

805. *The Reformatsky Reaction on the Tetralones and Indanones.*

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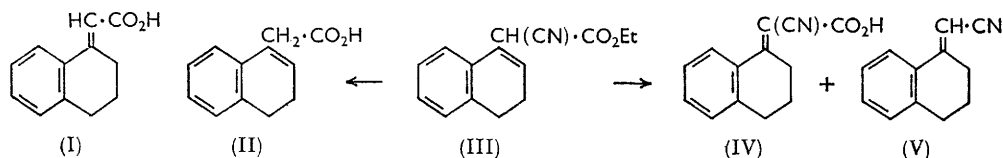
The constitutions of the unsaturated acids obtained by the interaction of ethyl bromoacetate and zinc with tetralones and indanones have been established.

By interaction of 1-tetralone and ethyl bromoacetate in the presence of zinc followed by dehydration of the resulting hydroxy-ester Schroeter¹ obtained a mixture of unsaturated acids which he claimed to have separated into "sehr reine Säuren" m. p. 90—92°, 106°, and 163—164°. To two of these he assigned the respective structures (I) and (II), but for the third he advanced only the formula $C_{12}H_{12}O_2$. von Braun *et al.*² had previously, by the same reaction, isolated an acid, m. p. 100°, which they considered to be the endo-unsaturated acid (II), but which Schroeter considered to be a mixture. Schroeter's work

¹ Schroeter, *Ber.*, 1925, **58**, 713.

² von Braun, Gruber, and Kirschbaum, *Ber.*, 1922, **55**, 3664.

is not entirely convincing, notably his evidence for the structure of the acid (II) by converting it into a keto-aldehyde for which he gave no structural proof beyond the formation of a semicarbazone, the analytical figures of which were poor.



We have therefore repeated Schroeter's work and in part have substantiated his conclusions. Three acids were obtained, m. p. 90—100°, 106°, and 162—163°, and Schroeter's structure (II) for the acid, m. p. 106°, was confirmed by the similarity of its spectrum to that of 1,2-dihydronaphthalene,³ by its decarboxylation with dilute sulphuric acid to 1,2-dihydro-4-methylnaphthalene, and by the colourless acylurea it gives with di-(*p*-dimethylaminophenyl)carbodi-imide.⁴ It forms a dibromide and cannot be isomerised to the exo-unsaturated acid by alkali.

The acid, m. p. 162—163°, is a carboxylic acid (ν_{\max} . 1687 cm^{-1}) although it is not extracted from ether by sodium carbonate.⁵ It is an $\alpha\beta$ -unsaturated acid (I) since it forms a yellow acylurea,⁴ yields 1-tetralone with ozone, and although containing a double bond conjugated to the benzene ring reacts extremely slowly with bromine. It is not isomerised by alkali. Its configuration is probably that represented in formula (I) since its absorption spectrum, λ_{\max} . 271 $\text{m}\mu$ ($\log \epsilon$ 4.19), is strikingly similar to that⁶ of *trans*-cinnamic acid, λ_{\max} . 273 $\text{m}\mu$ ($\log \epsilon$ 4.32) and different from that of *cis*-cinnamic acid, λ_{\max} . 264 $\text{m}\mu$ ($\log \epsilon$ 3.42).

Like Schroeter, we obtained by laborious purification a small quantity of an acid, m. p. 90—92° (capillary). On the Kofler hot-plate, however, although much of the acid melted in this range the m. p. was 90—100° and even at 110° a few crystals still remained. The acid is probably the endo-unsaturated acid (II) contaminated with a little exo-isomer (I). The presence of the former acid was established by the formation of the dibromide, the strong absorption at 264 $\text{m}\mu$, the formation of a very pale yellow acylurea contaminated by colourless crystals, and (less conclusively) by paper chromatography. The exo-unsaturated acid was detected by formation of 1-tetralone on ozonolysis.

