chloride, there was added dropwise at 0° with good stirring a solution of 6.4 g. (0.04 mole) of bromine in 25 ml. of carbon tetrachloride. The solvent was removed on a steam bath and the residue was dried under high vacuum. After the addition of 25 ml. of methanol and 15 g. of dimethyl sulfate, there was added dropwise with stirring 12 g. of potassium hydroxide in 40 ml. of water. The final solution was made basic and extracted with ether. After drying and removing the ether on a steam bath, the product distilled at 88° (1 mm.). Infrared showed that this product was identical with that prepared by the bromination of I. The bromo compound was dissolved in 30 ml. of anhydrous ether and 3 g. of magnesium was added. A solution of 6 g. of ethyl iodide in 15 ml. of ether was added dropwise under gentle reflux, and the resulting mixture was refluxed for 30 min. and then added to a large excess of Dry Ice in a beaker. After 3 hr., excess concentrated hydrochloric acid was added, and the mixture was extracted with ether. The ether extract was washed with a dilute solution of sodium hydroxide and the aqueous phase was acidified and placed in the refrigerator overnight. The crystals were filtered, air-dried, sublimed at 180° (0.05 mm.), and recrystallized from petroleum ether (30–60°) to give colorless crystals, 1 g., m.p. 184°.

Oxidation of Acylphenones.—The methyl and ethyl ketones (II III, VI, and VII) were converted to the corresponding benzoic acids by hypobromite oxidation.[15,25] The isopropyl ketones (IV and VIII) gave the benzoic acids by bromination (hypobromite), hydrolysis by aqueous alkali, and cleavage of the crude anhydrous α-hydroxy ketone by lead tetraacetate.[26] The acids obtained were purified as described above and compounds II, III, and IV gave an acid identical with X. Compounds VI, VII, and VIII gave an acid, m.p. 151–152°. A mixture melting point with the acid prepared from 5-methylvanillin[16,27] showed no depression.

Acknowledgment.—The authors gratefully acknowledge support of this work by the Robert A. Welch Foundation and the Lamar Research Center.

(25) R. Levine and J. R. Stephens, *J. Am. Chem. Soc.*, **72**, 1642 (1950).
(26) D. Y. Curtin and S. Leskowitz, *ibid.*, **73**, 2635 (1951).
(27) Sample kindly supplied by Professor Burger.

Synthesis and Study of Pseudo-Aromatic Compounds. II. The Synthesis of Indeno[5′,6′-4,5]-2,7-dicarboethoxytropone

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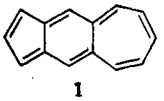
The synthesis of indeno[5′,6′-4,5]-2,7-dicarboethoxytropone is described. From the n.m.r. and ultraviolet spectra of this compound, as well as its failure to incorporate deuterium from deuterium oxide, it is concluded that it does not enolize to give a substituted anthrazulene.

The fact that simple, molecular-orbital and valence-bond approximation methods fail to satisfactorily predict the π-electronic properties of nonalternant cyclic and polycyclic conjugated polyenes has resulted in the use of rules to qualify these calculations. Thus two rules, Craig's rule[1] and the $4n + 2$[2] rule, are commonly used as criteria to predict aromaticity.

Although the $4n + 2$ rule has no formal validity for polycyclic systems,[1,3] it is still applied to them under the assumption that polycyclic systems are not too severe a perturbation of a monocyclic system.[3,4]

The anthrazulene ring system (**1**) is an interesting example of a nonalternant hydrocarbon which concurs with both the $4n+2$ rule and Craig's rule for aromaticity, but has defied synthesis by routes commonly useful for the synthesis of aromatic systems. Thus, attempted dehydrogenation of indano[5′,6′-1,2]cyclohepta-1,3-diene gave no traceable products and it was concluded that anthrazulene must be nonaromatic.[5,6]



