with two 10-ml. portions of dichloromethane. The combined dichloromethane layers were washed with 20 ml. of 5% aqueous sodium bicarbonate and 10 ml. of water, then dried over magnesium sulfate, and evaporated to dryness *in vacuo* to give 0.5 g. of a sirup which had an infrared spectrum very similar to that of an authentic sample of tetrahydro-3aH-cyclopenta-1,3-oxathiolan-2-one (V).[3]

Treatment of crude V with methanolic sodium methoxide in the manner described previously[3] gave 0.25 g. (43% based on VI) of *cis*-2-mercaptocyclopentanol (IV), b.p. 75–85° (6–7 mm.), that had an infrared spectrum in complete agreement with that of an authentic sample.[3]

The distilled IV gave an 87% yield of a crystalline bisurethan, m.p 173–174°; there was no melting point depression when mixed with the authentic bisurethan of III.[3]

Methyl 2-O-(phenylthiocarbamoyl)-3,5-O-isopropylidene-β-D-xylofuranoside (VIII).[5] A solution of 2.7 g. of methyl 3,5-*O*-isopropylidene-β-D-xylofuranoside (VII)[3] in 27 ml. of toluene and 13.2 ml. of 1*N* methanolic sodium methoxide was evaporated to dryness *in vacuo*. The residue was dissolved in 27 ml. of hot toluene and re-evaporated to dryness *in vacuo*. The residual sodium salt was dissolved in 27 ml. of toluene at 80° and 1.73 ml. of phenyl isothiocyanate was added. Rapid precipitation of a gelatinous sodium salt took place before all the thiocyanate could be added. The thick gel was thinned by the addition of 27 ml. more of toluene and the mixture was heated in a bath at 85° for 15 min. while protected from moisture. After the addition of 1.7 ml. of acetic acid and 50 ml. of water, the mixture was shaken until the solids dissolved. The separated toluene layer was washed with water, then evaporated to dryness *in vacuo* to give 3.7 g. of an oil which contained unreacted phenyl isothiocyanate. The oil darkened on standing but crystallized after 8 days. The waxy solid was dissolved in 25 ml. of warm benzene, then diluted with 75 ml. of hexane. The solution was clarified with Norit, then diluted with an additional 25 ml. of hexane

The solution was stored at 3° overnight to afford, after filtering and washing with 15% benzene in hexane, 2.0 g. (45%) of product, m.p. 92–96°.

A second recrystallization gave the analytical sample, m.p. 94–96° (resolidifies and remelts at 101–102°); $\lambda_{max(\mu)}^{Nujol}$ 6.19 (phenyl), 6.42 (NH of thiourethan), 6.65 (phenyl + C = S).

Anal. Calcd. for $C_{16}H_{21}NO_6S$: C, 56.7; H, 6.25; N, 4.13; S, 9.43. Found: C, 56.8; H, 6.08; N, 4.07; S, 9.06.

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[5] Prepared originally at Southern Research Institute by one of the authors (B. R. B.).

Synthesis of 2-Indenylacetic Acid

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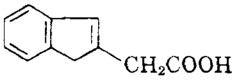
For some synthetic experiments, 2-indenylacetic acid (I) was required. Its formation as a by-product in the treatment of 1-hydroxy-2-indenylacetic acid with hydrobromic acid, has been claimed[1]; however, the reported melting point (150–160°) is not that of authentic (I). Very recently,[2] I has been obtained in 23% over-all yield, among other products in the Reformatsky reaction between 2-hydrindone and ethyl bromoacetate; the hydroxy ester (II) formed was dehydrated with formic acid and the unsaturated ester so obtained hydrolyzed to I. We report here on some alternative possibilities for the preparation of I.

