threne (XVI), separated as white shiny needles (2.27 g., 39%), m.p. 219–220.8°. Concentration of the mother liquor gave a further 0.8 g. (14%) of a light tan solid, m.p. 218–221°. Recrystallization from dioxane gave shiny needles melting at 223–223.6° (lit.[7] 219°).

2,3-Dihydro-2-hydroxy-1H-cyclopenta(*l*)phenanthrene (XVII).—To a suspension of the ketone XVI (0.75 g.) in methanol (50 ml.) was added a solution of sodium borohydride (1.0 g.) in methanol (30 ml.). A vigorous effervescence occurred, and after about 30 seconds all of the suspended solid material had gone into solution. The resulting solution was allowed to stand at room temperature for 2 days, and the solution was brought to *p*H 7 by addition of dilute hydrochloric acid. The solution was poured into water (300 ml.), and the dense white precipitate was removed by filtration and washed well with water. On air-drying, impure XVII was obtained as a fine white powder (0.72 g., 95%), m.p. 184.6–186.1°. Two recrystallizations from 95% ethanol gave fine colorless needles of XVII (0.6 g., 80%), m.p. 187.1–188.0°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.16; H, 6.02. Found: C, 87.11; H, 5.82.

When the above alcohol (100 mg.) was heated under reflux on a steam-bath for 3 hr. with 100% formic acid and then poured into water, the corresponding formate separated (103 mg., 92%). Recrystallization from 95% ethanol gave long white needles (59 mg., 53%), m.p. 179.5–180°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.30; H, 5.53.

When the alcohol XVII (1.0 g.) was warmed at 100° with acetic anhydride and then poured onto ice, the corresponding acetate (1.19 g., 98%), m.p. 158–159.2°, was obtained. Recrystallization from 95% ethanol gave white needles, m.p. 160–161° (685 mg., 57%).

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.40; H, 5.96.

1H-Cyclopenta(*l*)phenanthrene (XIII).—A mixture of the alcohol XVII (0.5 g.) and boric acid (2.0 g.) was heated at atmospheric pressure in a metal-bath until a liquid melt was obtained. The tube was cooled, the pressure reduced and the solid mass was heated slowly at first to 180–190° (0.4 mm.) and then to 300° (0.1 mm.). A brownish-yellow sublimate (370 mg., 79%) was collected. It was resublimed at 100–120° (0.05 mm.), the sublimate weighing 101 mg. (22%), m.p. 143–147.5°. This product was dissolved in benzene and passed through a column of activated alumina. Elution of the column with benzene afforded 94 mg. of a white solid, m.p. 146.1–148.5°. Three recrystallizations from isopropyl alcohol gave 27 mg. of XIII, m.p. 149.9–151.9°. A mixture of this product with XIII, obtained by degradation of XII (m.p. 150.2–152.8°), melted at 150–152.7°. The synthetic sample of XIII and the sample obtained by degradation had identical infrared spectra.

2,3-Dihydro-1H-cyclopenta(*l*)phenanthrene (XIV).—To a solution of potassium hydroxide (1.2 g.) in diethylene glycol (6 ml.) was added the ketone XVI (1.0 g.) and 2 ml. of 85% hydrazine hydrate. The mixture was heated at 160–165° for 1.5 hr. The excess hydrazine hydrate was removed by heating to 205–210° and the mixture was heated at 205° for an additional period of 3.5 hr. The mixture was diluted with water and acidified with hydrochloric acid. A brown powder that weighed 0.96 g. after air-drying was obtained. Recrystallization from 95% ethanol (Norit) yielded XIV (0.57 g., 58%) as colorless needles, m.p. 145.1–147.9°. Two more recrystallizations from absolute ethanol raised the melting point to 149.1–149.9° (420 mg.) (lit.[8] 150°). The hydrocarbon XIV synthesized by this method and the sample obtained by the degradation XI → XII → XIII → XIV described above were identical according to mixed melting point and comparison of infrared spectra.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Rearrangement of Allyl Groups in Three-carbon Systems. VII. Diethyl α-Allyl-2-naphthalenemalonate

BY ARTHUR C. COPE, JAY E. MEILI AND D. W. H. MACDOWELL[1]

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Diethyl α-allyl-2-naphthalenemalonate (I) has been observed to rearrange on heating at 273° to the diethyl ester of 3-carboxy-2,3-dihydro-1H-benz(*e*)indene-2-acetic acid (II). Evidence establishing the structure of II was obtained by degrading the corresponding acid III to 1,2-naphthalenedicarboxylic acid and to 2,3-dihydro-1H-benz(*e*)indene (VII). The conversion of III to a geometric isomer VI and an intramolecular anhydride IV was found to parallel exactly transformations of related model compounds in the indan series (XI, XII and XIII). Final proof of structure of the acid III was obtained by synthesis.

The preceding paper[2] reports the thermal rearrangement of diethyl α-allyl-9-phenanthrenemalonate to an isomeric ester containing the 2,3-dihydro-1H-cyclopenta(*l*)phenanthrene ring system. Before the structure of the rearrangement product was known, the thermal rearrangement of diethyl α-allyl-2-naphthalenemalonate (I) was studied as an analogous case in which the structure of the product might be established more simply. The results obtained and an investigation of some indan derivatives that are structurally related to the rearrangement product are described in this paper.

Ethyl 2-naphthaleneacetate was condensed with diethyl carbonate in the presence of dry sodium ethoxide with removal of the ethanol formed by distillation,[3] and the resulting enolate was alkylated with allyl bromide to give diethyl α-allyl-2-naphthalenemalonate (I) (97%). This ester was converted to diethyl α-propyl-2-naphthalenemalonate by quantitative hydrogenation. Saponification of the ester I followed by acidification at 0–5° resulted in decarboxylation and formed α-allyl-2-naphthaleneacetic acid (70%), from which the ethyl ester was prepared.

