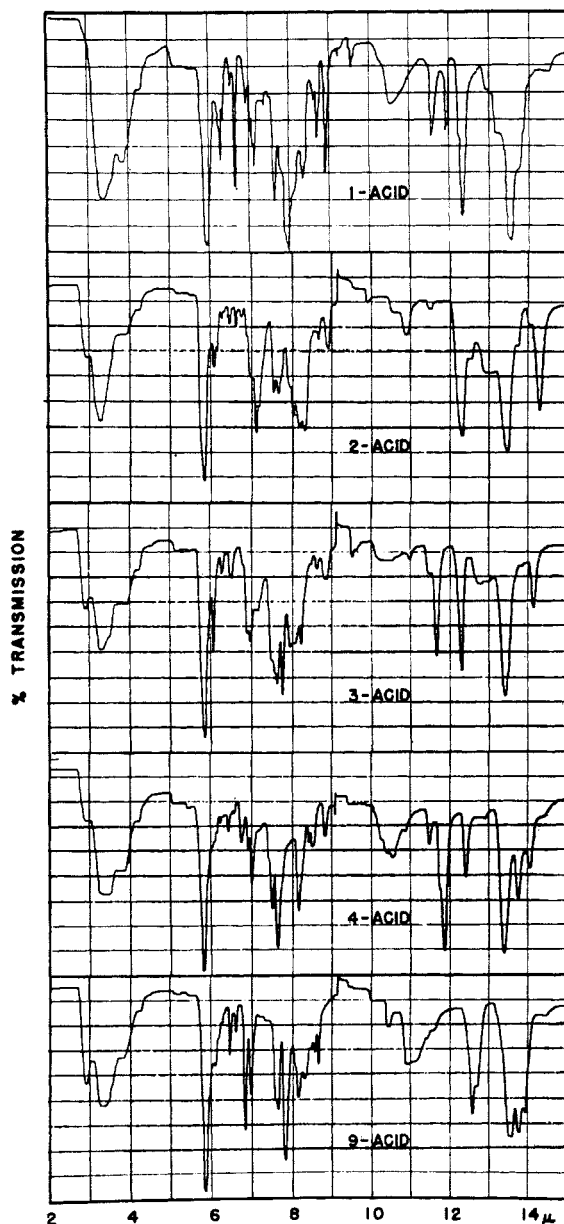

Fig. 1.   Infrared spectra of the monocarboxylic acids of phenanthrene

Phenanthrene-1-carboxylic acid. This acid was prepared from 4-(α-naphthyl)butanoic acid by the synthetic route designed by Rutherford and Newman[20] for the synthesis of phenanthrene-4-carboxylic acid. The crude methyl ester was fractionally distilled in a Piros-Glover Spinning Band column (obtained from H. S. Martin Co., Evanston, Illinois). After two crystallizations from methanol the methyl 1-phenanthrene carboxylate had m.p. 55.0–55.7°.

Anal. Calcd. for $C_{16}H_{12}O_2$, saponification equiv. 236. Found, 233. Saponification of the ester yielded the acid, m.p. 234.7–235.2°.

were heated at 230–260° for 2 hr. A small Claisen head was attached to the flask and the crude ketone was distilled (97% yield; b.p. 195–200° at 1.5 mm).

Phenanthrene-3-carboxylic acid. 2-Acetylphenanthrene (30 g., 0.14 mole) was oxidized by treatment with refluxing Clorox (*ca.* 5% sodium hypochlorite) for 24 hr. The unchanged ketone (9.2 g.) was filtered and the filtrate acidified. The crude acid which precipitated weighed 16.4 g.,

