Maleic Anhydride Adduct of *trans*-Piperylene (VII).—A solution containing maleic anhydride (1 mole), 0.5 g. of picric acid, and a mixture of *cis*- and *trans*-piperylene (2 moles) in 500 ml. of benzene was heated to reflux.[7] Attempts to purify the product by recrystallization, after removing benzene and *cis*-piperylene, were not successful, but the pure adduct melting 61–62° (lit.[7] m.p. 61°) could be obtained by two distillations at 127–129° (0.5 mm.).

The n.m.r. spectrum of the adduct in $CDCl_3$ as solvent exhibited a doublet for the C-3-methyl hydrogens at τ 8.66, slightly nonequivalent vinyl hydrogens at 4.09, C-1 and C-2 hydrogens at approximately 6.6, and the C-3 and C-6 hydrogens at approximately 7.5. The doublet for the C-3-methyl hydrogens using DMSO-d_6 as solvent occurred at τ 8.74.

The acid from VII, m.p. 154–157° (lit.[8] m.p. 156–158°), was isolated by heating 6 g. of the adduct in 35 ml. of boiling water for 10 min. and allowing the solution to stand overnight at room temperature.

The n.m.r. spectrum of the acid in DMSO-d_6 as solvent exhibited a doublet for the C-3-methyl hydrogens at τ 8.97.

Maleic Anhydride Adduct of *cis*-Piperylene (VIII).—A mixture of 33.2 g. of VII from *trans*-piperylene and 0.33 g. of dimethylaniline was heated 4 hr. at 190° (bath temperature).[8] Dimethylaniline was removed by distillation under reduced pressure, and the product was collected at 108° (0.75 mm.). The n.m.r. spectrum of a $CDCl_3$ solution indicated that only 40% isomerization had occurred as measured by the ratio of the peak areas for the C-3-methyl group in VIII at τ 8.73 and in VII at 8.66 using $CDCl_3$ as solvent.

Repetition of the base-catalyzed isomerization at 280–290° for 10 min. gave 22.2 g. of product, isolated by distillation at 134–136° (3.5 mm.), which consisted of 75% VIII and 25% unchanged VII.

The pure acid from VIII, m.p. 160–162° (lit.[8] m.p. 161–162°), was isolated by hydrolyzing 22 g. of the adduct mixture in 120 ml. of boiling water for 5 min., collecting the insoluble product after cooling, and recrystallizing the acid from 70 ml. of water at room temperature.

The n.m.r. spectrum of the acid in DMSO-d_6 as solvent exhibited only one doublet corresponding to the C-3-methyl group at τ 8.92.

Acknowledgment.—We wish to thank Mrs. M. T. Neglia for the n.m.r. spectra and Dr. R. Feinland for the v.p.c. data.

Synthesis and Study of Pseudo-Aromatic Compounds. IV. A Synthetic Approach to Anthrazulene[1]

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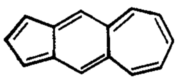
The synthesis of 5,7-diphenyl-1-anthrazulenium ion and attempts to convert this ion to 5,7-diphenylanthrazulene are described. The limited data available indicates that the anthrazulene ring system is extremely reactive to electrophilic attack.

The theoretical relevence of anthrazulene (1) lies in the fact that this molecule should serve as a criterion



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for the validity of applying empirical rules to predict aromatic character. Both Craig's rule[2] and the $4n + 2$ rule[3] are commonly used as a basis for predicting the presence or absence of stabilization in the ground state due to π-electron delocalization in cyclic conjugated polyenes. Since anthrazulene is predicted to possess a high π-electron delocalization energy from molecular orbital calculations (2.254 γ, 74.1 kcal./mole)[4] and has a $4n + 2$ periphery and totally symmetrical ground state, as predicted by Craig's rule, it would be expected to be aromatic. However, both these empirical rules and quantum mechanical approximation methods fail to take into account a high reactivity which might be associated with certain structural characteristics. Thus anthrazulene may possess a substantial π-electron delocalization energy in accordance with prediction, but may be highly reactive due to facile conversion to a benzenoid aromatic system by reaction with its environment, or it may possess essentially no π-electron delocalization energy and be unstable for the same reason.

It has been established that dehydrogenation of indano[5′,6′:1,2]cyclohepta-1,3-diene does not lead to anthrazulene and that it is not aromatic from a classical standpoint[5,6] (*i.e.*, it does not possess a high π-electron delocalization energy which is associated with a lowering of the ground-state energy in relation to its environment). Also it has been demonstrated that the anthrazulene ring system is a substantially higher energy species than related systems in which the central ring is formally benzenoid.[7]

In order to attempt to determine the ground-state properties of anthrazulene the synthesis of 5,7-diphenylanthrazulene has been investigated and the results of this investigation are reported herein.