When diethyl α-allyl-2-naphthalenemalonate was heated at 273° for 24 hr., an isomeric ester II was formed in 65% yield. This ester gave negative unsaturation tests with potassium permanganate and on saponification yielded a crystalline dicarboxylic acid, III, m.p. 235.0–235.8° dec. Esterification of the acid III with ethanol re-formed the ester II.

The dicarboxylic acid III was not decarboxylated by heating alone or mixed with copper powder at 220–250°, or by boiling with copper powder in quinoline, and accordingly could not be a malonic

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[1] Visking Corporation Fellow, 1953–1954.

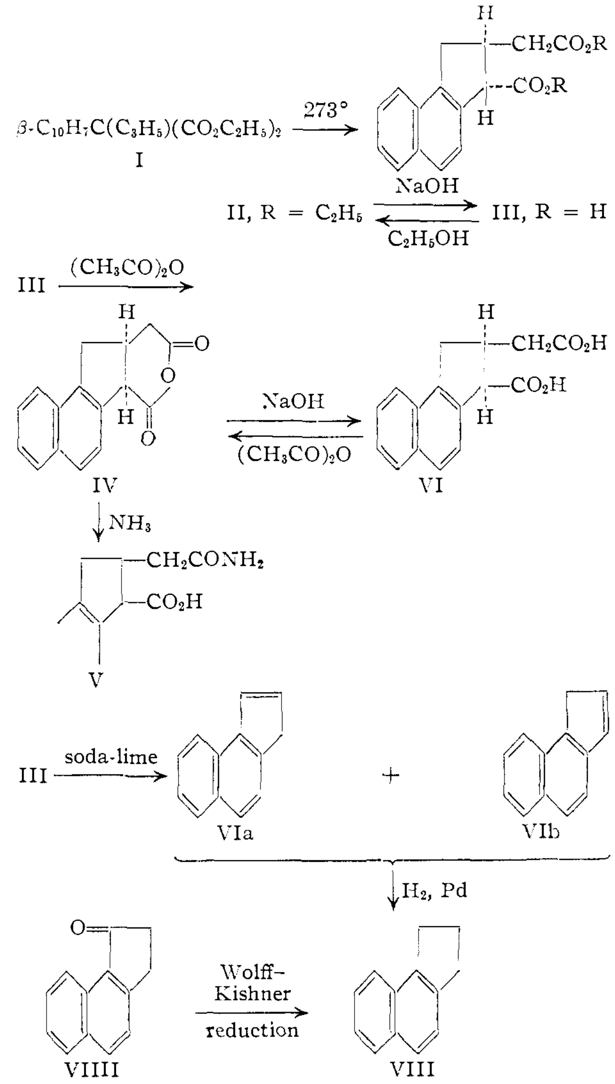
[2] A. C. Cope, L. Field, D. W. H. MacDowell and M. E. Wright, THIS JOURNAL, **78**, 2547 (1956).

[3] A procedure described for similar cases by V. H. Wallingford, A. H. Homeyer and O. M. Jones, *ibid.*, **63**, 2056 (1941).

acid derivative. On heating with acetic anhydride the acid III formed an anhydride IV, m.p. 151.2–152.8°, that was shown to be an intramolecular anhydride by treatment with liquid ammonia, which formed the dicarboxylic acid monoamide V. Saponification of the anhydride IV yielded a dicarboxylic acid VI, m.p. 213.5–214.0°, that was isomeric but not identical with the acid III formed by saponification of the ester II. The acid VI reformed the anhydride IV on treatment with acetic anhydride. The lower melting acid VI was converted into the higher melting isomer III by boiling with aqueous sodium hydroxide, while III was recovered unchanged after such treatment. These facts indicate that the acids III and VI are *trans* and *cis* isomers and that III has the more stable of the two configurations. Since both acids formed the same intramolecular anhydride, the anhydride formation probably involves closure of a ring system in which a *cis* ring juncture is more stable than *trans*, and the acid VI obtained by hydrolysis of the anhydride is the *cis* isomer. Accordingly, the ester II and the corresponding acid III have *trans* configurations. This conclusion is supported by evidence based on syntheses described later in this paper.

The facts that the rearrangement product II contains no olefinic double bond and that it is an isomer of the allyl-substituted ester I require the formation of a new ring in the conversion of I to II. Oxidation of the acid III with alkaline potassium ferricyanide showed that the ring had closed on the 1-position of the naphthalene nucleus, for the product was 1,2-naphthalenedicarboxylic acid. When the sodium salt of the acid III was heated with soda-lime at 250°, a mixture of crystalline hydrocarbons (VIa and VIb) was formed. Quantitative hydrogenation of the mixture yielded the known hydrocarbon, 2,3-dihydro-1H-benz(*e*)indene (VII).[4] The hydrocarbon VII obtained by this route and an authentic sample prepared by Wolff–Kishner reduction of the ketone VIII had the same physical properties, including infrared spectra, and formed identical picrates, m.p. 108–109°. Recrystallization of the mixture of hydrocarbons VIa and VIb, m.p. 39.8–46.5°, resulted in separation of one pure isomer, m.p. 61.4–62.4°. Since structure VIa has been assigned to a hydrocarbon prepared by another route melting at 48.5–50°,[5] the high-melting isomer presumably corresponds to VIb.

