yield a crude purple-black product. This material was recrystallized from ethyl acetate, and then from high-boiling petroleum ether to yield 0.57 g. of Langenbeck's compound (32%), m.p. 160°. The infrared spectrum of this product was superimposable upon that of the product m.p. 165° obtained by pyrolysis of benzilic acid. Use of 2-hydroxy-4,4'-dimethoxydiphenylacetic acid lactone (IX, R = OCH_3) in place of 3-phenylisocoumaranone in the above reaction did not lead to any *o*-quinodimethan analog of Langenbeck's compound. The only products recovered were the starting isocoumaranone and other colorless unidentified materials.

The Dipiperidine Derivative (XXI).—Eighty milliliters of freshly distilled piperidine, b.p. 105–107°, was added to 5 g. of Langenbeck's compound, and solution was effected with the aid of gentle warming on a steam-bath. The resulting dark-red solution was stoppered and allowed to remain at room temperature for three days at which time the color of the solution had faded to a straw-yellow. The excess piperidine was removed *in vacuo*, and the resulting red residue was triturated with 20 ml. of ligroin. Continued washing with ligroin resulted in the formation of an almost white product m.p. 208° dec. (reported m.p. 212°).

2-Hydroxy-4-diphenylhydroxymethylbenzophenone (XVII) by the Action of Periodic Acid on the Dipiperidine Derivative.—To a solution of 3.7 g. of piperidine salt (XXI) in 100 ml. of peroxide-free dioxane was added a solution of 1.8 g. of periodic acid in 40 ml. of water. The mixture was refrigerated for one week, then diluted with water and extracted with ether. The ether extract was washed with aqueous bisulfite, dried and concentrated *in vacuo*. The resulting oily residue was dissolved in hot alcohol and reprecipitated with water. Repetition of this process and recrystallization of the amorphous precipitate from *n*-heptane yielded 50 mg. of a crystalline product, m.p. 132–133°.

Anal. Calcd. for $C_{26}H_{20}O_3$: C, 82.08; H, 5.30. Found: C, 82.00; H, 5.49.

This compound shows bands at 2.8 and 6.13 μ in the infrared, is soluble in dilute alkali, and gives a deep brown coloration with ferric chloride.

Methyl 3-Hydroxy-4-formylbenzoate (XV, R = CH_3).—Eight hundred milligrams of 3-hydroxy-4-formylbenzoic acid prepared by the method of Tiemann[24] was dissolved in 100 ml. of absolute methanol, and 0.5 ml. of concentrated sulfuric acid was added. After refluxing this mixture overnight and removal of solvent, a solid residue was obtained which was crystallized from ethyl alcohol yielding needles (30%), m.p. 135–135.5°.

Anal. Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.48. Found: C, 59.70; H, 4.41.

2-Hydroxy-4-diphenylhydroxymethylbenzhydrol (XVI).—Phenylmagnesium bromide was prepared from 0.882 g. of magnesium turnings in 20 ml. of anhydrous ether and 5.7 g. of bromobenzene in 10 ml. of ether. To the suspension was added 1.08 g. of methyl 3-hydroxy-4-formylbenzoate in 50 ml. of ether. The mixture was refluxed for 30 minutes, and then allowed to stand overnight. A mixture of 30 ml. of water and 30 ml. of acetic acid was then added. The yellow ether layer was separated, washed with aqueous bicarbonate solution and then evaporated to dryness, yielding a yellow oil. The oil was further purified by chromatography on an alumina column using 50% ether–petroleum ether as an eluant. Recrystallization of the amorphous solid thus obtained from *n*-heptane yielded 0.57 g. (25%) of solid, which melted unsharply at 68–70°. The infrared absorption spectrum of this product shows no bands in the carbonyl region and is identical with the spectrum of the alcohol derived by lithium aluminum hydride reduction of the ketone XVII.

Anal. Calcd. for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80. Found: C, 81.17; H, 6.13.

Reduction of the Ketone XVII by Lithium Aluminum Hydride.—Fifty milligrams of lithium aluminum hydride was suspended in 50 ml. of anhydrous ether, and to the mixture was added 89 mg. of 2-hydroxy-4-diphenylhydroxymethylbenzophenone dissolved in 15 ml. of anhydrous ether. The reaction mixture was stirred for 1 hr., and then allowed to stand overnight. The excess lithium aluminum hydride and lithium salt were decomposed by the addition of aqueous acetic acid, and the ether layer separated. The ether solution was washed with aqueous bicarbonate, dried over sodium sulfate and the dried solution was concentrated to an oil. By chromatography on an alumina column using ether–petroleum ether as eluant, a product was obtained (15 mg.) which was identical (comparison of infrared spectra) with the product XVI obtained by the action of excess phenylmagnesium bromide on methyl 3-hydroxy-4-formylbenzoate.

2-Hydroxy-4-diphenylhydroxymethylbenzophenone (XVII) by Synthesis.—To a solution of 0.159 g. of 2-hydroxy-4-diphenylhydroxymethylbenzhydrol (XVI) in 35 ml. of dry acetone and 50 ml. of dry benzene, was added 0.5 g. of freshly prepared aluminum isopropoxide. The reaction mixture was refluxed for 22 hours and then allowed to stand overnight at room temperature. The resulting solution was evaporated to dryness *in vacuo*, the residue acidified with 6 *N* sulfuric acid and then extracted with ether. Evaporation of the dried ether solution yielded a brown oil which was converted to a crystalline solid (90 mg.) m.p. 130° by crystallization from *n*-heptane. The infrared spectrum of this product was identical with that of the ketone XVII, m.p. 130–132°, obtained by periodic acid oxidation of the dipiperidene derivative XXI.