Indane-5,6-dialdehyde[7] readily condenses with 1,3-diphenylacetone in the presence of base to give the corresponding indano[5′,6′:4,5]-2,7-diphenyltropone (2). This procedure has been shown to be a general method for the synthesis of 4,5-benzotropones.[8] The experimental molecular weight indicated that the product resulted from condensation of 1 mole of aldehyde and 1 mole of ketone. The n.m.r. (Figure 1) and infrared spectra are completely consistent with the proposed structure 2.

This indanotropone reacted with N-bromosuccinimide to give an unstable bromination product which lost hydrogen bromide upon attempts to recrystallize

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(1) Part III: D. J. Bertelli and C. Golino, *J. Org. Chem.*, **30**, 368 (1965).

(2) D. P. Craig, *J. Chem. Soc.*, 3175 (1951).

(3) E. Huckel, *Z. Physik*, **70**, 204 (1931); *Z. Electrochem.*, **43**, 752 (1937).

(4) G. Berthier, B. Pullman, and J. Baudet, *J. Chim. Phys.*, **50**, 209 (1953).

(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**, (1953); *Chem. Abstr.*, **49**, 3116 (1955).

(7) D. J. Bertelli, *J. Org. Chem.*, **29**, 3032 (1964).

(8) J. Thiele and J. Schneider, *Ann.*, **369**, 287 (1909); J. Thiele and E. Weitz, *ibid.*, **377**, 1 (1910); W. Reid and H. Bender, *Ber.*, **89**, 1574 (1956).

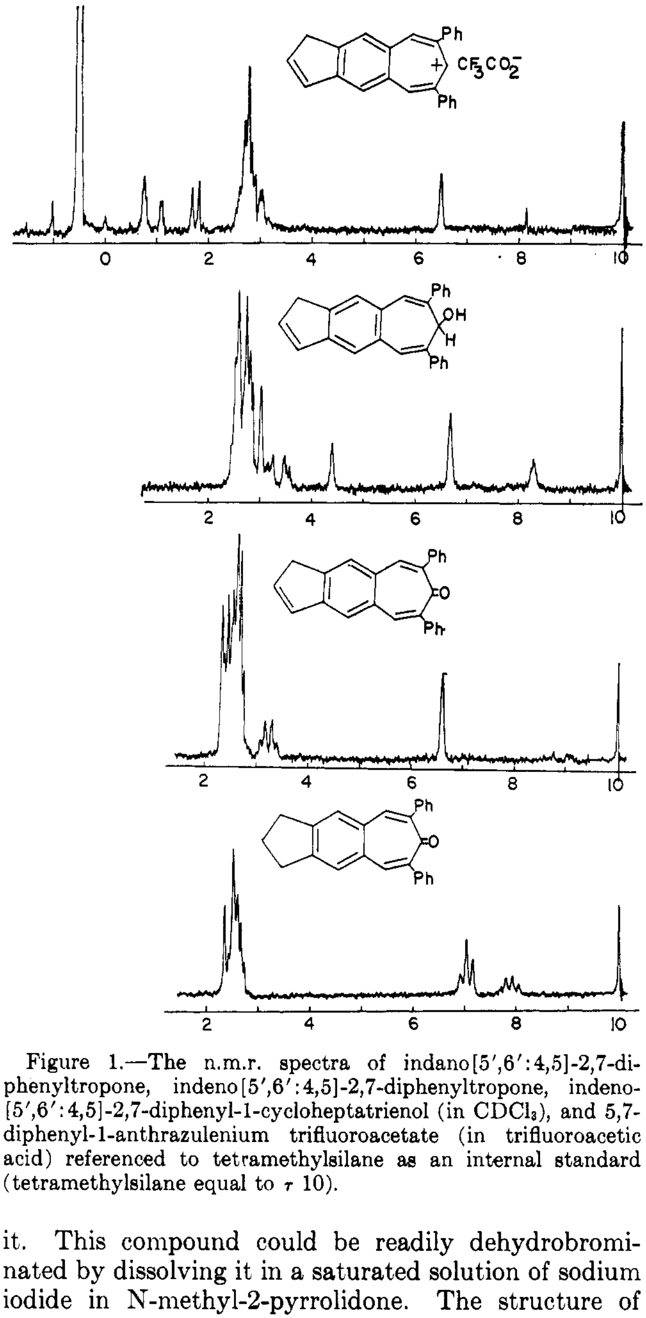
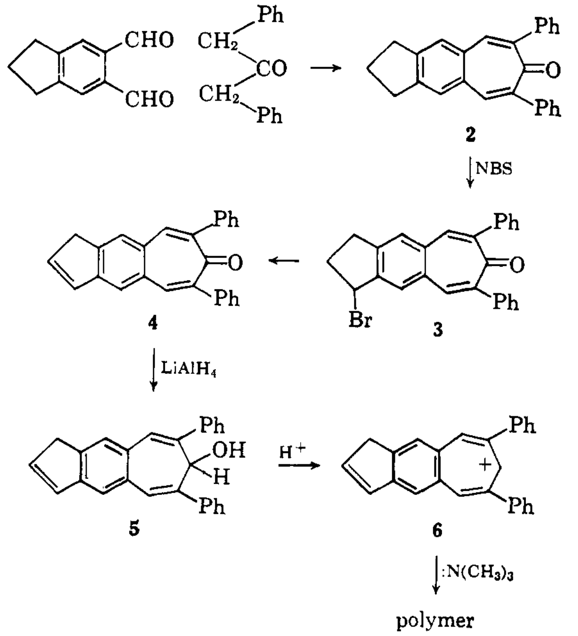


