

The ether layer was washed with a saturated sodium bicarbonate solution and water, dried over sodium sulfate, and evaporated to dryness. Crystallization from ether yielded XXVIII (88 mg., m.p. 180–182°, 68%). A sample was recrystallized for analysis

from ether; m.p. 183–185°, $[\alpha]_D^{25} +119^\circ$ (c 0.21, CHCl_3), $\lambda_{\text{max}}^{\text{EtOH}}$ 240 m μ (15,400); $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.85, 6.00, 6.18 μ .

Anal. Calcd. for $\text{C}_{19}\text{H}_{26}\text{O}_2$: C, 79.68; H, 9.15. Found: C, 79.51; H, 9.42.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH.]

Protonation and Substitution Studies on Cyclopenta[*c*]thiapyran and 2-Phenyl-2-pyrindine¹⁻³

By ARTHUR G. ANDERSON, JR., AND WILLIAM F. HARRISON⁴

RECEIVED AUGUST 31, 1963

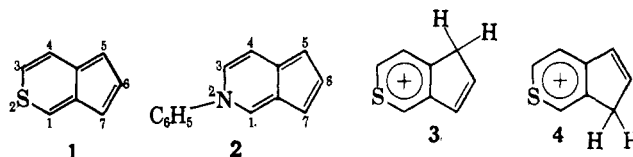
The behavior of the compounds in the title, which are iso- π -electronic hetero-analogs of azulene, with certain acids and bases is reported. The ultraviolet and n.m.r. spectra and comparisons with azulene indicate the probable positions of protonation. The successful electrophilic substitution of cyclopenta[*c*]thiapyran by a number of reagents, the positions of substitution as indicated by the n.m.r. spectra of the products, the effects of different substituents on the visible spectrum, and some reactions involving nucleophilic reagents are described and discussed.

The syntheses of the first simple π -excessive heterocyclic analogs of azulene, cyclopenta[*c*]thiapyran (1), and 2-phenyl-2-pyrindine (2), and a comparison of some of their physical properties with those of azulene were described in the previous paper.⁵ The similarities observed in the comparison led to the investigation of some of the chemical properties of the heterocycles and the present paper deals with results of these studies.

Behavior with Acids and Bases.—At the time we began these experiments, the basicity of azulene was well known and theoretical calculations, considerations of the spectral and proton magnetic resonance changes that occurred upon reaction with strong acids, and the analogy of electrophilic substitution provided strong evidence that protonation occurred in the 1-position.⁶ In the early n.m.r. work by Frey,⁷ however, the absorptions attributed to the 2- and 3-protons were not separately resolved and the assignment of the highest field absorption to water impurity appeared to be incorrect. Also the infrared spectral data of Bauder and Gunthard⁸ on dideuterioazulene did not seem to be really definitive with regard to this question. Therefore the proton magnetic resonance spectra of azulene in both 98% sulfuric acid and 70% deuterated 98% sulfuric acid were examined. The results (Fig. 1) obtained were clearly consistent only with complete, reversible protonation at the 1- (3-) position. Except that no coupling between the 1,1- and the 2- or 3-hydrogens was detectable, the spectrum in sulfuric acid was very similar to that in trifluoroacetic acid subsequently reported by Danyluk and Schneider.⁹ The proton exchange rate in the former solvent is thus appreciably the faster and the mean life-time of the ion is only a fraction of a second. The spectrum in deuterated acid did not change after 15 min. and showed deuteration at both the 1- and 3-positions.

These results plus the earlier analysis of the n.m.r. spectrum of cyclopenta[*c*]thiapyran⁵ provided a basis for the interpretation of the spectrum of this compound in acid (Fig. 2). The lack of symmetry in the molecule served to separate the absorptions for most of the dif-

ferent hydrogens, but it also meant that, depending on the relative stabilities of the ions formed by protonation at the 5- (3) or the 7-positions (4), there might be an appreciable concentration of one or two organic cationic species present. The spectrum obtained appeared to represent a single ion and therefore either predominantly one ion was formed or the electronic shielding of the corresponding hydrogens in the 5- and 7-protonated ions was essentially the same. The analysis of the spectrum was therefore as shown (Fig. 2).



The singlet of twice unit intensity at 5.99 τ was attributed to the 5,5-hydrogens in 3 (or the 7,7-hydrogens in 4). The doublets of unit intensity at 1.99 and 2.48 τ were assigned to the vinylic 6- and 7-hydrogens in 3 (or the 5- and 6-hydrogens in 4). These latter absorptions lie within 0.1 p.p.m. of those found for the corresponding 2- and 3-hydrogens of the azulenum ion. The rather poorly defined doublet at 1.19 τ was interpreted to arise from the 4-hydrogen, which would be coupled with the 3-hydrogen. The absorption in the region near 0.47 τ was explained as representing the superposition of a singlet from the 1-hydrogen and a doublet from the 3-hydrogen. It might be expected that the positions adjacent to the sulfur atom of a thiapyrylium system would be the least shielded. Two further aspects of the assignments should be noted. The relative positions of the peaks attributed to the 3- and 4-hydrogens is the reverse of that deduced for the spectrum of the unprotonated compound⁵ (wherein the absorption for the 3-hydrogen was well upfield from that of the 4-hydrogen). The present conclusion was based on the following series of experiments. First, conditions (7 *M* potassium *t*-butoxide in O-deuterated absolute *t*-butyl alcohol at 120–130° for ca. 18 hr.) were found which gave deuterium exchange in the 1-, 2-, 3-, 5-, and 7-positions of azulene¹⁰ (determined by

(1) Supported in part by a grant from the National Science Foundation.

(2) A portion of this work was reported in a preliminary communication: A. G. Anderson, Jr., and W. F. Harrison, *Tetrahedron Letters*, No. 2, 11 (1960).

(3) From the Ph.D. thesis of William F. Harrison.

(4) Standard Oil of California Fellow, summer, 1958; National Science Foundation Predoctoral Fellow, 1959–1960.

(5) A. G. Anderson, Jr., W. F. Harrison, and R. G. Anderson, *J. Am. Chem. Soc.*, **85**, 3448 (1963).

(6) For a discussion and references see E. Heilbronner, "Non-Benzenoid Aromatic Compounds," ed. by D. Ginsburg, Interscience Publishers, Inc., New York, N. Y., 1959, Chapter V.

(7) H. M. Frey, *J. Chem. Phys.*, **25**, 600 (1956).

(8) A. Bauder and H. H. Gunthard, *Helv. Chim. Acta*, **41**, 889 (1958).

(9) S. S. Danyluk and W. G. Schneider, *Can. J. Chem.*, **40**, 1777 (1962).