Infrared Absorption Spectra.—All infrared absorption spectra were determined on a Perkin-Elmer recording spectrophotometer, model 21.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Steric Effect of Methylene Groups. VII

BY STUART W. FENTON, ARTHUR E. DEWALD[1] AND R. T. ARNOLD

RECEIVED AUGUST 12, 1954

In previous papers of this series chemical and physical evidence has been presented to show that the steric effect of a methylene group in a five-membered ring is smaller than that in a corresponding six-membered ring. Rates of saponification of esters derived from hydrindene-4-carboxylic acid, 5,6,7,8-tetrahydro-1-naphthoic acid, and the 7- and 4-dimethylamino derivatives of these two acids, respectively, have now been determined and completely support the conclusions drawn from our earlier work.

It has been assumed tacitly during the development of classical stereochemistry that the steric effect of a particular substituent (such as methyl, nitro, etc.) exhibits a reasonably constant steric influence. Considerable success has been achieved in correlating the experimental steric effectiveness of groups with their calculated sizes.[2]

Earlier publications from this Laboratory[3] dealing with comparative studies in the hydrindene and tetralin series have shown that the methylene groups in these substances exert different steric influences on *ortho* substituents attached to the benzenoid ring, and that the methylene group in the five-membered ring has the smaller effect. With re-

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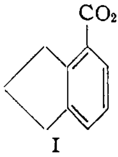
[1] Smith, Kline and French Fellow, 1950–1953.

[2] W. M. Stanley and R. Adams, THIS JOURNAL, **52**, 1200 (1930).

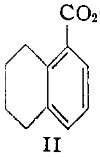
[3] R. T. Arnold, V. J. Webers and R. M. Dodson, *ibid.*, **74**, 368 (1952).

spect to hydrogen, therefore, the methylene groups in the above two series must be assigned different but perhaps constant values.

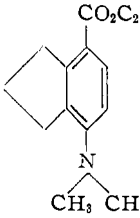
In the present study, saponification rates have been determined for the esters I–IV.



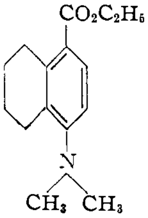
I



II



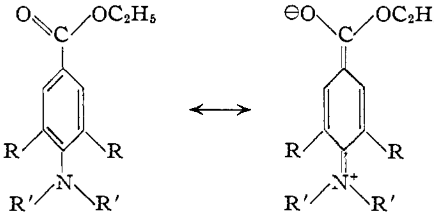
III



IV

It is to be expected that the smaller steric influence of the methylene group in I should lead to relative rates such that $k_{\text{I}} > k_{\text{II}}$.

Westheimer and Metcalf[4] have made a quantitative study of the diminution of saponification rates for benzoic esters brought about by the resonance interaction of the amino and carbonyl groups.



A

Since the rate determining-step for saponification involves an attack of hydroxide ion on the carbonyl carbon atom of the ester grouping, steric inhibition of resonance in (A) brought about by repulsion between R and R′ diminishes the magnitude of the negative charge in the neighborhood of the ester group and increases, therefore, the rate of saponification.

TABLE I

Compound	$k \times 10^3$, l. mole^{-1} min.$^{-1}$ $k_{25°}$	$k_{55°}$	log PZ	E, kcal. mole^{-1}	$\Delta H^{\ddagger}$, kcal. mole^{-1}	$\Delta S^{\ddagger}$, cal. mole^{-1} deg.$^{-1}$
Ethyl benzoate	59.2 ± 1.0	750 ± 12	10.9	16.5 ± 0.2	15.8 ± 0.2	−19.3
I	8.55 ± 0.16	121 ± 2	10.5	17.2 ± .2	16.5 ± .2	−20.8
II	2.69 ± .06	41.1 ± 0.5	10.4	17.7 ± .2	17.0 ± .2	−21.4
III	1.68 ± .04	29 ± 1.1	10.8	18.5 ± .4	17.8 ± .4	−19.7
IV	1.16 ± .05	19.5 ± 0.5	10.5	18.3 ± .4	17.7 ± .4	−20.8

If, as we believe, the methylene groups in the five-membered ring of III are sterically smaller than those in the corresponding six-membered ring of IV, one is led to an interesting conclusion, namely, that the two methylene groups *ortho* to the benzenoid ring in III play a dual role and simultaneously facilitate and hinder saponification of this ester. The methylene group *ortho* to the ester group in III is not so effective as the corresponding methylene group in IV in blocking the attack by hydroxide ion. The methylene group in III, *ortho* to the dimethylamino substituent, however, does not interfere so effectively as the corresponding methylene group in IV with the resonance interaction of the amino and ester groups and relatively should diminish the rate of saponification. Mathematically, therefore, it is to be expected that $k_{\text{I}}/k_{\text{II}} > k_{\text{III}}/k_{\text{IV}}$. Examination of the data in Table I shows that the above expectations have been realized.

It is noteworthy that the ultraviolet spectra of the compounds under investigation offer independent support for the kinetic data with regard to conclusions reached concerning the relative steric size of methylene groups in five- and six-membered rings. In all cases it is clear, from the values recorded in Table II, that for those bands in which quinoidal structures play a dominant role in the "activated state,"[5,6] the intensities for the hydrindene derivatives are consistently higher than those of the analogous tetralin compounds. These data reflect the greater steric inhibition of resonance effected by the larger methylene group in the six-membered ring of the tetralin compounds over that found in the hydrindene analogs.

TABLE II[a]

Compound	λ_{max}, mμ	E_{max}	λ_{max}, mμ	E_{max}
Ethyl 5,6,7,8-tetrahydro-1-naphthoate	237	8,000	286	1,600
Ethyl hydrindene-4-carboxylate	236	10,200	288	2,400
Ethyl 1-N,N-dimethylamino-5,6,7,8-tetrahydro-4-naphthoate	233	10,000	294	9,700
Ethyl 4-N,N-dimethylamino-hydrindene-7-carboxylate	236	10,500	306	15,400
5,6,7,8-Tetrahydro-1-naphthoic acid	235	6,000	285	1,300
Hydrindene-4-carboxylic acid	234	8,600	287	2,200
1-N,N-Dimethylamino-5,6,7,8-tetrahydronaphthalene-4-carboxylic acid	230	9,200	288	7,300
4-N,N-Dimethylaminohydrindene-7-carboxylic acid	233	10,100	300	12,000

[a] The spectra were recorded with a Beckman model DU spectrophotometer with ethanol (95%) as a solvent.