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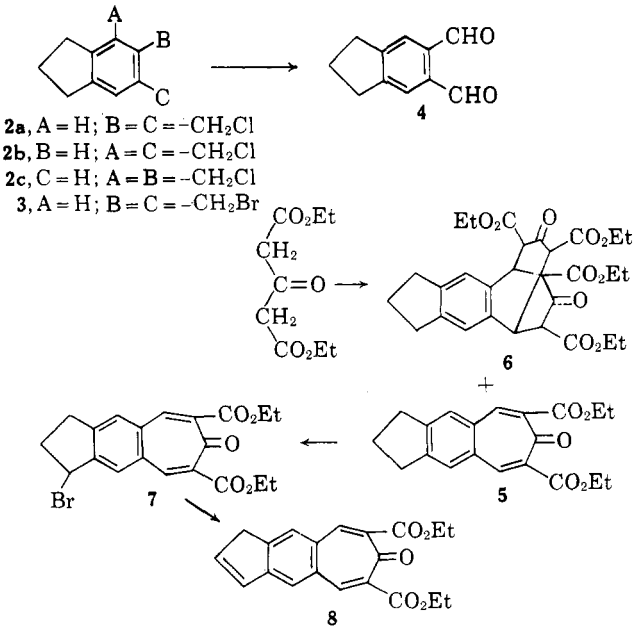
The fact that anthrazulene has a high-predicted, π-electron delocalization energy (2.245γ,[7] 74.1 kcal./mole; 4.895β,[8] 80.8 kcal./mole) which even after correction for strain energy (21.7 kcal./mole)[8] is still substantially high (52.4, 59.1 kcal./mole), indicated that further study of this ring system would be of value. This paper reports the synthesis of indeno-[5′,6′-4,5]-2,7-dicarboethoxytropone (**8**) which is a tautomer of the anthrazulene ring system.

The dichloromethylation of indane yields three products (**2**) which were detected by hydrogenation to the methylindanes and analysis by vapor phase chromatography. The components were found in a ratio of 60:30:10. Oxidation of the mixture of dichloromethyl compounds with 30% nitric acid, methylation of the resulting carboxylic acids with diazomethane, and separation by column chromatography over alumina, yielded the tetramethyl esters of pyromellitic acid (39%) and prehnitic acid (3%). From these data the predominant dichloromethylindane produced was assumed to be the 5,6-isomer (**2a**) and the product formed in the second highest amount the 4,6-isomer (**2b**). The remaining isomer is most likely the 4,5-isomer (**2c**) although no mellophanic acid was detected as an oxidation product.

Further confirmation of the structural assignment of the most predominant isomer (**2a**) was obtained. The dichloride mixture was recrystallized until the vapor phase chromatographic analysis of the hydrogenation product contained only a single peak which corresponded to the isomer that was originally most abundant. Hydrolysis of this component to the dialcohol and oxidation with chromic acid in acetone gave a lactone[9] and thus showed the *ortho* relationship of the two groups.

(1) D. P. Craig, *J. Chem. Soc.*, 3175 (1951).
(2) E. Huckel, *Z. Physik.*, **70**, 204 (1931); *Z. Elektrochem.*, **43**, 752 (1937).
(3) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., (1961) p. 288.
(4) The bridging bond converting a monocyclic system to a polycyclic system does not introduce *too* severe a perturbation on the monocyclic system for a qualitative analogy.
(5) A. D. Campbell and S. M. Slater, *J. Chem. Soc.*, 4353 (1952).
(6) S. Gupta, *Current Sci.* (India), **5**, 133 (1936); S. Dev, *J. Indian Chem. Soc.*, **30**, 729 (1953); *Chem. Abstr.*, **49**, 3116 (1955).
(7) G. Berthier, B. Pullman, and J. Baudet, *J. chim. phys.*, **50**, 209 (1953).
(8) Private communication from H. J. Dauben, Jr., University of Washington.
(9) V. I. Stenberg and R. J. Perkins, *J. Org. Chem.*, **28**, 323 (1963).



Reaction of 5,6-dichloromethylindane with the sodium salt of 2-nitropropane[10] resulted in the isolation of an oil, in low yield, which was shown by n.m.r. analysis to be a mixture of a dialdehyde and monoaldehydechloromethyl compound. Attempts to separate the mixture by crystallization were unsuccessful and separation by vapor phase chromatography was impractical because the aldehyde decomposed excessively at the high temperature required. Since longer reaction times led to formation of side products, dibromomethylindane (**3**) was used instead.

The dibromomethylation of indane proceeded analogously to the dichloromethylation reaction, giving the same three isomeric products in the same ratio. Again the mixture was analyzed by hydrogenation to the dimethylindane mixture and vapor phase chromatography. Recrystallization of the crude dibromomethylindanes resulted in isolation of a product which upon hydrogenation and analysis by vapor phase chromatography was shown to be the same hydrocarbon as derived from the 5,6-dichloromethylindane. Reaction of 5,6-dibromomethylindane with the sodium salt of 2-nitropropane gave a 19.5% yield of indane-5,6-dialdehyde (**4**). In the reaction of both the dibromethyl- and the dichloromethylindane the predominant products resulted from partial carbon alkylation, rather than oxygen alkylation, to give the corresponding nitroalkanes.

