in an oil-bath, and the apparatus was fitted with thermometers to measure the temperatures of the bath, of the reaction mixture and of the distilling vapors. The bath temperature was raised directly to 160°, at which point boiling commenced in the reaction mixture. The further progress of the reaction is shown in Table III.

TABLE III

Total time in hours	Temperature, °C. Bath	Pot	Vapor	Remarks
0	160	110	98	Started boiling. H_2O started distilling
1.25	158	129	104	
2.25	163	143	100	
3.25	170	150	100	
4.50	177	160	88	Distillation practically stopped
5.00	180	162	90	
5.50	185	165	123	
6.50	187	170	151	Dimethylformamide started distilling
7.75	187	175	133	
8.50	187	177	91	
10.50	185	178	64	Distillation practically stopped. Shut off

Following the period of heating, the reaction mixture was allowed to cool somewhat (it solidifies if allowed to cool to room temperature) and was poured into about twice its volume of water. This gave a milky suspension of oily unreacted ketone and product; acidification with hydrochloric acid removed the milkiness. On cooling, the unreacted ketone solidified; it was removed by filtration and dried. It weighed 86.4 g. (43.5%), and was of purity sufficient so that it could be used directly in another reaction.

The solution containing the product was made strongly alkaline with sodium hydroxide and was steam-distilled. The distillate was extracted with three portions of ether, and the combined ether extracts were washed with water and dried over anhydrous magnesium sulfate. The ether was evaporated, and the amine distilled at reduced pressure. The product was a colorless oil of b. p. 120–122° (14 mm.), and weighed 88.1 g. (38.6% conversion or 68.4% adjusted yield).

In other preparations of II according to the improved procedure, conversions[9] of 28, 46, 31, 33 and 36% and adjusted yields[9] of 73, 68, 97, 61 and 61%, respectively, have been obtained.

Preparation of II by the Eschweiler[12] Reaction.—*p*-Bromo-α-methylbenzylamine hydrochloride (0.02 mole) (prepared from *p*-bromoacetophenone by the Leuckart reaction) was sealed in a Pyrex tube with 4 g. of 40% formaldehyde solution, and the tube was heated three hours at 130°. The product was isolated as its picrate (m. p. 151.5–152°) in 34.5% yield. A mixed melting point with the picrate of II prepared from *p*-bromoacetophenone and dimethylamine was not depressed.

Acknowledgment.—To Miss Bonnie Souther the authors express their appreciation for her assistance in several of these experiments.

Summary

It is shown that the Leuckart reaction is a useful method for the synthesis of tertiary amines from ketones and dialkylformamides. Magnesium chloride catalysis is necessary.

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(12) Eschweiler, German Patent 80,520 (Dec. 17, 1893); Stevens, *J. Chem. Soc.*, 2107 (1930).

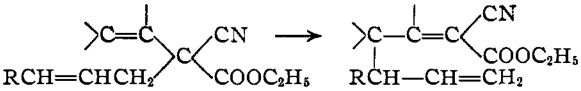
PORTLAND, OREGON RECEIVED SEPTEMBER 20, 1948

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

The Rearrangement of Allyl Groups in Three-Carbon Systems. V. Ethyl (3-Indenyl)-allylcyanoacetate

BY ARTHUR C. COPE AND LAMAR FIELD[1]

A number of (substituted vinyl)-allylcyanoacetic esters have been observed to rearrange in the following manner on heating at 170–200°[2]



(R = H or CH_3)

This paper reports an investigation of the rearrangement of ethyl (3-indenyl)-allylcyanoacetate (III), a crystalline ester previously prepared by Ingold and Thorpe.[3]

In the synthesis of III, 1-indanone (I) was condensed with ethyl cyanoacetate in the presence of ammonium acetate to give an ester (II) which could have either the α,β-unsaturated structure IIA or the β,γ-unsaturated structure IIB. Ingold and Thorpe considered that IIB was the correct formula because the ester formed a sodium enolate and could be alkylated to give III. It is now recognized that such evidence is inconclusive, because alkylidene cyanoacetic esters (such as IIA) can form sodium enolates by three-carbon tautomerism and can be alkylated. Comparison of the ultraviolet absorption spectra of the ester II and the alkylation product III obtained by treating II with sodium ethoxide and allyl bromide furnished convincing evidence concerning the structures of both compounds. The spectrum of III (curve 1, Fig. 2), coincides closely with the spectrum reported for indene itself,[4] which has the same conjugated system. The ester II, on the other hand, absorbs strongly at much longer wave lengths (curve 3, Fig. 2), and accordingly can be assigned structure IIA, in which the nitrile and carbethoxyl groups are included in the conjugated system.