An attempt was made to prepare some or all of the above acids by hydrolysis of the product (III) obtained by condensing 1-tetralone with ethyl cyanoacetate.⁷ The cyano-dihydro-ester (III) failed to give tetralone on ozonolysis and was hydrolysed by alkali to the endo-unsaturated acid (II), m. p. 106—107°. With concentrated hydrochloric acid or a mixture of sulphuric acid, acetic acid, and water the ester underwent hydrolysis to 1-tetralone, but with hydrochloric acid and ethanol it yielded the cyano-acid (IV) and the unsaturated nitrile (V). Both products contain an exo-double bond since they exhibit phenyl conjugation and yield 1-tetralone on ozonolysis, while in addition the acid forms a yellow acylurea. Double-bond migration in the presence of acid is, of course, well known,⁸ but the bond migration observed when the ester is treated with hydrochloric acid is perhaps unexpected.

The unsaturated acid (VI) obtained on interaction of ethyl bromoacetate, zinc, and 2-tetralone was assigned this constitution on the basis of its styrene-like absorption.⁹ Repetition of this work gave the expected hydroxy-ester, probably mixed with some unsaturated ester. Alkaline hydrolysis gave the hydroxy-acid, which was dehydrated by acetic anhydride to the unsaturated acid (VI). Dehydration of the hydroxy-ester with

³ Morton and Gouveia, *J.*, 1934, 916.

⁴ Zetzsche and Röttger, *Ber.*, 1939, 72, 1599; Campbell and Crombie, *Chem. and Ind.*, 1959, 600.

⁵ Cf. Johnson, Petersen, and Schneider, *J. Amer. Chem. Soc.*, 1947, 69, 74.

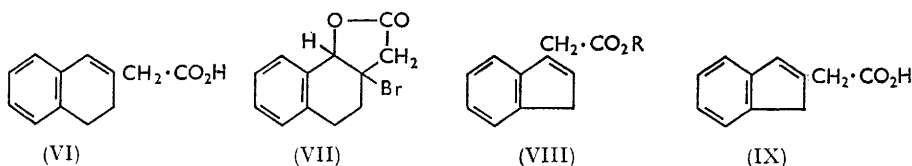
⁶ Gillam and Stern, "Electronic Absorption Spectroscopy," Arnold Ltd., London, 1957, p. 269.

⁷ Cf. Johnson, Johnson, and Petersen, *J. Amer. Chem. Soc.*, 1946, 68, 1929.

⁸ *E.g.*, Rupe *et al.*, *Ber.*, 1902, 35, 4265; 1907, 40, 2813.

⁹ Dauben and Teranishi, *J. Org. Chem.*, 1951, 16, 550.

thionyl chloride and pyridine, anhydrous formic acid, or acetic anhydride gave the unsaturated ester, which on saponification yielded the acid (VI), whose structure was established by its phenyl conjugation (λ_{max} , 270 m μ ; $\log \epsilon$ 3.98), formation of a colourless acylurea, and failure to detect 2-tetralone after ozonolysis. Bromine added spontaneously to the $\beta\gamma$ -unsaturated acid with the formation of the bromo-lactone (VII). Unlike the 3,4-dihydro-1-naphthylacetic acid (II), the acid (VI) did not undergo decarboxylation with dilute sulphuric acid, possibly because it is not sterically hindered.¹⁰ The acid was unchanged by hot dilute alkali.



1,1-Dimethyl-2-tetralone with ethyl bromoacetate and zinc gave the expected hydroxy-ester, but neither the ester nor the acid was dehydrated by formic acid, thionyl chloride and pyridine, or acetic anhydride. This is in marked contrast to 1-hydroxy-2,2-dimethylcyclohexylacetic acid which is readily dehydrated by acetic anhydride to 2,2-dimethylcyclohexylideneacetic acid.¹¹

Indan-1-one similarly gave an unsaturated ester, reported to contain an exo-double bond since it was oxidised by potassium permanganate to indan-1-one.¹² The ester was stated to resinify in alkali and with dilute sulphuric acid to yield mostly 3-methylindene and a trace of an acid, m. p. 85–86°, which was not analysed but for which von Braun suggested the exo-double-bond structure. The unsaturated ester is probably the endo-unsaturated compound (VIII; R = Et), since as just stated it yields 3-methylindene with sulphuric acid and with alkali, contrary to von Braun's statement, gives 3-indenylacetic acid (VIII; R = H), m. p. 95–96°, identical with the acid obtained by the reduction of benzofulvene carboxylic acid,¹³ whose structure is proved by the similarity of its ultraviolet absorption spectrum to that of indene,¹⁴ its colourless acylurea, and its formation of an anisylidene derivative with *p*-anisaldehyde.