Figure 1.—The n.m.r. spectra of indano[5′,6′:4,5]-2,7-diphenyltropone, indeno[5′,6′:4,5]-2,7-diphenyltropone, indeno-[5′,6′:4,5]-2,7-diphenyl-1-cycloheptatrienol (in $CDCl_3$), and 5,7-diphenyl-1-anthrazulenium trifluoroacetate (in trifluoroacetic acid) referenced to tetramethylsilane as an internal standard (tetramethylsilane equal to τ 10).

it. This compound could be readily dehydrobrominated by dissolving it in a saturated solution of sodium iodide in N-methyl-2-pyrrolidone. The structure of this bromination product **3** was readily established by its n.m.r. spectrum which confirmed that substitution had occurred on the five-membered ring. The product of dehydrobromination of **3** was shown to be indeno[5′,6′:4,5]-2,7-diphenyltropone (**4**) by its n.m.r. spectrum (Figure 1). The multiplet at *ca.* τ 2.7 is assigned to the benzenoid and the 3,6-protons of the tropone ring. The multiplets at τ 3.2 and 3.3 are assigned to the vinyl protons of the five-membered ring and the singlet at τ 6.7, to the methylene of the five-membered ring. These latter values are in excellent agreement with the positions of the corresponding protons in indene. They are also in excellent agreement with the small coupling constant between the vinyl and methylene protons of indene. As was the case for the corresponding 2,7-dicarboethoxyindenotropone[7] there was no detectable tendency for the diphenyl compound **4** to enolize.

The diphenylindenotropone could be readily reduced by lithium aluminum hydride to the corresponding substituted 1-cycloheptatrienol **5**. This compound



could not be crystallized, but again the structure could be confirmed by the n.m.r. spectrum (Figure 1). The multiplet at τ 2.7 is assigned again to the benzenoid protons, and the singlet at τ 3.04 is assigned to the vinyl protons of the cycloheptatrienol ring. The multiplet at τ 3.2 and 3.5 and the peak at τ 6.7 are assigned to the five-membered ring protons. The peaks at τ 4.4 and 8.2 are assigned, respectively, to the hydroxyl and alkyl protons of the cycloheptatrienol ring.

Treatment of indenyl[5′,6′:4,5]-2,7-diphenylcycloheptatrienol (**5**) with trifluoroacetic acid produced an immediate color change. The n.m.r. spectrum of solutions of **5** in trifluoroacetic acid (Figure 1) demonstrates that the species produced from this reaction is 5,7-diphenylanthrazulenium ion. The peaks due to the 5,7-phenyl groups and the methylene of **6** are shifted downfield slightly but are readily recognizable. The vinyl protons of **5** have shifted downfield somewhat upon conversion to the carbonium ion and are partially overlapped by the 5,7-phenyl groups. The multiplet at τ 0.75 is due to the 4,8-protons of the seven-membered ring and the triplet at τ 1.05 is the 6-proton of this ring. The two peaks at τ 1.75 are the protons of the indenyl benzene ring and are not equivalent due to the dissymmetry caused by the five-membered ring.[9] The protons of the seven-membered ring are split, showing some 1,3-coupling (J = *ca.* 2 c.p.s.). The apparent quartet for the 4,8-protons is again due to the dissymmetry caused by the five-membered ring and consists of two overlapping doublets. This assignment is confirmed by the n.m.r. spectrum of indano[5′,6′:4,5]-2,7-diphenyltropenium ion which exhibits a triplet for the 1-proton of the seven-membered ring and a doublet (J = *ca.* 2 c.p.s.) for the 3,6-protons of this ring. (This compound will be discussed more fully later.)