Establishment of the ring system present in the hydrocarbon left only the position of three carbon atoms to be determined to permit assignment of a complete structure to the dicarboxylic acid III. The fact that the rearrangement product II was readily saponified to III suggested that neither carbethoxyl group was attached to a tertiary carbon atom. A negative Kuhn–Roth C-methyl determination eliminated some possible structures. Ready formation of an anhydride from the acids III and VI suggested that they were substituted succinic or glutaric acids. These considerations, plus the requirement of structural features that might permit loss of three carbon atoms on heating the sodium salt of III with soda-lime, led to structure II as the most probable one for the rearrangement product, and III–VI for compounds derived from it.



Prior to confirmation of structure III by synthesis, the properties of related compounds in the indan series were determined, since the synthetic problems in that series were less complicated, in order to obtain indirect evidence concerning the validity of the interpretations upon which the structures of II and III were based.

Methyl 3-indenecarboxylate (IX) was prepared by esterification of 3-indenecarboxylic acid.[6] Evidence that this acid has the α,β-unsaturated structure shown was furnished by the fact that it was recovered unchanged after boiling with aqueous sodium hydroxide and by the position of the ester carbonyl band at 1720 cm.$^{-1}$ in the infrared spectrum of IX, indicating conjugation of the carbonyl group with the alicyclic double bond. Michael addition of dimethyl malonate to IX in the presence of sodium methoxide formed dimethyl 1-carbomethoxy-2-indanmalonate (X) in 70% yield. The ad-

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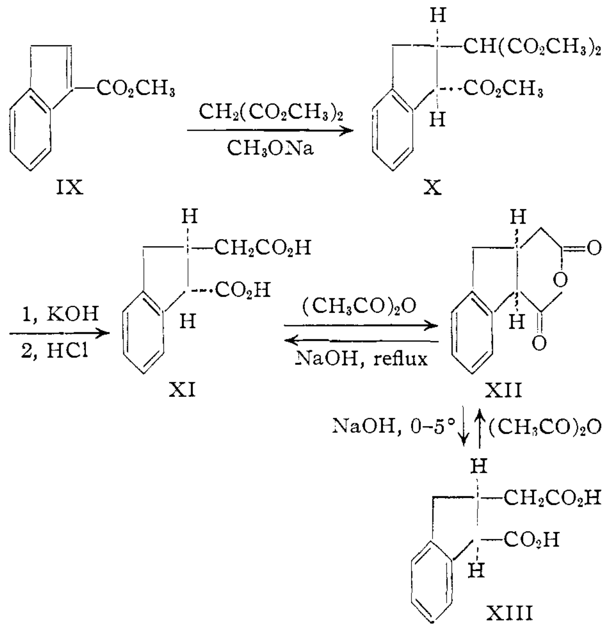
(4) J. W. Cook and C. L. Hewitt, *J. Chem. Soc.*, 1111 (1933).

(5) C. F. Koelsch and R. A. Scheiderbauer, THIS JOURNAL, **65**, 2312 (1943).

(6) W. S. Knowles, J. A. Kuck and R. C. Elderfield, *J. Org. Chem.*, **7**, 374 (1942).

duct X is believed to have the *trans* configuration; the fact that Michael addition of diethyl malonate to ethyl 1-cyclopentenecarboxylate leads exclusively to a *trans* adduct[7] supports this conclusion. Saponification of X followed by decarboxylation of the tricarboxylic acid by heating with hydrochloric acid yielded 1-carboxy-2-indanacetic acid (XI) (83%). This acid on treatment with acetic anhydride formed the anhydride XII (74%). Saponification of the anhydride XII with sodium hydroxide in aqueous ethanol at the boiling point re-formed the acid XI. However, when the saponification was conducted at 0–5°, an isomeric acid XIII was formed and accordingly is assigned the *cis* configuration. The acids XI and XIII had different infrared spectra as well as different melting points, and mixtures of them melted over a broad range.

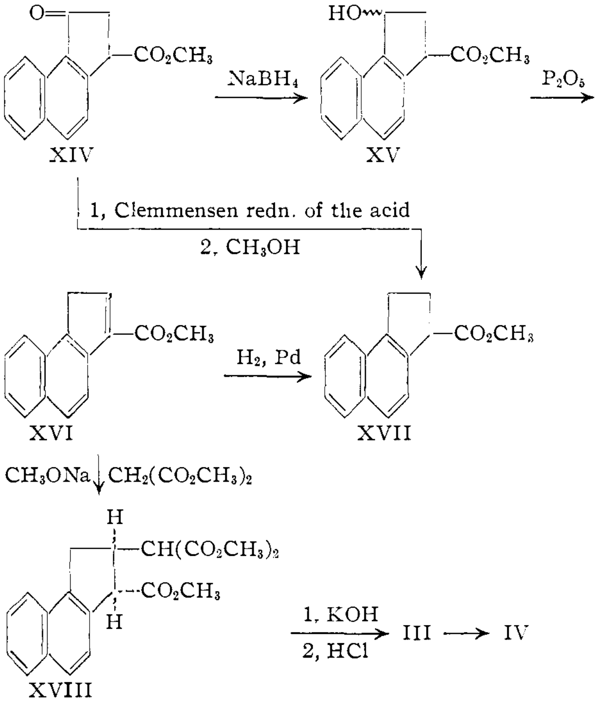
When the sodium salt of XI was heated with soda-lime, indene was formed in 63% yield, and identified as the picrate. These reactions in the indan series exactly paralleled those formulated above for III–VII and provided strong supporting evidence for structures II and III.