(10) These are precisely the positions of exchange predicted if the mechanism involves attack by the alkoxide ion at the 4- (8-) position as is observed for nucleophilic reaction with alkyl- and aryllithium reagents (K. Hafner, C. Bernhard, and R. Müller, *Ann.*, **650**, 35 (1961)). The deuterium exchange values for the different positions (68% maximum exchange possible) were 1- and 3- (ca. 68%); 2- (53%); 5- and 7- (64%); 4-, 6-, and 8- (ca. 0%). The absorptions for the 1-, 3-, and 6-positions were not completely resolved and the percentages for these are based on the fact that the total exchange for this region corresponded to complete equilibration for two hydrogens. It is possible that the value for the 1- and 3-positions is some less than 68% and the value for the 6-position is some larger than zero. No exchange was observed when azulene was heated under reflux with 2 *M* sodium methox-

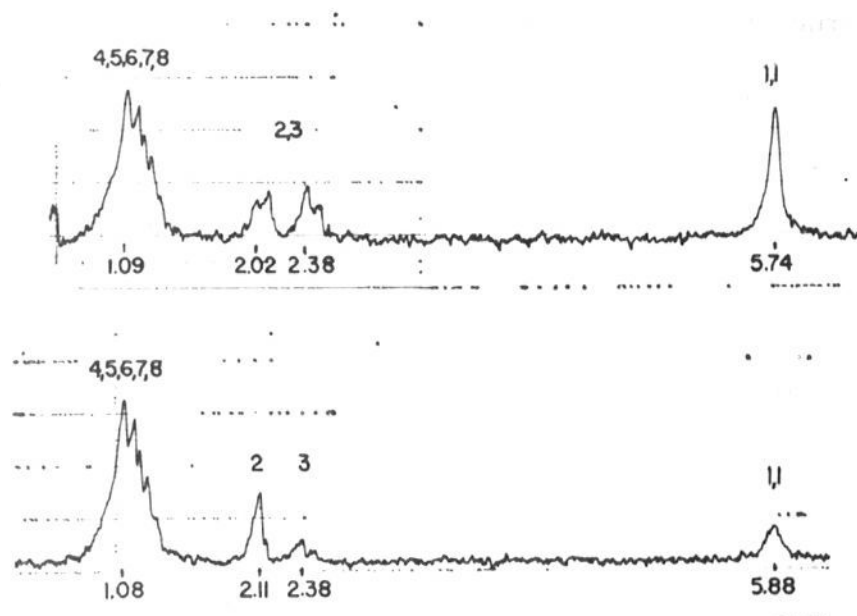


Fig. 1.—N.m.r. spectra of azulene in 98% sulfuric acid (upper curve) and in 70% deuterated 98% sulfuric acid (lower curve).

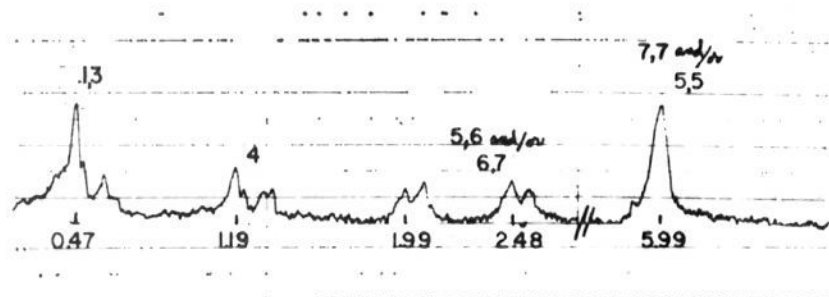
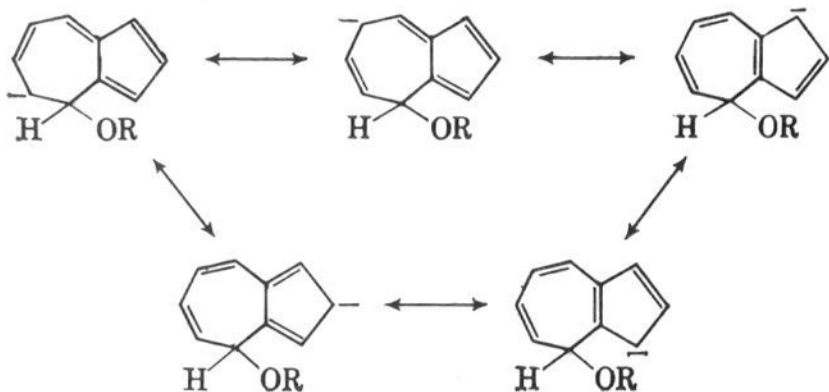


Fig. 2.—N.m.r. spectrum of cyclopenta[*c*]thiapyran in 98% sulfuric acid.

n.m.r.). Treatment of cyclopenta[*c*]thiapyran with the same strength of *t*-butoxide in 95% O-deuterated *t*-butyl alcohol at room temperature for 3 hr. resulted in greater than 90% exchange at the 1- and 3-positions and less than 5% exchange at the 4-, 5-, 6-, and 7-positions (Fig. 3).¹¹ The analysis of this spectrum in comparison with that of the nondeuterated compound confirmed the original assignments.⁵ Protonation of the 1,3-dideuterio substance afforded the species needed for comparison with the nondeuterated cation. The n.m.r. spectrum observed for the 1,3-dideuterio compound in sulfuric acid (Fig. 4) showed no absorption for the 1- and 3-positions in the region at 0.47 τ , and the

ide in 1:1 CH₃OH-CH₃OD for 2 days. Other workers (A. VanTets and H. H. Günthard, *Helv. Chim. Acta*, **45**, 457 (1962); W. Treibs and C. Weiss, *Naturwissenschaften*, **48**, 551 (1961)) have obtained somewhat different results under different reaction conditions.



(11) A mechanism which would exclude exchange at other than the 1- and 3-positions is not apparent *via* the usual modes of reaction. Selective proton abstraction at these positions would require the additional feature that the negative charge formed would not be distributed by resonance to other (e.g., 5-) positions such that exchange would occur. Nucleophilic attack by the alkoxide at the 5- or 7-position possesses this same limitation but is otherwise preferable. Attack at other positions leads to predictions which deviate even more from the results obtained. Attempts to determine the position of nucleophilic attack by reactions with phenyllithium and benzylolithium and subsequent treatment with chloranil gave unstable red oils which could not be characterized. It was noted that solutions of cyclopenta[*c*]thiapyran in 7 *M* potassium *t*-butoxide gradually deepened in color (to dark red) on prolonged standing in a sealed tube under reduced pressure.

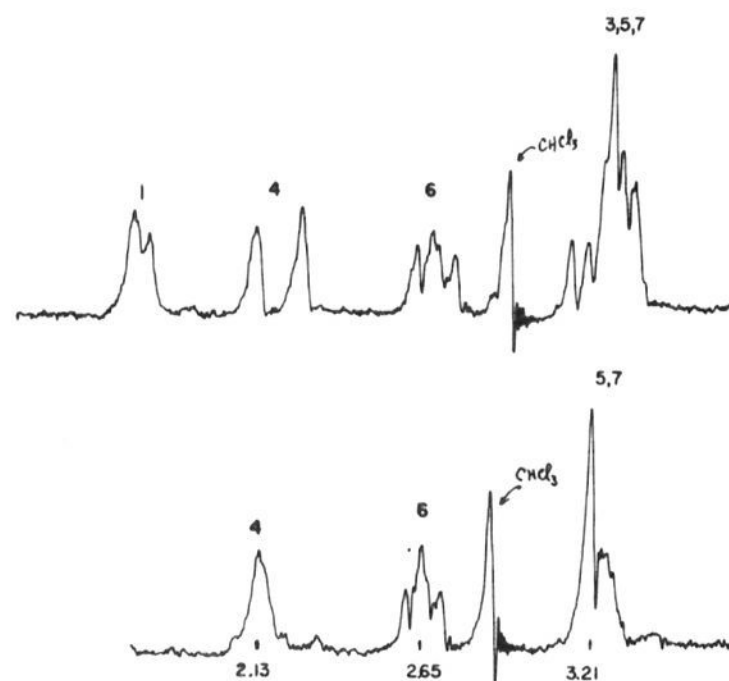


Fig. 3.—N.m.r. spectra of cyclopenta[*c*]thiapyran (upper curve) and 1,3-dideuteriocyclopenta[*c*]thiapyran (lower curve) in partially deuterated chloroform with hexamethyldisiloxane as the internal reference.