Confirmation of the structure of III was obtained by a synthetic route, beginning with hydro-

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(1) Socony-Vacuum Oil Co. Fellow, 1947-1948.

(2) Cope and Hardy, THIS JOURNAL, 62, 441 (1940); Cope, Hoyle and Heyl, *ibid.*, 63, 1843 (1941); Cope, Hofmann and Hardy, *ibid.*, 63, 1852 (1941).

(3) Ingold and Thorpe, *J. Chem. Soc.*, 115, 143 (1919).

(4) Morton and de Gouveia, *ibid.*, 911 (1934).

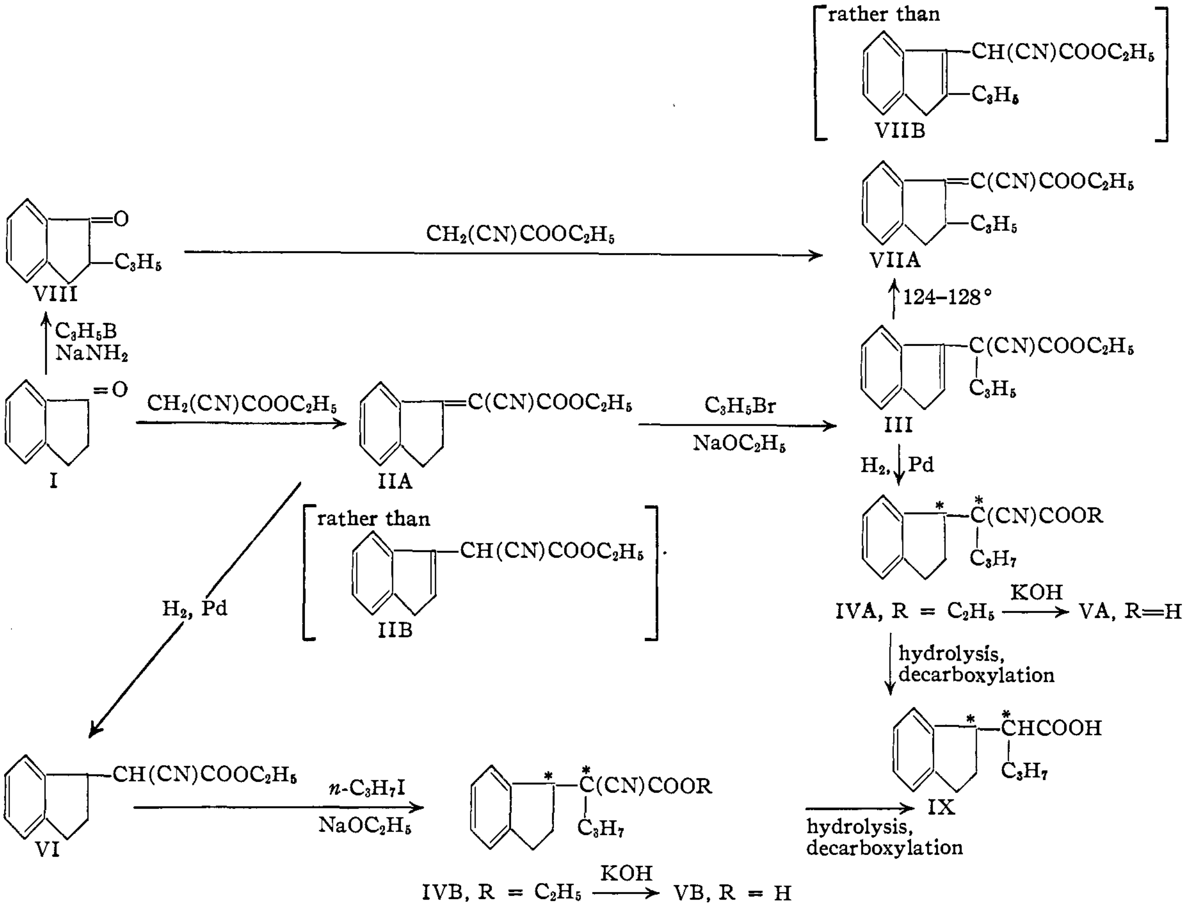

Fig. 1.—Asymmetric centers which make two diastereomers possible in IV, V and IX are indicated by an asterisk (*).