Indan-2-one with ethyl bromoacetate and zinc yielded the hydroxy-ester, which was hydrolysed to the hydroxy-acid and was dehydrated by formic acid to an unsaturated ester. Hydrolysis of this ester and acidification yielded 2-indenylacetic acid (IX), whose constitution followed from its phenyl conjugation, formation of a colourless acylurea, and failure to obtain indan-2-one by ozonolysis.

Our results indicate that the unsaturated acids obtained from the tetralones and indanones contain the double bond in the ring, except that some exo-unsaturated acid is obtained from 1-tetralone. This is in harmony with the conclusions of previous workers on 2-phenyl-1-tetralone¹⁵ and 2-phenylindan-1-one,¹⁶ both of which yield the endo-unsaturated acid. It is plausible to assume that in the hydroxy-esters and -acids obtained by the Reformatsky reaction on the tetralones the $\text{CH}_2\text{CO}_2\text{Et}$ and the OH group attach themselves to the nucleus by an equatorial and axial bond respectively. Models¹⁷ show that water may then be lost to give either an endo- or an exo-double bond, since the necessary planar four-centre grouping is present. In the indane series also there seems no stereochemical reason why an endo- or an exo-bond should be preferentially formed. It therefore seems difficult to predict the course taken to yield unsaturated acids, though

¹⁰ Schubert, Donohue, and Gardner, *J. Amer. Chem. Soc.*, 1954, **76**, 9.

¹¹ Elliott and Linstead, *J.*, 1938, 776.

¹² von Braun, Danziger, and Koehler, *Ber.*, 1917, **50**, 56.

¹³ Thiele and Rüdiger, *Annalen*, 1906, **347**, 282.

¹⁴ Donbrow, *J.*, 1959, 1964.

¹⁵ Newman, *J. Amer. Chem. Soc.*, 1938, **60**, 2947.

¹⁶ Campbell and Ciganek, *J.*, 1956, 3834.

¹⁷ Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21.

it might be hazarded that the products where possible would contain the carboxyl group conjugated with the phenyl nucleus. This obviously does not obtain. It was expected, however, from the observation that 1-tetralone gave some exo-unsaturated acid, that the indanones would also furnish some exo-unsaturated acid since Brown *et al.*¹⁸ have suggested that five-membered rings favour exo-double-bond formation when compared with their six-membered analogues. No such double bonds could be detected. This is in keeping with the failure of 3-indenylacetic acid to isomerise with alkali, which led Wüest¹⁹ to conclude that five-membered rings are reluctant to replace an endo- by an exo-double bond. It is to be noted that phenyl conjugation occurs in all our unsaturated acids and, in one instance, the hydroxy-acid from 1,1-dimethyl-2-tetralone where such conjugation could not result, no dehydration was effected.

EXPERIMENTAL

M. p.s, unless otherwise stated, were determined on the Kofler apparatus. Acylureas were prepared from the acids and di-(*p*-dimethylaminophenyl)carbodi-imide.⁴ In the Reformatsky reactions zinc wool, washed with dilute hydrochloric acid, water, acetone, and then dried was used.