Attempts to prepare an isolable salt of 5,7-diphenyl-1-anthrazulenium ion met with only limited success. Treatment of the cycloheptatrienol **5** with hexachloroplatinic acid in ethyl acetate immediately precipitated a dark red salt. The identity of this salt could be confirmed by the ultraviolet spectrum which was identical

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[9] This symmetry effect is also observed in the n.m.r. spectrum of indeno[5′,6′:4,5]-2,7-dicarboethoxytropone. See ref. 7.

with that produced by treating the cycloheptatrienol **5** with trifluoroacetic acid. However, the salt was extremely insoluble in all solvents tried and could not be recrystallized. This insolubility also made it useless as an intermediate for further reaction studies. Addition of the cycloheptatrienol **5** to either 70% perchloric acid or 45% fluoroboric acid again caused immediate precipitation of a red salt. These salts could again be verified as 5',7-diphenyl-1-anthrazulenium derivatives by n.m.r. and ultraviolet spectra but were unstable unless in the presence of strong acids. Thus, extraction of the reaction mixture produced by adding indeno[5',6':4,5]-2,7-diphenylcycloheptatrienol to either perchloric or fluoroboric acid with dichloromethane and subsequent evaporation of the solvent allowed isolation of the salts of ion **6**. However, they decomposed rapidly in the air and upon readdition of dichloromethane were no longer totally soluble. Attempts to prepare the fluoroborate or perchlorate salts in ether led to almost immediate decomposition of the salts into brown polymeric species. The apparent stability of the hexachloroplatinate salt under these same conditions is most likely a reflection of the insolubility of this latter salt. These salts also decomposed upon dissolving in acetonitrile. This data indicates that salts of 5,7-diphenyl-1-anthrazulenium ion are readily prepared but are labile to reaction with bases and that atmospheric moisture, ether, and acetonitrile are sufficiently basic to carry out this reaction.

When solutions of the trifluoroacetate, fluoroborate, or perchlorate salts of ion **6** in dichloromethane were added to a cold solution of excess trimethylamine in the same solvent, the intense red color of the ion changed to a light orange which darkened to a bright red in a few minutes. Attempts to concentrate these solutions by either a stream of deoxygenated nitrogen or distillation in a vacuum line led to the deposition of a pale yellow polymer. The ultraviolet spectrum of these solutions (Figure 2) taken a few minutes after mixing was identical with the ultraviolet spectrum of the polymer taken after removal of the solvent. Thus the species formed from the reaction of ion **6** and trimethylamine polymerizes in a few minutes. This conclusion is substantiated by the fact that addition of a dichloromethane solution of the reaction product of ion **6** with trimethylamine to excess trifluoroacetic acid does not lead to re-formation of **6** even if this acidification is carried out within a few minutes after the initial reaction. This could be verified by both the n.m.r. and ultraviolet spectra of the solutions resulting from acidification.

The polymeric species obtained by treating ion **6** with trimethylamine were pale yellow in color and partially soluble in dichloromethane and chloroform. The n.m.r. spectrum of these solutions showed a broad band from *ca.* τ 2.3 to 3.5 and, by integration, diffuse absorption in the aliphatic regions. The n.m.r. spectrum also eliminated the possibility of this product being a simple ammonium salt formed by addition of the amine to the carbonium ion. The ultraviolet spectrum of the polymer (Figure 2) is similar to that of the cycloheptatrienol **5** exhibiting a small bathochromic shift. This ultraviolet spectrum is consistent with a 1–5 or 1–9 polymer which would be expected to result from electrophilic polymerization of anthrazulene. The molecular weight of this polymer was *ca.* 1170 indicating that the polymer chains are relatively short. There is ample evidence that deprotonation of substituted tropenium ions[10,11] by trimethylamine is a general and rapid process. Thus, these data are consistent with the interpretation that 5,7-diphenyl-1-anthrazulenium ion is deprotonated by trimethylamine but rapidly polymerizes under the conditions employed above.