When 2-hydrindone was heated with malonic acid, pyridine, and piperidine, only self-condensation took place.[3]

Condensation of the not very stable enamine (III) of 1-hydrindone with ethyl bromoacetate[4] resulted in an ester of the expected composition (IV), but only in 14% yield (calculated on 1-hydrindone).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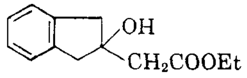
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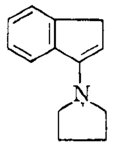
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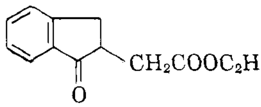
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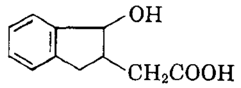
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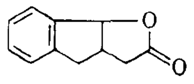
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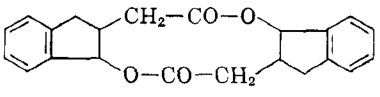
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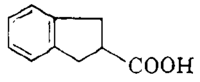
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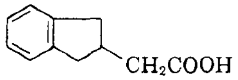
IX

A promising starting material appeared to be 1-hydroxy-2-hydrindylacetic acid (V) which is obtained[1] from ethyl acetoacetate and indene bromohydrin. However, V gave with hydrobromic acid or oxalic acid or under the conditions of reduction with hydriodic acid in glacial acetic acid, only the lactone (VI) which had been described before by Peacock and Menon[1] and was also formed when the methyl ester of V was treated with thionyl chloride or phosphorus oxychloride in pyridine. The lactone (VI) remained unchanged when heated with 85%

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[1] D. H. Peacock and B. K. Menon, *J. Chem. Soc.*, 1296 (1934).

[2] H. Ahmed and N. Campbell, *J. Chem. Soc.*, 4115 (1960).

[3] Ch. K. Ingold and J. F. Thorpe, *J. Chem. Soc.*, **115**, 143 (1919).

[4] According to the general method of G. Stork, R. Terrell, and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954).

phosphoric acid at 100°. Heating of V with potassium hydrogen sulfate in toluene gave a high melting (above 300°) product which may be a dimeric lactone (VII).

The acid (I) was finally obtained in an overall yield of 53% by the following conventional method: Hydrindene-2-carboxylic acid (VIII), which is available from *o*-xylylene dibromide and ethyl acetoacetate[5] or diethyl malonate[6] in 55 and 69% yield, respectively, was subjected to the Arndt-Eistert reaction and yielded in 88% yield 2-hydrindylacetic acid (IX). Its methyl ester gave with *N*-bromosuccinimide the methyl ester of I in 80% yield.

EXPERIMENTAL

2-Carbethoxymethyl-1-hydrindone (IV). A mixture of 1 mole of 1-hydrindone, 2 moles of pyrrolidine and 600 ml. of benzene was subjected to azeotropic distillation. The enament (III) boiled at 142–144° (2 mm.); 165° (5 mm.); yield, 65 g. (35%). As the product proved to be unstable, it was immediately treated as follows: A mixture of 61 g. of the enamine, 55 g. of ethyl bromoacetate, and 180 ml. of benzene was heated on the water bath at 80° for 15 min. Water (90 ml.) was added and the benzene layer separated and distilled. B.p. 127–133° (0.01 mm.); yield, 30 g. (41%).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.6; H, 6.4. Found: C, 70.2; H, 6.5.

1-Hydroxy-2-hydrindylacetic acid (V) was prepared according to the literature[1] and recrystallized from chloroform or water, m.p. 131°.

The methyl ester was prepared with diazomethane, b.p. 118° (0.005 mm).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.9; H, 6.8. Found: C, 69.8; H, 6.5.

We also prepared the following derivatives of V.

1-Hydroxy-2-hydrindylacetamide. A mixture of 6 g. of the methyl ester of V and concentrated ammonia was kept at room temperature for 2 days and the solid product recrystallized from ethanol; m.p. 170–171°, yield, 3 g. (55%).

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.1; H, 6.8. Found: C, 69.2; H, 7.5.

1-Hydroxy-2-hydrindylacetonitrile. A mixture of 6 g. of the amide and 6 g. of phosphorus pentoxide was distilled *in vacuo* (b.p. 170–200°, 20 mm.) and the distillate dissolved in benzene. The solution was washed with water, dried, and concentrated and the solid residue recrystallized from ethanol, m.p. 73°.

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.3; H, 6.4. Found: C, 76.1; H, 5.8.

The lactone (VI), m.p. 73° from toluene or petroleum ether, b.p. 100° (0.5 mm), was formed in the following experiments: (a) from 20 g. of the acid (V) in 100 ml. of anhydrous alcohol with gaseous hydrogen bromide for 6 hr.; yield, 15 g. (83%); (b) from 5 g. of the acid (V) and 10 g. of oxalic acid in 125 ml. of boiling toluene; (c) from 5 g. of the acid (V), 0.75 g. of red phosphorus, 0.25 g. of iodine, 12.5 ml. of glacial acetic acid, and 0.25 ml. of water at boiling temperature for 3 hr.; yield, 3.5 g. (78%); (d) from 10 g. of the methyl ester of V with 7 ml. of phosphorus oxychloride in 16 ml. of pyridine; (e) from 11 g. of the methyl ester of V with 4 g. of thionyl chloride in 4 g. of pyridine at 100° for 1 hr.; yield, 7 g. (77%).