Reformatsky Reaction with 1-Tetralone.—1-Tetralone (50 g., 0.343 mole) was added with vigorous stirring to zinc wool (18 g., 0.277 g.-atom), benzene (300 ml.), and ethyl bromoacetate (60 g., 0.36 mole) previously warmed to 60°. After the initial vigorous reaction had subsided the mixture was boiled for 1½ hr. The hot solution was decanted, methanol was added until a clear solution was obtained, and dilute sulphuric acid (400 ml.) added. The aqueous solution was twice extracted with benzene (50 ml.), and the combined benzene solutions were washed with water, dried, and distilled. Ethyl 1,2,3,4-tetrahydro-1-hydroxy-1-naphthylacetate (50 g.) distilled at 185—190°/10 mm. The ester (5 g.) in water (20 ml.) and 40% methanolic potassium hydroxide (5 ml.) were kept at room temperature for 24 hr. and then warmed to 60° for 20 min. Addition of water and dilute hydrochloric acid gave the hydroxy-acid as a colourless oil [*acylurea*, prismatic needles (from acetone), m. p. 172—173° (Found: N, 11.3. C₂₉H₃₄N₄O₃ requires N, 11.5%)]. The ester (40 g.) was heated with anhydrous formic acid (120 ml.) for 15 min., and the formic acid was removed by blowing air through the hot solution. The unsaturated esters (30 g.) distilled at 190—195°/8 mm., and were boiled for 2 hr. with 10% methanolic potassium hydroxide (200 ml.). Most of the alcohol was removed by distillation. Addition of water and hydrochloric acid gave a mixture of unsaturated acids (18 g.), m. p. 84—98°. The ether layer was shaken with sodium hydrogen carbonate solution. The ether layer yielded 1,2,3,4-tetrahydro-1-naphthylideneneacetic acid (1.2 g.), prismatic needles (from light petroleum), m. p. 162—163° (Found: C, 76.2; H, 6.6. C₁₂H₁₂O₂ requires C, 76.6; H, 6.4%), λ_{max.} 270—271 mμ (log ε 4.19) in EtOH, ν (in Nujol) 1687 cm.⁻¹ (Ar-CH:CH-CO₂H) [*acylurea*, yellow needles (from acetone), m. p. 176—177° (Found: N, 11.5. C₂₉H₃₂N₄O₂ requires N, 12.0%), λ_{max.} 272 mμ (log ε 4.57) in EtOH. Ozonolysis of the acid yielded 1-tetralone (dinitro-phenylhydrazone, m. p. 258—259°). The aqueous layer with dilute hydrochloric acid gave a mixture of acids, 10 g. of which were repeatedly boiled with water (200 ml.), the hot clear solutions being decanted. The oily residue from boiling light petroleum (b. p. 80—100°) gave 3,4-dihydro-1-naphthylacetic acid, m. p. 106—107° (Schroeter¹ gives m. p. 106°); the filtrate on concentration gave an impure acid, m. p. 90—92° (capillary) after repeated crystallisation from light petroleum. The combined decanted aqueous solutions, when cold, deposited 3,4-dihydro-1-naphthylacetic acid (6 g.), prismatic needles (from light petroleum), m. p. 107°, λ_{max.} 262 mμ (log ε 3.85) [*acylurea*, colourless prisms (from acetone), m. p. 162—163° (Found: N, 11.6. C₂₉H₃₂N₄O₂ requires N, 12.0%)]. The acid (5 g.), when boiled with dilute sulphuric acid (100 ml.) until the evolution of carbon dioxide ceased, gave 1,2-dihydro-4-methylnaphthalene (2.5 g.), b. p. 105—107°/14 mm., λ_{max.} 262 mμ (log ε 3.83) in EtOH, which with chloranil in boiling xylene (4 hr.) yielded 1-methylnaphthalene [picrate, m. p. 141—142° (lit., 141—142°); trinitrobenzene derivative, m. p. 154° (lit., 154°)]. The ozonolysis product could not be

¹⁸ Brown, Brewster, and Shechter, *J. Amer. Chem. Soc.*, 1954, **76**, 467; Brown, *J. Org. Chem.*, 1957, **22**, 439; Gil-av and Shabtai, *Chem. and Ind.*, 1959, 1630; Turner and Garner, *J. Amer. Chem. Soc.*, 1958, **80**, 1424.

¹⁹ Wüest, *Annalen*, 1918, **415**, 299.

identified. The acid (1 g.), on treatment in cold ether (15 ml.) with bromine followed by precipitation with light petroleum, gave the *dibromide*, prisms (from ether–light petroleum), m. p. 148–150° (decomp.) (Found: Br, 45.5. $C_{12}H_{12}Br_2O_2$ requires Br, 45.9%).

The three acids were “spotted” on a sheet of Whatman No. 1 paper and ethanol, concentrated ammonia, and water (80:4:16) were allowed to run down the paper (16 hr.). The paper was dried and sprayed with Bromocresol (sodium salt). The acids, m. p. 106–107° and 90–92°, travelled at the same rate and gave yellow spots with a violet fluorescence in ultra-violet light. The other isomer could not be traced. This suggests that the acid, m. p. 90–92°, is an impure sample of the acid, m. p. 106–107°.

