solvent from the filtrate gave the saturated ketone XXXI (524 mg.) as a colorless oil. The 2,4-dinitrophenylhydrazone was prepared and recrystallized from methanol to give a mat of fine yellow needles which changed to stout prisms on standing in the solution; m.p. 146–147°.

Anal. Calcd. for $C_{20}H_{26}O_4N_4$: C, 62.16; H, 6.78. Found: C, 62.20; H, 6.95.

(b) Oxidation of the Alcohol XXXVII.—A solution of 219 mg. of the saturated alcohol XXXVII (m.p. 120–121°) in 2.2 ml. of pyridine was added to a suspension of the chromic acid–pyridine complex prepared by adding 224 mg. of chromic anhydride to 2.2 ml. of pyridine. The mixture was left at room temperature for 23 hours and dry ether was then added. The solids were collected and washed with dry ether. The filtrate was washed with dilute hydrochloric acid and water, dried over anhydrous sodium sulfate and gave, after removal of the solvent, 190 mg. of the ketone XXXI as a yellowish oil. The 2,4-dinitrophenylhydrazone was prepared and recrystallized from methanol; m.p. 146–147°. The melting point was not depressed on admixture with the 2,4-dinitrophenylhydrazone of the ketone obtained by reduction of the enone XXXVI.

Reduction of the Ketone XXXI.—The saturated ketone XXXI (164 mg.) was added in ether solution to a stirred suspension of 0.40 g. of lithium aluminum hydride in ether (total volume 30 ml.). The mixture was stirred under reflux for 17 hours and then cooled. Excess lithium aluminum hydride was decomposed with an aqueous sodium sulfate solution and anhydrous sodium sulfate was added. The solids were collected and washed with dry ether and the filtrate was evaporated to give 140 mg. of a colorless solid, m.p. 118–120°. One recrystallization from petroleum ether gave 96 mg. of colorless needles, m.p. 120–121°. One

further recrystallization from petroleum ether did not raise the melting point. The melting point was not depressed on admixture with the saturated alcohol XXXVII obtained from the β-diketone XXXIV and the infrared spectra were identical.

Preparation of Cedrol from the Ketone XXXI.—Methyllithium was prepared by adding 6 ml. of methyl iodide to 1.8 g. of lithium (in 6 pieces) in 40 ml. of dry ether, with stirring and cooling in ice. When the initial vigorous reaction had subsided the mixture was refluxed with stirring for 4 hours. The mixture was then cooled and the unreacted lithium (0.90 g.) was removed (calculated amount of methyllithium: 0.06 mole).

The ketone XXXI (446 mg., 0.0021 mole) in dry ether was added slowly to the solution of methyllithium and the mixture was refluxed with stirring for 18.5 hours. Excess methyllithium was decomposed by adding aqueous sodium sulfate solution containing some sodium thiosulfate to the stirred, ice-cooled solution. Water was added and the ether layer was separated and washed well with water, dried over anhydrous sodium sulfate and evaporated to give 480 mg. of crude cedrol as a solid residue. The crude product was recrystallized from methanol–water four times to give colorless needles: 1. obtained 380 mg., m.p. 80–81°; 2. obtained 340 mg., m.p. 83–87°; 3. obtained 284 mg., m.p. 85–87°; 4. obtained 215 mg., m.p. 86–87°.

Natural cedrol was also recrystallized from methanol–water to give colorless needles, m.p. 86–87°.[20] The mixture melting point of natural and synthetic cedrol was 86–87° and the infrared spectra were identical. The rotations were measured in chloroform solution: natural cedrol: $[\alpha]^{28}D$ 9.9 ± 0.4° (c 5.00); synthetic cedrol: $[\alpha]^{28}D$ 10.5 ± 0.8° (c 5.00); reported[20] values include +9° 31' and +10° 30' in chloroform solution.

# N,N'-Disubstituted-1-amino-7-imino-1,3,5-cycloheptatrienes, a Non-classical Aromatic System

BY W. R. BRASEN, H. E. HOLMQUIST AND R. E. BENSON

N.N'-Disubstituted-1-amino-7-imino-1,3,5-cycloheptatrienes are stable, highly colored compounds that are readily accessible from the tetrafluorocycloheptadienes derived from tetrafluoroethylene and cyclopentadiene. Chemical studies of these aminoimines have established that they have appreciable aromatic character. Although structurally related to tropolone, the reasons for aromaticity in these two systems appear to be fundamentally different. Whereas aromaticity in tropolone has been attributed to resonance forms containing the sextet, n.m.r. and infrared spectral data together with dipole moment studies of the aminoimines clearly rule out a major contribution from sextet forms. The evidence appears more consistent for a peripheral 10 π-electron system involving hybridization of the two non-bonding electrons on nitrogen of the NHR substituent with the 8 π-electrons of the double bonds.

A new synthesis of tropolone recently was reported from these laboratories, based on the hydrolysis of the tetrafluorocycloheptadienes accessible from cyclopentadiene and tetrafluoroethylene.[1]
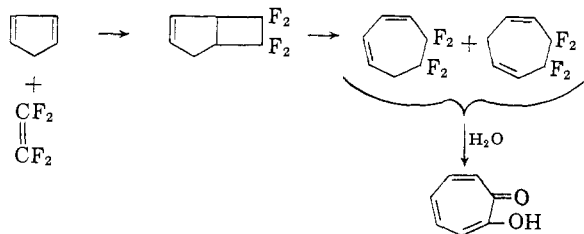
The tetrafluorocycloheptadienes are also intermediates for the synthesis of the 1-amino-7-imino-1,3,5-cycloheptatrienes (I),[2] a little-studied class of

compounds that is not conveniently accessible from tropolone or its derivatives. The disubstituted aminoimines are stable, highly colored compounds
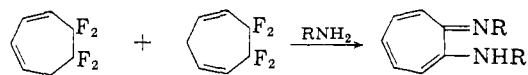
I, R = H, alkyl, aryl

that exhibit aromatic reactivity similar to that of tropolone itself.[3] It appears, however, that the reasons for aromaticity in these two systems are fundamentally different.[4] The present paper describes additional studies of the aminoimines.

The previously reported examples of 1-amino-7-imino-1,3,5-cycloheptatrienes are the compounds II–IV.

(1) J. J. Drysdale, W. W. Gilbert, H. K. Sinclair and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 3672 (1958).

(2) W. R. Brasen, H. E. Holmquist and R. E. Benson, *ibid.*, **82**, 995 (1960).

(3) Excellent reviews of the chemistry of tropolone include (a) P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955); (b) T. Nozoe, *Fortschr. Chem. Org. Naturstoffe*, **13**, 232 (1955); and (c) T. Nozoe in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Editor, Interscience Publishers, Inc., New York, N. Y., 1959.
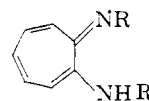
(4) R. E. Benson, *J. Am. Chem. Soc.*, **82**, 5948 (1960).

TABLE I

1-Amino-7-imino-1,3,5-cycloheptatrienes

| 1:	Formula	HF acceptor	Yield, %	M.p., °C	Color (crystal)	Calculated				Found			
						C	H	N	Mol. wt.	C	H	N	Mol. wt.
H[a,b]·1/2H$_2$O	C$_7$H$_8$N$_2$·1/2H$_2$O	NH$_3$	30	112–113	Yellow	65.09	7.02	21.69	..	65.01	6.93	21.54	.....
H·CF$_3$COOH (salt)	C$_9$H$_9$N$_2$O$_2$F$_3$			228–229				11.96		...	...	11.95	.....
H·HCl (salt)	C$_7$H$_9$N$_2$Cl			269–272		53.67	5.79	17.89		53.41	5.77	17.68	
H·CH$_3$COOH (salt)	C$_9$H$_{12}$O$_2$N$_2$			217–219		59.98	6.71	15.55		60.10	6.83	15.40	
Methyl	C$_9$H$_{12}$N$_2$	CH$_3$NH$_2$	75	66.5–67	Yellow	72.93	8.16	18.91	148	73.05	8.26	18.92	146, 147
Isobutyl	C$_{15}$H$_{24}$N$_2$	i-C$_4$H$_9$NH$_2$	36	d	Yellow	77.53	10.41	12.06	..	76.78	10.50	11.82	.....
Benzyl[b,c]	C$_{21}$H$_{20}$N$_2$	C$_7$H$_7$NH$_2$	47	81.5–82	Yellow	83.96	6.71	9.33	300	83.86	6.74	9.34	305
Phenyl	C$_{19}$H$_{16}$N$_2$	(C$_2$H$_5$)$_3$N	43	86.5–87	Yellow	83.78	5.92	10.29	272	83.38	5.93	10.05	296, 318
p-Tolyl	C$_{21}$H$_{20}$N$_2$	(C$_2$H$_5$)$_3$N	62	143–144	Orange	83.96	6.71	9.33	..	83.89	6.45	9.75	.....
p-Methoxyphenyl	C$_{21}$H$_{20}$N$_2$O$_2$	(C$_2$H$_5$)$_3$N	30	112.5–113	Red	...	...	8.43	332			8.42	346, 361
p-Chlorophenyl	C$_{19}$H$_{14}$N$_2$Cl$_2$	(C$_2$H$_5$)$_3$N	70	168–170	Red	66.87	4.13	8.21	341	66.71	4.22	8.13	365, 374
p-Dimethylaminophenyl	C$_{23}$H$_{28}$N$_4$	(C$_2$H$_5$)$_3$N	59	174.5–176	Dark red	77.06	7.31	...	..	76.99	7.38	...	.....
p-Phenylazophenyl	C$_{31}$H$_{24}$N$_6$	(C$_2$H$_5$)$_3$N	30	180.5–181.5	Greenish black	...	...	17.49	481	...	...	17.05	531, 552
p-Nitrophenyl	C$_{19}$H$_{14}$N$_4$O$_4$	(C$_2$H$_5$)$_3$N	40	<300	Brick red	62.98	3.89	...	..	62.77	3.79	...	.....