An outline of the synthetic routes employed is shown below. Since the structures of a few of the key starting materials are well established, the interrelationships demonstrated amongst the various compounds leave little doubt about the formulas assigned to them.

Acknowledgment.—The authors wish to thank Dr. Glenn E. Ullyot and the Smith, Kline and French Company of Philadelphia for support of this study through a graduate fellowship.

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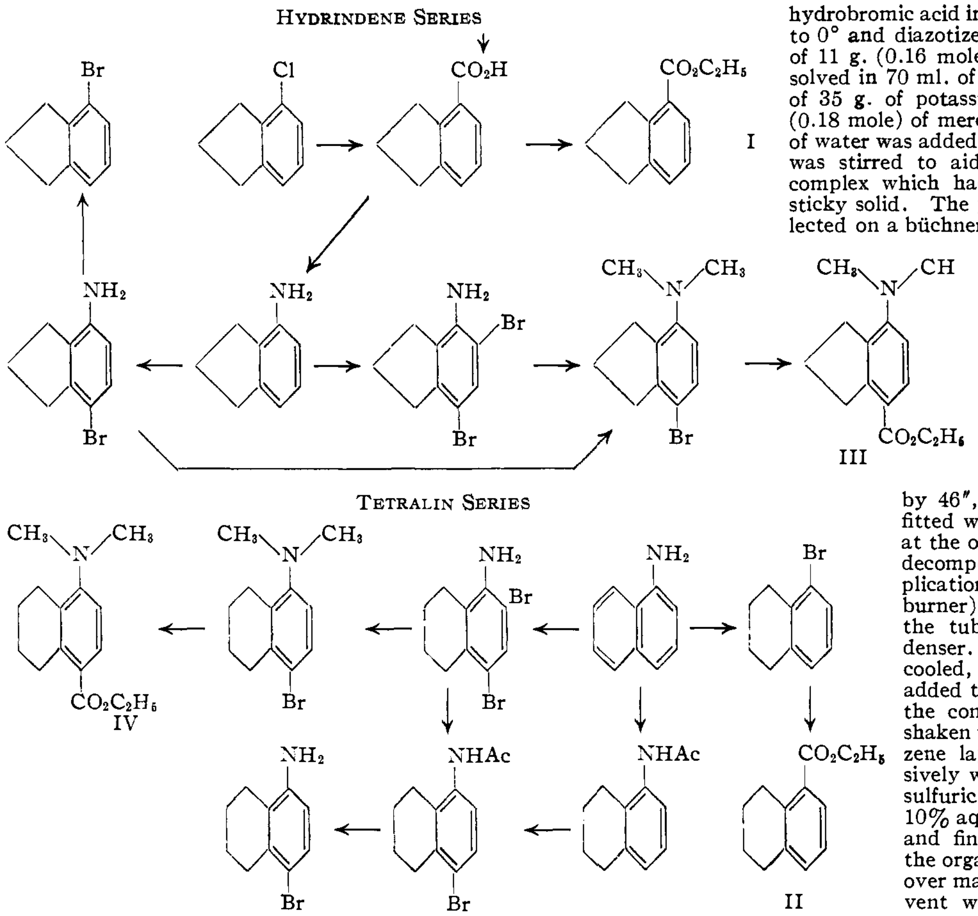
(4) F. H. Westheimer and R. P. Metcalf, THIS JOURNAL, **63**, 1339 (1941).

(5) W. R. Remington, *ibid.*, **67**, 1838 (1945).

(6) R. T. Arnold and P. N. Craig, *ibid.*, **72**, 2728 (1950).



Experimental

Kinetic Measurements.—The solvent used for the kinetic study was prepared by the addition of freshly boiled distilled water to absolute ethanol purified according to Manske's procedure.[7] This solvent was 69.98% ethanol by weight, as determined from its specific gravity (sp. g. 25/25 = 0.86597).

The alkaline hydrolyzing agent was prepared in 500-ml. quantities by dissolving metallic sodium in the 70% ethanol. This reagent (approximately 0.04 *N*) was standardized with acid prepared from constant boiling hydrochloric acid.

The acid used to quench the reaction aliquots was approximately 0.024 *N* and was prepared from constant boiling hydrochloric acid. A stock solution of carbonate-free sodium hydroxide (approximately 0.02 *N*) was used for the back titrations. Its concentration was checked periodically against potassium acid phthalate using 0.1% phenolphthalein (in 70% ethanol) as indicator.

Analytical samples of esters, prepared as described below, were used in the kinetic study.

New Pyrex volumetric flasks were calibrated at 25° to allow for the volume occupied by the weighing capsule used for that run. The pipets were calibrated at the temperature at which they were used.

The temperature baths were maintained at 25 + 0.05° and 55 ± 0.05° and good second-order kinetics were observed throughout.

1-Amino-5,6,7,8-tetrahydronaphthalene.—This amine was prepared by a method previously employed in this Laboratory.[3]

1-Bromo-5,6,7,8-tetrahydronaphthalene.—It was found that application of the general method of Schwecten[8] to this example gave much better yields than the Sandmeyer procedure.