The only method that was found to be satisfactory for the isolation of the dialdehyde was extraction of the crude product with a 40% aqueous solution of sodium bisulfite and then regeneration of the free aldehyde. The bisulfite addition compound was decomposed with formaldehyde rather than acid or base because either of the latter methods led to decomposition of the free aldehyde.

Condensation of indane-5,6-dialdehyde with diethyl acetonedicarboxylate gave two products, indano-[5′,6′-4,5]-2,7-dicarboethoxytropone (**5**) and a biscondensation product **6** in 32 and 8.9% yield, respectively. The identity of these two products was established by their n.m.r. spectra (Table I). The

(10) H. B. Hass and M. L. Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949).

TABLE I

N.M.R. SPECTRA[a]

Compd.	Seven-membered ring protons	Benzene protons	Five-membered ring protons
5	1.9 (s, 2)	2.32 (s, 2)	6.93 (t, 4, benzylic) 7.83 (q, 2)
6	(5.3–6.3)[b]	3.05 (s, 2)	7.2 (t, 4, benzylic) 8.0 (q, 2)
7	1.9 (s, 2)	2.18 (s, 1) 2.32 (s, 1)	4.41 (t, 1, bromobenzylic) 6.87 (m, 2, benzylic) 7.32 (m, 2)
4,5-benzotropone[c]	3.08 (AB d, 4)	2.48 (s, 4)	
2,7-dicarboethoxy-4,5-benzotropone[c]	1.9 (s, 2)	2.27 (d, 4)	

[a] The spectra were taken in deuteriochloroform using tetramethylsilane as an internal reference (TMS = τ 10). The positions of the ethyl protons were consistently the same and are not included (for these values see Fig. 1). All positions are in τ-units and the number in parenthesis indicates relative area (s, singlet; d, doublet; t, triplet; q, quintet; m, multiplet). [b] These protons overlapped the methylene protons of the ethoxy groups, which themselves were not all equivalent, and no assignment could be made. [c] J. Thiele and J. Schneider, *Ann.*, **369**, 287 (1909); J. Thiele and E. Weitz, *ibid.*, **377**, 1 (1910).

structure of **6** as a biscondensation product was established by the fact that the n.m.r. spectrum showed that 2 moles of diethyl acetonedicarboxylate had added to the aldehyde. Also the absence of vinylic protons established the structure as **6** rather than a product resulting from addition of 2 moles of diethyl acetone dicarboxylate without cyclization.

Bromination of the indanotropone (**5**) with N-bromosuccinimide gave 1′-bromoindano[5′,6′-4,5]-2,7-dicarboethoxytropone (**7**) in 69% yield. The position of bromination was readily established by the n.m.r. spectrum of the product (Table I).

The bromide **7** could be readily dehydrohalogenated by dissolving it in a saturated solution of sodium iodide in N,N-dimethylformamide and allowing the solution to remain at room temperature, under nitrogen, for 36 hr. Using the same conditions, except omitting the sodium iodide, resulted only in isolation of unreacted bromide. Thus the elimination step is probably preceded by exchange of iodide for bromide and then dehydrohalogenation.[11]

The structure of the product resulting from dehydrohalogenation of **7** as indeno[5′,6′-4,5]-2,7-dicarboethoxytropone (**8**) was established by its n.m.r. spectrum (Fig. 1). The peak at τ 1.9 (2 protons) is assigned to the seven-membered ring protons by analogy to 2,7-dicarboethoxy[4,5]benzotropone (Table I). The two peaks centered at τ 2.25 (2 protons) are the benzene ring protons. The quartet at τ 5.6 (4 protons) and the triplet at 8.6 (6 protons) are due to the ethoxy groups. The AB doublet at τ 3.1 (1.6 protons) and the peak at 6.45 (1.8 protons) are assigned to the protons of the five-membered ring and are in good agreement with the τ-values for indene. The small coupling constant between the methylene and vinyl

(11) Work is presently under way on the study of the mechanism of this elimination reaction.