[a] 1-Amino-7-imino-1,3,5-cycloheptatriene isolated as hemihydrate. [b] These compounds were also prepared by amine interchange. [c] Prepared by amine interchange by Dr. E. W. Bousquet. [d] B.p. 102° (0.07 mm.).
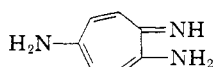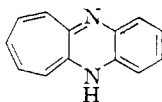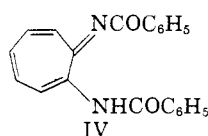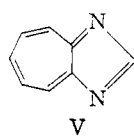
II   III   IV   V

The 5-amino derivative II was obtained by successive nitrosation, oximation and reduction of tropolone,[5] and the o-phenylene derivative III was synthesized by condensation of 2-chlorotropone or 2-methoxytropone with o-phenylenediamine.[6] Compound III is reported to be colorless, whereas the aminoimines synthesized in this work were found to be highly colored derivatives. Unfortunately, our attempts to prepare III from the tetrafluorocycloheptadienes were unsuccessful. Nozoe[7] and co-workers have also prepared the diazaazulene V and a number of its substituted derivatives. Recently, the dibenzoyl derivative IV of 1-amino-7-imino-1,3,5-cycloheptatriene was prepared from the diazaazulene V by reaction with benzoyl chloride.[8] Attempted hydrolysis of IV yielded 2-phenyl-1,3-diazaazulene with either acidic or basic catalysts.

Synthesis.—The N,N'-disubstituted aminoimines I listed in Table I were obtained in 30–80% yields by reaction of the tetrafluorocycloheptadienes with primary amines in a variety of solvents preferably ethanol or acetonitrile. An excess of the amine served as the hydrogen fluoride acceptor and,

in the case of the weakly basic aromatic amines, higher yields were obtained when triethylamine was also present. Furthermore, the conjugated isomer 5,5,6,6-tetrafluoro-1,3-cycloheptadiene consistently gave higher yields of the aminoimines than the unconjugated isomer 6,6,7,7-tetrafluoro-1,4-cycloheptadiene.

The reaction with ammonia to give the parent aminoimine appears to represent a special case. Because of the high reactivity of this compound, difficulty was experienced in isolating the product in yields comparable to those obtained with most primary amines.

The formation of small amounts of aromatic byproducts was noted in several of the preparations, particularly those involving aliphatic amines. The products formed were shown to be derivatives of o-fluorobenzaldehyde. Rearrangements leading to aromatic derivatives in the tropolone series are well known[3a] and presumably a related rearrangement occurs to a varying extent in the reactions of tetrafluorocycloheptadienes with amines.

In the case of the secondary amine N-methylaniline, the rearranged product α,α-bis-(N-methyl-N-phenylamino)-o-fluorotoluene (VI) was the only product identified from the reaction.

VI

The identity of the amine VI was established by its synthesis from o-fluorobenzaldehyde and N-methylaniline.

Physical Properties.—As a class, the aminoimines I show strong infrared absorption in the 6–7 μ region indicative of aromatic structures. Compound I (R = CH$_3$) has strong absorption at 6.27, 6.50, 6.60 and 6.81 μ (KBr wafer, Fig. 1). The strong absorption at 13.5 and 14.25 μ provides additional evidence for aromatic character, since

(5) T. Nozoe, M. Sato, S. Ito, K. Matsui and T. Matsuda, *Proc. Japan Acad.*, **29**, 565 (1953); ref. 3a, p. 102.

(6) T. Nozoe, Y. Kitahara, K. Takase and M. Sasaki, *Proc. Japan Soc.*, **32**, 349 (1954); *C. A.*, **56**, 2805 (1956).

(7) T. Nozoe, T. Mukai and I. Murata, *J. Am. Chem. Soc.*, **76**, 3352 (1956).
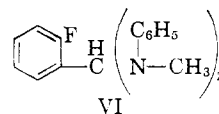
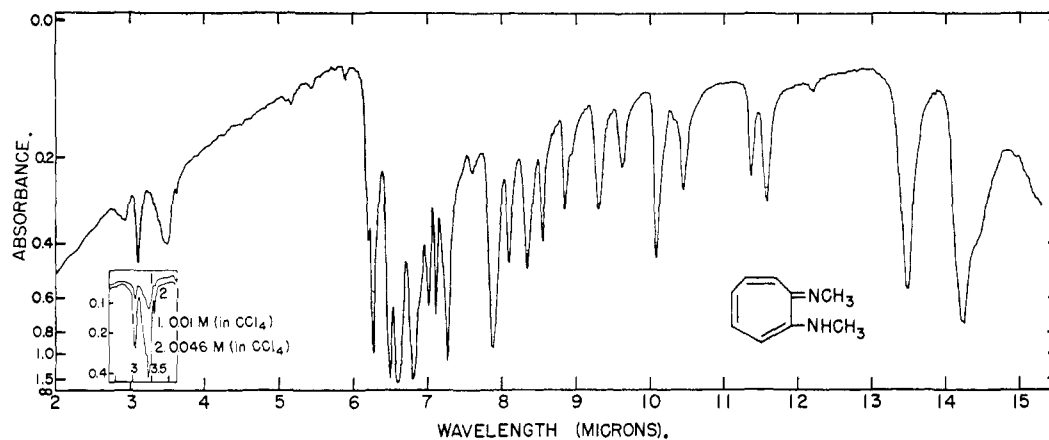(8) I. Murata, *Bull. Chem. Soc. Japan*, **32**, 841 (1959).

Fig. 1.

these bands are present in benzene derivatives having five adjacent hydrogen atoms. Furthermore, these bands are also present in tropolone, although shifted to 13.22 and 14.15 μ.

The absorption at 3.1 μ is attributable to NH (hydrogen bonded) and the broad absorption at 3.45 μ to CH (saturated and unsaturated). It appears that intramolecular hydrogen bonding is present extensively in the solid since the solution spectra of I (R = CH$_3$) show only a slight shift in the NH band, from 3.1 to 3.08 μ.[9] Furthermore, the similarity of the spectra in this region for 0.01 and 0.046 molar solutions in CCl$_4$ establishes that hydrogen bonding is intramolecular rather than intermolecular (Fig. 1 insert). To establish definitely that the absorption at 3.1 μ is attributable to NH and that there was no absorption due to unassociated NH in the 3.45 μ region, the N-deuterium derivative of I (R = CH$_3$) was prepared. The absorption at 3.45 μ was unchanged, the band at 3.08 was very weak, indicating the presence of a small amount of the NH compound, and a new band appeared at 4.1 μ, attributable to N-D.

Confirmation of strong hydrogen bonding in this structure was found in the proton nuclear magnetic resonance spectrum (Fig. 2). Only a single methyl resonance was observed, indicating that the methyl groups are equivalent[10] and, therefore, the nitrogen

(A)
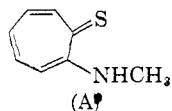
atoms to which they are attached are also equivalent. Such equivalence must arise from either intramolecular hydrogen bonding or rapid hydrogen exchange. Efforts to obtain a resolvable fine structure for the CH$_3$ resonance at temperatures down to −80° for both the N–H and N–D compounds in carbon tetrachloride solution were unsuccessful. Only a single methyl resonance was observed under these conditions. Since the rate of

(9) In this respect the aminoimine differs from tropolone, since the latter appears to have extensive intermolecular hydrogen bonding in the solid state. In solution the hydrogen bonding becomes intramolecular, however. See K. Kuratani, M. Tsuboi and T. Shimanouchi, *Bull. Chem. Soc. Japan*, **25**, 250 (1952); also ref. 3a, p. 22.

(10) The aminothioxo compound (A) shows a doublet methyl resonance; see W. R. Brasen and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3135 (1961).
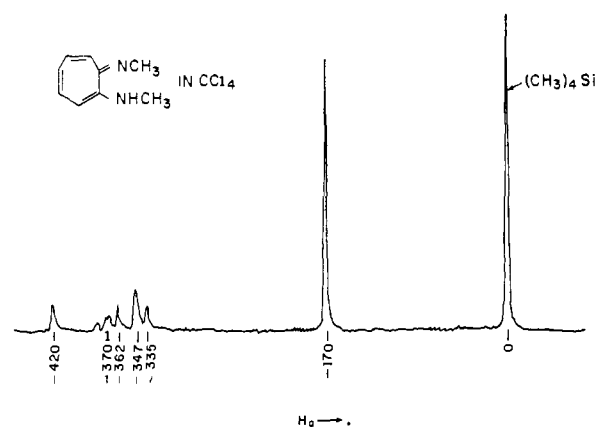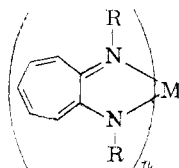

Fig. 2.—The n.m.r. data were obtained on a Varian Associates instrument HRS-60 operating at 56.4 megacycles and approximately 9400 gauss.

deuterium exchange should be appreciably lower than that of hydrogen, this evidence supports a symmetrical hydrogen bonded structure for I (R = CH$_3$) or an extremely fast intramolecular hydrogen (and deuterium) exchange.