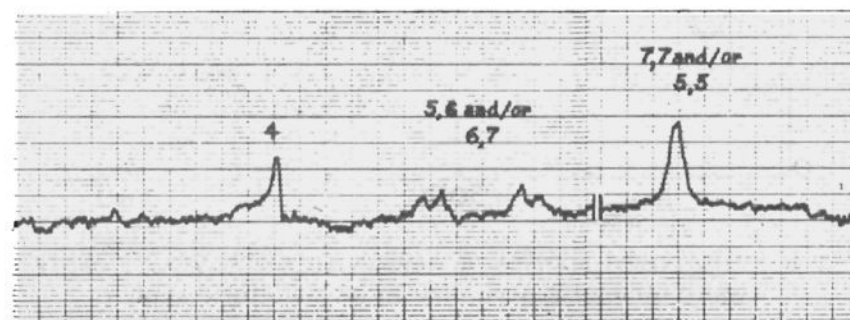


Fig. 4.—N.m.r. spectrum of 1,3-dideuteriocyclopenta[*c*]thiapyran in 98% sulfuric acid.

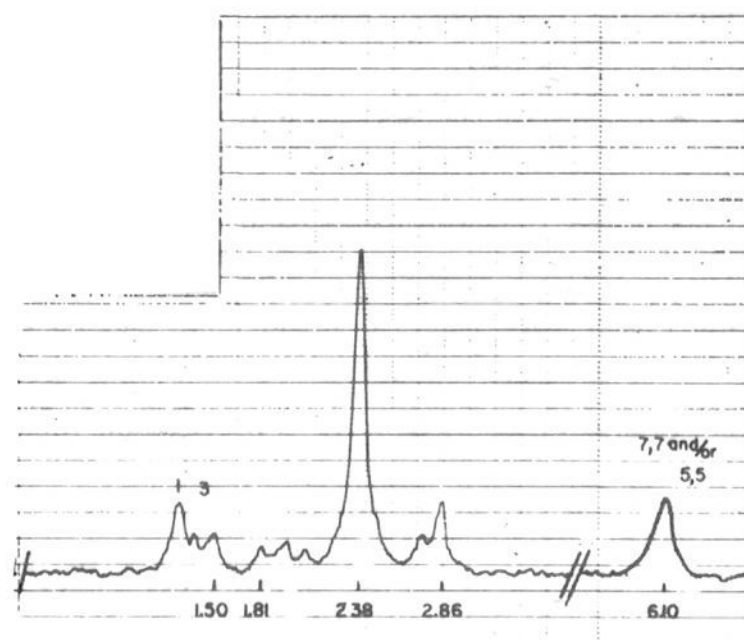


Fig. 5.—N.m.r. spectrum of 2-phenyl-2-pyridine in 98% sulfuric acid.

signal at *ca.* 1.2 τ assigned to the 4-hydrogen was now a singlet.

A second aspect of interest was the question of the position of protonation. An answer to this was sought through examination of the n.m.r. spectrum after treatment with partially (70%) deuterated sulfuric acid. The spectrum at the end of 15 min. corresponded to that expected for equilibration of the peak at 5.99 τ , and a reduction of the absorption at 2.48 τ approximating that for equilibration¹² also occurred. The latter was therefore attributed to the 7-hydrogen in **3** and/or the 5-hydrogen in **4**. The observance of

(12) The low intensities obtained relative to the variations in the base line did not permit an accurate measurement of the area in this region. The fact that the spectrum was unchanged after 24 hr. indicated equilibration had been attained. No exchange at positions 1, 3, 4, or 6 was detected.

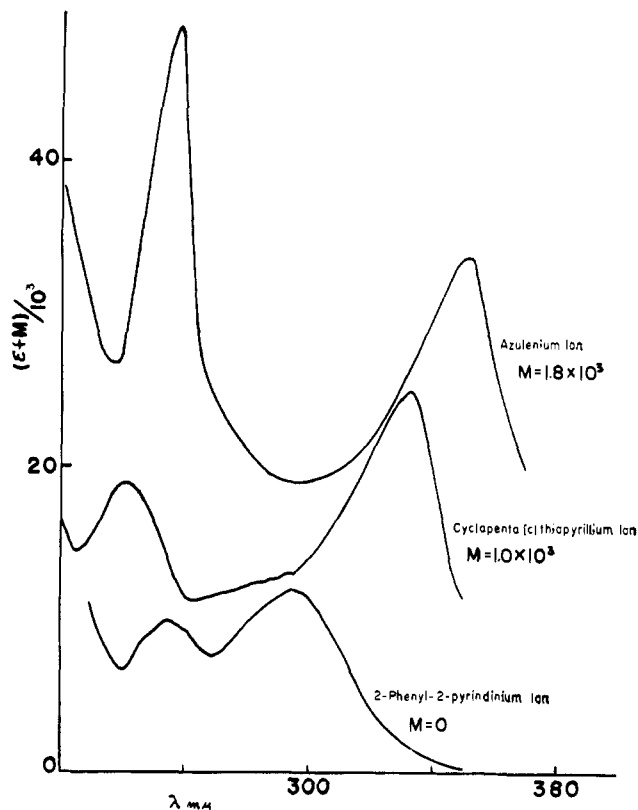
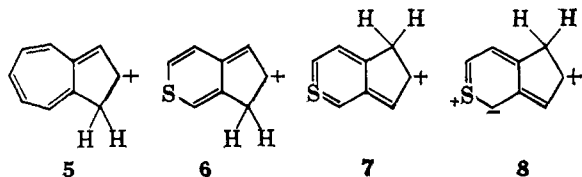


Fig. 6.—Ultraviolet spectra of azulene, cyclopenta[*c*]thiapyran, and 2-phenyl-2-pyridine in 98% sulfuric acid.

equilibration (or nearly so) at both the 5- and 7-positions within 15 min. is an indication that the stabilities of **3** and **4** are not grossly different but does not preclude the presence of predominantly one species in solution, and we feel this to be a more likely explanation of the simplicity of the spectrum than the fortuitous identity of the shielding of the corresponding hydrogens in the two ions.

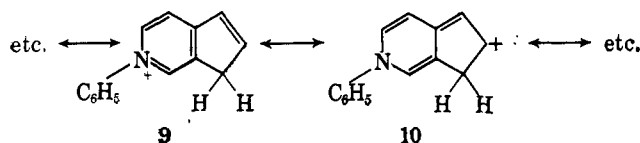
It was noted that the absorption due to the 2-hydrogen of the azulenium ion and that from the corresponding 6-hydrogen of the cyclopenta[*c*]thiapyrylium ion was in each case the lower field peak of those from the vinyl-type hydrogens in these systems. Insofar as this can be attributed to the contribution of resonance structures (*e.g.*, **5**, **6**, **7**, and **8**) wherein the positive charge is localized at these positions, the argument can be advanced (assuming the energies of the



ground states of **3** and **4** exclusive of contributions by structures such as **6**, **7**, and **8** are equal) that the participation of structures **7**, **8**, etc. (which involve either higher orbital bonding by sulfur or charge separation) would stabilize the 5-protonated ion **3** relatively less than the contribution of structure **6** would stabilize the 7-protonated ion **4**, and that the shielding of the 6-hydrogen in **3** and **4** would differ sufficiently to be detectable by n.m.r. Thus **4** is favored as the dominant species present.