(25) A. Burger and E. Mosettig, *J. Am. Chem. Soc.* **57**, 2731 (1935); **58**, 1857 (1936).
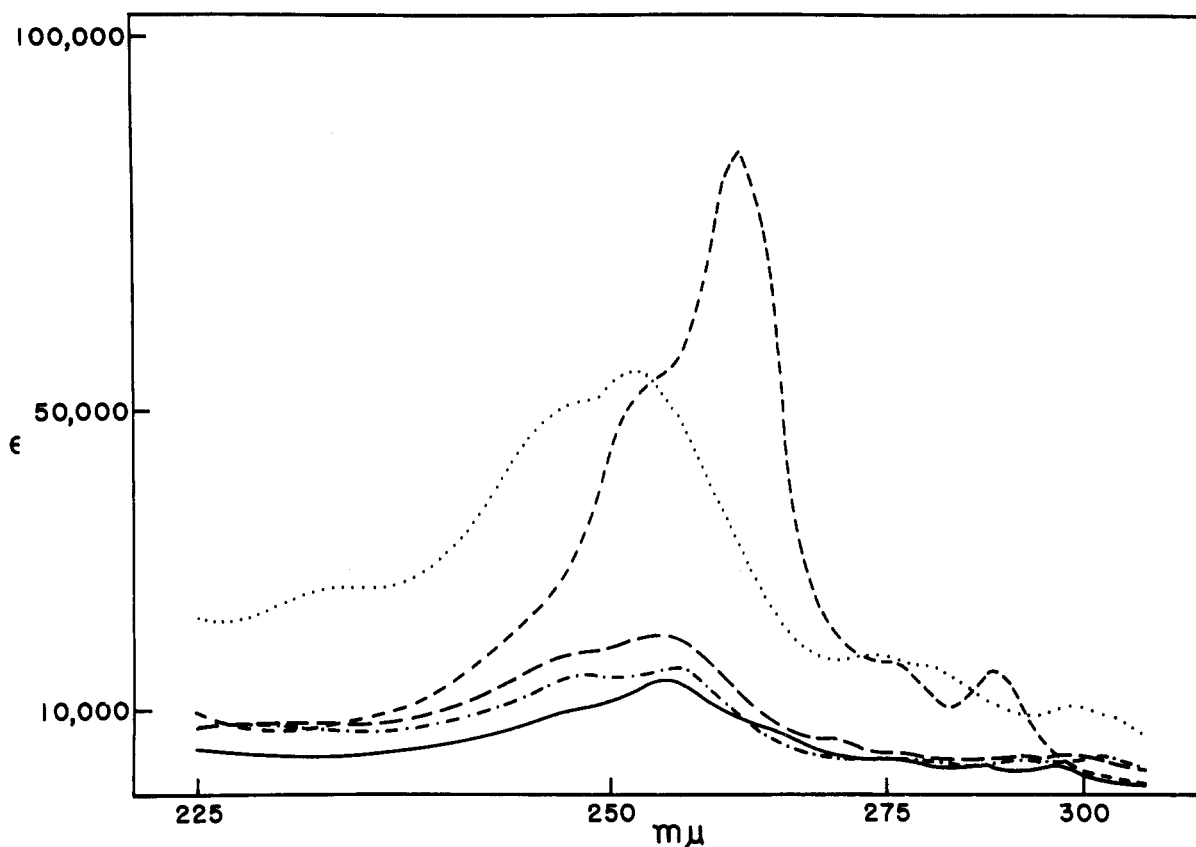
Fig. 2. Ultraviolet absorption spectra: 1-phenanthrene carboxylic acid (......); 2-phenanthrene carboxylic acid (———); 3-phenanthrene carboxylic acid (—·—·); 4-phenanthrene carboxylic acid (————); 9-phenanthrene carboxylic acid (– – – –); all in absolute ethanol

78% yield based on ketone consumed; m.p. 262–265°. The crude acid was added to an ethereal solution of diazomethane and the resulting ester was purified by distillation through a Piros-Glover spinning band column and by recrystallization of the distillation fractions from methanol, m.p. 96.7–98.2°, b.p. 176° (0.40 mm.).

Anal. Calcd. for $C_{16}H_{12}O_2$: Saponification equiv. 236. Found: 239. Pure phenanthrene-2-carboxylic acid was obtained by saponifying the ester with 0.4N potassium hydroxide in diethylene glycol and recrystallizing the acid from ethanol, m.p. 267.8–268.5°.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.1; H, 4.5; neut. equiv. 222. Found: C, 80.8; H, 4.5; neut. equiv. 220.