The n.m.r. spectrum of I (R = CH$_3$) in trifluoroacetic acid showed little change in the fine structure attributable to the ring protons, although the position of absorption was shifted down-field by approximately 70 c.p.s. This shift may be attributed to a deshielding effect, as has been observed in the case of the azulene–azulenium ion system.[11] As expected, the absorption attributable to the methyl groups was shifted very slightly (approximately 10 c.p.s.) and only a single resonance was observed.

It is believed that the strong resemblance of the spectrum of the unprotonated product to that of the unambiguously symmetrical protonated derivative (E) is indicative of a symmetrical structure in the case of the unprotonated product in which the symmetry is due either to a symmetrically hydrogen-bonded product or to a fast intramolecular hydrogen exchange. Furthermore, the fact that the fine structure attributable to the protons of the seven-membered ring is remarkably similar in both products indicates strongly that there is considerable

(11) S. S. Danyluk and W. G. Schneider, *ibid.*, **82**, 997 (1960).
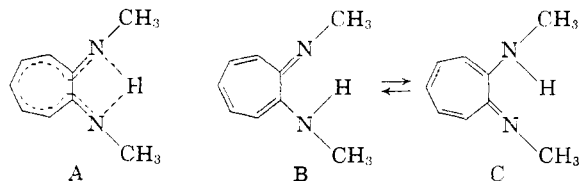
TABLE II

CHELATES OF AMINOIMINOCYCLOHEPTATRIENES

R	Formula	M	n	M.p., °C.	Calculated C	Calculated H	Calculated N	Analyses, % Mol. wt.	Found C	Found H	Found N	Found Mol. wt.
H	$C_{14}H_{14}N_4Ni$	Ni	2	>300	56.61	4.75	18.87	..	56.58	4.94	18.12	..
CH$_3$	$C_{18}H_{22}N_4Ni$	Ni[a]	2	182	61.23	6.28	15.87	..	61.01	6.51	16.19	..
p-Methoxyphenyl	$C_{42}H_{38}N_4O_4Ni$	Ni	2	228 d.	...	..	7.77	721	...	..	7.77	722
p-Chlorophenyl	$C_{38}H_{26}N_4Cl_4Ni$	Ni	2	245 d.	...	..	7.58	739	...	..	7.56	736
p-Chlorophenyl	$C_{38}H_{26}N_4Cl_4Co$	Co	2	218 d.	...	..	7.56	739	...	..	7.28	809
p-Chlorophenyl	$C_{38}H_{26}N_4Cl_4Cu$	Cu	2	280 d.	...	..	7.53	744	...	..	7.44	757
CH$_3$	$C_{27}H_{33}N_6Cr$	Cr[b]	3	325 d.	65.70	6.74	17.03	10.54[c]	65.05	6.82	16.72	10.32[c]

[a] Prepared either from the metal carbonyl or metal salt.   [b] Prepared from the corresponding metal carbonyl.   [c] Cr, %.

electron delocalization in I (R = CH₃). If there were little delocalization in this aminoimine, it is anticipated that this portion of the spectrum would be markedly altered, as in the case of the azulene-azulenium ion example.[11] Furthermore, the resonance of the ring protons is close to the region in which the benzenoid protons are observed (6.2–6.6 p.p.m. vs. 6.9 p.p.m. for benzene, tetramethylsilane reference).

In an attempt to gain further insight into the nature of the hydrogen atom in I (R = CH₃), the nickel chelate was prepared and its n.m.r. spectrum examined. The spectrum, determined at room temperature in carbon tetrachloride, is very unusual in that the bands are markedly shifted from their positions in the ligand. This behavior has been attributed to the presence of a thermally accessible triplet state.[12] However, at −70° the absorption attributable to ring protons is very similar to that of the unchelated product. This evidence is interpreted as indicating that the hydrogen is as effective as nickel for effecting electron delocalization in the seven-membered ring.

It is believed that the infrared and n.m.r. data are in accord for the symmetrical hydrogen-bonded structure represented by A, but the time-average structure of the rapid tautomeric process B ⇌ C cannot be eliminated unequivocally.[13,14] Although the interconversion B ⇌ C
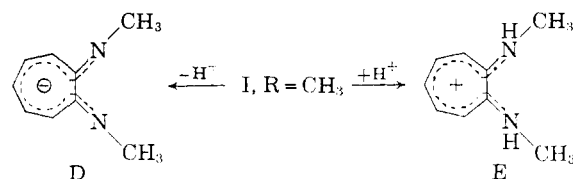

formally represents a tautomeric process, it is possible that because of a very favorable location of the hydrogen atom the structures B and C are more related as resonance forms than as conventional tautomers.
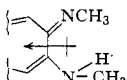

A priori, it might be expected that I (R = CH₃) would be an amphoteric substance in view of the high electron delocalization possible in the symmetrical structures D and E. In particular, if I (R = CH₃) had no appreciable delocalization energy, it would be expected to be an exceptionally strong base. Experimentally, it was found that the basic strength of the aminoimines approximated that of the amines from which they were derived. For example, I (R = CH₃) had pK_B of 3.8 vs. pK_B 3.4 for methylamine under similar conditions. This observation indicates that there is appreciable delocalization in I (R = CH₃) in agreement with the general characteristics of the infrared spectrum together with n.m.r. data regarding the similarity in fine structure of the ring proton resonance of I (R = CH₃) and compound E.

Study of the dipole moments of I (R = CH₃) and its 4-bromo derivative has led to the surprising conclusion that whereas the 7-membered ring in both tropolone and azulene is electropositive in the ground state, it is relatively electronegative in the aminoimine.[15] The observed moments together with those reported for tropolone and azulene are

(12) W. D. Phillips and R. E. Benson, J. Chem. Phys., 33, 607 (1960).

(13) Professor Trueblood of the University of California at Los Angeles is currently studying the X-ray crystal structure of I (R = CH₃) and 1 (R = p-ClC₆H₄).

(14) Only data relating to I (R = CH₃) have been cited for this discussion. However, essentially all of the aminoimines described in Table I have been examined by n.m.r. and only single resonances for the substituents on nitrogen have been found. Furthermore, the unsymmetrical aminoimine VIII shows only single resonances for the methyl and aryl groups, even at −80°.

(15) Molecular orbital calculations (LCAO–MO method) by Dr. H. E. Simmons using conventional assumptions (R. Daudel, R. Lefebre and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter IV) have given a value of 0.3 D. for 1 (R = CH₃), with the dipole directed into the ring. Values of the nitrogen Coulomb integral ($a_N = a_0 + \beta_0$) and carbon-nitrogen resonance integral ($\beta_{CN} = 1.2 \beta_0$) were used that have given reasonable results for other nitrogen-containing molecules. In view of the assumptions made, particularly regarding the location of the hydrogen on nitrogen, this result clearly indicates that contribution from a structure such as F is negligible.

given in Table III. The assumption that the dipole moment is directed into the ring of I (R = CH₃), together with the known group moment of 1.52 D. for bromine,[16] leads to a calculated value of 2.76 D. for the 4-bromo derivative, in good agreement with the observed value (2.52 D.). On the other hand, if the dipole is assumed to be directed away from the ring, the observed value should be about 0.3 D.

TABLE III

DIPOLE MOMENTS

	I, R = CH₃	4-Brl, R = CH₃	Tropolone	5-Bromo-tropolone	Azulene
Dipole[a] debyes	1.24	2.52	3.71[b]	2.07[c]	1.0[d]
Direction of dipole					

[a] All determinations were made in benzene at 25°.
[b] Y. Kurita, T. Nozoe and M. Kubo, *Bull. Chem. Soc. Japan*, 24, 10 (1951). [c] Y. Kurita, T. Nozoe and M. Kubo, *ibid.*, 26, 242 (1953). [d] G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, 17, 264 (1949).

Verification for the relative electronegative character of the seven-membered ring in I (R = CH₃) compared to that of tropolone was found in the n.m.r. spectrum. The ring protons have resonance at higher fields (6.2–6.6 p.p.m.) than those of tropolone (center at 7.3 p.p.m.) because of deshielding in the latter.

Clearly, the aromaticity observed in the aminoimines cannot be easily attributed to contributions from a resonance structure such as F, as has been done in the case of tropolone (G).[17]

F   G
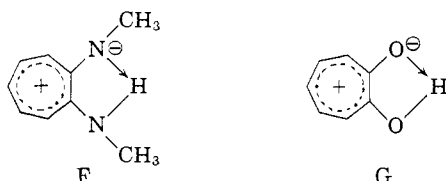
For this reason it is not surprising that although tropolone and the aminoimines I have both aromatic character and structural similarity, distinct differences do exist in their chemical reactivity. A possible explanation accounting for aromaticity in the aminoimines is considered after a discussion of their chemistry.

Like tropolone, the aminoimines I show strong absorption in the 300–400 mμ region. However, there is also additional absorption in the visible region. Thus, the aminoimine I (R = CH₃) has λₘₐₓ 263 mμ (ε 17,800), λₘₐₓ 346 mμ (ε 8,650), λₘₐₓ 360 mμ (ε 10,100) and λₘₐₓ 418 mμ (ε 6,820). The chelate derivatives showed stronger absorption at somewhat longer wave lengths; thus, the nickel chelate of I (R = CH₃) had absorption at 280 mμ (ε 30,900), λₘₐₓ 322 mμ (ε 20,500), λₘₐₓ 370 mμ (ε 18,900) and λₘₐₓ 475 mμ (ε 16,800).

In the case of the aryl-substituted aminoimines I, the ultraviolet absorption was shifted toward

(16) C. P. Smyth in "Physical Methods of Organic Chemistry," Vol. 1, Part 2, Second Edition, Edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1949, p. 1614.