Analogous reasoning is applicable to the interpretation of the spectrum of 2-phenyl-2-pyridine in 98% sulfuric acid (Fig. 5) in that only protonation at the 7-position (**9**) produces a pyridinium ion and also allows

structures having no charge separation to portray electron delocalization of the remaining double bond (**10**). On this basis assignments were made as follows: the singlet of twice unit intensity at 6.1 τ to the two



hydrogens at the 7-position, the doublet at 2.86 τ to the 5-hydrogen, the doublet near 1.5 τ to the 3-hydrogen, and the singlet at *ca.* 1.26 τ (which partially overlaps the adjacent doublet) to the 1-hydrogen. The absorption from the 4- and 5-hydrogens is less clearly defined and must be partially that observed near 1.8 τ and partially concealed by the large peak of the phenyl protons at 2.38 τ .

Solutions of azulenium ion in strong acids can be diluted with water or other bases and the liberated azulene can be recovered almost quantitatively. Boyd, in studies on benzocyclopenta[*b*]pyrans, had reported that these substances were stable to strong acid and to alcoholic hydroxide solutions, and were unstable to warm acetic acid, but had not commented further.¹³ Benzocyclopenta[*b*]thiapyrans and the corresponding pyridine compounds with phenyl substituents on the 2- and 4-positions of the heterocyclic ring were found to be stable to hot acetic acid as well as to strong acids and bases.¹⁴ When solutions of cyclopenta[*c*]thiapyrylium or 2-phenyl-2-pyridinium ion in concentrated sulfuric acid were diluted with water or other bases, only green polymer-like material could be recovered.¹⁵ Both substances were found to be stable in concentrated phosphoric acid and in >60% sulfuric acid, and also to 5% ethanolic potassium hydroxide. At intermediate acidities as in dilute sulfuric acid and in glacial acetic acid, however, decomposition rapidly occurred. The apparent explanation lies in the formation of some of the conjugate acid of the heterocyclic base in the presence of a sufficiently reactive nucleophile. In the decomposition which ensues, the latter could attack the conjugate acid at a position adjacent to the hetero-atom, with subsequent ring scission a probable result. The hetero-pseudoazulenes were also unstable to chromatography on Florisil, neutral alumina, and silica gel.¹⁶

The colorless to pale yellow appearance and ultraviolet spectra of solutions of azulene and **1** in concentrated sulfuric acid (Fig. 6) indicated that these were essentially completely in the protonated form. In acetic acid the initial ultraviolet and visible spectra showed the compounds to be present primarily as the free bases. In contrast, the initial spectrum of **2** was essentially the same in sulfuric (Fig. 6) and acetic acids. Thus azulene and **1** are appreciably weaker bases than acetate ion, and **2** is an appreciably stronger base than acetate ion.

Electrophilic Substitution.—The observed basicity of **1** and **2** with proton exchange at the 5- and 7-positions enhanced the likelihood that the similarity of these compounds to azulene would extend to electrophilic substitution at these positions. The relative quanti-

(13) G. V. Boyd, *Chem. Ind. (London)*, **37**, 1244 (1957); *J. Chem. Soc.*, 1978 (1958).

(14) G. V. Boyd, *ibid.*, 55 (1959).

(15) A quite low yield of cyclopenta[*c*]thiapyran was recovered when a solution of the conjugate acid of this in sulfuric acid was added dropwise to a slurry of aqueous potassium hydroxide and ether.

(16) An attempt to capture a possible fulvene aldehyde intermediate decomposition product in the ethereal eluate from chromatography on silica gel afforded a brown oil which gave a precipitate with 2,4-dinitrophenylhydrazine but could not be further identified.

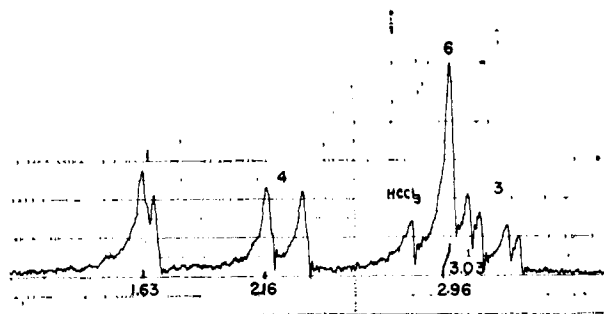
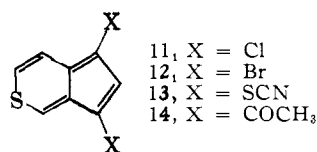


Fig. 7.—N.m.r. spectrum of 5,7-dichlorocyclopenta[*c*]thiapyran in partially deuterated chloroform with tetramethylsilane as the internal reference.

ties of the substances at hand and the absence of a second aromatic ring in **1** caused the selection of this compound for these studies. To avoid possible difficulties in the separation of isomeric monosubstitution products, attention was initially directed for the most part to reagents and conditions which had been found to give disubstituted products with azulene.

Treatment of **1** with two equivalents of *N*-chloro- or *N*-bromosuccinimide at room temperature formed a dichloro (66%) or a dibromo (50%) derivative, respectively. An attempt to effect trichlorination gave only a green polymer-like material. The ultraviolet and visible absorption spectra of the dihalo compounds closely resembled those of **1**. Reaction of **1** with excess thiocyanogen gave a 48% yield of a dithiocyano derivative. When the product from the treatment of **1** with mercuric acetate (probably the diacetoxymercuri derivative) was allowed to react with thiocyanogen, a compound having the same ultraviolet and visible spectrum as the dithiocyano derivative was formed in very low yield.¹⁷ Acetylation of **1** with excess acetic anhydride in the presence of stannic chloride gave a low (9%) yield of a diacetyl derivative.¹⁸

Evidence for the structures of these products as 5,7-disubstituted cyclopenta[*c*]thiapyrans (**11**–**14**) was obtained from examination of the n.m.r. spectra of the dichloro (**11**) and dithiocyano (**13**) compounds (Fig. 7 and 8). Conclusions based on a comparison of these



spectra with that of **1** depended on the assumption that the differences in the electronic distributions in the ground states of the parent system and the substitution products would not radically alter the relative absorptions of the hydrogens common to both. Thus in the spectrum of **11** (Fig. 7) absorptions with spin-spin couplings and relative intensities corresponding to those assigned to the 1-, 3-, and 4-hydrogens of **1** were found within 0.15 p.p.m. of the values for the latter.⁵ In place of the triplet at 2.58 τ for the 6-hydrogen in **1**, however, was a singlet of unit intensity at 2.96 τ . The structure of **11** as shown provided the only reasonable interpretation of the spectrum. It was gratifying to note that the quadruplet previously postulated for the 3-hydrogen in **1** but obscured in the spectrum of that compound⁵ was clearly revealed in the spectrum of

(17) The corresponding reaction with azulene gave a 97% conversion of the diacetoxymercuri compound to the dithiocyano derivative.

(18) It was subsequently discovered that stannic chloride caused the polymerization of **1**. This and the fact that the presence of an acid and a nucleophile at the same time could bring about decomposition (see above) probably account for the low yield.