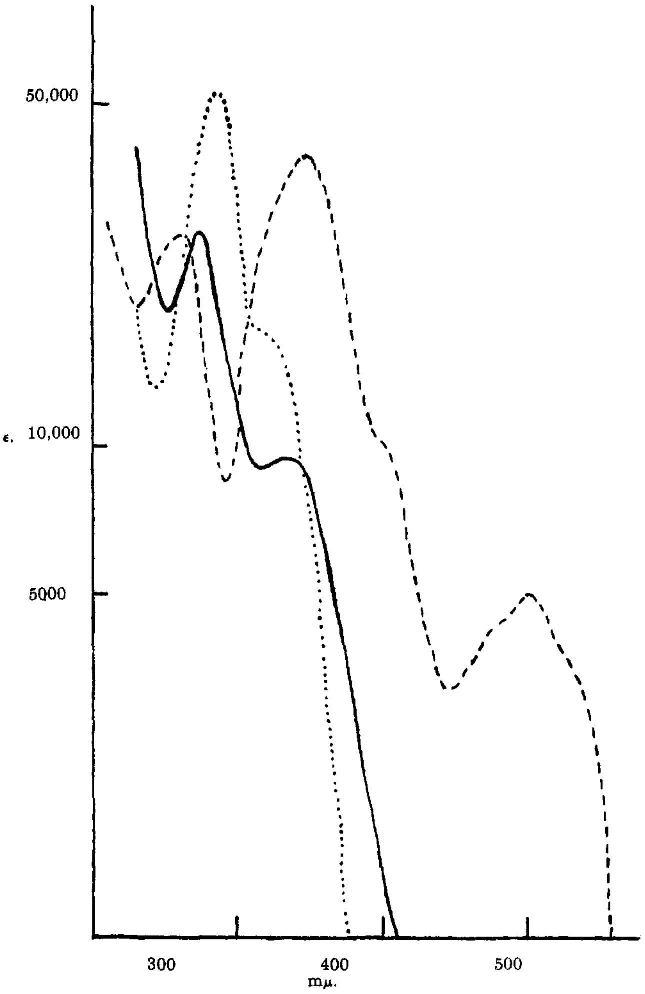

Figure 2.—The ultraviolet spectra of indeno[5',6'-4,5]-2,7-diphenyl-1-cycloheptatrienol (**5**) (in CH_2Cl_2) (· · · ·), 5,7-diphenyl-1-anthrazulenium hexachloroplatinate (**6**) (in H_2SO_4) (– – – –), and the polymer obtained from attempted deprotonation of 2,7-diphenyl-1-anthrazulenium ion (in CH_2Cl_2) (———).

Although filtration of the dichloromethane solutions obtained by addition of ion **6** to trimethylamine resulted in the isolation of trimethylammonium perchlorate or fluoroborate, this fact could not be taken as conclusive evidence for a deprotonation of ion **6** because of the inability to rule out the presence of traces of acid remaining in solutions of **6** from the original preparation of the ion.

These data clearly show that 5,7-diphenylanthrazulene is highly reactive toward the environment present under the reaction conditions described above, although it could not be established whether trace amounts of oxygen or trimethylammonium fluoroborate catalyzed the observed polymerization. However, the data do not allow any definite conclusion as

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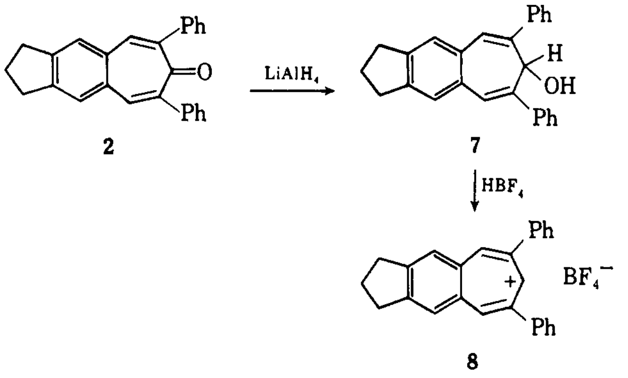
[10] H. J. Dauben, Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4657 (1961); H. J. Dauben, Jr., and R. B. Medz, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963, p. 75.

[11] K. Hafner, *Angew. Chem., Intern. Ed. Engl.*, **3**, 166 (1964).

to the presence or absence of an appreciable π-electron delocalization energy in the anthrazulene ring system. This observed instability of 5,7-diphenylanthrazulene can only be interpreted as demonstrating a relatively low activation energy to electrophilic attack, and thus comparable stabilities for ion **6** and 5,7-diphenylanthrazulene.