(17) G. L. Buchanan and D. R. Lockwood, *Chemistry & Industry*, 391 (1958); see also ref. 3a–c.

longer wave lengths and in the visible spectrum I (R = p-CH₃OC₆H₄) has λₘₐₓ 412 mμ (ε 14,300), and I (R = p-ClC₆H₄) has λₘₐₓ 414 mμ (ε 14,650). As expected, substitution of a ring hydrogen with bromine results in a bathochromic shift; thus, 4-bromo I (R = p-ClC₆H₄) has λₘₐₓ 427 mμ (ε 18,100).

Reactions Involving Nitrogen Atoms.—The skeletal structure of the aminoiminocycloheptatrienes was established by a two-step conversion to tropolone. Initial attempts to hydrolyze the aminoimine derived from p-chloroaniline to tropolone or a derivative thereof with 20% sulfuric acid or with 20% sodium hydroxide were unsuccessful, with essentially no hydrolysis taking place after refluxing in these media for six days. However, the aminoimine was converted to 2-(p-chlorophenylamino)-tropone by reaction with potassium acetate in refluxing acetic acid. Although the aminotropone was stable to hot aqueous acid, it was readily converted to tropolone by alkaline hydrolysis. The identity of the aminotropone was confirmed by its synthesis from p-chloroaniline and 2-chlorotropone.
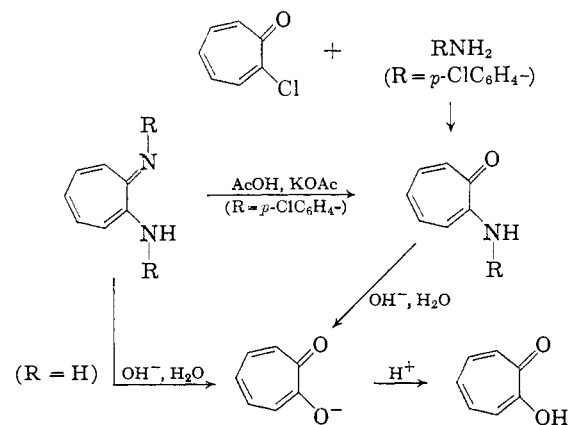
Hydrolysis of the unsubstituted aminoiminocycloheptatriene, unlike the substituted compounds, was found to proceed directly to tropolone anion under basic conditions.

Additional confirmation for the adjacency of the nitrogen atoms in the aminoimines was derived from formation of stable chelate derivatives.

VII
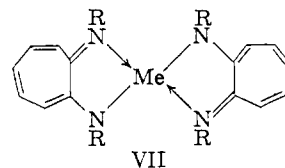
Bidentate structures were obtained from nickel, copper and cobalt salts. In addition, reactions of the aminoimines with several metal carbonyls yielded chelate derivatives. In the case of chromium hexacarbonyl, a product containing three moles of the ligand was formed. The chelates are stable, highly colored products having extinction coefficients of about 15,000–20,000. Preliminary study indicated that they are less stable to acidic conditions than the corresponding derivatives of tropolone.

The first step of the hydrolysis reaction described above is one example of a more general reaction

that the aminoiminocycloheptatrienes undergo with certain nucleophilic reagents. With primary amines an interchange yielding unsymmetrically substituted aminoiminocycloheptatrienes has been observed. With p-anisidine and I (R = CH₃) the reaction occurred readily in the presence of a small amount of acetic acid in dioxane solvent to give the unsymmetrical product VIII. Attempts to replace both methylamine functions were unsuccess-


VIII   IX
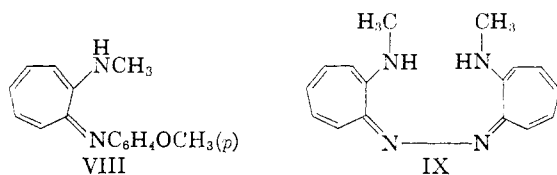
ful, even at temperatures up to 250°. Similarly, reaction with such bifunctional amines as hydrazine and p-phenylenediamine yielded aminoimines in which only one methylamine group was replaced, e.g., IX. However, reaction with the more basic benzylamine resulted in displacement of both methylamine groups to yield a symmetrically substituted product identical with that obtained from the tetrafluorocycloheptadienes and benzylamine.

X
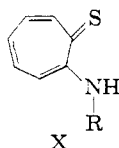
Reaction of the aminoimines with hydrogen sulfide yielded the previously unreported aminothioxocycloheptatrienes X, the subject of the following paper.[10]

Compounds containing the diazaazulene ring system can be prepared from the aminoimines. Thus, the action of trifluoroacetic anhydride on I (R = H) gave 2-trifluoromethyl-1,3-diazaazulene. Reaction of the aminoimine derived from methylamine with methylene iodide in the presence of pyridine yielded the diazaazulenium iodide XI, as


XI
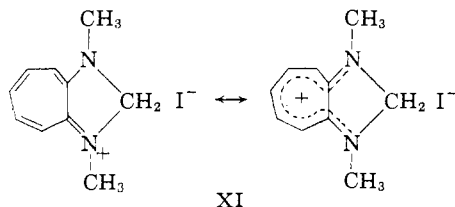
indicated by elemental and spectral analyses. The reaction of the aminoimine from benzylamine with methylene iodide yielded the analogous diazaazulene derivative. In addition, 1,3-dimethyl-1,3-diazaazulenium chloride was prepared from I (R = CH₃) and formalin in hydrochloric acid.

Reactions Involving the Cycloheptatriene Nucleus.—Unlike tropolone, which is reported to give a mixture of products with bromine,[3a-c] the aminoimines react with one mole of bromine under mild conditions to give a single product in high yield. Bromination of the p-chlorophenyl derivative at 0° in methylene chloride gave a monosubstituted derivative in 90% yield. It was established in-

directly that substitution had occurred at the 4-position.

5,5,6,6-Tetrafluoro-1,3-cycloheptadiene was brominated to give a dibromide, presumably 3,4-dibromo-6,6,7,7-tetrafluorocycloheptene, which upon hydrolysis yielded 5-bromotropolone.[18] It is considered unlikely that alternative dibromides derived from the tetrafluorocycloheptadiene would yield 5-bromotropolone. Reaction of the dibromo compound with p-chloroaniline yielded an aminoimine that was identical with that obtained by bromination of the aminoimine I (R = p-ClC₆H₄).
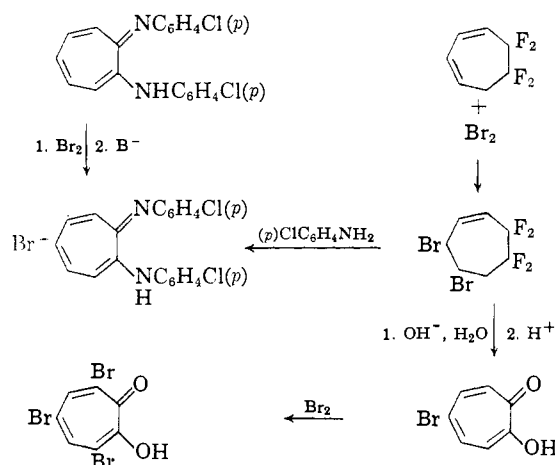
Similarly, chlorination of 1-(p-tolylamino)-7-(p-tolylimino)-1,3,5-cycloheptatriene yielded a monochloro compound, the 4-substituted derivative.[19]

Bromination of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene was found to proceed normally to yield a monobromo compound. It was established by n.m.r. that substitution had occurred at the 4-position. However, when chlorine in acetic acid was employed, participation of the methyl groups and subsequent cyclication was observed to give a product identified as 1-methyl-4,6,8-trichloro-1,3-diaza-2(1-H)-azulenone (XII).

XII
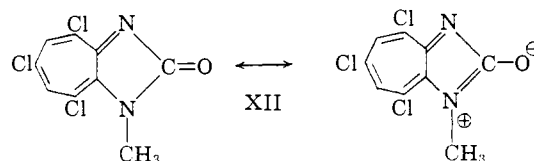
The infrared spectrum of this compound is similar to that of 1,3-dimethyl-1,3-diazaazulenium iodide (XI), indicating that the polarized structure is an important contributor to the resonance hybrid.

A cursory investigation of displacement reactions of 4-bromo-1-(p-tolylamino)-7-(p-tolylimino)-1,3,5-cycloheptatriene indicated that the bromine was moderately labile. Thus, reaction with either thiourea or hydrogen sulfide gave the sulfide XIII and reaction with malonitrile yielded the highly colored dicyanomethylene derivative XIV. Spec-

(18) The 4-position of the aminoimines is equivalent to the 5-position of tropolone, which is numbered as a cyclic ketone.