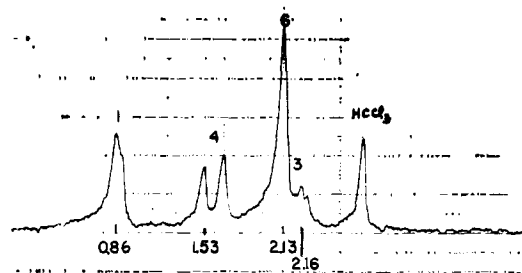
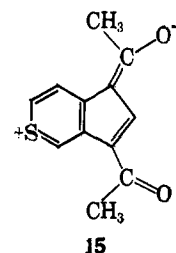


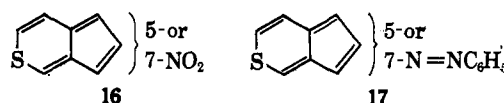
Fig. 8.—N.m.r. spectrum of 5,7-dithiocyanocyclopenta[*c*]thiapyran in partially deuterated chloroform with tetramethylsilane as the internal reference.

11. The n.m.r. spectrum of **13** (Fig. 8) was also readily interpreted only in terms of 5,7-substitution. The absorption envelope was similar to that of **11** but shifted *ca.* 0.8 p.p.m. to lower field. This shift probably reflects the large inductive effect of the two thiocyanogroups.¹⁹ Also the singlet from the 6-hydrogen was superimposed on the downfield portion of the absorption from the 3-hydrogen, and the splitting attributed to coupling between the 1- and 3-hydrogens was less than found for **11**. These data for **11** and **13** and the analogous mode of formation make structures **12** and **14** quite certain also.

The infrared spectrum of **14** showed a carbonyl absorption at 6.137 μ , an even longer wave length than that observed (6.103 μ) for 1,3-diacetylazulene. This indicates relatively more single bond character in the carbonyl groups of **14**, and thus that structures such as **15** contribute to the ground state of **14** more than the analogous structures do in the case of 1,3-diacetylazulene. This also suggests that the conjugate acid of **1** would be more stable relative to **1** than the azulonium ion is relative to azulene and, therefore, that **1** would be a stronger base than azulene.



Only a monosubstitution product (**16**) was obtained in 55% yield from the reaction of **1** and tetranitromethane. The properties of this compound did not provide a definitive distinction between 5- and 7-substitution, and extension of the arguments (above) favoring protonation at the 7-position to the nitration process provided the only basis of preference. Attempts to form a dinitro derivative with either tetranitromethane or nitric acid-acetic anhydride as the reagent were unsuccessful. Similarly, treatment of **1** with benzenediazonium fluoroborate gave only a monophenylazo derivative (**17**) in 78% yield.



It was of interest to examine the effects of the different substituent groups on the visible spectrum of **1** and compare these with the data from the corresponding azulene compounds. It was found that **1**⁵ and its substitution products displayed the same broad absorption curve with a number of low intensity maxima

(19) F. G. Bordwell and P. J. Bontan, *J. Am. Chem. Soc.*, **78**, 854 (1956).

(poorly resolved in the spectra of **13** and **16**) on the long wave length side. The maximum at the longest wave length was the most distinct and was therefore used for comparisons. As is the case with azulene derivatives²⁰ the position of this peak varied markedly with the nature of the substituent present (Table I). While the direction of the shift caused by a particular group was the same for derivatives of azulene and of **1**, the magnitude of the shift in each direction was uniformly less for the derivatives of **1**. The specific effects on the visible spectrum of different types of groups in the 1- and 3-positions of azulene have been successfully interpreted²¹ with the aid of the values calculated by Pariser for reversal of the direction of the dipole and the consequent changes in the ring atom electron densities accompanying excitation. The results in Table I,

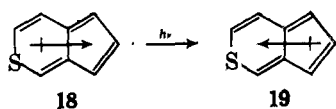
TABLE I

LONGEST WAVE LENGTH MAXIMA FOR 7- AND 5,7-SUBSTITUTED CYCLOPENTA[*c*]THIAPYRANS

5-, and or 7-substituent	λ_{\max} , $m\mu^a$	$\Delta\lambda_{\max}$, $m\mu^b$	$\Delta\nu_{\max}$, $cm.^{-1}b$	Corresp. azulene compound	
				$\Delta\lambda_{\max}$, $m\mu^b$	$\Delta\nu_{\max}$, $cm.^{-1}b$
None	565
Cl, Cl	616	52	-1492	58	-1544
Br, Br	606	41	-1197	45	-1241
COCH ₃ , COCH ₃	527	-38	1276	-60	1990
NO ₂	543	-22	717	-48	1556

^a *n*-Hexane solvent. This absorption was in most cases not resolved in polar solvents such as methanol and ether. ^b λ (or ν) of parent system - λ (or ν) of substituted compound.

and also the hypsochromic shift in the ultraviolet and visible spectra with increasing solvent polarity observed earlier,⁵ are indicative of similar characteristics for **1**: a dipole in the ground state oriented approximately along the long axis of the molecule (**18**), and a marked decrease, or even a reversal of the direction, of the dipole in the excited state (**19**) with a consequent decrease in the electron densities at the 5- and 7-positions. The fact that the spectral shifts are less with derivatives of **1** than with the corresponding azulenes suggests that in the former there may be a smaller net change in electron distribution involved.



Reaction of 1,3-Dibromoazulene and 5,7-Dichlorocyclopenta[*c*]thiapyran with Silver Nitrite.—In the course of concurrent studies on certain of the corresponding 1- and 1,3-substituted azulenes it was discovered that 1,3-dibromoazulene reacted with silver nitrite in ethanol to give a 63% yield of 1-nitro-3-bromoazulene, but no dinitroazulene was formed.²² This result was noteworthy in several respects. It was a nucleophilic substitution at a ring position known to be the most reactive to electrophilic species, and only one of the bromines was replaced with excess silver nitrite present. Further, the reaction provided a possible route to an unsymmetrically substituted nitrohalo derivative of **1**. To gain some indication of the nature of the reaction process involved, the kinetic dependence on the concentration of nitrite ion of the

(20) A. G. Anderson, Jr., R. G. Anderson, and T. S. Fujita, *J. Org. Chem.*, **27**, 4535 (1962); A. G. Anderson, Jr., and R. G. Anderson, *ibid.*, **27**, 3578 (1962), and references therein.

(21) A. G. Anderson, Jr., and B. M. Steckler, *J. Am. Chem. Soc.*, **81**, 4941 (1959).

(22) Subsequent to the completion of our experiments, similar results were reported for the reaction of 1,3-dibromoazulene derivatives with cuprous cyanide and silver thiocyanate: K. Hafner, H. Patzelt, and H. Kaiser, *Ann.*, **666**, 24 (1962).

reaction with 1,3-dibromoazulene was examined. The formation of the nitroazulene product was followed spectrophotometrically at 500 $m\mu$ and the optical density *vs.* time measured in runs made at 50° in aqueous dioxane with varying concentrations of nitrite ion (Table II). The total concentration of ions in all

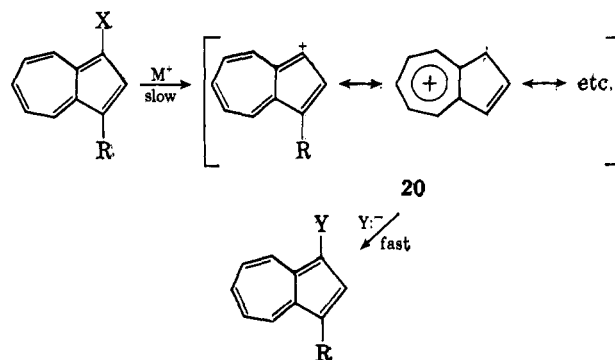
TABLE II

RATE DATA FOR 1,3-DIBROMOAZULENE PLUS SILVER AND NITRITE IONS

Run ^a	[Ag ⁺] ^b × 10 ²	[NO ₂ ⁻] ^c × 10 ²	D_{\max}^d			
			0 min.	125 min.	232 min.	1085 min.
1	1.05	1.05	0.33	0.85	1.23	1.96
2	1.05	6.95	.33	.90	1.15	1.83
3	1.05	18.75	.33	.65	0.88	1.63