genation of III to ethyl (1-indanyl)-propylcyanoacetate, IVA. Hydrolysis of the liquid ester IVA yielded the crystalline (1-indanyl)-propylcyanoacetic acid, VA. Alkylation of ethyl (1-indanyl)-cyanoacetate (VI) with *n*-propyl iodide gave a crystalline ester, ethyl (1-indanyl)-propylcyanoacetate, IVB, which must be a diastereomer of IVA, and on hydrolysis yielded a diastereomeric form of (1-indanyl)-propylcyanoacetic acid (VB) which was not identical with VA. It was possible to relate the two series by comparison of products obtained by more drastic hydrolysis and decarboxylation. The acid VB on hydrolysis with potassium hydroxide in aqueous diethylene glycol followed by distillation was converted to a crystalline diastereomer of (1-indanyl)-propylacetic acid (IX). Saponification of IVA under similar conditions followed by distillation yielded a sample of (1-indanyl)-propylacetic acid (IX) which was identical with the sample of IX derived from VB(m. p. and mixed m. p.).

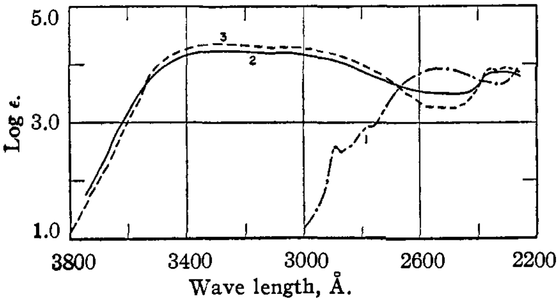

Fig. 2.—Ultraviolet absorption spectra: curve 1, ethyl (3-indenyl)-allylcyanoacetate (III); curve 2, ethyl (2-allyl-1-indanylidene)-cyanoacetate (VIIA); curve 3, ethyl (1-indanylidene)-cyanoacetate (IIA).

When the ester III was heated at 124–128° for three hours, an isomeric rearrangement product was isolated in 63% yield as a crystalline solid, m. p. 80.5–81°. The carbon skeleton of the rearrangement product was established beyond doubt by an independent synthesis of the same compound from the condensation of 2-allyl-1-indanone (VIII) with ethyl cyanoacetate (identity established by m. p. and mixed m. p.). The ultraviolet absorption spectrum of the rearrangement product (curve 2, Fig. 2) permits the assignment to it of the α,β-unsaturated structure VIIA, since the curve practically coincides with the curve for IIA and differs from the spectrum of III and indene. Accordingly, the shift of an allyl group in

III into the indene ring to give the α,β-unsaturated ester VIIA parallels exactly the previously observed rearrangements in which an allyl group migrated into an open-chain substituted vinyl group or a 1-cyclohexenyl group.[2]

Active hydrogen determinations on several of the esters in this series gave values which are consistent with the structures which are assigned to them. All of the esters liberated some methane from methylmagnesium iodide under the conditions used, presumably because of the acidity of the hydrogen in the 1-position of the indane or indene nucleus. However, the esters (IIA and VI) which could react to give enolates liberated one equivalent of methane, within experimental error (0.93 and 0.97 equivalent, respectively), while the others displaced fractional equivalents (III, 0.22 equivalent; IVB, 0.38 equivalent; IVA, 0.34 equivalent).

Experimental[5]

1-Indanone (I).—β-Phenylpropionyl chloride was prepared by the procedure of Ingold and Thorpe[3] and converted to I by a modification of procedures previously described.[6,7] A solution of 197.6 g. of β-phenylpropionyl chloride in 400 ml. of olefin-free dry commercial *n*-hexane was added to a suspension of 198 g. of anhydrous sublimed aluminum chloride in 75 ml. of hexane at the reflux temperature during ten minutes with mechanical stirring. The mixture was stirred for an additional ten minutes and poured onto ice. The product was extracted with ether and the solution was dried over magnesium sulfate. Upon concentration of the solution under reduced pressure 144.8 g. (93%) of I was obtained as a pale yellow solid, m. p. 35–38°.