(1-Naphthylmethyl)succinic acid.[23] Recrystallization did not remove the 3-(1-naphthyl)propanoic acid which formed as a byproduct in this synthesis. The mixture of acids was converted to the methyl esters and the desired dimethyl (1-naphthylmethyl)succinate was separated by fractional distillation, m.p. 93–95°.

Anal. Calcd. for $C_{17}H_{18}O_4$: Saponification equiv. 143. Found: 142.

The dimethyl ester was saponified. The diacid was crystallized from acetone-hexane; m.p. 182.5–184.0°; 45% yield based on the crude mixture of acids.

1-Keto-1,2,3,4-tetrahydrophenanthrene-3-carboxylic acid. Previous workers[23] cyclized the diacid to the keto acid using 85% sulfuric acid. However, this method gave only a 50% yield of the desired ketoacid. Use of anhydrous hydrogen fluoride resulted in an 85–90% yield. The diacid (31 g.) was dissolved in 300 ml. of anhydrous hydrogen fluoride and the latter was allowed to evaporate overnight. After washing the residue thoroughly with water, the solid product was recrystallized from ethanol, yield 25 g. m.p. 225–226°. The

melting point was not depressed by addition of the cyclization product obtained using 85% sulfuric acid.

Anal. Calcd. for $C_{15}H_{12}O_3$: Neut. equiv., 240. Found: Neut. equiv., 237.

Strong ketonic carbonyl absorption was observed at 5.93 μ[24] (corresponding absorptions for 7-butyl-1-tetralone and 1-indanone were observed at 5.90 μ and 5.82 μ respectively).

The ketone was reduced by the Clemmensen reduction[26]; m.p. 209.5–210°, yield 36%.

Phenanthrene-3-carboxylic acid. The methyl ester of 1,2,3,4-tetrahydro-3-phenanthrene carboxylic acid (7.8 g.) (prepared by direct esterification with methanol) and sulfur (2.1 g.) were heated at 240° for 40 min. Vacuum distillation gave 5.6 g. (75%) of distillate, b.p. 165–170° (0.3 mm.), m.p. 88–93°; repeated recrystallizations from hexane raised the melting point to 95.1–95.6°.

Anal. Calcd. for $C_{16}H_{12}O_2$: Saponification equiv. 236. Found: 240.

The purified ester was quantitatively saponified with 0.4N potassium hydroxide in diethylene glycol. After several recrystallizations from ethanol, the acid melted at 278.5–280.0°.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.1; H, 4.5; neut. equiv. 222. Found: C, 80.6; H, 4.7; neut. equiv. 221.

Phenanthrene-4-carboxylic acid. The synthesis of this acid was described by Rutherford and Newman.[20] The methyl phenanthrene-4-carboxylate was purified by fractional distillation, b.p. 155–160° at 0.10 mm. Saponification of the ester yielded the acid, m.p. 174.5–175.5°.

(26) E. L. Martin; *Org. Reactions,* **Vol. I,** 166 (1942).

<div align="center">TABLE I</div>

<div align="center">MELTING POINTS OF THE PHENANTHRENE CARBOXYLIC ACIDS AND METHYL ESTERS</div>

	Acid		Methyl Esters	
Isomer	Found	Lit.	Found	Lit.
1	234.7–235.2	228–233[4-7]	55.0–55.7	57[4]
2	267.8–268.5	254–260.3[8, 9, 10]	96.7–98.2	96.0–96.5[9]
3	278.5–280.0	269–272[8, 9, 19]	95.1–95.6	94.5–95.0[9]
4	174.5–175.5	170–174.5[10, 11, 20]	83.0–84.0	84.8–85.5[20]
9	259.2–260.0	246–256[8, 13-18]	116.2–116.8	115.5–116.0[9, 17]

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.1; H, 4.5; neut. equiv. 222. Found: C, 81.1; H, 4.5; neutralization equiv. 223.

1,1'-Bicyclohexenyl. The conjugated diene was prepared by dehydrating 195 g. of 1,1'-dihydroxy-1,1'-dicyclohexyl[27] over 19 g. of anhydrous copper sulfate at 130–150°. As the diene formed it distilled from the mixture; yield 177 g. (96%). After purification by washing with dilute sodium bicarbonate and fractional distillation the diene weighed 122 g. (77%), b.p. 87° (0.84 mm.), n_D^{25} 1.5349.