^a All runs at 50° in 63% dioxane-water. ^b Concentrations of silver and nitrite ions expressed in moles/liter. ^c Excess nitrite ions from added sodium nitrite. ^d Optical density at 500 $m\mu$.

runs was high compared to the difference in concentration between runs and it was felt that changes in ionic strength would not be critical. The slight deceleration of the rate found with increased nitrite ion concentrations indicated that this ion was not involved in the rate-determining step.²³ Kinetic studies on the reactions of silver salts with alkyl halides²⁴ point to an appreciable degree of carbonium ion character in the transition state. Therefore if a relatively stable positive ion could be formed, the rate-determining step might involve the abstraction of halide ion by silver ion alone. The product would be formed in a subsequent, more rapid combination of the positive ion with the nucleophile. In that the loss of a halide from a 1-haloazulene would form a positive species (**20**) which might be stabilized through the delocalization of the positive charge, such a mechanism is proposed for the reaction of 1-haloazulenes with appropriate metal salts. The necessity of sufficient stabilization of the positive charge in the transition state serves to



explain the nonreactivity of the 3-nitro-1-haloazulene products, and of analogous 3-cyano- and 3-thiocyano-1-halo compounds obtained by Hafner, *et al.*²² This interpretation is also applicable to the reaction of certain halophenols with silver nitrite to form nitrophenols.²⁵ An "ion-pair" mechanism involving "molecular" silver salt²⁴ is not excluded, however, and further studies in progress include the investigation of this possibility, and also the existence of unpaired electrons in **20**.

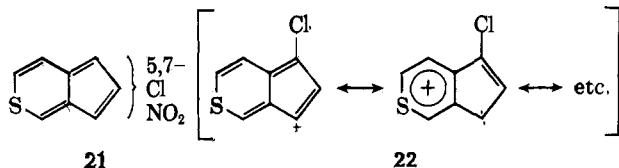
The analogous reaction of 5,7-dichlorocyclopenta[*c*]thiapyran (**11**) with silver nitrite was found to occur and gave a nitrochloro derivative (**21**) in 46% yield.

(23) Preliminary experiments showed the reaction to have a first-order dependence on silver nitrite and it was assumed that there was no specific dependence on "molecular" silver nitrite. D_{∞} was not determined in the kinetic runs (Table II) and therefore no *k*-values were calculated.

(24) G. S. Hammond, M. F. Hawthorne, J. H. Waters, and R. M. Graybill, *J. Am. Chem. Soc.*, **82**, 704 (1960); N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *ibid.*, **77**, 6269 (1955).

(25) M. Ringeissen, *Compt. rend.*, **198**, 2180 (1934);

A mechanism involving an intermediate ion (e.g., **22**) is also attractive for this case. What was probably the same compound (the ultraviolet and visible spectra, the melting points, and mixture melting point were essentially the same but the infrared spectra, though very similar, were not completely superimposable) was obtained from the reaction of the mononitro derivative (**16**) with N-chlorosuccinimide. Whether the product was the 5-chloro-7-nitro, or the 5-nitro-7-chloro compound was not determined. As mentioned earlier, the evidence available slightly favored the 7-position for mononitration and this would lead to the 5-chloro-7-nitro structure.



The obtaining of this unsymmetrically substituted derivative afforded an opportunity for a rough quantitative test of the additivity of the effects of two unlike groups on the long wave length absorption maximum in the visible region.²⁶ The spectral shift for a chloro group in the 5- or 7-position was assumed to be one-half of the amount found for the 5,7-dichloro compound. The calculated shift for **21** on this basis was +4 μ and this was very close to the observed value of +3 μ .

Experimental²⁷

t-Butyl Alcohol-*d*.—Deuterium oxide (40 g.) was equilibrated with dry *t*-butyl alcohol (74 g.) as described by Albin,²⁸ and 40 g. of product was recovered. The amount of exchange of the O-H hydrogen for deuterium was $95.4 \pm 1\%$ as determined by the ratio of the areas of the peaks for O-H absorption in the n.m.r. spectra of the deuterated and undeuterated material.

1,2,3,5,7-Pentadeuterioazulene.—Potassium metal (1.5 g., 38.4 mg.-atoms) was dissolved in 20 ml. of absolute *t*-butyl alcohol (70% deuterated) and 4.5 ml. (ca. 8.6 mmole) of potassium *t*-butoxide) of the solution thus formed was added to 87 mg. (0.68 mmole) of azulene in a thick walled glass tube. The sealed tube and contents were heated at 120–130° for 18 hr. At the end of this time an appreciable quantity of decomposition products had separated. The tube was cooled, opened, and 99.5% deuterium oxide was added to precipitate the azulene. The whole mixture was extracted with several portions of ether and the combined ether extracts were then washed with water and dried over sodium sulfate. After filtration, the solvent was removed under reduced pressure and a solution of the residue in *n*-pentane was chromatographed on Florisil with the same solvent as eluent. The percentage of deuterium exchange at the various positions of the azulene (28 mg.) obtained from the blue eluate fraction was determined from the ratio of the respective peak areas in the

(26) As cyclopenta[*c*]thiapyran is a nonalternant molecule which is iso- π -electronic with azulene, and as its spectral properties in the ultraviolet and visible regions closely parallel those of azulene, it might be expected that the remarkable additivity of the spectral shifts of individual groups found in poly-, and especially in 1,3-substituted azulenes (Plattner's Rule), would hold for the analogous 5,7-substituted heterocyclic analog. For references pertaining to this characteristic of azulenes see Pl. A. Plattner, A. Fürst, and K. Jirasek, *Helv. Chim. Acta*, **30**, 1320 (1947); A. J. Haagen-Smit, *Fortschr. Chem. Org. Naturstoffe*, **5**, 40 (1948); ref. 20. For a discussion of the interpretation of this phenomenon in terms of the nonsymmetrical spacing of the energy levels as indicated by simple MO theory see E. Heilbronner, "Non-Benzenoid Aromatic Compounds," ed. by D. Ginsburg, Interscience Publishers, Inc., New York, N. Y., 1959, pp. 231–245, and references therein.

(27) Melting points are corrected and boiling points are uncorrected unless otherwise indicated. Infrared spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer with a sodium chloride or calcium fluoride prism. Ultraviolet and visible spectra were taken on a Cary Model 11S or 14 spectrophotometer. Nuclear magnetic resonance spectra were recorded by Mr. B. J. Nist on a 60-Mc. Varian Associates spectrophotometer, Model V-K3507. Mass spectra were taken by Mr. B. J. Nist on a Type 21-103 Consolidated Engineering Corp. mass spectrometer. Microanalyses were performed by Drs. G. Weiler and F. B. Strauss, Oxford, England, Dr. Aldred Bernhardt, Max Planck Institute, Mülheim, Germany, or by B. J. Nist, L. Ho, A. Kuo, and C. H. Ludwig.