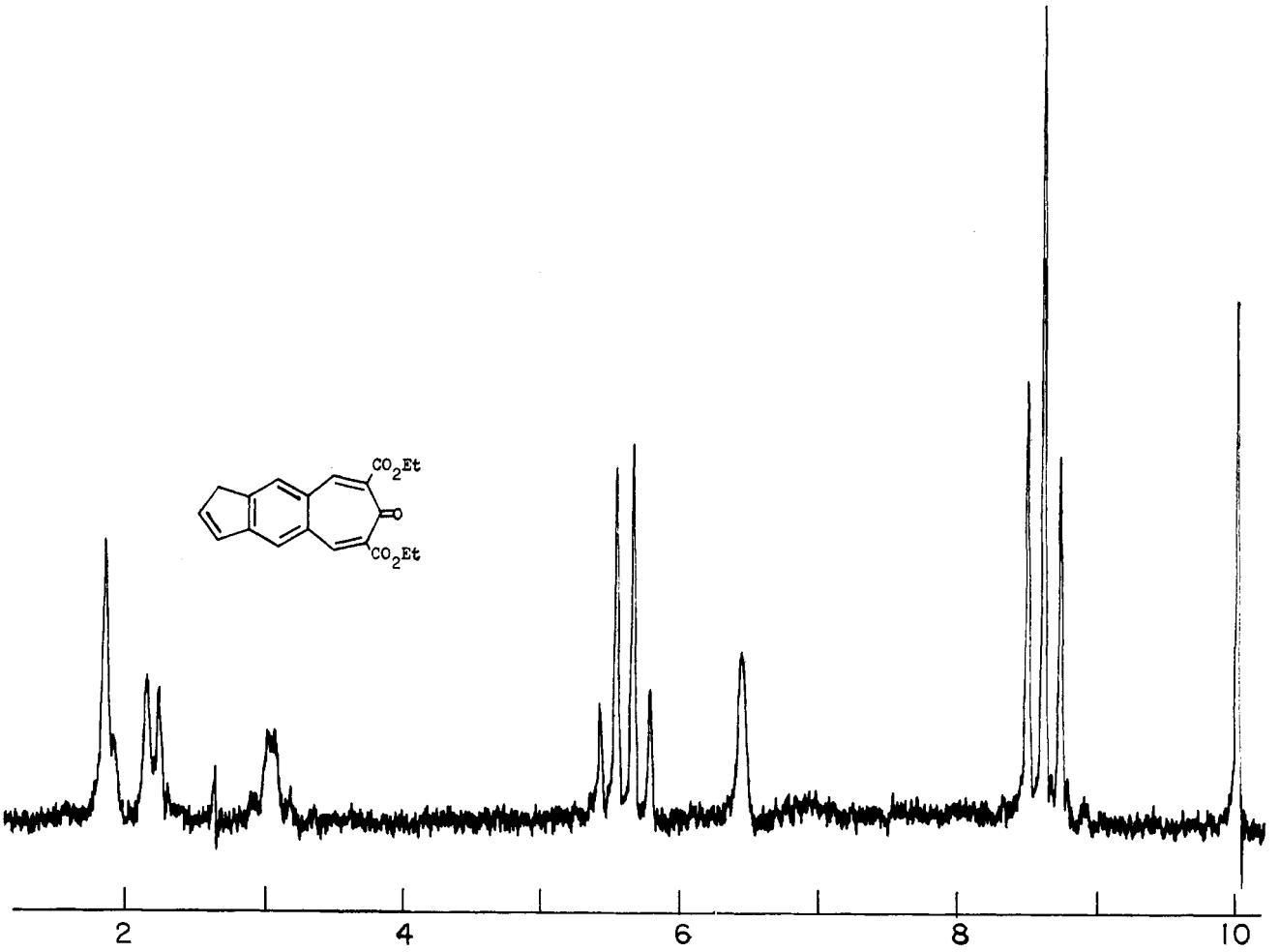


Figure 1.

protons of the five-membered ring is typical of both indene itself and 1-azulenium ion.[12] No hydroxyl proton could be detected in either the n.m.r. spectrum, which was examined to τ −8.0, or the infrared spectrum.

Indeno[5′,6′-4,5]-2,7-dicarboethoxytropone is somewhat unstable in solution and decomposes at a more rapid rate when heated. For this reason recrystallization of the compound resulted in some decomposition and loss of product. This lack of stability was also reflected in the n.m.r. spectrum by the diffuse absorption at *ca.* τ 7 (Fig. 1). This decomposition, which could not be avoided although several attempts were made, is probably due to reaction at the five-membered ring double bond which would reduce the intensity of the vinyl and methylene protons and cause absorption in the benzylic region (*ca.* τ 7) while leaving the number of aromatic protons unchanged. Thus the low intensity of the five-membered ring protons is assumed to be due to decomposition and error in electronic integration rather than enolization.