1,2,3,4,5,6,7,8,9,9a,10,10a-Dodecahydrophenanthrene-9-carboxylic acid. Acrylic acid (25 g.), 1,1'-bicyclohexenyl (27 g.), and 100 ml. of 95% ethanol were refluxed for 24 hr. On cooling, 24.3 g. (52%) of snow-white crystals precipitated, m.p. 168–170°.

Anal. Calcd. for $C_{15}H_{22}O_2$: Neut. equiv. 234. Found: 233. A second crop of crystals (14 g.) had a lower melting point and is believed to have been contaminated with the ethyl ester.

Phenanthrene-9-carboxylic acid. The dodecahydrophenanthrene-9-acid. (16.1 g.) and powdered sulfur (13.2 g.)

(27) E. E. Gruber and R. Adams, *J. Am. Chem. Soc.* **57**, 2555 (1935).

were heated for 3 hr. at 150–210°. The product was dissolved in 5% sodium carbonate solution. After filtration, the acid was recovered by acidification of the filtrate. Ten grams of the crude acid was converted to the methyl ester with diazomethane. The ester was fractionally distilled through a Piros-Glover spinning band column (b.p. 162° at 0.22 mm.). Repeated recrystallization from methanol of the best distillation fractions yielded 1.6 g. (16%) of ester, m.p. 116.2–116.8°.

Anal. Calcd. for $C_{15}H_{12}O_2$: Saponification equiv. 236. Found: 232. Saponification of the ester with 0.4N potassium hydroxide in diethylene glycol and three recrystallizations from ethanol gave colorless needles, m.p. 259.2–260.0°.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.1; H, 4.5; neut. equiv. 222. Found: C, 81.9; H, 4.5; neut. equiv. 221.

<div align="center">[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]</div>
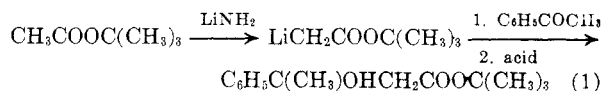
Synthesis of β-Hydroxy Esters from Ethyl Acetate and Ketones or Aldehydes by Means of Lithium Amide. Some Results with Other Esters[1]

<div align="center">WILLIAM R. DUNNAVANT AND CHARLES R. HAUSER</div>

Ethyl acetate was condensed with various ketones or aldehydes including certain α,β-unsaturated ketones or aldehydes by means of two equivalents of lithium amide in liquid ammonia to form the corresponding β-hydroxy esters. In general the yields were good. This method is considered more convenient than that involving the Reformatsky reaction. The products were saponified and/or dehydrated to give derivatives. The condensations of certain other esters with ketones or aldehydes were effected with one or two equivalents of lithium amide.

It has been previously shown[2] that lithio t-butyl acetate, prepared from molecular equivalents of the ester and lithium amide in liquid ammonia, can be condensed satisfactorily with various ketones or aldehydes in ether to form the β-hydroxy esters. For example, this aldol type of condensation was realized with the lithio ester and acetophenone in 76% yield (Equation 1).

$$CH_3COOC(CH_3)_3 \xrightarrow{\text{LiNH}_2} LiCH_2COOC(CH_3)_3 \xrightarrow[\text{2. acid}]{\text{1. } C_6H_5COCH_3}$$
$$C_6H_5C(CH_3)OHCH_2COOC(CH_3)_3 \quad (1)$$

It has similarly been observed[3] that even ethyl acetate can be condensed satisfactorily with acetophenone,[3] cyclohexanone,[3] or fluorenone[4] provided an extra equivalent of lithium amide is employed.

(1) Supported by the Office of Ordnance Research, U. S. Army.

(2) C. R. Hauser and W. H. Puterbaugh, *J. Am. Chem. Soc.*, **73**, 2972 (1951); *J. Am. Chem. Soc.*, **75**, 1068 (1953).

(3) C. R. Hauser and J. K. Lindsay, *J. Am. Chem. Soc.*, **77**, 1050 (1955).

(4) C. R. Hauser and D. Lednicer, *J. Org. Chem.*, **22**, 1248 (1957).