Dimeric anhydride (VII) (?). A mixture of 10 g. of the acid (V), 10.6 g. of potassium hydrogen sulfate, and 200 ml. of toluene was refluxed azeotropically for 4 hr. The resulting product was washed with water, dried, and concentrated and the remaining solid product (4 g.; 40%) recrystallized from chloroform m.p. about 300°.

Anal. Calcd. for $C_{22}H_{20}O_4$: C, 75.9; H, 5.8. Found: C, 75.7; H, 6.1.

Hydrindene-2-carboxylic acid (VIII), from water, m.p. 130, was obtained in 55% yield from *o*-xylylene dibromide, ethyl acetoacetate, and sodium ethoxide according to Scherks[4] and in 69% yield with diethyl sodiomalonate *via* hydrindene-2,2-dicarboxylic acid, m.p. 193°, according to Baeyer and Perkin.[6]

Chloride. A mixture of 22.5 g. of VIII and 50 ml. of thionyl chloride was gently heated until dissolution. Then the excess of thionyl chloride was removed *in vacuo* and the residue twice dissolved in benzene and again concentrated *in vacuo*, b.p. 90–94° (0.7 mm); 108° (2.5 mm). The chloride crystallized upon standing; m.p. 38°. Yield, 19.5 g. (83%).

2-Hydrindylacetic acid (IX). At a temperature of −10°, 18.5 g. of the chloride of VIII was added slowly to an ethereal solution of excess diazomethane (from 61.8 g. of nitrosomethylurea). After 12 hr. at room temperature, the ether was evaporated. The remaining yellowish needles of the diazoketone melted at 47° dec.. It was dissolved in a mixture of 35 ml. of benzyl alcohol and 35 ml. of collidine and decomposed in batches of 5 ml. at 180°. To the combined resulting solutions, 100 ml. of benzene was added and the solution washed with dilute hydrochloric acid and water and freed from benzene. The product was hydrolyzed for 4 hr. with 25 ml. of 50% aqueous potassium hydroxide and 50 ml. of methanol, diluted with water and, after extraction with ether. acidified. Yellowish crystals, which melted at 91° after recrystallization from petroleum ether (b.p. 60–80°) or nitromethane. Yield, 14.5 g. (88%).

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.0; H, 6.8. Found: C, 75.4; H, 7.3.

The *methyl ester* was prepared from 17.9 g. and diazomethane in 75% yield (14.5 g.), b.p. 90° (0.7 mm); $n_D^{26.5}$ 1.5168.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4. Found: C, 75.4; H, 7.7.

Methyl 2-indenylacetate (as I). A mixture of 13.6 g. of the foregoing ester, 12.8 g. of *N*-bromosuccinimide and 125 ml. of carbon tetrachloride was refluxed for 90 min., filtered, and concentrated. The residue was refluxed for 2 hr. with 15 ml. of pyridine and 40 ml. of benzene. The solution was washed with dilute hydrochloric acid and water and concentrated, and the product distilled *in vacuo*, b.p. 95–96° (0.01 mm.);[2] $n_D^{26.5}$ 1.5441. Yield, 11 g. (80%).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.6; H, 6.4. Found: C, 76.3; H, 6.3.

2-Indenylacetic acid (I), obtained by alkaline hydrolysis of the ester, was recrystallized from nitromethane and melted at 124°(lit.,[2] m.p. 116–117°); yield, practically quantitative.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.9; H, 5.8. Found: C, 75.9; H, 5.9.

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The Synthesis of Some *vic*-Dihalo-1,2-dihydrodicyclopentadienenitroso Halides

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During the course of an investigation of the monomerization of the nitroso chloride dimer (I) of *endo*-dicyclopentadiene, we had occasion to prepare

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(5) E. Scherks, *Ber.*, **18**, 378 (1885).

(6) A. N Baeyer and H. W. Perkin, *Ber.*, **17**, 122 (1884).