(19) Since the completion of this work, n.m.r. studies of the nickel chelates of the mono ring-substituted derivatives have established that the substituent is invariably at the 4-position. This work will be described in a forthcoming publication.
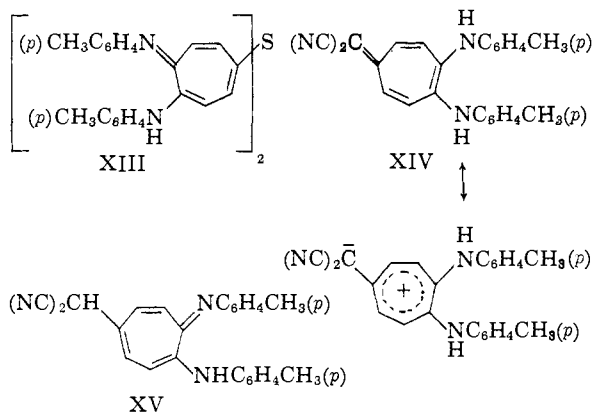
tral and chemical evidence favor the exomethylene structure XIV over the tautomeric isomer XV. The compound is insoluble in dilute acids and did not form chelate derivatives under conditions successfully used for the aminoimines.
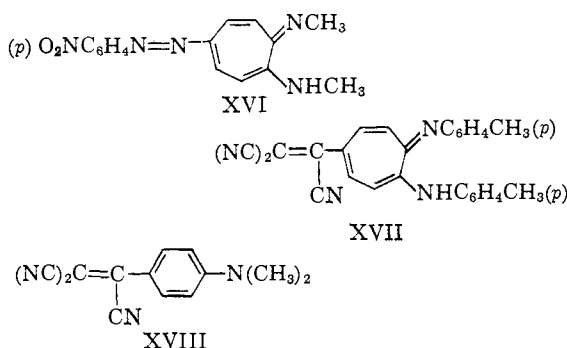
A distinct similarity in reactivity of the amino-imine products with that of tropolone was found. Thus, condensation with a diazonium compound gave the azo derivative XVI by substitution at the 4-position.[17] Tropolone has been shown to react exclusively at the 5-position with diazonium salts to give azo derivatives.[20]

An unusual reaction of nitrous acid with 1-methyl amino-7-methylimino-1,3,5-cycloheptatriene was observed. 5-Nitrosotropolone was isolated in 23% yield by reaction of one mole of the aminoimine with one mole of nitrous acid. The amino groups presumably are removed after ring substitution has occurred, since efforts to hydrolyze the aminoimine to tropolone with strong acids or strong bases were unsuccessful.

A similarity between the aminoimine I, R = p-CH$_3$C$_6$H$_4$, and N,N-dialkylarylamines was shown in the reaction with tetracyanoethylene to obtain a tricyanovinylaminoimine XVII. The reaction of N,N-dimethylaniline with tetracyanoethylene has been shown to yield the tricyanovinyl compound XVIII.[21] Tetracyanoethylene with tropolone under similar conditions fails to give identifiable products.[22]

Experimental

In the preparation of the aminoimines, yields have been calculated on the basis of the tetrafluorocyclohepta-

(20) Reference 3a, p. 45.
(21) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).
(22) Unpublished observation of Dr. W. W. Gilbert.

diene content of the fluorocarbon mixture. The yield of aminoimine depends to a large extent upon the purity of the starting material and ranges from about 5% yield with material containing 20% of the diene, to 60–75% yield with material containing over 90% of the diene. Purity of the dienes was determined by vapor phase chromatography.[1]

The physical properties and analyses of the aminoimines are given in Table I.

1-Amino-7-imino-1,3,5-cycloheptatriene Hemihydrate.— To a solution of 75 ml. of methanol in 200 ml. of ammonia was slowly added with stirring a solution of 15 g. of 5,5,6,6-tetrafluoro-1,3-cycloheptadiene in 25 ml. of methanol while the temperature rose from −15 to +10°. The mixture was stirred an additional 2 hours, during which time it was allowed to warm to room temperature. Ether (200 ml.) was added and the insoluble material was removed by filtration. The filtrate was evaporated rapidly under reduced pressure and the residue was taken up in 150 ml. of ether. The resulting solution was decanted from a small amount of insoluble residue and the liquid was saturated with anhydrous hydrogen chloride. The gummy precipitate which separated was combined with the initial insoluble residue and dissolved in 100 ml. of hot water. The solution was decolorized with activated carbon and made basic with 20% sodium hydroxide to precipitate the product. The yield of combined product from two experiments was 7.0 g. The hemihydrate was purified by recrystallization from ether or by sublimation. The infrared spectrum has absorption at 2.95, 3.05 and 3.15 μ (OH, NH$_2$ and NH), 6.15, 6.25 and 6.65 μ (NH$_2$ and conjugated C=C and/or C=N). The aminoimine was characterized also by its hydrochloride, acetate and trifluoroacetate salts.

1-Methylamino-7-methylimino-1,3,5-cycloheptatriene (I, R = CH$_3$).—To a solution of 200 ml. of methylamine in 100 ml. of ethyl alcohol, cooled by an ice-bath, was added with stirring a solution of 30.7 g. of 5,5,6,6-tetrafluoro-1,3-cycloheptadiene in 30 ml. of ethyl alcohol over a 30-minute period. The addition was carried out under a condenser packed with solid carbon dioxide–acetone, and the temperature of the reaction solution varied from 0 to 14°. The ice-bath and condenser were removed and stirring was continued for 2 hours. The resulting mixture was poured into about 1 l. of ice-water to give 20.6 g. of I, R = CH$_3$, as a yellow solid. Recrystallization was most readily effected from the minimum amount of methanol. The infrared and ultraviolet absorption data are reported in the Physical Properties section.

1-(p-Tolylamino)-7-(p-tolylimino)-1,3,5-cycloheptatriene (I, R = p-CH$_3$C$_6$H$_4$).—To a solution of 47 g. of p-toluidine and 89 g. of triethylamine in 150 ml. of methanol was added a solution of 35 g. of a fluorocarbon fraction containing approximately 33 g. of 5,5,6,6-tetrafluoro-1,3-cycloheptadiene in 50 ml. of methanol during 1 hour. After addition was complete, the mixture was refluxed for 30 minutes and then cooled in ice to precipitate most of the product. Addition of 100 g. of ice caused more solid to separate. The solid was collected by filtration, washed with methanol, and recrystallized by dissolving it in the minimum amount of methylene chloride, adding twice the volume of hot ethanol, and heating until the methylene chloride had been removed by distillation. The yield of I, R = p-CH$_3$C$_6$H$_4$, was 37 g.

The α,α-Bis-(N-methyl-N-phenylamino)-o-fluorotoluene (VI).—A solution of 16.6 g. (0.08 mole) of tetrafluorocycloheptadienes (80% purity) and 10 ml. of acetonitrile was added to a solution of 21.4 g. (0.2 mole) of methylaniline and 30 g. (0.27 mole) of triethylamine in 50 ml. of acetonitrile. The resulting solution was cooled in ice and the temperature kept below 25°. When the initial reaction had subsided the solution was heated to 50° and then cooled. The white precipitate which resulted was recrystallized from acetonitrile to yield 5 g. (20% yield) of VI, m.p. 158.5–159°.

Anal. Calcd. for C$_{21}$H$_{21}$N$_2$F: C, 78.71; H, 6.61; N, 8.75; mol. wt., 320. Found: C, 79.08; H, 6.73; N, 8.70; mol. wt.,316.

The product decomposed in dilute hydrochloric acid to yield an oil which formed a 2,4-dinitrophenylhydrazone, m.p. 210.5–212°. A mixed melting point with the 2,4-dinitrophenylhydrazone of o-fluorobenzaldehyde, m.p. 210–210.5°, was 210–211.5°.

An alternate synthesis of VI was accomplished by combination of 2.5 g. of o-fluorobenzaldehyde with 4.04 g. of

methylaniline and 2 drops of triethylamine in a mixture of 25 ml. of benzene and 25 ml. of acetonitrile. The solution was refluxed and the benzene and acetonitrile removed by distillation in an attempt to remove water as the azeotrope. Apparently, however, no water was eliminated and no noticeable reaction took place during this time. The solution was allowed to stand for 1 week, after which time a precipitate had formed which was recrystallized from acetonitrile to yield 3 g. (50% yield) of VI, identical with the product of the reaction of methylaniline with the tetrafluorocyclo-heptadienes, m.p. 160.5–162°; mixed melting point, 159–160°.

Hydrolysis of 1-(p-Chlorophenylamino)-7-(p-chloro-phenylimino)-1,3,5-cycloheptatriene.—A solution of 6.4 g. of the aminoimine and 20 g. of potassium acetate in 100 ml. of acetic acid was refluxed for 6 days. The yellow solution was added to 150 ml. of ice-water and the mixture was cooled to 0°. The greenish-yellow precipitate was recovered by filtration, dissolved in methanol, and 30 ml. of 10% ammonium hydroxide was added. The mixture was cooled and filtered and the solid was dissolved in methanol. The methanol solution was decolorized, diluted with water, and allowed to cool slowly. The resulting yellow crystals weighed 3.5 g. Recrystallization from methanol–water yielded 3.3 g. (80%) of yellow 2-(p-chlorophenylamino)-tropone, m.p. 147°.

Anal. Calcd. for $C_{13}H_{10}NOCl$: N, 6.04. Found: N, 6.05.

The mother liquor from the first recrystallization was concentrated and cooled to yield 3 g. (95%) of p-chloroacetanilide. A sample after recrystallization melts at 182–182.5°, lit.[23] m.p. 179°. A mixed melting point with an authentic sample was not depressed.

An authentic sample of 2-(p-chlorophenylamino)-tropone was prepared by refluxing a solution containing 0.5 g. of 2-chlorotropone, 0.5 g. of p-chloroaniline and 0.5 g. of tri-ethylamine in 10 ml. of ethanol for 3 days. The resulting solution was diluted with an equal volume of water and cooled. The yellow precipitate was recrystallized twice from methanol–water and dried to yield 0.45 g. of 2-(p-chlorophenylamino)-tropone, m.p. 148°. A mixed melting point with the product obtained by hydrolysis of 1-(p-chlorophenylamino)-7-(p-chlorophenylimino)-1,3,5-cyclo-heptatriene was not depressed.