The route by which the acids XI and III lose three carbon atoms in forming the hydrocarbons indene and VIa and VIb, respectively, can be considered as a reverse Michael reaction, in which carbon dioxide and acetic acid are eliminated. It is uncertain which fragment is lost first; speculative mechanisms can be written for either course. The sodium salt of 3-indenecarboxylic acid yielded indene (20%) when heated with soda-lime, but this result may have no bearing on the path by which XI forms indene.

Final proof of structure of the rearrangement product II was obtained by synthesis of the corresponding acid III by the method shown below. Methyl 2,3-dihydro-1-oxo 1-H-benz(*e*)indene-3-carboxylate (XIV) was reduced to the hydroxy ester XV with sodium borohydride, and XV was dehydrated by treatment with phosphorus pentoxide in benzene. The product is formulated as the α,β-unsaturated ester XVI because the infrared carbonyl band occurs at 1720 cm.$^{-1}$, but the isomeric β,γ-unsaturated structure is not rigorously excluded. The unsaturated ester XVI was catalytically hydrogenated to the saturated ester XVII, which was identical with an authentic sample prepared from XIV by Clemmensen reduction of the keto acid corresponding to XIV followed by esterification. Michael addition of dimethyl malonate to XVI formed the adduct XVIII, which was saponified and then decarboxylated to the *trans*-acid III, which was identical with III obtained from II according to melting point, mixed melting point and comparison of infrared spectra. Samples of III from both sources also formed the same anhydride IV.

Only speculative mechanisms can be written for the rearrangement of I to II, and for the analogous rearrangement in the phenanthrene series described in the preceding paper. However, it seems very likely that in both instances an allyl group rearranges from the malonic ester grouping to the adjacent reactive position of the aromatic nucleus (the 1-position of naphthalene and the 10-position of phenanthrene) and that the esters so formed undergo cyclization and further rearrangement at the high temperatures required in both series.



Experimental[8]

Diethyl α-Allyl-2-naphthalenemalonate (I).—A solution of sodium ethoxide was prepared from 11.1 g. of sodium and 250 ml. of absolute ethanol in a flask which was fitted with a 25 × 1.5-cm. helix-packed column with a variable take-off head. The ethanol was removed by distillation under reduced pressure, and to the dry sodium ethoxide was added 300 ml. of diethyl carbonate and 95.3 g. of ethyl 2-naphthaleneacetate. The mixture was heated under reflux and the ethanol formed in the reaction was distilled until only

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(7) A. H. Cook and R. P. Linstead, *J. Chem. Soc.*, 956 (1934).

(8) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

diethyl carbonate was being removed (2.8 hr.). The solution was cooled to 70°, allyl bromide (55 ml.) was added and the mixture heated under reflux for 1 hr. The mixture was cooled, 5 ml. of water was added and the precipitated sodium bromide was removed by filtration and washed with ether. The ether washings were added to the crude reaction product, which was purified by distillation, yielding diethyl α-allyl-2-naphthalenemalonate (I) (141.3 g., 97%), b.p. 198–207° (1.5 mm.), $n^{25}\mathrm{D}$ 1.5520–1.5530.

Diethyl 2-naphthalenemalonate was prepared from ethyl 2-naphthaleneacetate and diethyl carbonate in the presence of ethanol-free sodium ethoxide by a procedure similar to the one described above, and the ester was isolated by acidification with acetic acid, extraction with ether and crystallization from hexane. The yield was 54%, m.p. 101.6–102.4°, lit.[9] 99–100°.

Diethyl α-allyl-2-naphthalenemalonate also was prepared from the sodium enolate of diethyl 2-naphthalenemalonate (14.2 g.) and allyl bromide (8.7 g.) in absolute ethanol. The product was isolated by extraction with ether and purified by short-path distillation at a bath temperature of 190° and 0.25 mm. Diethyl α-allyl-2-naphthalenemalonate was obtained in a yield of 14.3 g. (88%), $n^{25}\mathrm{D}$ 1.5520, d^{25}_{4} 1.114.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found: C, 73.60; H, 6.81.

Diethyl α-Propyl-2-naphthalenemalonate.—Hydrogenation of a solution of 1.37 g. of diethyl α-allyl-2-naphthalenemalonate in 10 ml. of 95% ethanol in the presence of 50 mg. of 10% palladium-on-Norit was complete in 1.5 hr. and 103% of one molar equivalent of hydrogen was absorbed. Distillation yielded 1.12 g. (82%) of diethyl α-propyl-2-naphthalenemalonate as a colorless liquid, b.p. 148–151.8° (0.34 mm.), $n^{25}\mathrm{D}$ 1.5420–1.5423. An analytical sample had b.p. 149.5–151.5° (0.34 mm.), $n^{25}\mathrm{D}$ 1.5421, d^{25}_{4} 1.098.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 72.98; H, 7.39.

α-Allyl-2-naphthaleneacetic Acid.—Diethyl α-allyl-2-naphthalenemalonate (2.10 g.) was heated under reflux with a mixture of 40 ml. of 25% sodium hydroxide and 20 ml. of ethanol. At the end of 5 hr., the reaction mixture was cooled and poured with stirring into a mixture of ice and concentrated hydrochloric acid (20 ml.). The resulting solid was separated by filtration and recrystallized from water; the yield of α-allyl-2-naphthaleneacetic acid was 1.02 g. (70%), m.p. 81.0–82.2°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.23; neut. equiv., 226. Found: C, 79.87; H, 6.39; neut. equiv., 224.