A solution of 1-amino-5,6,7,8-tetrahydronaphthalene (22.4 g., 0.15 mole) and 70 ml. (*ca.* 0.48 mole) of 40% aqueous hydrobromic acid in 1 l. of water was cooled to 0° and diazotized by the rapid addition of 11 g. (0.16 mole) of sodium nitrite dissolved in 70 ml. of cold water. A solution of 35 g. of potassium bromide and 65 g. (0.18 mole) of mercuric bromide in 110 ml. of water was added. The resulting mixture was stirred to aid crystallization of the complex which had formed initially as a sticky solid. The yellow complex was collected on a büchner funnel, partially dried, and then washed with 250 ml. of ether. The resulting solid was divided into small portions and mixed intimately with 100 g. of powdered potassium bromide. The mixture was in turn divided into two portions. Each portion was transferred to a Pyrex tube $1^3/_4''$ by 46″, sealed at one end and fitted with a long air condenser at the other. The complex was decomposed by the gradual application of heat (using a bunsen burner), starting at the end of the tube fitted with the condenser. After the tube had cooled, sufficient water was added to dissolve the solid, and the contents of the tube were shaken with benzene. The benzene layer was washed successively with water, concentrated sulfuric acid (until colorless), 10% aqueous sodium carbonate, and finally with water. After the organic layer had been dried over magnesium sulfate, the solvent was removed at reduced pressure. Distillation of the residue through a 10-cm. Vigreux column yielded 24.5 g. (76.4%) of 1-bromo-5,6,7,8-tetrahydronaphthalene, b.p. 95.5-97° (2.5 mm.), n^{25}_{D} 1.5821.

Fieser and Hershberg[9] reported that treatment of the above diazonium bromide with cuprous bromide gave a product (b.p. 135-140° (16 mm.)) in 52% yield.

5,6,7,8-Tetrahydro-1-naphthoic Acid.—A solution of 24.5 g. (0.12 mole) of 1-bromo-5,6,7,8-tetrahydronaphthalene in 100 ml. of anhydrous ether was added, during a period of 45 minutes, to 1.78 g. (0.26 g. atom) of lithium in 125 ml. of dry ether contained in a 500-ml., three-necked, round-bottomed flask fitted with a Trubore stirrer, a condenser and a dropping funnel. The resulting dark mixture was stirred at the reflux temperature for 80 minutes, and then was poured on crushed Dry Ice. After the Dry Ice had evaporated, the ether solution was shaken with 1% aqueous potassium hydroxide. Acidification of the aqueous layer with concentrated hydrochloric acid yielded 13.9 g. (68%) of colorless solid, m.p. 149-151°. Sublimation at 5 mm. with a block temperature of 120° followed by recrystallization from nitromethane gave 5,6,7,8-tetrahydro-1-naphthoic acid as colorless needles, m.p. 150.5-151.5°.

Calcd.: neut. equiv., 176.2. Found: neut. equiv., 176.1. V. Braun[10] and Sergievskaya and Nikhamkina[11] reported m.p. 150-151°.

Ethyl 5,6,7,8-Tetrahydro-1-naphthoate.—An ethereal solution of diazoethane (containing approximately 0.055 mole of diazoethane) was added to 8.0 g. (0.045 mole) of 5,6,7,8-tetrahydro-1-naphthoic acid dissolved in 125 ml. of dry ether at 0°. The resulting pale yellow solution was maintained at 0° for two hours and then allowed to warm to room temperature in the course of 20 hours. The solution was concentrated at reduced pressure and dried over mag-

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[7] R. H. Manske, THIS JOURNAL, **53**, 1106 (1931).

[8] H. W. Schwecten, *Ber.*, **65**, 1605 (1932).

[9] L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **59**, 2333 (1937).

[10] J. V. Braun, *Ber.*, **55**, 1700 (1922).

[11] S. I. Sergievskaya and E. G. Nikhamkina, *J. Gen. Chem.* (*U.S.S.R.*), **15**, 940 (1945).

nesium sulfate. The solvent was removed at reduced pressure and the colorless residue was distilled through a 10-cm. Vigreux column yielding 8.4 g. (90.5%) of colorless liquid, b.p. 124.5–127.5° (2 mm.), $n^{25}\mathrm{D}$ 1.5304–1.5324. Redistillation through a 30-cm. spiral wire column gave 6.4 g. of analytically pure 1-carbethoxy-5,6,7,8-tetrahydronaphthalene, b.p. 118–119° (1.6 mm.), $n^{25}\mathrm{D}$ 1.5326. Sergievskaya and Nikhamkina[11] reported b.p. 128–129° (4 mm.).

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.56; H, 7.93.

1-Amino-2,4-dibromo-5,6,7,8-tetrahydronaphthalene.—Freshly distilled 1-amino-5,6,7,8-tetrahydronaphthalene (31.9 g., 0.22 mole) was dissolved in 325 ml. of glacial acetic acid contained in a 1-l. three-necked flask fitted with a Trubore stirrer, a dropping funnel and a condenser. Dropwise addition of bromine (70.3 g., 0.44 mole) dissolved in 180 ml. of glacial acetic acid to the vigorously stirred solution gave an immediate white precipitate. The reaction was slightly exothermic. The first half of the bromine solution was added at room temperature during a period of one hour. The reaction mixture was then warmed to 55–60° and the remainder of the bromine was added in the course of four hours. The orange mixture was stirred for an additional 1.5 hours at 65–70° and then cooled to room temperature. The solid was separated by filtration and washed with cold ether. The yield of colorless 1-amino-2,4-dibromo-5,6,7,8-tetrahydronaphthalene hydrobromide was 79.3 g. (94.9%); m.p. 228–233° dec.

To 75 g. of the hydrobromide suspended in 450 ml. of 95% ethanol, sufficient 10% aqueous sodium hydroxide was added to give an alkaline solution. The gradual addition of water to this ice-cooled solution precipitated the free amine in crystalline form. Reprecipitation of this material from an alkaline ethanol–water medium yielded 55.8 g. (94%) of colorless crystals, m.p. 42.5–43.0°. Recrystallization of a portion of this solid from ethanol–water gave an analytical sample of 1-amino-2,4-dibromo-5,6,7,8-tetrahydronaphthalene as colorless needles, m.p. 43.2–43.8°.

Anal. Calcd. for $C_{10}H_{11}NBr_2$: C, 39.37; H, 3.64. Found: C, 39.66; H, 3.87.