Ethyl (1-Indanylidene)-cyanoacetate (IIA).—A mixture of 64.2 g. of ethyl cyanoacetate, 8.8 g. of ammonium acetate, 27.3 g. of glacial acetic acid, 115 ml. of benzene and 75 g. of 1-indanone was heated under vigorous reflux for seven hours, while the water formed was removed with a Dean and Stark type continuous separator.[8] The benzene solution was cooled, washed with water, dried over magnesium sulfate, treated with Darco and concentrated under reduced pressure. Crystallization of the solid residue from ethanol yielded 87.8 g. (68%) of IIA, m. p. 104–104.5°. After recrystallization from ethanol to constant m. p. IIA formed colorless needles, m. p. 104.5–105.5°. Ingold and Thorpe[3] report m. p. 104° for this compound (which they assigned structure IIB). A sample liberated 0.93 equivalent of methane in a Zerewitinoff determination, presumably forming an enolate through three-carbon tautomerism. A carbon tetrachloride solution of the unsaturated ester IIA did not decolorize a dilute solution of bromine and decolorized a more concentrated solution only with the evolution of hydrogen bromide. An acetone solution rapidly decolorized 2% aqueous potassium permanganate. This behavior is consistent with the α,β-unsaturated structure IIA.

Ethyl (3-Indenyl)-allylcyanoacetate (III).—A procedure similar to one used for the alkylation of a number of alkylidene-cyanoacetic esters[9] was employed for the preparation of III. IIA (20.0 g.) was added to a solution of sodium ethoxide prepared from 2.0 g. of sodium and 70 ml. of absolute ethanol, cooled to −5°. The mixture was stirred at −10 to −5° for forty-five minutes, after which 15.0 g. of allyl bromide was added and the mixture was heated rapidly to the reflux temperature, which was maintained for three minutes. The resulting suspension was cooled, poured into water, and extracted with ether. The extract was washed with water, dried over magnesium sulfate, treated with Darco and concentrated under reduced pressure. The sirup crystallized on seeding, and was recrystallized from a mixture of equal parts of pentane and hexane containing 15% of ether; yield 8.4 g. (36%), m. p. 59–60°. An analytical sample of III was obtained as fine colorless crystals with a constant m. p. of 59–60° by recrystallization from the same solvent and from cyclohexane. Ingold and Thorpe[3] report m. p. 65° for III.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.41; active hydrogen, none. Found: C, 76.23; H, 6.42; active hydrogen, 0.22 equivalent.

Ethyl (1-Indanyl)-cyanoacetate (VI) and (1-Indanyl)-cyanoacetic Acid.—A solution of 20.7 g. of ethyl (1-indanylidene)-cyanoacetate (IIA) in 180 ml. of purified dioxane absorbed hydrogen very slowly on catalytic reduction in the presence of 1.0 g. of palladium-on-Norite catalyst[10] at room temperature and pressure. The mixture was filtered, 3.0 g. of palladium-on-Norite was added, and the temperature was raised to approximately 70° during seven hours. After twenty-three hours 2.72 l. (133%) of hydrogen had been absorbed. The catalyst was separated and the solution was concentrated under reduced pressure. A solution of the residue in benzene was washed with 1 *N* hydrochloric acid, aqueous potassium bicarbonate, water, and dried over magnesium sulfate. After concentration under reduced pressure the oil was distilled from a Hickman molecular-type pot still at a pressure of 3–5 microns and a bath temperature of 102–128°. The yield of VI was 8.8 g. (51%), $n^{25}D$ 1.5271.

Anal. Calcd. for $C_{14}H_{15}O_2N$: C, 73.34; H, 6.60; N, 6.11; active hydrogen, one equivalent. Found: C, 73.34; H, 6.28; N, 6.25; active hydrogen, 0.97 equivalent.