Ethyl α-Allyl-2-naphthaleneacetate.—A solution of α-allyl-2-naphthaleneacetic acid (3.47 g.), absolute ethanol (30 ml.) and *p*-toluenesulfonic acid monohydrate (0.1 g.) was heated at the reflux temperature for 15 hr. The water formed was removed by co-distillation with toluene, and a solution of the residual oil in ether was washed with sodium carbonate solution, water and dried over magnesium sulfate. Distillation yielded 3.49 g. (89%) of the ester, $n^{25}\mathrm{D}$ 1.5649, m.p. 25.2–27.0°. The product from a similar preparation with b.p. 153–155° (1.4 mm.) was analyzed.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.34; H, 7.35.

Rearrangement of Diethyl α-Allyl-2-naphthalenemalonate.—The ester I (58.7 g.) was divided into three approximately equal portions and each portion was heated separately at 273° for 24 hr. under a positive pressure of 1200 p.s.i. of hydrogen. The products were combined and distilled through a 25 × 1.5-cm. Vigreux column. The total recovery of material amounted to 45.4 g. (77%). Low-boiling fractions (4.7% of this amount) had boiling points, refractive indices and infrared spectra very similar to diethyl α-allyl-2-naphthalenemalonate. The ester II formed by rearrangement (38.0 g.), b.p. 173–184° (0.49 mm.), $n^{25}\mathrm{D}$ 1.5580–1.5602, was isolated in 65% yield. A fraction with b.p. 179° (0.29 mm.), $n^{25}\mathrm{D}$ 1.5592, was analyzed.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found: C, 73.71; H, 6.74.

Saponification of II.—A solution of II (2.38 g.) in 95% ethanol (25 ml.) and 20% sodium hydroxide (25 ml.) was swirled for 5 minutes. Considerable solid material separated, and the reaction mixture was allowed to stand at room temperature for 26 hr. The solid was removed by filtration and washed with ethanol. It was then dissolved in water and acidified with iced hydrochloric acid. The solid was removed by filtration, washed with water and air-dried to give the acid III, 1.59 g. (81%), m.p. 233.8–235.2° dec. An analytical sample, m.p. 235.0–235.8° (dec., inserted at 216°), was obtained by one recrystallization from acetonitrile.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; neut. equiv., 135. Found: C, 71.30; H, 5.38; neut. equiv., 138.

Re-esterification of the Acid III.—A mixture of the acid (2.62 g.), *p*-toluenesulfonic acid (0.1 g.) and absolute ethanol (40 ml.) was heated under reflux for 31 hr. Toluene was added and distilled to remove water, and the processes of heating with absolute ethanol and removal of the water by codistillation with toluene were repeated twice. A solution of the residue in ether was washed with 5% sodium bicarbonate solution, dried over sodium sulfate and distilled. The yield of II, a yellow liquid with b.p. 185–187° (0.6 mm.), $n^{25}\mathrm{D}$ 1.5584–1.5590, was 2.39 g. (76%). An analytical sample had $n^{25}\mathrm{D}$ 1.5587, d^{25}_{4} 1.144.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found: C, 73.65; H, 6.80.

Anhydride of the Acid III.—A mixture of the acid III (960 mg.) and acetic anhydride (30 ml.) was heated under reflux for 2.5 hr. The acetic anhydride was removed under reduced pressure, and the resulting solid was sublimed at 0.4 mm. with a heating block temperature of 150° to give the anhydride IV (730 mg., 81%). Two crystallizations from benzene–hexane yielded the pure anhydride (550 mg., 61%), m.p. 151.2–152.8°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80; sapn. equiv., 126. Found: C, 76.06; H, 4.94; sapn. equiv., 123.1.

Ammonolysis of the Anhydride IV.—A mixture of the anhydride IV (136 mg.) and liquid ammonia was allowed to stand in a Dewar flask for a total of 5 days, with periodic additions of liquid ammonia to replace the amount lost by evaporation. The residual solid was acidified with aqueous hydrochloric acid and the product was crystallized twice from aqueous ethanol to yield 75 mg. (52%) of the dicarboxylic acid monoamide V, m.p. 200.8° dec. An analytical sample was recrystallized twice from aqueous ethanol, m.p. 202.8–204° (dec., inserted at 191°).

Anal. Calcd. for $C_{16}H_{15}O_3N$: C, 71.36; H, 5.62; N, 5.20; neut. equiv., 269. Found: C, 71.05; H, 5.81; N, 5.06; neut. equiv., 268.

The structure of the amide is tentatively designated as V, on the assumption that ammonolysis would attack the least hindered carbonyl group of the anhydride IV.

Saponification of the Anhydride IV.—Saponification of 159 mg. of the anhydride with 4 ml. of 1.0 *N* sodium hydroxide in a mixture of ethanol and water at 85° for 1 hour yielded, after acidification, 140 mg. (82%) of the acid VI, m.p. 213.5–214° (dec., inserted at 205°).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; neut. equiv., 135. Found: C, 71.08; H, 5.48; neut. equiv., 134.

The acid VI (185 mg.) was treated with acetic anhydride in the same manner as the acid III and yielded 131 mg. of the anhydride IV, m.p. 145–148.5° after sublimation. After several crystallizations from benzene–hexane the melting point of the anhydride IV was 150–151.5°, undepressed on admixture with a sample of IV prepared from the acid III.

Conversion of the Lower Melting Acid VI to the Higher Melting Isomer III.—A solution of 40 mg. of the acid VI, m.p. 213–214°, in 10% aqueous sodium hydroxide was heated under reflux for 18 hr. Acidification yielded 29 mg. (73%) of the higher melting isomer III, m.p. 231.6–233.1°, identical with the sample of III previously described (mixed m.p.). Identical treatment of the higher melting acid III resulted in no change and 81% recovery of III.