1-N,N-Dimethylamino-4-bromo-5,6,7,8-tetrahydronaphthalene.—1-Amino-2,4-dibromo-5,6,7,8-tetrahydronaphthalene (30.5 g., 0.1 mole) was dissolved in 400 ml. of glacial acetic acid contained in a 1-l. round-bottomed flask fitted with an off-set dropping funnel and a reflux condenser. Sixty milliliters of 40% aqueous formaldehyde and 150 g. of amalgamated zinc[12] were added, and the mixture was heated to the reflux temperature. Concentrated hydrochloric acid (300 ml.) was added during a period of seven hours. Seventeen additional hours at the reflux temperature converted the initially dark brown reaction mixture to a pale yellow solution. This solution was decanted from the zinc and cooled to 0°. Sufficient 50% aqueous sodium hydroxide was added to dissolve the zinc hydroxide formed, and the resulting solution was shaken with benzene. The benzene layer was dried over magnesium sulfate, the solvent was removed at reduced pressure, and the residue was distilled through a 10-cm. Vigreux column yielding 22.6 g. (89%) of colorless liquid which darkened on prolonged contact with air; b.p. 133–136° (2–3 mm.), $n^{25}\mathrm{D}$ 1.5863. Redistillation gave an analytical sample of 1-N,N-dimethylamino-4-bromo-5,6,7,8-tetrahydronaphthalene, b.p. 102° (0.2 mm.), $n^{20}\mathrm{D}$ 1.5885.

Anal. Calcd. for $C_{12}H_{16}NBr$: C, 56.70; H, 6.35. Found: C, 56.83; H, 6.22.

This material was identical with that obtained by the direct methylation of 1-amino-4-bromo-5,6,7,8-tetrahydronaphthalene with methyl iodide.

1-N,N-Dimethylamino-5,6,7,8-tetrahydro-4-naphthoic Acid.—Lithium (1.1 g., 0.16 g. atom) was added to 50 ml. of anhydrous ether contained in a 500-ml. three-necked flask fitted with a Trubore stirrer, a dropping funnel and a reflux condenser closed by calcium chloride drying tubes. Sixteen grams (0.06 mole) of 1-N,N-dimethylamino-4-bromo-5,6,7,8-tetrahydronaphthalene dissolved in 50 ml. of anhydrous ether was added dropwise, during a period of 20 minutes, with vigorous stirring. The reaction proceeded rapidly accompanied by the separation of lithium bromide. The dark mixture was stirred at reflux temperature for 40 minutes, and poured on crushed Dry Ice. Following evaporation of the Dry Ice, the ethereal residue was shaken with 150 ml. of 1% aqueous potassium hydroxide. Acidification of the aqueous layer to *p*H 6 (*p*H indicator paper) led to the precipitation of 6 g. of nearly colorless solid. An additional 3.4 g. of reddish solid was obtained by concentration of the filtrate, readjustment to *p*H 6, then ether extraction followed by removal of the solvent. The yield of crude 1-N,N-dimethylamino-5,6,7,8-tetrahydro-4-naphthoic acid (m.p. 164.5–166°) was 68%. Sublimation at 5 mm. with a block temperature of 155° followed by recrystallization from nitromethane gave an analytical sample, m.p. 165.8–166.3°.

Anal. Calcd. for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.81; neut. equiv., 219.3. Found: C, 71.47; H, 7.97; neut. equiv., 218.2.

Ethyl 1-N,N-Dimethylamino-5,6,7,8-tetrahydro-4-naphthoate.—1-N,N-Dimethylamino-5,6,7,8-tetrahydro-4-naphthoic acid (8.8 g., 0.04 mole) was partially dissolved in 200 ml. of anhydrous ether at 0°. Sufficient cold ethereal diazoethane (about 0.05 mole) was added to give the solution a permanent pale yellow color. After 20 hours, the ether was removed at reduced pressure and the yellow residue was distilled through a 10-cm. Vigreux column yielding 9.6 g. (97%) of pale yellow liquid, b.p. 160.5–163.5° (2 mm.), $n^{25}\mathrm{D}$ 1.554–1.555. Redistillation of this material through a 30-cm. spiral wire column gave a colorless analytical sample, b.p. 125.5–128° (0.4 mm.), $n^{25}\mathrm{D}$ 1.5552.

Anal. Calcd. for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.86; H, 8.73; N, 5.76.

A portion of this ester was dissolved in ether and shaken with anhydrous potassium carbonate. The potassium carbonate was separated by filtration. Removal of the solvent at reduced pressure gave the ester as a colorless solid, m.p. 19–20°.

1-Amino-4-bromo-5,6,7,8-tetrahydronaphthalene.—Attempted bromination of 1-acetamido-5,6,7,8-tetrahydronaphthalene using chloroform as solvent[13] gave very unsatisfactory results. The use of dioxane for this bromination proved to be ideal.

1-Acetamido-5,6,7,8-tetrahydronaphthalene (28.4 g., 0.15 mole) was dissolved in 550 ml. of commercial dioxane in a 1-l. three-necked flask fitted with a Trubore stirrer, a dropping funnel and a condenser. Bromine (24.5 g., 0.153 mole) was added at room temperature with stirring followed by 50 ml. of dioxane. A white precipitate started to separate within 15 minutes. The reaction was slightly exothermic but evolution of hydrogen bromide was not observed.