A sample of VI dissolved in a 5% excess of 10% aqueous sodium hydroxide within a few minutes. The solution was allowed to stand at room temperature for thirty hours, extracted with ether, and acidified. The solid acid which separated was purified by sublimation and by crystallization from carbon tetrachloride and from a mixture of equal parts of benzene and cyclohexane. The (1-indanyl)-cyanoacetic acid which was obtained had a constant m. p. of 109.5–110.5° and decomposed with evolution of carbon dioxide at about 145°.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51. Found: C, 71.18; H, 5.51.

Ethyl (1-Indanyl)-propylcyanoacetate (IVB).—Ethyl (1-indanyl)-cyanoacetate (VI, 8.3 g.) was added dropwise with stirring to a cold solution of sodium ethoxide prepared from 0.87 g. of sodium and 15 ml. of absolute ethanol. A solid enolate separated. The mixture was stirred at room temperature until it became homogeneous, after which 6.5 g. of *n*-propyl iodide was added and the mixture was heated under reflux for three hours. The mixture was cooled, poured into water, and extracted with benzene. The extracts were washed with water, dried over magnesium sulfate, boiled with 0.5 g. of Darco and concentrated under reduced pressure. The dark oil was shaken with 14 ml. of 10% aqueous sodium hydroxide for thirty minutes at room temperature to remove any VI which was present and extracted with ether. The extracts were washed with water, dried over magnesium sulfate and evaporatively distilled at a bath temperature of 125–130° (0.06 mm.). The yield of a partially crystalline product was 7.7 g. (79%). The oil was removed by pressing the product on hard paper and recrystallizing the solid from 2:1 pentane–hexane; yield 4.0 g. (41%) of large colorless prisms, m. p. 51.5–52.5°. An analytical sample was recrystallized to constant melting point from aqueous ethanol and pentane–hexane; m. p. 52.5–53.5°.

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(5) Melting points are corrected and boiling points are uncorrected. We are indebted to Mr. S. M. Nagy, Mr. Philip H. Towle and Mrs. Louise W. Spencer for elemental analyses.

(6) Thiele and Wanscheidt, *Ann.*, **376**, 269 (1910).

(7) Ingold and Piggott, *J. Chem. Soc.*, 1483 (1923).

(8) A condensation procedure used by Cope, Hofmann, Wyckoff and Hardenbergh, THIS JOURNAL, **63**, 3453 (1941).

(9) Cope and Hancock, *ibid.*, **60**, 2904 (1938).

(10) "Organic Syntheses," Vol. 26, John Wiley, New York, N. Y., 1946, p. 32.

Anal. Calcd. for $C_{17}H_{21}O_2N$: C, 75.24; H, 7.80; N, 5.16; active hydrogen, none. Found: C, 75.27; H, 7.95; N, 5.22; active hydrogen, 0.38 equivalent.

The oil absorbed on the paper was extracted with ether and again evaporatively distilled to give 1.64 g. (17%) of a yellow oil, n^{25}D 1.5138, which crystallized only to a small extent on seeding with IVB. The oil proved to be analytically pure, and is presumed to be a mixture of the diastereomers IVA and IVB.

Anal. Calcd. for $C_{17}H_{21}O_2N$: C, 75.24; H, 7.80. Found: C, 75.16; H, 8.03.

(1-Indanyl)-propylcyanoacetic Acid ("Allo" Form, VB).—The solid ethyl (1-indanyl)-propylcyanoacetate (IVB, m. p. 52.5–53.5°) (0.5 g.) was heated at the reflux temperature for twenty-four hours with one molar equivalent of 5% ethanolic potassium hydroxide. The solution was poured into water containing a small amount of sodium hydroxide, extracted with ether and acidified with hydrochloric acid. An ether extract of the oily acid was washed with water, dried over magnesium sulfate and concentrated to an oil which crystallized; yield 0.35 g. (78%), m. p. 133–134.5°. Recrystallization to constant melting point from benzene–cyclohexane gave small needles, m. p. 135–135.5°. An acetone solution of VB did not decolorize 2% aqueous potassium permanganate.

Anal. Calcd. for $C_{15}H_{17}O_2N$: C, 74.04; H, 7.05. Found: C, 73.91; H, 7.10.