Hydrolysis of 2-(p-Chlorophenylamino)-tropone to Tropo-lone.—A solution of 1 g. of 2-(p-chlorophenylamino)-tropone in 20 ml. of methanol was added to a solution of 4 g. of sodium hydroxide in 20 ml. of water. The resulting solution was refluxed for 2 hours and the methanol was removed by distillation. The solution was diluted with 70 ml. of water and extracted with ether. The ether was removed by distillation to yield 0.32 g. (60%) of p-chloro-aniline. The acetyl derivative was prepared, m.p. 181.5–182.5°. A mixed melting point with an authentic sample of p-chloroacetanilide was not depressed.

The original water solution was acidified to pH 2 and extracted with methylene chloride. After drying the extract over magnesium sulfate and removal of solvent by distillation, the oily residue crystallized. The product was recrystallized from petroleum ether to yield 0.47 g. (89% yield) of tropolone, m.p. 52–53°. A mixed melting point with an authentic sample of tropolone was not depressed.

Hydrolysis of 1-Amino-7-imino-1,3,5-cycloheptatriene.—A solution of 0.5 g. of the aminoimine and 1 g. of sodium hydroxide in 5 ml. of ethanol and 5 ml. of water was heated on a steam-bath for 5 hours. The solution was cooled, diluted to a volume of 20 ml. with water and acidified with hydrochloric acid. This solution was extracted with methylene chloride and the organic layer was dried over magnesium sulfate. Removal of the methylene chloride by distillation yielded a yellow oil which was taken up in petroleum ether. Cooling of this solution yielded 0.2 g. (40% yield) of tropolone, m.p. 50–51°. A mixed melting point with an authentic sample was not depressed.

Amine Interchange—7-(p-Methoxyphenylimino)-1-methylamino-1,3,5-cycloheptatriene (VIII).—A solution of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (0.74 g., 0.005 mole), p-anisidine (1.23 g., 0.01 mole) and acetic acid (15 drops) in dioxane (25 ml.) was refluxed for 40 hours.

(23) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 238.

The cooled solution was poured into ice-water and the mixture extracted four times with ether. The organic layers were combined, dried over magnesium sulfate and filtered. The ether was removed by distillation to give 1.0 g. of crude product which was recrystallized from petroleum ether to give 0.47 g. (39% yield) of VIII as orange crystals, m.p. 79–81°. An analytical sample from petroleum ether had m.p. 80.5–81.5°.

Anal. Calcd. for $C_{15}H_{16}ON_2$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.70; H, 6.69; N, 11.65.

With Bifunctional Compounds.—The general procedure was that of refluxing a solution containing 3 g. (0.02 mole) of I (R = CH_3) with 0.01 mole of the bifunctional amine in 40 ml. of dioxane containing 2 drops of acetic acid. Reaction time was 2 to 4 days. The products were isolated by dilution of the reaction mixture with water and recrystal-lization of the resulting precipitate from methylene chloride–ethanol. The product (IX) from hydrazine crystallized as deep red needles (0.3 g.), m.p. 210° dec.

Anal. Calcd. for $C_{16}H_{18}N_4$: C, 72.15; H, 6.81; N, 21.04; mol. wt., 266. Found: C, 72.28; H, 6.66; N, 19.86; mol. wt., 272.

The product from p-phenylenediamine crystallized as metallic orange leaflets (0.7 g.), m.p. 208° dec.

Anal. Calcd. for $C_{22}H_{22}N_4$: C, 77.17; H, 6.48; N, 16.37; mol. wt., 342. Found: C, 77.44; H, 6.38; N, 16.33; mol. wt., 336.

Chelate Derivatives. A. From Metallic Salts.—The chelates were prepared by mixing a solution of two molar equivalents of the aminoimine in methylene chloride with an ethanol–water solution of one molar equivalent of the metallic halide and two molar equivalents of sodium acetate. The resulting mixture was heated until the lower boiling solvent was removed, hot water was added and the precipitated crystalline solid recrystallized by dissolving in boiling benzene and adding an equal volume of ethanol. The yields were practically quantitative in all cases. The physical properties and analytical data are given in Table II.

B. From Metal Carbonyls.—The chelates were prepared by mixing the aminoimine with a 10% excess of the appropriate metal carbonyl in methanol and refluxing the resulting solution under nitrogen for 24 hours. The products precipitated during the course of the reaction and were recrystallized from methylene chloride and petroleum ether. The physical properties and analytical data are given in Table II.

2-Trifluoromethyl-1,3-diazaazulene.—To a solution of 1-amino-7-imino-1,3,5-cycloheptatriene hemihydrate (1.0 g., 0.008 mole) in chloroform (15 ml.) was added trifluoro-acetic anhydride (6.3 g., 0.03 mole). The precipitate that formed initially dissolved on refluxing the mixture for 3 hours. The solution was concentrated by distillation to obtain a semi-solid which was crystallized from ethyl ace-tate–petroleum ether to give 0.92 g. (60% yield) of the diazaazulene as pale yellow crystals, m.p. 180° with subli-mation. Recrystallization from ethyl acetate–petroleum ether gave a sample, m.p. 180.5–180.7° in a sealed capillary.

Anal. Calcd. for $C_9H_5N_2F_3$: C, 54.55; H, 2.54; N, 14.14; F, 28.77. Found: C, 55.07; H, 2.79; N, 14.09; F, 29.02.

1,3-Dimethyl-1,3-diazaazulenium Iodide (XI).—A solution of 3 g. (0.02 mole) of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene, 6 g. (0.022 mole) of methylene iodide and 3.2 g. (0.4 mole) of pyridine in 20 ml. of aceto-nitrile was allowed to stand for 2 weeks at room temperature. The dark supernatant liquid was decanted from the precipitated crystals and eventually deposited several additional crops of product. The combined product was recrystallized from ethanol to yield red needles of XI, m.p. 249.5° dec.

Anal. Calcd. for $C_{10}H_{13}N_2I$: C, 41.68; H, 4.55; N, 9.71. Found: C, 41.97; H, 4.73; N, 9.72.

The infrared spectrum (KBr wafer) showed strong absorption at 6.25 (C=C and/or C=N) and 13.3 μ. There was also medium absorption at 6.75, 8.30, 8.35, 9.1 and 10.85 μ, and weak absorption at 6.4, 6.65, 6.95 (shoulder at 7.05 μ), 7.5 (shoulder at 7.6 μ), 7.9, 8.1, 8.95, 9.5, 9.9, 11.0, 11.3 and 13.75 μ. The ultraviolet absorption spectrum, determined in acetonitrile, showed λ_{max} 280 mμ (ϵ 31,100), λ_{max} 353 mμ (shoulder, ϵ 7,780), λ_{max} 322 mμ (ϵ 10,900), λ_{max} 370 mμ (ϵ 3,550), λ_{max} 375 mμ (ϵ 3,575).

The product also could be obtained by refluxing the pyridine solution for 4 hours. In this case, however, it was more difficult to purify.

1,3-Dimethyl-1,3-diazaazulenium Chloride.—To 8 ml. of 90% formic acid, cooled by an ice-bath, was added 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (7.4 g., 0.05 mole) and then 10 ml. of 36% aqueous formaldehyde. The solution was warmed rapidly to 92°, whereupon vigorous gas evolution commenced. The heating was stopped until the gas evolution subsided. The temperature then was brought to 96–99° for 4 hours. After cooling, 30 ml. of 4 N hydrochloric acid was added and the solution was evaporated to dryness under reduced pressure to give a tacky, orange solid which was recrystallized from ethanol to give 2.8 g. (29%) of orange needles, m.p. 238–240°.

Anal. Calcd. for $C_{10}H_{13}N_2Cl$: C, 61.06; H, 6.66; N, 14.24; Cl, 18.02. Found: C, 61.66; H, 6.61; N, 14.40; Cl, 17.96.

The infrared spectrum of the chloride derivative closely resembled that of the corresponding iodide. The chloride could also be prepared by addition of concentrated hydrochloric acid to a suspension of the aminoimine in formalin and heating on the steam-bath for a short time.

1,3-Dibenzyl-1,3-diazaazulenium Iodide.—A solution of 1-benzylamino-7-benzylimino-1,3,5-cycloheptatriene (1.5 g., 0.0056 mole) in pyridine (30 ml.) was stirred and refluxed for 3 hours. The orange solid (1.9 g., 86%) was collected by filtration and recrystallized from methylene chloride–petroleum ether; m.p. 200–201° dec.

Anal. Calcd. for $C_{22}H_{21}N_2I$: C, 60.00; H, 4.81; N, 6.36. Found: C, 60.36; H, 5.18; N, 6.09.

Synthesis of 4-Bromo-1-(p-chlorophenylamino)-7-(p-chlorophenylimino)-1,3,5-cycloheptatriene. A. By Bromination of 1-(p-Chlorophenylamino)-7-(p-chlorophenylimino)-1,3,5-cycloheptatriene.—To a solution of 7.8 g. of the aminoimine in 50 ml. of methylene chloride was added a solution of 3.2 g. of bromine in 20 ml. of methylene chloride. Very little evolution of heat occurred and only a slight deepening of the red color of the solution was observed. Addition of 100 ml. of ethanol followed by concentration of the solution precipitated 10 g. (90%) of an orange hydrobromide. Treatment of a small portion of this product with dilute aqueous ammonia followed by crystallization from ethanol yielded the bromoaminoimine, m.p. 181–182°; mixed melting point with the product obtained from 3,4-dibromo-5,5,6,6-tetrafluorocycloheptene and p-chloroaniline, 181–182°.