After being stirred for 20 hours at room temperature, the precipitate was collected on a büchner funnel, and washed with a cold dioxane–water mixture (1:4) until colorless. The yield of material (m.p. 162–175°) was 28.5 g. An additional 6.9 g. of brown solid (m.p. 160–165°) was obtained by dilution of the filtrate with water. The total yield of crude 1-acetamido-4-bromo-5,6,7,8-tetrahydronaphthalene was 35.4 g. (88%). Recrystallization from 95% ethanol gave colorless material which melted at 184.5–185.5°. The reported m.p. is 180–181°.[13]

To 15.8 g. of the recrystallized bromo compound contained in an erlenmeyer flask were added 50 ml. of 95% ethanol and 50 ml. of concentrated hydrochloric acid. The mixture was heated on a steam-cone for two hours. The solvent was evaporated and the hydrochloride separated from the cold mixture by filtration. The hydrochloride was suspended in 95% ethanol and sufficient 5% aqueous potassium hydroxide was added to make the solution alkaline. Dilution of this cold mixture with water yielded 12.9 g. (96.7%) of slightly pink 1-amino-4-bromo-5,6,7,8-tetrahydronaphthalene, m.p. 41.5–42.0°. Sublimation at room temperature (5 mm.) removed the light pink coloration but did not change the melting point. The reported value[13] is 42°.

1-Bromo-5,6,7,8-tetrahydronaphthalene.—1-Amino-4-bromo-5,6,7,8-tetrahydronaphthalene (2.26 g., 0.01 mole) was dissolved in 30 ml. of ether contained in a 500-ml. erlenmeyer flask. Gaseous hydrogen bromide was bubbled into the solution to precipitate the hydrobromide. The ether was removed with an air stream. Fifteen milliliters of 40% aqueous hydrobromic acid and 100 ml. of water were added. Diazotization with sodium nitrite (0.8 g. in 10 ml.

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[12] E. L. Martin, This Journal, **58**, 1440 (1936).

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of water) at ice-bath temperature gave a pale yellow solution. Fifteen milliliters of cold 50% hypophosphorous acid was added and the mixture was stored in the refrigerator for two days. After nine hours at room temperature, the brown oil which had separated was extracted with benzene. The benzene layer was washed with concentrated sulfuric acid to remove phenolic compounds leaving a colorless organic layer which was then washed free of acid with 10% aqueous sodium carbonate. The benzene layer was dried over magnesium sulfate and the solvent was removed at reduced pressure. The residue was distilled through a 30-cm. spiral wire column yielding 0.91 g. (43.3%) of colorless liquid; b.p. 73–75° (2–3 mm.), n^{25}D 1.5815. Redistillation through the same column gave 0.8 g. of 4-bromo-5,6,7,8-tetrahydronaphthalene, b.p. 67–69° (2 mm.), n^{25}D 1.5823.

1-Bromo-5,6,7,8-tetrahydronaphthalene prepared by Schwecten's procedure[8] from 1-amino-5,6,7,8-tetrahydronaphthalene had n^{25}D 1.5822.

4-Chlorohydrindene.—This compound was prepared essentially by the method of Fieser and Hershberg.[14]

Hydrindene-4-carboxylic Acid.—To 3.5 g. (0.5 g. atom) of lithium and 200 ml. of anhydrous ether contained in a 500-ml., three-necked, round-bottomed flask fitted with a Trubore stirrer, a condenser and a dropping funnel was added, during a period of 45 minutes, a solution of 35.2 g. (0.23 mole) of purified 4-chlorohydrindene in 100 ml. of dry ether. The reaction proceeded slowly, due undoubtedly to the formation of a black coating on the lithium. The resulting dark mixture was stirred under reflux for 11 hours, then poured on crushed Dry Ice. Following evaporation of the Dry Ice, the ethereal residue was shaken with 1% aqueous potassium hydroxide. Acidification of the aqueous layer gave 21.6 g. of nearly colorless hydrindene-4-carboxylic acid, m.p. 150–151.5°. Sublimation of this material at 5 mm. with a block temperature of 120° yielded 20.7 g. (55.3%) of colorless acid, m.p. 151.5–153°. Further purification, by recrystallization of the sublimate from nitromethane, gave colorless needles, m.p. 152.5–153.5°.

Calcd.: neut. equiv., 162.2. Found: neut. equiv., 162.0.

Fieser and Hershberg[14] obtained this substance by acid hydrolysis of 4-cyanohydrindene, m.p. 152.5–153.5°.

From the neutral reaction product there was isolated di-(4-hydrindyl) ketone in a yield of 16%; m.p. 78.2–78.8°. The reported value[14] is 77–78°.

Ethyl Hydrindene-4-carboxylate.—To 8.1 g. (0.05 mole) of hydrindene-4-carboxylic acid, m.p. 152.5–153.5°, dissolved in 140 ml. of anhydrous ether at 0°, was added ethereal diazoethane (about 0.06 mole) until a pale yellow color persisted. After 20 hours, the solvent was removed at reduced pressure and the colorless residue was distilled through a 30-cm. spiral wire column yielding 9.2 g. (96.8%) of colorless liquid; b.p. 110–112° (2 mm.), $n^{25.5}$D 1.5310–1.5313. Redistillation through the same column gave analytically pure 4-carbethoxyhydrindene, b.p. 108–109° (1.8 mm.), n^{25}D 1.5315.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 76.05; H, 7.57.

4-Aminohydrindene.—Hydrindene-4-carboxylic acid (13.6 g., 0.084 mole) was dissolved in 30 ml. of concentrated sulfuric acid contained in a 200-ml. three-necked flask fitted with a glass stirrer, a thermometer and a bubbler tube leading into 10% aqueous sodium hydroxide. Dry chloroform (60 ml.) was added to the well-stirred, yellow-brown solution followed by 7.8 g. (0.12 mole) of dry sodium azide at a rate such that the temperature of the reaction mixture was raised to 50–55°, by immersion in a water-bath, and maintained there until evolution of gas ceased. The dark reaction mixture, containing some solid, was poured on to ice and made alkaline with 50% aqueous sodium hydroxide. The product was extracted with ether and dried over magnesium sulfate. Following removal of the solvent at reduced pressure, distillation of the ether residue through a 10-cm. Vigreux column yielded 9.6 g. (86.5%) of colorless 4-aminohydrindene, b.p. 73–74° (2.5 mm.), n^{25}D 1.5884.