Saponification under similar conditions of the oily mixture of diastereomers from which IVB had been separated gave a mixture of diastereomeric acids, m. p. 105–110°, which could not be purified by recrystallization.

Anal. Calcd. for $C_{15}H_{17}O_2N$: C, 74.04; H, 7.05. Found: C, 74.42; H, 7.10.

Reduction of Ethyl (3-Indenyl)-allylcyanoacetate (III) to Ethyl (1-Indanyl)-propylcyanoacetate (IVA).—A solution of 3.0 g. of III in 10 ml. of aldehyde-free glacial acetic acid absorbed 105% of two molar equivalents of hydrogen on shaking with 0.5 g. of palladium-on-Norite catalyst for seven hours at room temperature and pressure. Benzene (25 ml.) was added, the catalyst was removed by filtration and the filtrate was poured into water. Benzene extracts containing the hydrogenated ester were washed with potassium bicarbonate solution, water, dried over magnesium sulfate and concentrated under reduced pressure. The residual oil was evaporatively distilled at 0.17 mm. and a bath temperature of 130° and yielded 2.63 g. (87%) of IVA as a nearly colorless oil, n^{25}D 1.5132.

Anal. Calcd. for $C_{17}H_{21}O_2N$: C, 75.24; H, 7.80; N, 5.16; active hydrogen, none. Found: C, 75.04; H, 7.78; N, 5.17; active hydrogen, 0.34 equivalent.

Hydrogenation of III in absolute ethanol in the presence of palladium-on-Norite gave similar results and also yielded an oil which could not be crystallized.

(1-Indanyl)-propylcyanoacetic Acid ("Normal" Form, VA).—A sample (0.49 g.) of the ester IVA prepared by hydrogenation (described in the preceding paragraph) was heated under reflux for twenty-six hours with a 10% excess of 5% ethanolic potassium hydroxide, and the acid formed was isolated in the same manner as VB. The crude acid (0.40 g., m. p. 104–120°) was recrystallized three times from benzene–cyclohexane to yield 0.19 g. (43%) of VA, m. p. 128–130°. An analytical sample crystallized to constant m. p. from benzene–cyclohexane, chloroform and from carbon tetrachloride had m. p. 130.5–131°, which was depressed to 109–130° by its diastereomer VB. An acetone solution of VA did not decolorize 2% aqueous potassium permanganate.

Anal. Calcd. for $C_{15}H_{17}O_2N$: C, 74.04; H, 7.05. Found: C, 74.27; H, 7.30.

(1-Indanyl)-propylacetic Acid (IX). (a) From 1-Indanylpropylcyanoacetic Acid ("Allo" Form, VB).—Saponification of IVB with a 10% ethanolic solution of four molar equivalents of potassium hydroxide for seventeen hours at the reflux temperature resulted only in the formation of the substituted cyanoacetic acid VB, isolated in 93% yield.

A solution of 0.421 g. of VB and 0.58 g. of potassium hydroxide in 0.6 ml. of water and 4 ml. of diethylene glycol was heated under reflux for twenty-nine hours. The light brown mixture was cooled and diluted with 20 ml. of water. After extraction with ether, the cooled aqueous layer was acidified with hydrochloric acid. An ether extract of the oil which separated was washed with small portions of water until the washings were neutral, and was treated with magnesium sulfate and Darco. After filtration and evaporation of the solvent, there was obtained 0.286 g. of a yellow oil which was evaporatively distilled at 127–154° (0.1 mm.). A benzene solution of the distillate was extracted with aqueous potassium hydroxide. The aqueous layer was extracted with ether and then acidified with hydrochloric acid. The oil which separated was extracted with ether. After washing the ether extract with water until the washings were neutral, it was dried over magnesium sulfate, and concentrated to give 0.209 g. of a yellow oil.

On standing, the oil became semi-solid and was washed twice with pentane at −70° by centrifugation and decantation. There was obtained 0.102 g. of (1-indanyl)-propylacetic acid (IX), m. p. 67.5–69.5°. The solid was recrystallized three times from pentane at −70°, and once from aqueous ethanol by chilling nearly to the freezing point. Fine colorless crystals with a constant m. p. of 68.5–70° were obtained.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.25; H, 8.32.