The reactivity of ion **6**, which we attribute to deprotonation and subsequent polymerization, is markedly different from that of indano[5′,6′:4,5]-2,7-diphenyltropenium fluoroborate (**8**) which is easily isolated under reaction conditions that fail to yield ion **6**. Reduction of indano[5′,6′:4,5]-2,7-diphenyltropone with lithium aluminum hydride gave the corresponding alcohol **7** which again could not be induced to crystallize. Treatment of this alcohol in ether with fluoroboric acid immediately produced a bright red-orange salt **8**, the structure of which was verified by its n.m.r. spectrum. The only difference between the π-electron systems of **6** and **8** is the additional double bond in **6**. It appears reasonable that the delocalization energy of both **6** and **8** are very nearly identical. This supposition is supported by the n.m.r. spectrum of **6** which indicates very little charge delocalization into the five-membered ring. If one then equates the delocalization energies of **6** and **8**, the higher reactivity of **6** may be attributed to the relatively lower energy associated with anthrazulene relative to the hypothetical system which would result by deprotonation of **8**. This leads one to the conclusion that there is some stabilization by formation of the fully cyclic anthrazulene system which may be in excess of a simple polyolefin. However, the actual magnitude may be quite small and is not available from the present data.



Experimental

The following analyses were performed by Alfred Bernhardt Microanalytical Laboratories, Mülheim, Germany, and West Coast Analytical Laboratories, El Cerrito, Calif. The melting points are uncorrected.

Indano[5′,6′:4,5]-2,7-diphenyltropone.—Indane-5,6-dialdehyde (3.67 g., 0.0211 mole) and 1,3-diphenylacetone (4.40 g., 0.021 mole) were dissolved in 50 ml. of anhydrous methanol. A pellet of sodium hydroxide was added to this solution and the flask was shaken until the sodium hydroxide dissolved. After approximately 30 min. a yellow oil separated from the solution. After 1 hr. approximately 10 ml. of ether was added while the solution was stirred with a glass rod. This caused the oil to crystallize. The crystalline product was collected on a filter and recrystallized from benzene–ligroin (b.p. 60–90°) resulting in pale yellow needles (4.65 g., 63%), m.p. 160.5–162.5°. An analytical sample was obtained by several recrystallizations from acetic acid.

Anal. Calcd. for $C_{26}H_{20}O$: C, 89.62; H, 5.78; mol. wt., 348. Found: C, 89.65, 89.49; H, 5.79, 5.82; mol. wt., 361, 346.

Infrared spectrum (KBr) had 1620 (C=O) and 1590 (C=C) cm.$^{-1}$; and ultraviolet spectrum (95% ethanol), 292 mμ (ϵ 43,800) and 255 mμ (ϵ 31,900).

1′-Bromoindano[5′,6′:4,5]-2,7-diphenyltropone.—Indano[5′,6′:4,5]-2,7-diphenyltropone (1.0 g., 2.86 mmoles), N-bromosuccinimide (0.55 g., 3.09 mmoles), and 10 mg. of azobisisobutyronitrile were added to 20 ml. of carbon tetrachloride. This mixture was refluxed for 20 min.; at this time the succinimide was floating at the surface of the solution. The solution was cooled and filtered to remove the succinimide. Evaporation of this carbon tetrachloride solution on a rotary evaporator gave a yellow oil which would not crystallize. An attempted recrystallization resulted in loss of hydrogen bromide. The n.m.r. spectrum of a sample of the crude material exhibited peaks at *ca.* τ 2.7 (multiplet, the phenyl and tropone hydrogens), 4.57 (triplet, the bromobenzylic hydrogen), and 7.18 (multiplet, the hydrogens of the five-membered ring) which established the structure as **3**.

Indeno[5′,6′:4,5]2,7-diphenyltropone.—Crude 1′-bromoindano[5′,6′:4,5]-2,7-diphenyltropone, prepared by using the above quantities and conditions, was dissolved in 10 ml. of N-methyl-2-pyrrolidone. Sodium iodide was then added to this solution, with stirring, until excess solid was present. The resulting solution was allowed to stand at room temperature for 12 hr. under nitrogen. After this period the solution was poured into 50 ml. of water and extracted with 30-ml. of chloroform. The chloroform solution was isolated and washed with an additional 50 ml. of water. The chloroform solution was then concentrated to a semisolid residue on a rotary evaporator. Ethanol (50 ml.) was added to this residue and the mixture was heated to boiling. Chloroform was then added until the solids dissolved at the boiling point of the solution. Cooling caused crystallization of yellow needles or plates (0.59 g., 60%). This material was recrystallized three additional times to give buff-colored needles, m.p. 173–176° dec.

Anal. Calcd. for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 89.95, 89.82; H, 5.49, 5.52.

Infrared spectrum had (KBr) ν 1610 (C=O) and 1580 (C=C) cm.$^{-1}$ in $CHCl_3$; ν (C=O) and ν (C=C) were the same and had no hydroxyl peak. The ultraviolet spectrum (95% ethanol) had λ_{max} 300 mμ (ϵ 43,900) and 266 mμ (ϵ 37,050).