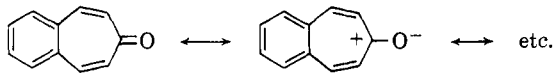
From the n.m.r. data as well as the failure to detect the presence of a hydroxyl group in the infrared spectrum it is assumed that **8** is in the keto form and shows no tendency to enolize. Furthermore, the fact that the aromatic protons of **8** integrate to exactly four protons indicates that there is no enol content present which would raise this value. However, the presence of a few per cent of the enol would probably be undetected. Also, the small bathochromic shift in the ultraviolet spectrum of **8** relative to that of **6** (Fig. 2) indicates the similarity of the two π-electron systems and the difference appears consistent with the addition of a conjugated vinyl group. Since the enol form of **8** would be expected to exhibit a considerably different π-electronic energy system from that of **6**, the ultraviolet spectrum also indicates that **8** is predominantly in the keto form.

As a final attempt to determine if **8** was in equilibrium with the enol form, a solution of **8** in hexadeuterioacetone containing 10% D_2O was allowed to stand for 24 hr. at 40°. If an equilibrium mixture were present it would be expected that the α-protons of the five-membered ring would exchange for deuterium under these conditions. The compound was not sufficiently soluble in acetone to obtain a solution of satisfactory concentration to determine the n.m.r. spectrum directly, but isolation of **8** after 24 hr. by evaporation of the deuterioacetone and D_2O and taking the n.m.r. spectrum in deuteriochloroform showed the vinyl and methylene protons had not exchanged. Furthermore, the infrared spectrum of the same sample showed no C–D absorption. Thus, **8** apparently fails to enolize to any appreciable extent.

It is difficult to estimate the delocalization energy of the keto form of **8**. The delocalization energy of 2,7-dimethyl-4,5-benzotropone has been determined from heat of combustion data and a value of 82.7 kcal./

(12) S. S. Danyluk and W. C. Schneider, *J. Am. Chem. Soc.*, **82**, 997 (1960).

mole has been reported.[13] Although this value appears high with respect to the other physical properties of benzotropones[14,15] it must be concluded that 4,5-benzotropone has an appreciable resonance energy. However, this delocalization energy in excess of that attributable to the benzene ring must be largely due to dipolar resonance forms (**9b**). The substitution of the two carboethoxy groups at the two and seven



9a **9b**

positions would be expected to substantially lower the contribution from **9b** and thus the over-all π-electron delocalization energy. This assumption is substantiated by the fact that **5** readily undergoes addition of a second mole of diethyl acetonedicarboxylate to give the bis adduct **6**, which can be made the sole product by using 2 moles of diethyl acetonedicarboxylate. These carboethoxy groups might also be expected to lower the resonance energy of the anthrazulene system because of the predicted over-all π-electron polarization away from the seven-membered ring toward the five-membered ring.[7] However, this latter factor would be expected to be somewhat less important in the enol form than the keto form of **8**.

The available data indicates that the ground-state energy of the keto form of **8** must be substantially lower than the enol form. However, since no measurable concentration of the enol form was detected, it is not possible to calculate a relative delocalization energy of the enol form from these data.

Work is presently in progress to synthesize the hydrocarbon from intermediates used in the above synthetic sequence.

Experimental

The following melting points have been corrected. The elemental analyses were performed by Alfred Bernhardt Microanalytical Laboratory, Mulheim, Germany.

5,6-Dichloromethylindane.—Indane, 100 g. (0.847 mole), was added to a mixture of paraformaldehyde, 60 g. (2 moles), and 600 ml. of concentrated hydrochloric acid. This mixture was heated to 110° for 36 hr. with vigorous stirring. The reaction mixture was then cooled and extracted with 200 ml. of ligroin (b.p. 60–110°). The organic layer was washed with 500 ml. of water and then dried over magnesium sulfate. The resulting solution was concentrated on a rotary evaporator to *ca.* 150 ml. and then distilled under vacuum. An initial fraction, 35 g. (b.p. 60–115° at 1 mm.), which consisted of indane and 5-chloromethylindane, was collected and then a second fraction, 111 g. (b.p. 115–138°, 61%) was collected. Cooling the second fraction in a freezer caused crystallization. The crude product was recrystallized three times from ligroin (b.p. 60–110°) to give colorless needles, 21 g. (11.5%), m.p. 73–74°.