Oxidation of the Acid III.—A mixture of potassium ferricyanide (14.2 g.), potassium hydroxide (2.5 g.), the acid III (0.30 g.) and 52 ml. of water was heated at 60–70° for 42 hr. with stirring. The acid formed was isolated by filtering the mixture, acidifying and extracting with ether. Sublimation yielded 104 mg. (48%) of 1,2-naphthalenedicarboxylic acid anhydride, which was reconverted to the dicar-

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(9) M. F. Ansell and D. H. Hey, *J. Chem. Soc.*, 1683 (1950).

boxylic acid. The 1,2-naphthalenedicarboxylic acid obtained had the properties described by Fieser.[10]

Decarboxylation of the Acid III with Soda-lime.—The sodium salt of III, prepared from 2.03 g. of the acid and aqueous sodium hydroxide, was powdered and mixed with 8.5 g. of soda-lime. The mixture was heated in a sublimation apparatus at a bath temperature of 245–250° and 0.3 mm. for 6.5 hr. The sublimate which collected on a Dry Ice cooled condenser was dissolved in pentane and the solution was passed through a column of alumina and concentrated. Sublimation of the residue at 1.5 mm. with a heating block temperature of 80° yielded 944 mg. (75%) of a yellow solid. After one crystallization from aqueous ethanol the product (a mixture of VIa and VIb) melted at 42.4–46°. Repeated recrystallization from aqueous ethanol and resublimation yielded a small amount of the higher melting isomer VIb as a white solid, m.p. 61.4–62.4°.

Anal. Calcd. for $C_{13}H_{10}$: C, 93.94; H, 6.06. Found: C, 93.67; H, 5.97.

2,3-Dihydro-1H-benz(*e*)indene (VII).—A mixture of the hydrocarbons VIa and VIb, obtained by decarboxylating the acid III as described above (502 mg., m.p. 39.8–46.5°), was dissolved in ethyl acetate and hydrogenated in the presence of 10% palladium-on-Norit. Reduction was complete in 0.5 hour and 95.5% of one molar equivalent of hydrogen was absorbed. The product was distilled through a semi-micro column and amounted to 428 mg. (84%) of VII, b.p. 85–87° (0.45 mm.), $n^{25}D$ 1.6268–1.6289. The picrate of the hydrocarbon VII, after recrystallization from 95% ethanol, had m.p. 108–109°, and was identical (mixed m.p.) with an authentic sample which was prepared as follows.

To β-2-naphthalenepropionic acid[11] (13.2 g.) in a polyethylene beaker was added anhydrous hydrogen fluoride (200 ml.). The mixture was allowed to stand at room temperature for 18 hr. and then neutralized with sodium carbonate. The 2,3-dihydro-1-oxo-1H-benz(*e*)indene (VIII) was extracted with methylene chloride and purified by recrystallization from 95% ethanol (7.05 g., 59%), m.p. 105.2–106.6°, lit.[4] m.p. 102–103°.

A solution of 30 ml. of diethylene glycol, 4 ml. of 85% hydrazine hydrate, 4 g. of potassium hydroxide and 1.68 g. of the above ketone VIII was heated under reflux for 0.8 hr. Water was removed by distillation, and the mixture was then heated under reflux for a further 3.5 hr. It was then cooled, diluted with water and poured into ice and hydrochloric acid. The 2,3-dihydro-1H-benz(*e*)indene (VII) was extracted with pentane and purified by distillation; the yield was 926 mg. (60%), b.p. 85.5–88.5° (0.45 mm.), $n^{25}D$ 1.6299–1.6306. The picrate had m.p. 108–109°, lit.[4] 109–110°.

Dimethyl 1-Carbomethoxy-2-indanmalonate (X).—Methyl 3-indenecarboxylate (IX) was prepared in 74% yield by esterification of 3-indenecarboxylic acid[6] with methanol in the presence of *p*-toluenesulfonic acid, removing the water formed by co-distillation with benzene; b.p. 139–140° (12 mm.), $n^{25}D$ 1.5625 (lit.[12] b.p. 153–154° at 23 mm.).

A solution of 22.7 g. of dimethyl malonate in 20 ml. of dry methanol was added with stirring in a nitrogen atmosphere to the sodium methoxide prepared from 1.32 g. of sodium and 50 ml. of dry methanol. A solution of 10.0 g. of methyl 3-indenecarboxylate in 10 ml. of dry methanol was added, and the mixture was heated in a bath at 65–70° with stirring for 3 hr. and allowed to stand overnight at room temperature. Glacial acetic acid (3 ml.) was added, followed by water, and the product was extracted with ether. The extracts were washed with sodium bicarbonate solution and water, dried over magnesium sulfate, and concentrated. Distillation of the residue separated a forerun of dimethyl malonate from 12.1 g. (70%) of X as a pale yellow oil, b.p. 135–137° (0.1 mm.), $n^{25}D$ 1.5128.

Anal. Calcd. for $C_{16}H_{18}O_6$: C, 62.74; H, 5.88. Found: C, 62.73; H, 5.97.

1-Carboxy-2-indanacetic Acid (XI).—The above malonic ester derivative (2.8 g.) was added to 60 ml. of 5% potassium hydroxide in 1:1 aqueous methanol. The solution was heated under reflux for 14 hr. and concentrated to remove methanol. The aqueous residue was cooled and acidified with hydrochloric acid; a light brown solid separated from the solution. An equal volume of concentrated hydrochloric acid was added and the suspension was heated under reflux for 48 hr. The clear solution was decanted to separate a solid, and the yellowish needles that separated on cooling were collected (0.65 g., m.p. 204.5–206.5°). The residual undissolved material was again treated with 20% hydrochloric acid under reflux, and an additional 1.15 g. of XI was obtained, m.p. 205–208°. The products were combined and recrystallized once from acetonitrile (Norit) to give 1.46 g. (73%) of XI as colorless needles, m.p. 206.1–207.7°. An analytical sample was recrystallized several times from acetonitrile and melted at 207.2–208.6°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49; neut. equiv., 110.1. Found: C, 65.30; H, 5.54; neut. equiv., 108.5.