(b) From Ethyl (1-Indanyl)-propylcyanoacetate (IVA).—A solution of IVA (0.490 g.) and 0.61 g. of potassium hydroxide in 4 ml. of diethylene glycol and 0.6 ml. of water was heated at the reflux temperature for twenty-nine hours. The mixture was worked up in the manner described under (a) and there was obtained 0.138 g. of a pasty yellow solid which after washing with cold pentane gave 0.052 g. of IX, m. p. 65.5–68°. After two recrystallizations from cold pentane, very fine nearly colorless crystals were obtained with an m. p. of 67–68.5°, which was undepressed (mixed m. p., 67.5–69.5°) by the sample of (1-indanyl)-propylacetic acid prepared from VB.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.38; H, 8.40.

Rearrangement of III to Ethyl (2-Allyl-1-indanylidene)-cyanoacetate (VIIA).—III (4.0 g.) was heated under nitrogen at 124–128° for three hours in a sealed Pyrex tube. The solid which separated on cooling was washed with cold pentane, pressed on hard paper, and recrystallized from 1:1 pentane-hexane containing 15% of ether. The yield of VIIA, m. p. 79.5–80.5°, was 2.5 g. (63%). An analytical sample recrystallized to constant m. p. from the same solvent, cyclohexane and hexane, had m. p. 80.5–81°.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.41. Found: C, 76.36; H, 6.67.

2-Allyl-1-indanone (VIII).—The sodamide prepared from 4.7 g. of sodium and liquid ammonia was suspended in 120 ml. of dry ether. A solution of 30.0 g. of freshly distilled 1-indanone, b. p. 114–115° (10 mm.), in 45 ml. of dry ether was added and the mixture was stirred and heated at the reflux temperature for three and one-half hours. The slurry of the enolate was cooled in a nitrogen atmosphere, 24.7 g. of allyl bromide in 100 ml. of dry ether was added, and the mixture was warmed until a reaction began which caused refluxing for one hour. After stirring and heating under reflux on a steam-bath for an additional threee hours, the mixture was cooled and 20 ml. of water was added. The ether layer and an ether extract of the aqueous layer were washed with salt solution, dried over magnesium sulfate and concentrated under reduced pressure. Three distillations, the last through a 15 × 1.6 cm. jacketed Vigreux column with a total-condensation, partial take-off head separated 1-indanone and higher boiling products from 2-allyl-1-indanone (VIII); yield 4.06 g. (12%), b. p. 95–98.5° (0.6 mm.), n^{25}D 1.5532.

Anal. Calcd. for $C_{12}H_{12}O$; C, 83.68; H, 7.03. Found: C, 83.87; H, 7.13.

VIII (0.2 g.) was dissolved in 8 ml. of ethanol and converted to the 2,4-dinitrophenylhydrazone by treatment with a solution of 0.16 g. of 2,4-dinitrophenylhydrazine in 0.8 ml. of sulfuric acid and 1.2 ml. of water, diluted with 4 ml. of ethanol. The mixture was heated at the reflux temperature for two hours after the appearance of a precipitate. On cooling, filtering and washing with cold alcohol a yield of 0.25 g. (88%) of the dinitrophenylhydrazone was obtained, m. p. 169–170°. After recrystallization from ethanol–ethyl acetate, acetonitrile and chloroform–carbon tetrachloride, the derivative was a crystalline crimson powder with a constant m. p. of 177–178°.

Anal. Calcd. for $C_{18}H_{16}O_4N_4$: C, 61.36; H, 4.58. Found: C, 61.34; H, 4.70.

Synthesis of Ethyl (2-Allyl-1-indanylidene)-cyanoacetate (VIIA) as a Proof of Structure.—A mixture of 2.0 g. of VIII, 1.28 g. of ethyl cyanoacetate, 0.18 g. of ammonium acetate, 0.54 g. of glacial acetic acid and 5 ml. of benzene was heated under reflux for nineteen hours, while the water formed was removed from the refluxing benzene with a small Dean and Stark type continuous separator. During the period of heating, seven additional portions of ammonium acetate (0.18 g.) and one of acetic acid (0.54 g.) were added.[11] The mixture was poured into 25 ml. of benzene and washed with ten 5-ml. portions of water. The benzene solution was combined with a benzene extract of the water washings, dried over magnesium sulfate and concentrated under reduced pressure. The residue crystallized on seeding, and after washing with cold pentane containing 10% of ether amounted to 0.32 g. (10%), m. p. 76–78°. An additional 0.19 g. (6%) of VIIA was obtained from the mother liquors by evaporative distillation and recrystallization. Crystallization to constant melting point from cyclohexane gave colorless needles of VIIA, m. p. and mixed m. p. with the sample of VIIA obtained by rearrangement of III, 80.5–81°.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.41. Found: C, 76.24; H, 6.53.