By Reaction of 3,4-Dibromo-5,5,6,6-tetrafluorocycloheptene with p-Chloroaniline.—A solution containing 3.26 g. of 3,4-dibromo-5,5,6,6-tetrafluorocycloheptene, 5 g. of triethylamine and 5 g. of p-chloroaniline in 10 ml. of ethanol was heated on a steam-bath for 1 hour. The deep red solution was cooled and diluted with 5 ml. of water to precipitate a red solid. Recrystallization of this product from ethanol gave 1.54 g. (37% yield) of 4-bromo-1-(p-chlorophenylamino)-7-(p-chlorophenylimino)-1,3,5-cycloheptatriene, red needles, m.p. 180–181°.

Anal. Calcd. for $C_{19}H_{13}N_2Cl_2Br$: N, 6.67. Found: N, 6.88.

Preparation and Hydrolysis of 3,4-Dibromo-5,5,6,6-tetrafluorocycloheptene.—A solution of 104 g. of a fluorocarbon mixture containing 83 g. (0.5 mole) of 5,5,6,6-tetrafluoro-1,3-cycloheptadiene in 200 ml. of methylene chloride was stirred vigorously and irradiated with two sunlamps while a methylene chloride solution containing 120 g. (0.75 mole) of bromine in 100 ml. of solvent was added. The addition was stopped when evolution of hydrogen bromide began, at which time 0.51 mole of bromine had been consumed during 30 minutes. After removal of solvent, distillation of the product yielded 118.3 g. (72% yield) of 3,4-dibromo-5,5,6,6-tetrafluorocycloheptene, b.p. 101–105° (8 mm.), $n^{25}D$ 1.4940.

Anal. Calcd. for $C_7H_6F_4Br_2$: Br, 49.04. Found: Br, 48.69.

A mixture of 8.3 g. of the dibromo compound and 60 ml. of 10% aqueous potassium hydroxide solution was stirred for 1 hour. The resulting dark brown mixture was acidified, cooled, and the solid recovered by filtration. Recrystallization from ethanol and water afforded 3.6 g. (72% yield) of 5-bromotropolone, m.p. 188.5–189.5°, reported[3a] m.p. 190–191°. The product gave the characteristic green

color with alcoholic ferric chloride. A small amount of 5-bromotropolone when treated with aqueous bromine gave the yellow 3,5,7-tribromotropolone, m.p. 122–123° after recrystallization from ethanol–water; lit.[3a] m.p. 125°.

7-Dicyanomethylene-3,4-di-(p-tolylamino)-1,3,5-cycloheptatriene (XIV).—1-(p-Tolylamino)-7-(p-tolylimino)-1,3,-5-cycloheptatriene was brominated as described above for the p-chlorophenyl analog to yield 4-bromo-1-(p-tolylamino)-7-(p-tolylimino)-1,3,5-cycloheptatriene in 90% yield, m.p. 152–153°.

Anal. Calcd. for $C_{21}H_{19}N_2Br$: Br, 21.07. Found: Br, 21.31.

A solution of 12 g. of the bromoaminoimine and 2.2 g. of malononitrile in 40 ml. of dimethylformamide was heated to 95–100° on the steam-bath. A total of 5 ml. of triethylamine was added to this solution in 1-ml. portions at 5-minute intervals. The resulting solution was heated for 10 minutes and poured into 100 g. of ice with stirring. The resulting gummy solid was triturated with methanol, isolated by filtration and taken up in methylene chloride. The product was recrystallized by adding hot acetonitrile to the methylene chloride solution and boiling to remove the bulk of the lower-boiling solvent. Compound XIV was obtained as a dark red, crystalline solid (11.6 g., 95% yield), m.p. 209° dec.

Anal. Calcd. for $C_{24}H_{20}N_4$: C, 79.09; H, 5.53; N, 15.38. Found: C, 78.92; H, 5.58; N, 15.63.

The infrared spectrum showed principal absorption at 2.95 μ (NH), 3.3 μ (=CH), 3.45 μ (saturated C—H), 4.5 μ (conjugated C≡N), 6.25, 6.35 and 6.6 μ (conjugated C=C and/or C=N), 12.45 μ (p-substituted aromatic). The ultraviolet spectrum determined in acetonitrile showed major absorption at λ_{max} 283 (ε 18,500) and λ_{max} 440 (ε 28,500). The product is insoluble in dilute hydrochloric acid and did not form chelate derivatives with ferric or nickelous ions. Addition of aqueous sodium hydroxide to a dilute alcoholic solution of the product produced a fleeting, deep red color.

Synthesis of Bis-[1-(p-tolylamino)-7-(p-tolylimino)-1,3,5-cycloheptatrienyl] Sulfide (XIII).—A solution of 11.4 g. of the bromoaminoimine, 4 g. of thiourea and 10 ml. of triethylamine in 40 ml. of dimethylformamide was heated overnight on the steam-bath. The dark red solution was poured onto 100 g. of ice, and the resulting gummy solid was isolated by filtration. Recrystallization from methylene chloride by addition of hot acetonitrile and removal of the lower-boiling solvent gave 7 g. (74% yield) of XIII as fluffy orange needles, m.p. 188–190°.

Anal. Calcd. for $C_{42}H_{38}N_4S$: C, 79.96; H, 6.07; N, 8.88; S, 5.08; mol. wt., 631. Found: C, 79.97; H, 6.07; N, 9.16; S, 5.08; mol. wt., 670.

4-Bromo-1-methylamino-7-methylimino-1,3,5-cycloheptatriene.—A solution of bromine (50 g., 0.31 mole) in acetic acid (200 ml.) was added with stirring over 1.5 hours to a solution of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (43.2 g., 0.29 mole) in acetic acid (300 ml.). After 5 hours of additional stirring, the mixture was filtered to give 79.9 g. (89% yield) of the hydrobromide, m.p. 205–210°. A sample recrystallized from ethanol–ether had m.p. 208–213°.

Anal. Calcd. for $C_9H_{12}N_2Br_2$: C, 35.09; H, 3.93; N, 9.10. Found: C, 35.72; H, 4.17; N, 9.00.

A 3.6-g. portion of the salt was dissolved in water and made basic with 5% sodium hydroxide to precipitate the free base (2.5 g., 94%), m.p. 97–101°. Recrystallization from chloroform–petroleum ether gave the bromoaminoimine as yellow-orange needles, m.p. 101°.

Anal. Calcd. for $C_9H_{11}N_2Br$: C, 47.60; H, 4.88; N, 12.34. Found: C, 47.82; H, 4.78; N, 12.42.

4-Chloro-1-(p-tolylamino)-7-(p-tolylimino)-1,3,5-cycloheptatriene.—A solution of 1-(p-tolylamino)-7-(p-tolylimino)-1,3,5-cycloheptatriene (16 g., 0.053 mole) in acetic acid (500 ml.) was treated with chlorine (15 g., 0.42 mole) over a 15-minute period. Part of the product crystallized on cooling the solution. The remainder was obtained by evaporation of the solvent. The total yield of orange crystals of the chloroaminoimine was 4.3 g. (24%), m.p. 225–226° after recrystallization from ethanol.

Anal. Calcd. for $C_{21}H_{19}N_2Cl$: N, 8.37; Cl, 10.59. Found: N, 8.06; Cl, 10.20.

1-Methyl-4,6,8-trichloro-1,3-diaza-2(1-H)-azulenone (XII).—A solution of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (25 g., 0.17 mole) in acetic acid (400 ml.) was treated with a stream of sulfuric acid-washed chlorine for 4 hours. The solution warmed and darkened and finally became pale orange. The solution was concentrated under reduced pressure to give 10.8 g. (24%) of tan solid. Two recrystallizations from ethanol gave XII as light tan needles, m.p. 200°. The infrared absorption spectrum showed strong absorption at 6.22 and 12.97 μ, and medium absorption at 6.40, 6.83, 7.29, 7.45 (with shoulder at 7.56), 8.23 and 8.82 μ.

Anal. Calcd. for $C_9H_5ON_2Cl_3$: C, 41.02; H, 1.91; N, 10.63; Cl, 40.36; mol. wt., 263. Found: C, 41.11; H, 1.95; N, 10.79; Cl, 40.02; mol. wt., 278.

4-p-Nitrophenylazo-1-methylamino-7-methylimino-1,3,5-cycloheptatriene (XVI).—To a solution of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (1.5 g., 0.01 mole) and sodium acetate trihydrate (1.5 g., 0.01 mole) in ethanol (45 ml.) and water (10 ml.) was added a slurry of p-nitrobenzenediazonium fluoroborate (2.5 g., 0.01 mole) in water (40 ml.). The mixture was allowed to stand for an hour in an ice-bath with occasional stirring. The dark brown phenylazo compound (1.0 g., 33%) was collected by filtration and recrystallized twice from ethanol; m.p. 175–178° dec.

Anal. Calcd. for $C_{15}H_{15}O_2N_5$: C, 60.59; H, 5.09. Found: C, 60.31; H, 4.85.

Degradation to 5-Nitrosotropolone.—To a solution of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (2.96 g., 0.02 mole) in 6 N hydrochloric acid (10 ml.) was added a solution of sodium nitrite (1.40 g., 0.02 mole) in water (5 ml.) with stirring over a 20-minute period. The stirring was continued overnight after which a solid (0.7 g., 23%) was collected by filtration. Two recrystallizations from acetic acid gave golden crystals identified as 5-nitrosotropolone, m.p. 185–187° dec., lit.[24] m.p. 180°. The infrared spectrum is identical with that of an authentic sample of 5-nitrosotropolone.