Anhydride of 1-Carboxy-2-indanacetic Acid (XII).—One gram of 1-carboxy-2-indanacetic acid (XI) and 30 ml. of acetic anhydride were heated under reflux for 1 hr. The excess acetic anhydride was removed and the residue was sublimed at 120–125° (0.25 mm.). A sublimate weighing 822 mg. was collected, m.p. 93–94.9°. Resublimation at 85° (0.55 mm.) yielded 680 mg. (74%) of the anhydride XII, m.p. 94.6–95.5° after one crystallization from petroleum ether.

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.27; H, 4.98. Found: C, 71.26; H, 5.13.

Saponification of the Anhydride XII to the Higher Melting Acid XI.—The anhydride (20 mg.) was heated under reflux for 3 hr. with a mixture of 25 ml. of 4% aqueous sodium hydroxide solution and 15 ml. of ethanol. The solution was concentrated, cooled and acidified with hydrochloric acid. The higher melting acid XI crystallized on standing at 5°; the yield was 14 mg., m.p. 205.1–206.1°, undepressed on admixture with a sample of XI prepared from X.

Saponification of the Anhydride XII to the Lower Melting Acid XIII.—The anhydride XII (400 mg.) was stirred with a mixture of 10 ml. of ice-cold 4% aqueous sodium hydroxide and 10 ml. of ethanol for 10 minutes, and the mixture was allowed to stand overnight at 5°. The ethanol was removed at room temperature and the residual solution was cooled in ice and acidified with cold hydrochloric acid. A dense white precipitate separated and was allowed to stand overnight at 5° and removed by filtration. The acid XIII weighed 405 mg. (93%) after drying and melted at 185.0–188.6°. An analytical sample prepared by several recrystallizations from acetonitrile melted at 191.6–192.8°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49; neut. equiv., 110.1. Found: C, 65.49; H, 5.79; neut. equiv., 109.0.

A mixture of this acid, XIII, and the higher melting isomer XI with m.p. 207.2–208.6° melted at 179–196.4°.

Re-formation of the Anhydride XII from the Acid XIII.—From 28 mg. of the acid XIII and 5 ml. of acetic anhydride, there was obtained, after sublimation at 70–80° and 0.6 mm., 14 mg. (54%) of XII, m.p. 94.9–95.9°, undepressed on admixture with a sample of the anhydride XII described above.

Decarboxylation of 1-Carboxy-2-indanacetic Acid (XI).—The sodium salt of 1-carboxy-2-indanacetic acid prepared from 1.0 g. of the acid and aqueous sodium hydroxide was powdered and mixed with three times its weight of powdered soda-lime. The mixture was heated in a sublimation apparatus which was attached to a trap cooled with a Dry Ice–acetone mixture. The mixture was first heated at 260° and 0.5–0.6 mm. for 1 hr. and then at 310° for 2 hr. The distillate, which had the characteristic odor of indene, was dissolved in ether, washed with water, dried over magnesium sulfate and concentrated. The residue of 0.33 g. (63%) of impure indene was characterized as the picrate, prepared in ethanol, m.p. and mixed m.p. with an authentic sample 97–97.6°. A similar pyrolysis of the sodium salt of 3-indenecarboxylic acid yielded impure indene (20%).

Methyl 1H-Benz(*e*)indene-3-carboxylate (XVI).—A solution of 2.5 g. of sodium borohydride in 100 ml. of methanol was added to a solution of 10.0 g. of methyl 2,3-dihydro-1-oxo-1H-benz(*e*)indene-3-carboxylate (XIV)[13] in 400 ml. of methanol at 15–20°. The mixture was allowed to stand

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[10] L. F. Fieser, This Journal, **51**, 940 (1929).

[11] F. Mayer and A. Sieglitz, *Ber.*, **55**, 1855 (1922).

[12] R. Weissgerber, *ibid.*, **44**, 1436 (1911).

[13] R. H. Martin and P. Lambert, *Bull. soc. chim. Belg.*, **61**, 132 (1950).

overnight at room temperature, concentrated to about 120 ml. under reduced pressure and added to 50 ml. of water. The solution was adjusted to *p*H 7 with hydrochloric acid and extracted with ether. The extracts were washed with water, dried over magnesium sulfate and concentrated. The residue was the impure hydroxy ester, a mixture of an oil and a crystalline solid which melted at 118–119.2° after crystallization from aqueous acetone, but was not analytically pure. A solution of 1.6 g. of the crude hydroxy ester (the oil described above) in 25 ml. of dry benzene was treated with 1.0 g. of phosphorus pentoxide at room temperature for 15 minutes with intermittent shaking, which was continued for 2 hr. longer after addition of another 1.0-g. portion of phosphorus pentoxide. The organic layer was removed by decantation, and the solid residue was treated with water (50 ml.) and extracted with ether and then with benzene. The organic extracts were combined, washed with water and dried over magnesium sulfate. Removal of the solvents under reduced pressure gave a light yellow oil which on trituration with cold ether gave a white solid (100 mg., 7%), m.p. 267–269.2°, which was removed by filtration. Recrystallization from acetonitrile gave an analytical sample, m.p. 268.5–269.3°, of a by-product of unknown structure which is an isomer of the normal dehydration product described below.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.44. Found: C, 80.14; H, 5.62.