Ultraviolet Absorption Spectra.—The absorption curves in Fig. 2 were obtained with solutions of IIA, III and VIIA (prepared by rearrangement of III) in 95% ethanol, using a Beckman Model DU quartz ultraviolet spectrophotometer.

Active Hydrogen Determinations.—Values for molar equivalents of active hydrogen which are cited were obtained by shaking samples of the compounds with an excess of methylmagnesium iodide in diisoamyl ether at room temperature for one hour and at 80–100° for forty minutes, and measuring the methane evolved. For VI the times were thirty minutes at room temperature and twenty minutes at 80–100°.

Summary

Ethyl (3-indenyl)-allylcyanoacetate (III) has been prepared by the alkylation of ethyl (1-indanylidene)-cyanoacetate (IIA). The skeletal structure of III has been confirmed by reduction and hydrolysis to (1-indanyl)-propylacetic acid which was synthesized by an independent method. Rearrangement of III was observed to occur at 125°, with migration of the allyl group to give ethyl (2-allyl-1-indanylidene)-cyanoacetate (VIIA), the skeletal structure of which was established by an independent synthesis. Evidence supporting the structure of III and indicating the position of the double bonds in IIA and VIIA was obtained from their ultraviolet absorption spectra.

CAMBRIDGE 39, MASS. RECEIVED DECEMBER 31, 1948

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[11] Based on a procedure for condensing ethyl cyanoacetate with unreactive ketones to be published later by E. J. Cragoe, Jr., Charles M. Robb and James M. Sprague.

[CONTRIBUTION FROM NORTH DAKOTA STATE COLLEGE, FARGO, N. D., AND LEHIGH UNIVERSITY, BETHLEHEM, PENNA.]

Dibenzofuran-2-sulfonic Acid. I. The Free Acid and its Alkali Salts

BY RAY WENDLAND AND CHARLES H. SMITH, WITH RAFFAELE MURACA

Dibenzofuran-2-sulfonic acid has been prepared in this Laboratory as a pure compound, this being apparently its first indubitable preparation. The compound is a strong acid which possesses the advantageous property, unusual for sulfonic acids, of being easily crystallizable from cold water. Contrary to reports[1] it is not particularly hygroscopic and can be vacuum dried to a composition exhibiting a neutral equivalent of 249 ± 1 (theor., 248.25). This preparation melts sharply at 147.0 to 147.5°.

Earlier studies of dibenzofuran sulfonic acids are those of Zehenter,[1] Gilman and co-workers,[2,3,4] and Hoffmeister.[5] Zehenter obtained a product closely approximating the monosulfonic acid in composition by the action of fuming sulfuric acid on 2,2′-dihydroxydiphenyl, but his acid melted variously over the range 115 to 165°. Gilman's studies produced compounds with the following orientations: 2-sulfo,[2] 2,8-disulfo by the method of Hoffmeister,[5] 4,6-disulfo,[3] and 3-sulfo.[4]

This important work is meritorious for having determined the orientation influences within the ring system. However, since we have a free sulfonic acid of sharp melting point, there is a question whether Gilman and co-workers prepared their sulfonation products as free sulfonic acids in view of the physical constants presented. The following summary of their work should be examined:

(a) The 2-sulfonic acid was supposedly isolated by acidification of a solution of the sodium salt. The decomposition of the product above 300° without melting implied only the metal salt present; (b) the 4,6-disulfonic acid was prepared by oxidation of the sulfinic acid with potassium permanganate, whereby the potassium salt must have been formed. The product isolated showed only decomposition at 300° with no melting, implying again a metal salt; (c) the 3-sulfonic acid

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[1] J. Zehenter, *J. prakt. Chem.*, **131**, 331 (1931).

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