5,7-Diphenyl-1-anthrazulenium Hexachloroplatinate.—Lithium aluminum hydride (200 mg., 5.25 mmoles) was added to indeno[5′,6′-4,5]-2,7-diphenyltropone (200 mg., 0.575 mmole) suspended in 25 ml. of ether. The resulting mixture was allowed to stand 20 min. after which 20 ml. of a saturated solution of ammonium chloride was added, dropwise. The ether layer was then isolated and dried over anhydrous magnesium sulfate. The dried ether solution was then filtered and concentrated on a rotary evaporator to an amorphous solid. This material would not crystallize. The n.m.r. spectrum was completely consistent with the structure of this compound as indeno[5,′6′:4,5]-2,7-diphenyl-1-cycloheptatrienol. The ultraviolet spectrum (CH_2Cl_2) had λ_{max} 320 mμ (sh, ϵ 17,000) and 284 mμ (ϵ 52,800). This alcohol (100 mg., 0.286 mmole) was dissolved in 2 ml. of ethyl acetate. A solution of hexachloroplatinic acid was prepared by dissolving chloroplatinic acid (3.54 g.) in 10 ml. of concentrated hydrochloric acid. This hexachloroplatinic acid soluion was added to 2 ml. of acetic acid. Addition of the ethyl acetate solution of the cycloheptatrienol to the acetic acid solution of hexachloroplatinic acid caused the immediate precipitation of a maroon precipitate (81 mg., 53%), m.p. *ca.* 200° (slowly turns black above with no sharp transition). This material was too insoluble, in all solvents tried, to recrystallize it. An analysis was obtained on the crude material. The ultraviolet spectrum (96% H_2SO_4) had λ_{max} 500 mμ (ϵ 4960), 344 mμ (ϵ 39,200), and 260 mμ (ϵ 27,000).

Anal. Calcd. for $(C_{26}H_{19})_2Cl_6Pt$: C, 58.32; H, 3.58. Found: C, 57.80, 57.50; H, 3.32, 3.59.

The same carbonium ion could also be prepared by dissolving the cycloheptatrienol in trifluoroacetic acid, or by adding a methanolic solution of the cycloheptatrienol to either 70% perchloric acid or 48% fluoroboric acid. Addition of the cycloheptatrienol to fluoroboric or perchloric acid caused immediate separation of a precipitate which was taken up in dichloromethane and dried over anhydrous magnesium sulfate. The dichloromethane solution was then used for subsequent reactions. The ultraviolet and n.m.r. spectra demonstrated that these products have the assigned structure.

Deprotonation of 5,7-Diphenyl-1-anthrazulenium Ion.—When solutions of either the fluoroborate, perchlorate, or trifluoroacetic salts of the 5,7-diphenyl-1-anthrazulenium ion in dichloromethane were added to a cooled solution (−65°) of trimethylamine (5 g.) in 25 ml. of dichloromethane, the color changed from the intense red characteristic of the ion to pale orange. The solutions darkened to a bright red in a few minutes. The ultraviolet spectrum of these solutions which were taken within 5 min. after initial reaction gave the spectrum in Figure 2. Isolation of a polymeric material after evaporation of the solvent gave an identical ultraviolet spectrum.

Anal. Found: C, 89.01; H, 5.91; mol. wt., 1170, 1172.

The analytical data indicates that the polymer chain is short. The low carbon content is explained by the short polymer chains since termination will leave a positive ion which must be accompanied by an inorganic anion which will cause a low carbon analysis.

Indano[5′,6:4,5]-5,7-diphenyltropenium Fluoroborate.—Indane[5′,6′:4,5]-2,7-diphenyltropone (200 mg., 0.575 mmole) was added to a suspension of lithium aluminum hydride (0.2 g. 5.25 mmoles) and allowed to stand for 20 min. Then 20 ml. of a saturated solution of ammonium chloride was added dropwise. The ether layer was isolated and dried over anhydrous magnesium sulfate. The ether was then removed on a rotary evaporator to give an amorphous solid which would not crystallize. This solid was dissolved in 5 ml. of ether and *ca.* 0.5 ml. of fluoroboric acid was added dropwise causing an immediate precipitation of a bright orange solid in quantitative yield. This compound could be recrystallized from acetonitrile, m.p. 218–220° dec.

Anal. Calcd. for $C_{26}H_{21}BF_4$: C, 74.30; H, 5.04. Found: C, 73.98, 73.95; H, 5.13, 5.19.