The filtrate remaining after removal of the above compound was concentrated and the residue sublimed at 100–140° (0.3 mm.). The white sublimate amounted to 550 mg. (42%) of XVI, m.p. 126.9–127.7°. Recrystallization from ether yielded an analytical sample, m.p. 127.8–128.4°, as fine white needles.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.44. Found: C, 80.09; H, 5.56.

A solution of 100 mg. of the ester XVI in 20 ml. of ethyl acetate was hydrogenated in the presence of 30 mg. of 10% palladium-on-Norit at room temperature. Hydrogen absorption amounted to 91% of one molar equivalent in 50 minutes. The product XVII was purified by crystallization from 30–60° petroleum ether with cooling in Dry Ice and amounted to 92 mg. (92%). The ester formed clusters of white needles, m.p. and mixed m.p. with an authentic sample of XVII described below, 34.1–35°.

Methyl 2,3-Dihydro-1H-benz(*e*)indene-3-carboxylate (XVII).—2,3-Dihydro-1H-benz(*e*)indene-3-carboxylic acid[14] was esterified with methanol in the presence of *p*-toluenesulfonic acid. The ester XVII was obtained in 81% yield after crystallization from 30–60° petroleum ether. An analytical sample had m.p. 34.6–34.8°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.23. Found: C, 79.46; H, 6.17.

Michael Addition of Dimethyl Malonate to Methyl 1H-benz(*e*)indene-3-carboxylate (XVI).—To a solution of sodium methoxide prepared from sodium (0.093 g.) and 25 ml. of anhydrous methanol was added a solution of dimethyl malonate (2.5 g.) in anhydrous methanol (25 ml.). A solution of methyl 1H-benz(*e*)indene-3-carboxylate (0.90 g.) in a mixture of dry toluene (90 ml.) and anhydrous methanol (10 ml.) was added rapidly with stirring. After the reaction mixture had been heated under reflux for 16 hr., it was cooled and glacial acetic acid (5 ml.) was added. The mixture was dissolved in ether, and the solution was washed with sodium bicarbonate solution, water and dried over magnesium sulfate. Removal of the solvent gave a dark colored oil (0.9 g.) which was subjected to a short-path distillation under reduced pressure. The unreacted starting material XVI (380 mg.) sublimed first and was removed. A pale yellow very viscous oil distilled at 200–230° (0.1 mm.) (442 mg., 53% of the slightly impure ester XVIII, based on the amount of methyl 1H-benz(*e*)indene-3-carboxylate that was not recovered).

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.44; H, 5.66. Found: C, 68.06; H, 5.76.

3-Carboxy-2,3-dihydro-1H-benz(*e*)indene-2-acetic Acid (III).—One hundred and eighty milligrams of the tricarboxylic acid ester described above was heated under reflux for 33 hr. with 20 ml. of 5% potassium hydroxide in 1:3 aqueous methanol. Removal of the methanol, followed by acidification with hydrochloric acid, precipitated a brown solid. An equal volume of concentrated hydrochloric acid was added, followed by glacial acetic acid (5 ml.), and the suspension was heated under reflux for 4 hr. The solution was separated from some dark undissolved material by decantation through glass wool, and the filtrate was allowed to stand overnight at 5°. A light brown solid was obtained (82 mg., 65%), m.p. 232.6–233.6°. Two recrystallizations from acetonitrile gave white crystals of III, m.p. 234.5–235.1°. A mixture of this acid with III obtained by saponification of the thermal rearrangement product of diethyl α-allyl-2-naphthalenemalonate (m.p. 234.5–235.2°) melted at 234.7–235.2°. The infrared spectra of samples of the acid from both sources were identical. The acid prepared by this method on treatment with acetic anhydride by the procedure described above formed the anhydride IV, identical with a sample of IV derived from the rearrangement product II.

Cambridge, Massachusetts

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[14] W. H. Linnell, D. W. Mathieson and D. T. Modi, *J. Chem. Soc.*, 3257 (1953).

[Contribution from the Organic Chemicals Division, St. Louis Research Department, Monsanto Chemical Co.]

Preparation of Some New 2-Chloroacetamides

By A. J. Speziale and P. C. Hamm

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The synthesis of some new N-substituted 2-chloroacetamides and 2′-chloroacetanilides is described. Some new intermediates used in the preparation of this new class of herbicides are also presented.

A study of the phytotoxicity of N-substituted 2-chloroacetamides has shown that many of them possess outstanding effectiveness and selectivity for the control of annual grasses.[1] The synthesis of those 2-chloroacetamides and intermediates which were prepared during the course of this study but not previously reported is presented here.

The 2-chloroacetamides listed in Table I were prepared from the appropriate amine and chloroacetyl chloride by the method given for N-butyl-2-chloroacetamide. Slight modifications of this method were used depending on the nature of amine and final product. Where the amine hydrochloride was available, it was used directly, the quantity of sodium hydroxide being altered accordingly.

The 2-chloroacetanilides bearing negative groups were prepared by the method of Jacobs and Heidelberger[2] or by refluxing equimolar amounts of the aniline derivative and chloroacetyl chloride in dry benzene. This latter method is described for 2,2′-dichloro-4-nitroacetanilide.

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[1] P. C. Hamm and A. J. Speziale, 127th Meeting, American Chemical Society, Cincinnati, Ohio, March 30–April 2, 1955.

[2] W. A. Jacobs and M. Heidelberger, This Journal, **39**, 1439 (1917).