Anal. Calcd.: C, 61.41; H, 5.62; Cl, 32.96. Found: C, 61.32; H, 6.09; Cl, 32.76.

Hydrogenation of the crude dichloride mixture with palladium on carbon gave a mixture of dimethylindanes which was analyzed by vapor phase chromatography on a DEGS column indicating three components in a ratio of 6:3:1. Hydrogenation of a product obtained by recrystallization of the crude dichloride mixture three times and vapor phase chromatographic analysis showed the component to be at least 95% pure.

(13) R. W. Schmid, E. Kloster-Jensen, E. Kovacs, and E. Heilbronner, *Helv. Chim. Acta*, **39**, 806 (1956).

(14) H. H. Rennhard, C. DiModica, W. Simon, E. Heilbronner, and A. Eschenmoser, *ibid.*, **40**, 957 (1957).

(15) G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1959).

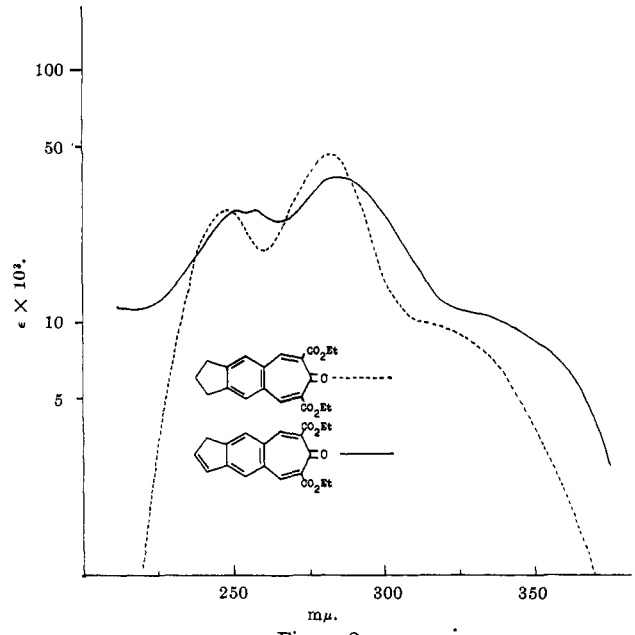


Figure 2.

Crude dichloride mixture (5 g.) was added to a solution of 50 ml. of concentrated nitric acid in 100 ml. of water and refluxed for 16 hr. The reaction mixture was concentrated by distillation to *ca.* 25 ml. and then transferred to an evaporating dish and heated on a steam bath to dryness. The residue was redissolved in 25 ml. of water and again evaporated to dryness. This latter procedure was repeated two more times to remove most of the residual nitric acid. The crude carboxylic acids were suspended in ether, and diazomethane in ether was added until the solution remained yellow. This solution was allowed to stand for 30 min.; then formic acid was added to decompose excess diazomethane. The ether was then evaporated and the residue was chromatographed on alumina (Merck neutral) with benzene. The first fractions contained the methyl ester of pyromellitic acid, which was recrystallized from methanol to give white plates (2.8 g., 39% yield), m.p. 141–143° (lit. m.p. 141.5°). Later fractions gave the tetramethyl ester of prehnitic acid which was recrystallized from methanol to give colorless needles (0.22 g., 3% yield), m.p. 134–135° (lit. m.p. 133–135°).

Recrystallized 5,6-dichloromethylindane, 2.5 g. (0.0117 mole), was added to a solution of potassium acetate, 3 g. (0.0303 mole), in 100 ml. of dry ethanol and refluxed for 12 hr. Then a solution of 5 g. of potassium hydroxide in 20 ml. of water was added and the resulting solution was refluxed for an additional 24 hr. The reaction mixture was then cooled and concentrated to *ca.* 25 ml. on a rotary evaporator. This residue was added to 200 ml. of water and extracted with 50 ml. of chloroform. The chloroform layers were combined, dried with magnesium sulfate, and evaporated to an oil. The crude diol was dissolved in 50 ml. of acetone and oxidized by dropwise addition of 5 ml. of aqueous 8 *N* chromic acid. The acetone was then decanted from the chromium salts and evaporated to a solid residue. This residue was recrystallized from 95% ethanol to give 0.58 g. (28%) of a lactone; infrared spectrum, ν 1750 cm.$^{-1}$ (C=O).