The same amine was obtained by degradation of the acid with hydroxylamine hydrochloride in polyphosphoric acid,[15] and by treatment of 4-hydrinyllithium with O-methylhydroxylamine.[16] The yields, however, were 35 and 23%, respectively.

4-Amino-5,7-dibromohydrindene.—Fourteen grams (0.1 mole) of freshly distilled 4-aminohydrindene was dissolved in 200 ml. of glacial acetic acid contained in a 500-ml., three-necked, round-bottomed flask fitted with a Trubore stirrer, a condenser and a dropping funnel. A solution of 35.4 g. (0.22 mole) of bromine in 80 ml. of glacial acetic acid was added during a period of two hours. The first half of the bromine was added at room temperature, the last half at 50–55°. The orange colored mixture was heated at 65–70° for three hours and then stirred for 14 hours at room temperature. The precipitated hydrobromide was collected on a büchner funnel, washed until colorless with cold ether, and dried. The solid was transferred to a beaker and suspended in 250 ml. of 95% ethanol. Sufficient 10% aqueous sodium hydroxide was added to make the solution alkaline. Dilution of this ice-cooled alkaline solution with water gave 4-amino-5,7-dibromohydrindene melting at 56.5–57.5° in 93.6% yield. Two recrystallizations of this material from 50% ethanol–water produced an analytical sample as fine colorless needles, m.p. 57.5–58°.

Anal. Calcd. for $C_9H_9NBr_2$: C, 37.14; H, 3.12. Found: C, 37.43; H, 3.39.

4-Acetamido-5,7-dibromohydrindene.—A mixture of 1 g. of 4-amino-5,7-dibromohydrindene and 4 ml. of acetic anhydride was heated at reflux temperature for 15 minutes, and poured with stirring into 50 ml. of water. The product was collected on a filter and washed with water. Three crystallizations from toluene gave an analytical sample of colorless 4-acetamido-5,7-dibromohydrindene, m.p. 222–222.5°.

Anal. Calcd. for $C_{11}H_{11}NOBr_2$: C, 39.67; H, 3.33. Found: C, 39.71; H, 3.52.

4-Acetamido-7-bromohydrindene.—4-Acetamidohydrindene (8.8 g., 0.05 mole) was dissolved in 100 ml. of purified dioxane contained in a 500-ml., three-necked, round-bottomed flask fitted with a Trubore stirrer, a reflux condenser and a dropping funnel. To this well-stirred solution was added 8.5 g. (0.053 mole) of bromine at room temperature followed by 20 ml. of dioxane. After 1.5 hours of vigorous stirring, a fine white precipitate appeared in the orange solution. The mixture was then stirred for an additional 12 hours. The precipitate was separated by filtration, washed with cold water and dried to give 7.5 g. of material, m.p. 166.8–167.6°. An additional 4 g. of solid (m.p. 167–168°) was obtained upon dilution of the filtrate with about 1 l. of water. The total yield was 11.5 g. (90%). A portion of this solid which was recrystallized twice from 95% ethanol gave an analytical sample of 4-acetamido-7-bromohydrindene as a colorless mat of fine silky needles, m.p. 168.2–169°.

Anal. Calcd. for $C_{11}H_{12}ONBr$: C, 51.99; H, 4.76. Found: C, 51.72; H, 4.82.

4-Amino-7-bromohydrindene.—4-Acetamido-7-bromohydrindene (6.2 g., 0.024 mole) was placed in a 125-ml. erlenmeyer flask fitted with a reflux condenser. Thirty milliliters of 95% ethanol and 25 ml. of concentrated hydrochloric acid were added and the mixture was heated on a steam-cone. Within ten minutes complete solution occurred. Shortly thereafter the crystalline amine hydrochloride separated. After two hours at the reflux temperature, the condenser was removed and the heating was continued in order to evaporate the ethanol and ethyl acetate. The hydrochloride was collected on a büchner funnel, partially dried, transferred to a beaker and suspended in 50 ml. of 95% ethanol. Sufficient 10% aqueous sodium hydroxide was added to make the solution alkaline. Dilution of this ice-cooled alkaline solution with water yielded 4.9 g. (94.8%) of 4-amino-7-bromohydrindene, m.p. 64–65°. Sublimation at 50° (5 mm.) followed by recrystallization from 95% ethanol gave an analytical sample, m.p. 64.5–65°.

Anal. Calcd. for $C_9H_{10}NBr$: C, 50.96; H, 4.75. Found: C, 51.12; H, 5.01.

Removal of the amino group through diazotization and treatment with hypophosphorous acid gave pure 4-bromohydrindene.

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[14] L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **59**, 396 (1937).

[15] H. R. Snyder, C. T. Elston and D. B. Kellom, *ibid.*, **75**, 2014 (1953).

[16] N. I. Sheverdina and K. A. Kocheshkow, *J. Gen. Chem. U.S.S.R.*, **8**, 1825 (1938).

4-N,N-Dimethylamino-7-bromohydrindene.—4-Amino-7-bromohydrindene (2.1 g., 0.01 mole) and 5.2 g. (0.1 mole) of 88% formic acid were heated in a 50-ml. erlenmeyer flask fitted with a reflux condenser on a steam-cone for two hours. Two grams of 40% aqueous formaldehyde was added and the heating was continued for 14 hours. Concentrated hydrochloric acid (2.5 ml.) was added and the reflux condenser was removed to permit the volatile material (excess formaldehyde and formic acid) to escape. The resulting mixture was removed from the steam-cone, diluted with water and made alkaline. The product was extracted with ether and dried over magnesium sulfate. Distillation of the ether residue at reduced pressure through a 30-cm. spiral wire column yielded 1.25 g. (52%) of a colorless liquid, b.p. 90–92 (2 mm.), $n^{25}\mathrm{D}$ 1.5914.