4-Tricyanovinyl-1-(p-tolylamino)-7-(p-tolylimino)-1,3,5-cycloheptatriene (XVII).—A solution of 1.7 g. (0.01 mole) of silver nitrate and 1.4 g. (0.011 mole) of tetracyanoethylene was added to 3 g. (0.01 mole) of 1-(p-tolylamino)-7-(p-tolylimino)-1,3,5-cycloheptatriene in 30 ml. of acetonitrile. The resulting solution immediately became blue-green and precipitated a highly colored solid. After heating on a steam-bath for 30 minutes the mixture was cooled and filtered to yield a blue-black solid. This product was purified by refluxing in 500 ml. of acetonitrile and filtering to remove metallic silver. The filtrate was concentrated by distillation until crystallization began. This procedure yielded 2.4 g. (60%) of the tricyanovinyl derivative, m.p. 258–262° dec.

Anal. Calcd. for $C_{26}H_{19}N_5$: C, 77.78; H, 4.77; N, 17.45. Found: C, 78.09; H, 4.72; N, 17.71.

The infrared spectrum showed no absorption attributable to NH; 3.25 μ (=CH), 4.5 μ (conjugated C≡N), 6.2, 6.25, 6.4, 6.5 and 6.65 μ (conjugated C=C and/or C=N), 3.4 μ (saturated CH), and 12.2 μ (p-disubstituted aromatic).

The product formed a deep blue solution in acetonitrile, ethanol or benzene and a red solution in dimethylformamide. When the reaction was carried out in dimethylformamide without the use of silver nitrate, a 25% yield of XVII was obtained after standing 16 hours at room temperature.

Discussion of Aromaticity

The facile ring substitution by such electrophilic reagents as bromine, chlorine and diazonium ion suggests that the aminoimines have appreciable delocalization energy. As previously discussed, confirmatory evidence has been obtained from infrared and nuclear magnetic resonance spectral studies that is in accord for a resonance-stabilized system.

In view of the structural similarities between the aminoimines and tropolone, it would be attractive *a priori* to attribute aromaticity in the aminoimines to contributions from forms such as F, as has been done in the case of tropolone. However, the dipole

moment studies clearly rule out major contributions from a 6 π-electron system and, in fact, indicate that the seven-membered ring is relatively electronegative.

Hückel's rule[25] for carbomonocyclic systems predicts that a conjugated 10 π-electron system would be appreciably stabilized by resonance, and this has been verified by Katz's[26] finding that cyclooctatetraeneyl dianion is resonance stabilized. Furthermore, Boekelheide[27] has shown that the cyclazine H
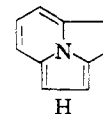
H

which contains a 10 π-electron system around the periphery of the molecule, has appreciable aromatic character.

It is noted that the aminoimines have potential for a conjugated 10 π-electron system (2 electrons from each of the 4 formal double bonds and a pair from the nitrogen of the NHR substituent). It is attractive to assume that some sort of hybridization occurs in these compounds so that a 10 π-electron system is attained involving the peripheral atoms. In this respect the aminoimines would resemble azulene, which is considered by Dewar[28] to be best regarded as a monocyclic 10 π-electron system in view of its low resonance energy and relatively long central bond. Furthermore, evidence for bonding between the nitrogen atoms has been obtained recently from valence bond calculations by Phillips.[29]

It is believed that all available data are consistent with the concept that the aminomines approach a peripherally conjugated 10 π-electron bicyclic system through hybridization of the formally nonbonding electrons of the amino nitrogen atom with those of the adjacent imino nitrogen atom. Thus, the aminoimines are most nearly represented by K, the average structure of the rapid tautomeric process exemplified by B ⇌ C, or of a symmetrically located hydrogen atom,[30] together with possible contribution from L.

(25) E. Hückel, Z. Elektrochem., 43, 752 (1937).

(26) T. J. Katz, J. Am. Chem. Soc., 82, 3784 (1960).

(27) R. J. Windgasser, Jr., W. H. Saunders, Jr., and V. Boekelheide, ibid., 81, 1459 (1959).

(28) M. J. S. Dewar, ibid., 74, 3345 (1952).

(29) Electron spin densities at the seven-membered ring carbon atoms of the paramagnetic Ni(II) chelates[12] of the aminoimines can be reproduced extremely well by a valence bond calculation that includes the five Kekulé structures plus the semi-long bond structure of the form J (private communication from Dr. W. D. Phillips).
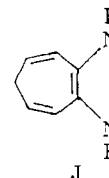
J

(30) A similar process probably is operating in the case of tropolone in solution. However, it does not appear that tropolone derives its unique chemistry from attainment of a 10 π-electron system but rather from contributions to the hybrid from a structure such as G. Dewar's initial concepts emphasized the importance of intramolecular hydrogen bonding, but this was shortly modified to recognize the importance of contributions from G (M. J. S. Dewar, Nature, 155, 50 (1945); 155, 479 (1945); see also ref. 3a, p. 12).

(24) Reference 3a, p. 48.

K   L
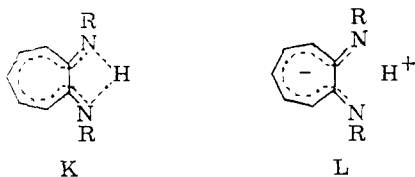
The fact that the aminoimines are more suscep-
tible to attack by electrophilic reagents than tro-
polone is readily interpreted on the basis that the
ring is more electronegative.[31] Thus, the com-
pounds undergo bromination and chlorination in
non-polar solvents to give single monosubstituted
products in high yield. Furthermore, in contrast
to tropolone,[3a,c] sulfonation[32] and nitration[33] are

(31) The fact that nitrogen is more capable of stabilizing a de-
veloping positive charge than oxygen may also be an important factor.

(32) Satisfactory analyses have not yet been obtained, but nuclear
magnetic resonance studies have established that the 4-substituted
derivative is formed.

(33) Unpublished result by Dr. A. D. Josey.

readily accomplished at room temperature. Lastly,
the reaction with tetracyanoethylene to give a
tricyanovinylaminoimine clearly is indicative of an
addition–elimination reaction attributable to the
electronegative character of the aminoimine. Un-
der similar conditions tropolone gives a mixture of
unidentified products.[22]

1-Amino-7-thioxo-1,3,5-cycloheptatrienes

By W. R. Brasen and R. E. Benson
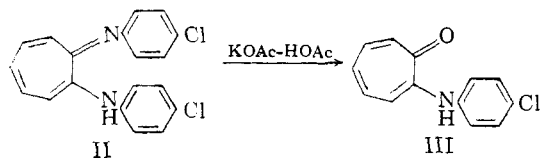
1-Amino-7-thioxo-1,3,5-cycloheptatrienes (IV), a previously unknown class of compounds, are accessible in good yields from the 1-amino-7-imino-1,3,5-cycloheptatrienes (I) by reaction with hydrogen sulfide. Although the thioxo compounds IV have considerable stability, they do not have the pronounced aromatic character associated with the aminoimines I.
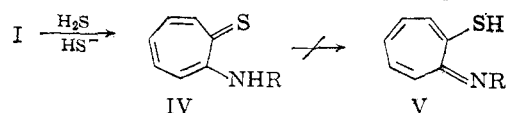
The synthesis of 1-amino-7-imino-1,3,5-cyclo-
heptatrienes was described in the previous paper.[1]

I
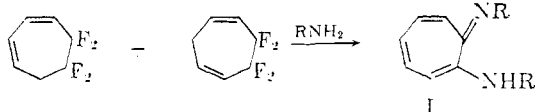
It was reported that the aminoimines were ex-
tremely stable to hydrolysis with strong acids or
bases, but that a diaryl derivative II underwent
hydrolysis readily in acetic acid in the presence of
potassium acetate to yield the arylaminotropone III.

II   III

Extension of the weak acid–weak base combina-
tion to the hydrogen sulfide–hydrosulfide system
has given 1-amino-7-thioxo-1,3,5-cycloheptatrienes
(IV), a previously unreported class of compounds.

IV   V

R = H, CH₃, p-CH₃OC₆H₄, p-CH₃C₆H₄

(1) W. R. Brasen, H. E. Holmquist and R. E. Benson, J. Am. Chem.
Soc., 83, 3125 (1961); see also ibid., 82, 995 (1960), for preliminary
note.

The most closely related compounds previously
reported appear to be thiotropolone (VI) and its S-
alkyl derivatives, prepared from 2-chlorotropone,[2]

VI   VII
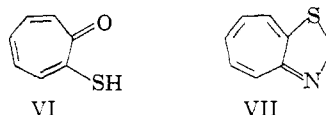
and derivatives of dihydro-1,3-thiaazulene (VII)
synthesized from 2-chlorotropone and thiourea.[3]

Verification that the displacement reaction had
proceeded without rearrangement was found in the
formation of stable chelates from the thioxo deriva-
tives IV with such metallic ions as copper, nickel
and cobalt. Furthermore, the aryl derivative IV
(R = C₆H₄CH₃-p) was converted to the corre-
sponding aminoimine I by reaction with p-toluidine.

The aminothioxo derivatives IV are colored
products that are readily soluble in dilute acid but in-
soluble in strong base, indicating that tautomeriza-
tion to the iminomercaptocycloheptatriene struc-
ture V is not favorable, even under these conditions.
This was verified by proton magnetic resonance
studies of IV, R = CH₃. In contrast with the
aminoimine I (R = CH₃) which shows a single
methyl resonance,[1] the thioxo compound IV (R =
CH₃) shows a doublet methyl resonance (3.05 and
3.16 p.p.m., tetramethylsilane reference). This

(2) T. Nozoe, M. Sato and K. Matsui, Proc. Japan Acad., 29, 22
(1953); 28, 407 (1952).

(3) T. Nozoe, Fortschr. Chem. Org. Naturstoffe, 13, 287 (1955).