The ultraviolet spectrum (96% H_2SO_4) had λ_{max} 473 mμ (ϵ 3800), 327 mμ (ϵ 64,800), and 249 mμ (ϵ 24,500); the n.m.r. spectrum (trifluoroacetic acid), τ 0.32 (doublet, the 3,6-hydrogens of the tropenium ion), 0.67 (triplet, the 1-hydrogen of the tropenium ion), 1.34 (singlet, the benzene hydrogens of the indane system), 2.3 (multiplet, the 2,7-phenyl hydrogens), 6.46 (triplet, the α-hydrogens of the five-membered ring), and 7.51 (quintuplet, the β-hydrogens of the five-membered ring).

Acknowledgment.—The author would like to express his indebtedness to the National Science Foundation for Research Grant N.S.F. GP758 which supported this work.

The Preparation of S-(1-Propynyl)-L-cysteine

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Pourcelot, *et al.*, reported that simple 2-propynyl sulfides isomerize in base to the corresponding 1-propynyl sulfides. We have found that this reaction takes place with S-(2-propynyl)-L-cysteine (I) which, in the presence of potassium *t*-butoxide in dimethylformamide at 0°, isomerizes to S-(1-propynyl)-L-cysteine (II).

S-(2-Propynyl)-L-cysteine was prepared by reaction of 3-bromopropyne with disodium cysteinate in ethanol. The structure of the compound was established by infrared (sharp absorption at 3290 cm.$^{-1}$ characteristic for a terminal triple bond) and by n.m.r. The proton on the α-carbon appears in the n.m.r. spectrum taken in 0.6 *M* sodium deuterioxide as a quartet centered at τ 6.53 (referred to sodium 3-(trimethylsilyl)-1-propanesulfonate) due to gauche-*trans* spin–spin coupling to the β-protons. The β-methylene protons occur as the AB portion of an ABX multiplet and are centered at τ 7.1. The γ-methylene protons occur as a sharp singlet at τ 6.67. The remaining protons exchange with deuterium of the solvent. Integration confirmed the assignment. In sodium hydroxide solution, the acetylenic proton occurs at *ca.* τ 7.4 as a broad band.

The structure of the isomerized compound II was established by disappearance of infrared absorption at 3290 cm.$^{-1}$ and by n.m.r. In 0.6 *M* sodium deuterioxide with the same reference as before, the n.m.r. spectrum again showed the α-proton as a quartet but slightly shifted downfield to τ 6.43. The protons of the β-carbon gave an ideal eight-line AB portion of an ABX multiplet and were centered at τ 7.05. The protons of the acetylenic methyl group gave a single sharp peak at τ 8.08. Integration confirmed the assignment.

$$\underset{\text{I}}{\mathrm{HC{\equiv}CCH_2SCH_2CH(NH_2)COOH}} \longrightarrow$$

$$[\mathrm{H_2C{=}C{=}CH{-}S}\ldots\ldots] \longrightarrow$$

$$\underset{\text{II}}{\mathrm{CH_3C{\equiv}CSCH_2CH(NH_2)COOH}}$$

As Pourcelot, *et al.*,[2] suggested, this type of isomerization may proceed through a series of prototropic changes *via* an allenic intermediate[3] (see preceding equation).

We have been unable to isolate any allenic compounds in this reaction. When dimethyl sulfoxide was substituted for dimethylformamide, only resinous material could be isolated.

We further characterized S-(2-propynyl)- and S-(1-propynyl)-L-cysteines by preparation of crystalline N-2,4,6-trinitrophenyl derivatives and the cyclohexylamine salts of the N-2,4-dinitrophenyl (DNP) amino acids. The latter compounds have large negative molecular rotations in acetic acid in agreement with the general rule[4] that DNP derivatives of L-α-amino acids, except alanine, have negative rotations in acetic acid. The values are also large for the S-substituted cysteines. The trinitrophenyl derivatives of the two new amino acids, however, have small positive rotations in acetic acid.

Attempted reduction of the triple bond of S-(1-propynyl)-L-cysteine (II) with sodium and liquid ammonia led to desulfurization with the production of L-alanine as the only amino acid product.

Experimental

S-(2-Propynyl)-L-cysteine.—The procedure used is an adaptation of the method of Theodoropoulos.[5] To a stirred suspension

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

[2] G. Pourcelot, P. Cadiot, and A. Willemart, *Compt. rend.*, **252**, 1630 (1961).

[3] Pourcelot, *et al.*,[2] isolated an allenic sulfide by isomerization of a 2-propynyl sulfide carrying a methyl substituent on the α-carbon.

[4] K. R. Rao and H. A. Sober, *J. Am. Chem. Soc.*, **76**, 1328 (1954); J. F. Carson and F. F. Wong, *J. Org. Chem.*, **26**, 4997 (1961).

[5] D. Theodoropoulos, *Acta Chem. Scand.*, **13**, 383 (1959).