Condensation of Ethyl Cyanoacetate with 1-Tetralone.—Tetralone (60 g.), ethyl cyanoacetate (46.6 g.), ammonium acetate (6.4 g.), acetic acid (19 g.), and benzene (150 ml.) were heated under a Dean and Stark water separator. Fractional distillation of the product yielded ethyl α -cyano-3,4-dihydro-1-naphthylacetate (36 g.), b. p. 202–206°/9 mm. This cyano-ester (2 g.) gave 1-tetralone when boiled (6 hr.) with concentrated hydrochloric acid (50 ml.) or with 40 ml. each of concentrated sulphuric acid, acetic acid, and water. When boiled with sodium hydroxide (5 g.) in water (40 ml.) and ethanol (20 ml.) until evolution of ammonia ceased the cyano-ester (2 g.) yielded 3,4-dihydro-1-naphthylacetic acid, m. p. and mixed m. p. 106–107°. Ozonolysis of the cyano-ester gave a product which certainly did not contain 1-tetralone.

The cyano-ester (5 g.) was boiled for 3½ hr. with ethanol (400 ml.) and concentrated hydrochloric acid (400 ml.). Water (500 ml.) was added and the mixture extracted several times with ether. The combined ether extracts were washed with water and shaken with sodium hydrogen carbonate solution. (a) The alkaline aqueous layer with dilute sulphuric acid gave α -cyano-1,2,3,4-tetrahydro-1-naphthylideneacetic acid, needles (from aqueous ethanol), m. p. 172–178° (decomp.) (Found: C, 73.8; H, 5.4; N, 6.3. $C_{13}H_{11}NO_2$ requires C, 73.3; H, 5.1; N, 6.6%), λ_{max} . 286 m μ (log ϵ 4.13) in EtOH [*acylurea*, yellow prisms, m. p. 150–151° (Found: N, 13.8. $C_{30}H_{31}N_5O_2$ requires N, 14.2%)]. The cyano-acid with ozone in ethyl acetate gave 1-tetralone. (b) The ether on evaporation gave 1-cyanomethylenetetralin, which after trituration with light petroleum in solid carbon dioxide–acetone crystallised from light petroleum or aqueous methanol, then having m. p. 69–70° (Found: C, 85.1; H, 6.6; N, 8.4. $C_{12}H_{11}N$ requires C, 85.15; H, 6.5; N, 8.35%), λ_{max} . 278 m μ (log ϵ 4.28) in EtOH. Ozonolysis in ethyl acetate yielded 1-tetralone.

Reformatsky Reaction on 2-Tetralone.—2-Tetralone was treated with zinc and ethyl bromoacetate according to the method of Dauben and Teranishi⁹ except that an initial addition of iodine (0.5 g.) was made. The product was shown by analysis and ultraviolet spectrum to be a mixture of hydroxy-ester and unsaturated ester. The mixed esters (5 g.), water (20 ml.), and 40% methanolic potassium hydroxide (4 ml.) were kept for 24 hr. and then warmed (20 min.). Working up in the usual way gave a mixture of two substances, m. p.s 56–60° and 80–84°. The mixture was dissolved in warm benzene which after some time deposited prisms, m. p. 58–60° (capillary), subliming at 57–59°, m. p. 81–85° in the Kofler apparatus. The analytical figures (C, 66.4; H, 6.6%) indicate that it is a mixture of the hydroxy-acid and its hydrate (Acid: C, 69.9; H, 6.8. Hydrate: C, 64.3; H, 7.0%). The lack of unsaturation in the product is confirmed by λ_{max} . 266 m μ (log ϵ 2.70) and λ_{max} . 273 m μ (log ϵ 2.75) and by formation of the *acylurea* of the hydroxy-acid as colourless prisms (from acetone), m. p. 154–155° (Found: N, 11.1. $C_{29}H_{34}N_4O_2$ requires N, 11.5%).