(28) J. R. Albin, Ph.D. Thesis, University of Washington, 1958.

n.m.r. spectra of the product and normal azulene recorded at the same concentration. The values found were 1- and 3- (ca. 68%), 2- (53%), 5- and 7- (64%), and 4-, 6-, and 8- (ca. 0%).¹⁰

1,3-Dideuteriocyclopenta[*c*]thiapyran.—Two milliliters of a solution prepared by the reaction of potassium (0.3 g., 7.38 mg.-atoms) in 10 ml. of 95% deuterated *t*-butyl alcohol was added to 68 mg. (0.508 mmole) of cyclopenta[*c*]thiapyran in a thick walled glass tube. The sealed tube and contents were kept at room temperature for 3 hr. The tube was opened and the organic material which precipitated upon the addition of 99.5% deuterium oxide was collected by filtration and washed with deuterium oxide. A solution of the wet product in 5 ml. of ether was dried over sodium sulfate. Removal of the solvent under reduced pressure left 30 mg. (44%) of product, m.p. 91–93°. Analysis of the n.m.r. spectrum of the product and comparison of the peak areas with the corresponding ones in the spectrum of undeuterated material taken at the same concentration indicated that greater than 90% exchange had occurred at the 1- and 3-positions (see the Discussion section). All maxima in the ultraviolet and visible absorption spectra were within 3 μ of those recorded for the undeuterated compound. The infrared spectra of the two species, however, were noticeably different.

Treatment of cyclopenta[*c*]thiapyran with potassium *t*-butoxide in *t*-butyl alcohol at higher temperatures brought about decolorization of the solution and complete loss of the thiapyran compound.

5,7-Dichlorocyclopenta[*c*]thiapyran (**11**).—To a stirred solution of cyclopenta[*c*]thiapyran (23 mg., 0.172 mmole) in 5 ml. of benzene was added dropwise over a period of 45 min. a solution of N-chlorosuccinimide (45.8 mg., 0.345 mmole) in 8 ml. of benzene, and stirring was continued for 14 hr. at room temperature. The red solution was then decanted onto a short column of alumina. Removal of the solvent under reduced pressure from the red eluate fraction which separated left a solid which was recrystallized twice from aqueous methanol and afforded 23 mg. (66%) of product **11** as red needles, m.p. 86–87°. A *n*-hexane solution showed λ_{\max} in $m\mu$ (log ϵ) at 234 (4.18), 252 (4.15), 260 (4.15), 281 (4.43), 291 (4.56), 329 (3.57), 333 (3.57), 339 (3.56), 356 (3.41), and 497 (3.19) with shoulders at 586 (2.67), 601 (2.46), and 617 (2.19). The infrared spectrum was recorded.

Anal. Calcd. for $C_8H_4SCl_2$: C, 47.31; H, 1.99; Cl, 34.92. Found: C, 47.04; H, 1.96; Cl, 34.87.

5,7-Dibromocyclopenta[*c*]thiapyran (**12**).—To a stirred solution of cyclopenta[*c*]thiapyran (11.3 mg., 0.0843 mmole) in 5 ml. of methylene chloride was added dropwise over a period of 1 hr. a solution of N-bromosuccinimide (29.7 mg., 0.167 mmole) in 9 ml. of methylene chloride. Stirring was continued at room temperature for an additional 1.5 hr. during which time some green material precipitated. The red solution was treated as described above for the analogous dichloro compound and recrystallization of the solid thus obtained twice from aqueous methanol gave 14.3 mg. (53%) of product **12** as red needles, m.p. 84–86° dec. A *n*-hexane solution showed λ_{\max} in $m\mu$ (log ϵ) at 232 (4.15), 253 (4.04), 261 (4.07), 283 (4.41), 293 (4.53), 330 (3.48), 339 (3.47), 357 (3.40), and 498 (3.20) with shoulders at 582 (2.67), 597 (2.48), and 608 (2.19). The infrared spectrum was recorded.

Anal. Calcd. for $C_8H_4SBr_2$: C, 32.90; H, 1.38. Found: C, 32.95; H, 1.62.

5,7-Dithiocyanocyclopenta[*c*]thiapyran (**13**).—A 2% solution of bromine in carbon tetrachloride was added slowly to a cold (0°), stirred suspension of lead thiocyanate (0.113 g., 0.35 mmole) in 2 ml. of carbon tetrachloride until the color of bromine just persisted. Sufficient lead thiocyanate to remove the excess bromine was then added.

The liquid decantate from the above mixture was added over a period of 5 min. to an ice-cold, stirred solution of cyclopenta[*c*]thiapyran (20.3 mg., 0.151 mmole). Stirring was continued for 2 hr. at 0° and then 30 min. at room temperature during which time some orange material precipitated. The supernatant orange solution was passed through a short column of neutral alumina and the orange fraction which was eluted with methylene chloride was collected. Removal of the solvent under reduced pressure and recrystallization of the residual solid twice from aqueous methanol yielded 18 mg. (48%) of product **13** as orange needles, m.p. 152–154°. An ether solution showed λ_{\max} in $m\mu$ (log ϵ) at 230 (4.25), 244 (4.20), 288 (4.40), 320 (3.64), and 453 (3.49). With *n*-hexane as the solvent and the use of 10-cm. cells, the peak in the visible region was shifted to 462 μ but no other maxima were resolved. The infrared spectrum (potassium bromide pellet) showed a sharp peak at 4.65 μ which was attributed to the thiocyanate groups.

Anal. Calcd. for $C_{10}H_4S_2N_2$: C, 48.36; H, 1.62. Found: C, 48.11; H, 1.28.

1,3-Dithiocyanazulene.—A solution of thiocyanogen in carbon tetrachloride, prepared as described above except that the initial amount of lead thiocyanate was 115.4 mg., was added to a cold (0°) stirred suspension of 71 mg. (0.11 mmole) of 1,3-diacetoxy-

mercuriazulene²⁹ in 2 ml. of carbon tetrachloride and the mixture was stirred for 2 hr. at 0° and then 2 hr. at room temperature. Treatment of the solution as described above for the isolation of 5,7-dithiocyanocyclopenta[*c*]thiapyran afforded 25.9 mg. (97%) of rose-red needles, m.p. 141–144°, from the methylene chloride eluate which were identical with an authentic sample.³⁰

5,7-Diacetylcyclopenta[*c*]thiapyran (14).—To a solution of cyclopenta[*c*]thiapyran (28.6 mg., 0.214 mmole) in 7 ml. of acetic anhydride was added stannic chloride (0.36 ml., 3.1 mmoles) and the mixture was allowed to stand at room temperature for 1 hr. The green solution which resulted was poured into a mixture of 77 ml. of 2 *N* sodium hydroxide and 50 g. of ice and the whole was shaken for 5 min. and then extracted with successive portions of ether until the extracts were colorless. The solvent was removed from the combined, dried (sodium sulfate) extracts under reduced pressure and the residual red oil was fractionally distilled onto the cold finger of a small sublimation apparatus at *ca.* 90° and 1 mm. The solid fraction was twice recrystallized from ether–hexane and gave 4 mg. (9%) of product 14 as orange needles, m.p. 183–184.5°. A *n*-hexane solution showed λ_{\max} in $m\mu$ ($\log \epsilon$) at 240 (4.25), 284 (4.67), 294 (4.43), 308 (4.38), 358 (3.46), 366 (3.53), and 470 (3.64), with shoulders at 508 (3.39), 517 (3.29), and 527 (3.09). The infrared spectrum (chloroform, calcium fluoride prism) showed strong absorption which was attributed to the carbonyl groups at 6.136 μ . The carbonyl absorption of 1,3-diacetylazulene under the same conditions was observed at 6.103 μ .