4-N,N-Dimethylamino-7-bromohydrindene.—To 5.8 g. (0.02 mole) of 4-amino-5,7-dibromohydrindene dissolved in 80 ml. of glacial acetic acid contained in a 500-ml. flask fitted with a reflux condenser and an off-set dropping funnel were added 45 g. of amalgamated mossy zinc and 15 ml. of 40% aqueous formaldehyde. Concentrated hydrochloric acid (10 ml.) was added and the gray mixture was heated to reflux temperature. An additional 75 ml. of concentrated hydrochloric acid was added during a period of 11 hours. After a reflux period of 24 hours, the acidic solution was decanted from the zinc, cooled and treated with sufficient aqueous sodium hydroxide to dissolve the zinc hydroxide which formed. The product was extracted with a benzene–ether mixture. After the organic layer had been dried over magnesium sulfate, the solvent was removed, and the residue was distilled at reduced pressure yielding 3.8 g. (79%) of colorless liquid; $n^{25}\mathrm{D}$ 1.5912. Redistillation of this material through a 30-cm. spiral wire column gave an analytical sample of colorless 4-N,N-dimethylamino-7-bromohydrindene, b.p. 93–93.5° (2.5 mm.), $n^{25}\mathrm{D}$ 1.5913.

Anal. Calcd. for $C_{11}H_{14}NBr$: C, 55.01; H, 5.88. Found: C, 55.18; H, 5.91.

4-N,N-Dimethylaminohydrindene-7-carboxylic Acid.—Lithium (0.71 g., 0.1 g. atom) was added to 50 ml. of anhydrous ether contained in a 500-ml. three-necked flask fitted with a Trubore stirrer, a dropping funnel and a reflux condenser. A solution of 10.95 g. (0.046 mole) of 4-N,N-dimethylamino-7-bromohydrindene in 50 ml. of dry ether was added during a period of 25 minutes with vigorous stirring. The reaction started within a few minutes. The dark mixture was stirred at reflux temperature for 45 minutes, then was poured on crushed Dry Ice. Following evaporation of the Dry Ice, the ether residue was shaken with 200 ml. of 1% aqueous potassium hydroxide. Acidification of the aqueous layer (*p*H 6) resulted in the separation of 6.1 g. of colorless solid. A second crop of 0.6 g. of reddish solid was obtained by concentration of the filtrate, ether extraction and removal of the solvent. Sublimation of the combined crops at 175° (5 mm.) yielded 6.2 g. (66%) of colorless solid, m.p. 182.5–184°. Two recrystallizations from nitromethane gave an analytical sample of 4-N,N-dimethylaminohydrindene-7-carboxylic acid as colorless needles, m.p. 183–183.8°.

Anal. Calcd. for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; neut. equiv., 205.2. Found: C, 69.94; H, 7.54; neut. equiv., 205.1.

Ethyl 4-N,N-Dimethylaminohydrindene-7-carboxylate.—To 8.2 g. (0.04 mole) of 4-N,N-dimethylaminohydrindene-7-carboxylic acid in 150 ml. of anhydrous ether at 0° was added sufficient ethereal diazoethane (approximately 0.05 mole) to impart a permanent yellow coloration to the solution. After 20 hours, the solvent was removed at reduced pressure and the yellow residue was distilled through a 30-cm. spiral wire column. The yield of colorless liquid, b.p. 132.5–135° (0.5 mm.), $n^{25}\mathrm{D}$ 1.5716, was 8.1 g. (87.1%). Redistillation gave material with $n^{25}\mathrm{D}$ 1.5716. This liquid was dissolved in anhydrous ether and shaken with anhydrous potassium carbonate. The potassium carbonate was separated by filtration. Removal of the solvent at reduced pressure gave 4-N,N-dimethylamino-7-carbethoxyhydrindene as a colorless solid. Recrystallization from absolute ether using a Dry Ice–acetone bath gave the ester, m.p. 44.5–45.5°, $n^{25}\mathrm{D}$ 1.5717.

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.03; H, 8.32; N, 6.25.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Tetraarylcyclopentadienes[1]

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A number of symmetrically substituted 1,2,4,5-tetraarylpentane-1,5-diones have been synthesized by coupling substituted α-phenylacetophenones with formaldehyde in a base-catalyzed reaction. Michael addition of substituted α-phenylacetophenones to α-phenylacrylophenone produced unsymmetrically substituted 1,5-diones. Conversion of the 1,5-diketones to tetraarylcyclopentadienes was effected *via* reductive cyclization with zinc in acetic acid to the corresponding 1,2,3,5-tetraarylcyclopentane-1,2-diols followed by their dehydration, or in the same steps, but without isolation of the diols.

Introduction

It is the purpose of this work to describe the synthesis of a number of 2,3,4,5-tetraarylcyclopentadienes which were desired in order to test their behavior as organic semi-conductors in the xerographic process. The synthesis of these compounds starts with the reductive cyclization of 1,5-diketones. Thus, the synthesis of the 1,5-diketones is the key step in the sequence. This leads to a division of the experimental work into the synthesis of 1,5-diketones, and their reductive cyclization to cyclopentanediols followed by their dehydration to cyclopentadienes or reductive cyclization and dehydration directly to cyclopentadienes.

Symmetrically Substituted 1,5-Diketones.—The symmetrical 1,5-diketones were synthesized by coupling two molecules of an α-phenylacetophenone with formaldehyde according to Wislicenus and Carpenter[4] as modified by Ziegler and Schnell[5] (equation 1). The α-phenylacetophenones were prepared according to literature procedures.

The yield of the 1,5-diketones varied from 32–94%. Table I summarizes most of the data. Typical procedures are given in the Experimental part.

Unsymmetrically Substituted 1,5-Diketones.—The direct adaptation of the procedure of Wislice-

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(2) Taken from the Dissertation presented by L. M. to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Ph.D. degree.

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(4) J. Wislicenus and H. Carpenter, *Ann.*, **302**, 223 (1898).

(5) K. Ziegler and B. Schnell, *ibid.*, **445**, 266 (1925).