The hydroxy-acid (1 g.) was warmed for 3 hr. with acetic anhydride (1.5 g.) and worked up in the usual way, to give 3,4-dihydro-2-naphthylacetic acid, m. p. and mixed m. p. 88–89°, identical with a sample prepared by saponification of the unsaturated ester. The acid, λ_{max} . 270 m μ (log ϵ 3.98), gave an *acylurea*, colourless needles, m. p. 138–139° (Found: N, 11.7. $C_{29}H_{32}N_4O_2$ requires N, 12.0%). The acid in ether was treated with bromine until absorption was complete. The ether was shaken with water and when slowly evaporated yielded 3a-bromo-2,3,3a,4,5,9b,hexahydronaphtho[1,2-b]furan-2-one (VII), needles (from light petroleum), m. p. 103–104° (Found: Br, 29.6. $C_{12}H_{11}BrO_2$ requires Br, 30.0%).

Reformatsky Reaction on 1,1-Dimethyl-2-tetralone.—1,1-Dimethyl-2-tetralone (21 g.) was added to zinc (9 g.), benzene (80 ml.), toluene (80 ml.), and ethyl bromoacetate (20 g.). After the initial violent reaction the mixture was boiled for 1 hr. and ethyl bromoacetate (20 g.) and zinc (18 g.) were added. Boiling was continued for 1 hr. and the addition of ester and zinc repeated. After further boiling (2 hr.) the mixture was cooled and decomposed by 3N-hydrochloric acid, and the aqueous layer was extracted with benzene (50 ml.). The combined

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organic layers were washed with water, dried (Na_2SO_4), and distilled to give the *ethyl 1,2,3,4-tetrahydro-2-hydroxy-1,1-dimethyl-2-naphthylacetate* (12 g.), b. p. 173—176°/10 mm. (Found: C, 74.3; H, 8.4. $\text{C}_{16}\text{H}_{22}\text{O}_3$ requires C, 73.3; H, 8.4%). The ester (2.5 g.), water (10 ml.), and 40% methanolic potassium hydroxide (2 ml.) were kept for 24 hr., then warmed at 60° for 20 min. Dilution with water and acidification gave a precipitate which was extracted with ether. Extraction of the ether with sodium hydrogen carbonate, followed by acidification, gave the *hydroxy-acid monohydrate*, needles (from benzene), m. p. 75—76° (capillary), subliming at *ca.* 75°, m. p. 101—102° (Kofler) (Found: C, 67.45; H, 7.85. $\text{C}_{14}\text{H}_{18}\text{O}_3 \cdot \text{H}_2\text{O}$ requires C, 66.7; H, 7.9%), λ_{max} 270 m μ (log ϵ 2.63), 262 m μ (log ϵ 2.63) (*acylurea*, m. p. 163—164°, identical with that described below). The hydroxy-ester (5 g.) was heated with anhydrous formic acid (25 ml.) for 20 min. Removal of the formic acid and fractionation gave a pale yellow liquid (3.5 g.), b. p. 170—175°/10 mm., which was hydrolysed by 40% methanolic potassium hydroxide. Addition of water and acidification gave the anhydrous *hydroxy-acid*, needles (from light petroleum, b. p. 60—80°), m. p. 101—102° (Found: C, 72.0; H, 7.75. $\text{C}_{14}\text{H}_{18}\text{O}_3$ requires C, 71.8; H, 7.7%), ν_{max} 3580 cm^{-1} , λ_{max} 272 (log ϵ 2.67), 265 m μ (log ϵ 2.67) [*acylurea*, colourless prismatic needles, m. p. 163—164° (Found: N, 11.4. $\text{C}_{31}\text{H}_{38}\text{N}_4\text{O}_3$ requires N, 10.9%)]. Attempts to dehydrate the acid were unsuccessful.