5,6-Dibromomethylindane.—Indane, 100 g. (0.847 mole), was added to a solution of paraformaldehyde, 60 g. (2 moles), in 700 ml. of 48% hydrobromic acid. The mixture was heated at 100° with vigorous stirring for 18 hr. The reaction mixture was then cooled, the organic layer was separated, and the aqueous layer was washed with 50 ml. of ether. The organic layers were then combined and distilled at reduced pressure. An initial fraction, collected at 110–150° (2 mm.), was a mixture of indane and monobromomethylindane, and a second fraction distilling at 160–171° (2 mm.) and consisting of a mixture of dibromomethylindanes was collected also. This second fraction was recrystallized three times from ligroin to give colorless prisms, m.p. 80–82°, 25.5 g. (10%).

Anal. Calcd. for $C_{11}H_{12}Br_2$: C, 43.45; H, 3.98; Br, 52.57. Found: C, 43.81; H, 4.06; Br, 52.20.

Hydrogenation, using palladium-on-carbon catalyst, of a sample of the crude dibromomethylindanes, and vapor phase chro-

matographic analysis of the resulting hydrocarbons on a DEGS column showed the mixture to contain the same products in the same ratio as obtained from dichloromethylation of indane. Hydrogenation of the recrystallized dibromomethylindane and vapor phase chromatographic analysis showed it to be at least 95% pure and consisting of the same hydrocarbon derived from 5,6-dichloromethylindane.

Indane-5,6-dicarboxaldehyde.—5,6-Dibromomethylindane, 21 g. (0.069 mole), was added to a solution of sodium 2-nitropropionate prepared by dissolving sodium metal, 3.1 g. (0.135 g.-atom) in 300 ml. of absolute ethanol and then adding 2-nitropropane, 12.2 g. (0.141 mole). The mixture was shaken vigorously from time to time and the temperature was controlled so that it did not exceed 25°. After 12 hr. the reaction mixture, which had turned bright yellow, was concentrated to an oil on a rotary evaporator, the temperature again being maintained below 25°. The solid–oil residue was extracted first with 100 ml. of ether, and then the remaining solid with 500 ml. of water. The two solutions were placed in a separatory funnel and the aqueous layer was withdrawn. The ether solution was then washed with 100 ml. of a 1% sodium hydroxide solution, concentrated to *ca.* 20 ml., and extracted with a 40% solution of sodium bisulfite. Addition of formaldehyde (34% aqueous solution) caused the separation of a yellow oil which was taken up in ether. Evaporation of the ether gave a yellow oil which crystallized from ligroin as yellow needles, 2.39 g. (19.8%), m.p. 50.5–52.5°.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.70; H, 5.82. Found: C, 75.63; H, 5.85.

Indano[5′,6′-4,5]-2,7-dicarboethoxytropone.—Indane-5,6-dialdehyde, 1.78 g. (0.01 mole), and diethyl acetonedicarboxylate 2.02 g. (0.01 mole, Aldrich), were dissolved in 40 ml. of 95% ethanol. Diethylamine, 2 drops, was added, causing the solution to warm slightly. After *ca.* 20 min., crystals started to precipitate. The reaction mixture was allowed to stand for 14 hr. and then concentrated to *ca.* 20 ml. with an air stream. The crystals were collected on a filter and washed with a few milliliters of 95% ethanol to give 0.585 g. Concentration of the mother liquor to an oil and chromatography on alumina (Merck neutral) using 50:50 benzene–ligroin gave an additional crystalline product which was recrystallized from 95% ethanol to give an additional 0.510 g. of tropone derivative (total 1.095 g., 32%). Recrystallization from 95% ethanol gave pale yellow needles: m.p. 176–177.5°; ultraviolet spectrum in 95% ethanol, 282 (ε 47,400) and 246 mμ (28,200).

Anal. Calcd. for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.51; H, 6.23.

Work-up of the mother liquor of the initial recrystallization after chromatography, by concentration, and cooling produced 0.456 g. (8.5%) of the bis adduct as white prisms, m.p. 143–145.5°.

Anal. Calcd. for $C_{29}H_{34}O_{19}$: C, 64.19; H, 6.32. Found: C, 64.33; H, 6.30.

1′-Bromoindano[5′,6′-4,5]-2,7-dicarboethoxytropone.—Indano-[5′,6′-4,5]-2,7-dicarboethoxytropone, 400 mg. (1.17 mmoles), N-bromosuccinimide, 220 mg. (1.24 mmoles), and azobisisobutyronitrile, 2 mg., were added to 8 ml. of carbon tetrachloride. After the mixture had been refluxed for 20 min., succinimide was floating at the surface. The succinimide was filtered off. Cooling of the resulting solution produced a white crystalline precipitate, 341 mg. (69%), which was satisfactory for further reaction. Recrystallization from carbon tetrachloride gave white needles: m.p. 150–152°; ultraviolet spectrum in 95% ethanol, 283 (ε 43,200) and 249 mμ (26,200).