Anal. Calcd. for $C_{12}H_{10}O_2S$: C, 66.03; H, 4.62. Found: C, 66.14; H, 4.54.

5- (or 7-) Nitrocyclopenta[*c*]thiapyran (16).—To a stirred solution of cyclopenta[*c*]thiapyran (16.3 mg., 0.12 mmole) in 0.5 ml. of pyridine and 10 ml. of ethanol was added 0.6 ml. of a 0.25 *M* solution of tetranitromethane in ethanol. The solution darkened and black material precipitated. After standing 10 min. at room temperature the mixture was concentrated almost to dryness under reduced pressure. The residue was taken up in benzene and the orange solution which resulted was passed through a short Florisil column. Elution with methylene chloride, removal of the solvent from the orange fraction under reduced pressure, and recrystallization of the residual solid twice from aqueous methanol gave 12 mg. (55%) of product 16 as orange needles, m.p. 147.5–150°. An ether solution showed λ_{\max} in $m\mu$ ($\log \epsilon$) at 223 (4.13), 249 (4.19), 259 (4.17), 321 (4.23), 350 (3.81), 3.64 (3.81), 390 (3.53), and 478 (3.72). With *n*-hexane as the solvent in 10-cm. cells shoulders were observed at 503, 522, 532, and 543 $m\mu$.

Anal. Calcd. for $C_8H_5NSO_2$: C, 53.03; H, 2.79. Found: C, 53.38; H, 2.88.

5- (or 7-) Phenylazocyclopenta[*c*]thiapyran (17).—To phenyldiazonium fluoroborate (29 mg., 0.115 mmole) was added a cold (0°) solution of cyclopenta[*c*]thiapyran (20 mg., 0.149 mmole) and sodium acetate (60 mg., 0.75 mmole) in 5 ml. of methanol. The resulting violet solution was stirred for 20 min. at 0°. The solvent was removed under reduced pressure and the residue was triturated with a few milliliters of methylene chloride. The colored solution thus obtained was chromatographed on a short column of neutral alumina with methylene chloride as the eluent. Removal of the solvent from the violet fraction and recrystallization of the residual solid twice from hexane gave 28 mg. (78%) of product 17 as violet prisms, m.p. 94–96°. A *n*-hexane solution showed λ_{\max} in $m\mu$ ($\log \epsilon$) at 234 (4.16), 290 (4.19), 297 (4.19), 396 (4.21), and 525 (3.83).

Anal. Calcd. for $C_{14}H_{10}SN_2$: C, 70.56; H, 4.23; N, 11.76. Found: C, 69.73; H, 4.49; N, 11.70.

(29) D. J. Gale. Ph.D. Thesis, University of Washington, 1957.

(30) A. G. Anderson, Jr., and R. N. McDonald, *J. Am. Chem. Soc.*, **81**, 5669 (1959).

1-Nitro-3-bromoazulene.—A mixture of 1,3-dibromoazulene³¹ (30.7 mg., 0.107 mmole) and silver nitrite (30.7 mg., 0.199 mmole) suspended in 8 ml. of ethanol and 3 ml. of water was heated under reflux for 18 hr. and then evaporated to dryness under reduced pressure. A solution of the residue in a little benzene was chromatographed on a column of neutral alumina. Elution with benzene removed unchanged 1,3-dibromoazulene (6.8 mg.); removal of the solvent from the colored fraction eluted with methylene chloride and recrystallization of the residual solid from methylene chloride–*n*-hexane gave 13.5 mg. (63%) of 1-nitro-3-bromoazulene, m.p. 184.5–187° (lit.³¹ 183–184°) which was identical (ultraviolet, visible, and infrared spectra) with an authentic sample.

Kinetic Dependence on Nitrite Ion of Reaction of 1,3-Dibromoazulene with Silver Nitrite.—Sufficient 1,3-dibromoazulene was dissolved in 50 ml. of 50% aqueous dioxane to give a spectroscopically determined (λ 630 $m\mu$, ϵ 400) concentration of 1.25×10^{-3} *M*. Three solutions were prepared as follows. Each contained 30 mg. of silver nitrite in 10 ml. of 75% dioxane–water and thus a silver ion concentration of 2.1×10^{-2} *M*. Solution A had no other ingredients and thus was 2.1×10^{-2} *M* in nitrite ion. Solution B contained 100 mg. of sodium nitrite in addition and was 13.9×10^{-2} *M* in nitrite ion. Solution C contained 300 mg. of sodium nitrite in addition and was 37.9×10^{-2} *M* in nitrite ion. Kinetic runs were made by combining 5.0 ml. of the dibromoazulene solution with 5.0-ml. portions of solutions A, or B, or C. The temperatures of the solutions prior to mixing and of the reaction mixture were kept at 50° in a constant temperature bath. Portions of the separate runs were withdrawn at the same time intervals and cooled quickly in ice water. The optical densities at 500 $m\mu$ (Table II) were determined on a Cary spectrophotometer.²⁷ D_{∞} values were not measured and therefore no *k*-values were calculated.

5- (7-) Chloro-7- (5-) nitrocyclopenta[*c*]thiapyran (21).—A mixture of 5,7-dichlorocyclopenta[*c*]thiapyran (30 mg., 0.149 mmole) and silver nitrite (130 mg., 0.845 mmole) suspended in 8 ml. of ethanol and 3 ml. of water was heated under reflux for 15 hr. and the solvent was then removed under reduced pressure from the orange solution which resulted. The residue was treated with a few milliliters of methylene chloride and the solution was chromatographed on a column of neutral alumina with the same solvent as the eluent. Removal of the solvent from the major orange fraction and recrystallization of the residual solid twice from aqueous methanol gave 14.5 mg. (46%) of product 21 as orange-red needles, m.p. 191.5–193°. An ether solution showed λ_{\max} in $m\mu$ ($\log \epsilon$) at 244 (4.07), 256 (4.11), 264 (4.12), 332 (4.23), 360 (3.70), 375 (3.72), 400 (3.57), and 495 (3.62). With *n*-hexane as the solvent, additional maxima were observed at 545, 556, and 568 $m\mu$. The infrared spectrum was recorded.

Anal. Calcd. for $C_8H_4ClO_2NS$: C, 48.36; H, 1.62. Found: C, 48.11; H, 1.28.

Reaction of 7- (5-?) Nitrocyclopenta[*c*]thiapyran with N-Chlorosuccinimide.—To a stirred solution of 7- (5-?) nitrocyclopenta[*c*]thiapyran (6.5 mg., 0.037 mmole) in 5 ml. of benzene was added slowly a solution of *N*-chlorosuccinimide (6 mg., 0.045 mmole) in 5 ml. of benzene. The mixture was stirred at room temperature for 5 hr. and then chromatographed on a short column of neutral alumina. Elution with methylene chloride gave an orange fraction which, after removal of the solvent under reduced pressure, yielded 6.5 mg. of orange needles, m.p. 165–190°. Recrystallization five times from aqueous methanol gave 1.5 mg. (17%) of product, m.p. 189–195°, which was indicated to be the same as that (21) from the reaction of 5,7-dichlorocyclopenta[*c*]thiapyran with silver nitrite (above) by a mixture melting point (189–193°) and the qualitative identity of the ultraviolet and visible absorption spectra of the two compounds. The infrared spectra, however, though very similar, were not completely superimposable.

(31) A. G. Anderson, Jr., J. A. Nelson, and J. J. Tazuma, *ibid.*, **75**, 4980 (1953).