Reformatsky Reaction on Indan-1-one.—Indan-1-one (26.5 g.), zinc (13 g.), benzene (150 ml.), and ethyl bromoacetate (33.4 g.) gave (?) *ethyl 3-indenylacetate*, b. p. 152—155°/9 mm. (Found: C, 76.8; H, 7.0. $\text{C}_{13}\text{H}_{14}\text{O}_2$ requires C, 77.2; H, 6.9%). The ester (10 g.) was boiled (2 hr.) with 6N-sodium hydroxide (12 ml.) in methanol (150 ml.). Most of the alcohol was distilled off and the solution acidified with dilute sulphuric acid. 3-Indenylacetic acid (6 g.) crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 95—96° (Thiele and Rudiger¹³ give 95—96°), λ_{max} 253 m μ (log ϵ 3.98) [*acylurea*, colourless prisms (from acetone), m. p. 163—164° (Found: N, 11.9. $\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_2$ requires N, 12.3%)]. The acid (3 g.) was boiled with dilute sulphuric acid (60 ml.) and yielded 3-methylindene, b. p. 72—74°/9 mm. (picrate, m. p. 77—79°, and 1-*p*-anisylidene derivative, m. p. 111—112°) (Thiele and Bühner²⁰ report 195—197°/710 mm., 76—78°, and 113° respectively). The acid (0.2 g.) and *p*-anisaldehyde (0.25 g.) in ethanol (5 ml.) with ethanolic potassium hydroxide (4 ml.) gave on acidification after 1 hr. the 1-*p*-anisylidene derivative, yellow prisms (from ethanol), m. p. 178—180° (decomp.) (Found: C, 78.0; H, 5.4. $\text{C}_{19}\text{H}_{16}\text{O}_3$ requires C, 78.1; H, 5.5%). The acid in ether reacted with bromine, to give the slightly impure *bromo-lactone*, prisms (from ether—light petroleum), m. p. 152—154° (Found: Br, 34.0. $\text{C}_{11}\text{H}_8\text{BrO}_2$ requires Br, 31.5%).

Reformatsky Reaction of Indan-2-one.—Indan-2-one (13.2 g.), zinc (6.5 g.), ethyl bromoacetate (16.7 g.), and benzene (150 ml.) were warmed on the water-bath. Iodine (0.5 g.) was added. Two additions of zinc (8 g.) and ethyl bromoacetate (20 g.) were made (after 1 and 2 hr.) and boiling was continued for 2 hr. The cooled solution was decomposed by 3N-hydrochloric acid (200 ml.). The aqueous layer was twice extracted by benzene (40 ml.), and the combined benzene extracts were dried (Na_2SO_4) and distilled. The residue with ether yielded a solid (1.2 g.), needles (from benzene), m. p. 216—217° (Found: C, 89.7; H, 5.7%; *M*, 326). The substance is possibly the condensation product, 1,3-di-(2-indanylidene)indane ($\text{C}_{27}\text{H}_{20}\text{O}$ requires C, 90.0; H, 5.6%; *M*, 360). Removal of the ether gave *ethyl 2-hydroxy-2-indanylacacetate*, b. p. 162—166°/10 mm. (33% yield) (Found: C, 71.4; H, 7.5. $\text{C}_{13}\text{H}_{16}\text{O}_3$ requires C, 70.9; H, 7.3%). The hydroxy-ester (5 g.) was warmed for $\frac{1}{2}$ hr. with formic acid (30 ml.). Distillation gave the unsaturated *ester* (3.5 g.), b. p. 150—153°/10 mm. (Found: C, 76.6; H, 7.3. $\text{C}_{13}\text{H}_{14}\text{O}_2$ requires C, 77.2; H, 7.0%). The ester (3 g.) was boiled for 2 hr. with 6N-sodium hydroxide (4 ml.) and ethanol (40 ml.). Removal of the alcohol and acidification gave 2-indenylacetic acid, prisms (from light petroleum), m. p. 116—117° (sinters at 100°) (Found: C, 75.6; H, 6.0. $\text{C}_{11}\text{H}_{10}\text{O}_2$ requires C, 75.8; H, 5.8%), λ_{max} 257 m μ (log ϵ 4.05) [*acylurea*, colourless prisms, m. p. 160—162° (Found: N, 12.1. $\text{C}_{28}\text{H}_{30}\text{N}_4\text{O}_2$ requires N, 12.3%)]. The acid with dilute sulphuric acid gave a white solid, possibly the *trimer* of 2-indenylacetic acid, compact prisms (from aqueous ethanol), m. p. 228—230° (Found: C, 75.2; H, 6.2%; *M*, 506. $\text{C}_{33}\text{H}_{30}\text{O}_6$ requires C, 75.8; H, 5.8%; *M*, 522).

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²⁰ Thiele and Bühner, *Annalen*, 1906, **347**, 266.