Anal. Calcd. for $C_{20}H_{19}BrO_5$: C, 57.29; H, 4.57; Br, 19.06. Found: C, 57.07; H, 4.66; Br, 19.96, 19.73.

Indeno[5′,6′-4,5]-2,7-dicarboethoxytropone.—1-Bromoindane-[5′,6′-4,5]-2,7-dicarboethoxytropone, 275 mg. (0.656 mmole) was dissolved in a suspension of 2 g. of sodium iodide in 15 ml. of N,N-dimethylformamide and allowed to stand at room temperature for 36 hr. under nitrogen. During this time the solution had turned red-orange. The reaction mixture was diluted with 25 ml. of chloroform and then 50 ml. of distilled water was added. The chloroform layer was separated and again washed with 50 ml. of water. After the chloroform solution had been dried with magnesium sulfate it was evaporated down to give a brown-red solid residue. This solid was recrystallized from 95% ethanol to give orange plates, 82 mg. (36%). A second recrystallization from 95% ethanol gave pale yellow plates: m.p. 165.5–168°; ultraviolet spectrum in 95% ethanol, 286 (ε 37,600), 255 (27,800), and 248 mμ (27,500). Attempts to obtain carbon and hydrogen analyses gave erratic results indicating carbon values *ca.* 1% too low. These results are attributed to the decomposition referred to in the discussion. When this compound was treated with hydrogen and palladium-on-carbon catalyst, 2.89 moles of hydrogen were absorbed. This hydrogenation product was identical with that obtained by hydrogenation of indano-[5′,6′-4,5]dicarboethoxytropone, which was verified by identical infrared spectra and mixture melting point determination.

Acknowledgment.—The author wishes to express his indebtedness to the National Science Foundation for Grant NSF GP 758 which supported this work.

Anthocyanins and Related Compounds. IV. The Synthesis of Coumestrol and Related Coumarinobenzofurans from Flavylium Salts

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Received May 19, 1964

Coumestrol and related coumarinobenzofurans have been synthesized by hydrogen peroxide oxidation of appropriately substituted 2′-hydroxy-3-methoxyflavylium salts.

Following the structural elucidation[2] of wedelolactone I in 1957, a number of phenolic coumarinobenzofuran derivatives have been identified in plant extracts. However, with the exception of the elegent wedelolactone synthesis recently described by Wanzlick and coworkers,[2] a satisfactory, generally applicable, synthetic route to these phenolic and partially O-alkylated coumarinobenzofurans has not previously been developed.[3]

Coumestrol, a constituent of alfalfa and other forage crops,[4] is of particular interest because of its estrogenic properties.[5] In a preliminary communication[6] a synthesis of coumestrol from 2′,4′,7-trihydroxy-3-methoxyflavylium chloride (II) was reported briefly. This flavylium salt, oxidized with hydrogen peroxide in

(1) A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) (a) T. R. Govindachari, K. Nagarajan, B. R. Pai, and P. C. Parthasarathy, *J. Chem. Soc.*, 545 (1957); (b) H. W. Wanzlick, R. Gritzky, and H. Heidepriem, *Chem. Ber.*, **96**, 305 (1963).

(3) For representative synthetic approaches, see T. R. Govindachari, K. Nagarajan, and P. C. Parthasarathy, *J. Chem. Soc.*, 548 (1957); O. H. Emerson and E. M. Bickoff, *J. Am. Chem. Soc.*, **80**, 4381 (1958); C. Deschamps-Vallet and C. Mentzer, *Compt. rend.*, **251**, 736 (1960); Y. Kawase, *Bull. Chem. Soc. Japan*, **32**, 690 (1959), *Chem. Abstr.*, **56**, 1437 (1962).

(4) E. M. Bickoff, R. L. Lyman, A. L. Livingston, and A. N. Booth, *J. Am. Chem. Soc.*, **80**, 3969 (1958).

(5) E. M. Bickoff, A. L. Livingston, and A. N. Booth, *Arch. Biochem. Biophys.*, **88**, 262 (1960).

(6) L. Jurd, *Tetrahedron Letters*, **No. 18**, 1151 (1963).