Chemical Co., Pittsburg, Calif.) performed the mass-spectrometric analyses; Mr. Fred Holling and Mrs. V. Krivoshein (Reed College) have helped us in translation from the Russian; for the NMR spectra we are indebted to Dr. Dietrich Heinert and Mr. Fred Anderson of the Illinois Institute of Technology. We have again exchanged data before publication with Professor R. M. Lagidze, whom we thank for his gracious and continued interest.

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PORTLAND 2, ORE.

[CONTRIBUTION FROM THE RESEARCH DIVISION, POLAROID CORP.]

Red Dyes of the Azabenzanthrone Series. 1-Substituted 2-Keto-3-alkyl-6-alkylamino-3-azabenzanthrones[1]

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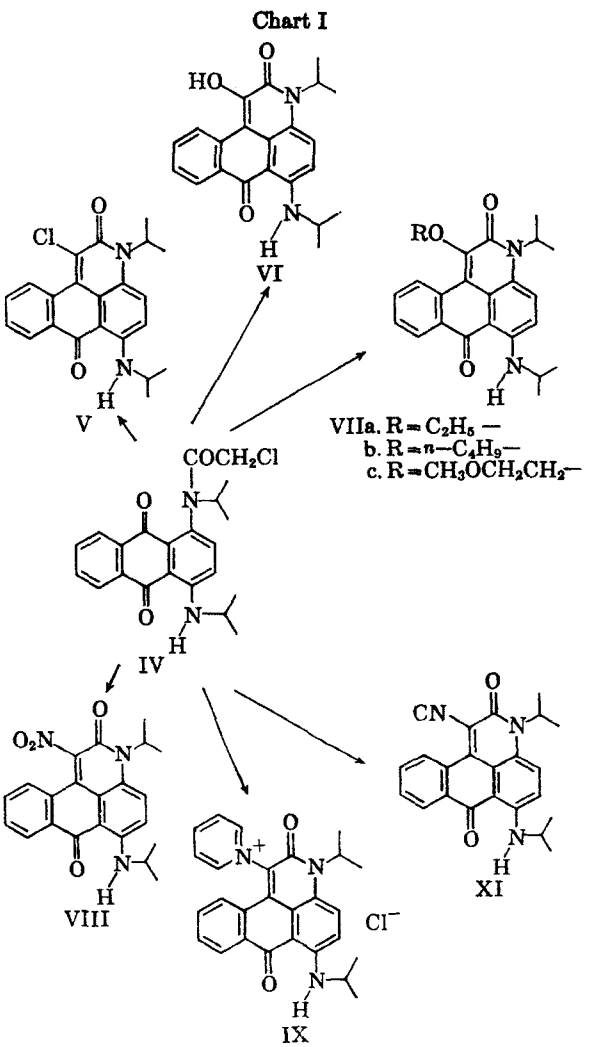
2-Keto-3-alkyl-6-alkylamino-3-azabenzanthrone dyes containing different substituents in the 1- position were synthesized A correlation between electronegativity of the 1-substituent and position of the visible absorption bands is noted. Several routes to a new type of 2-keto-3-azabenzanthrone dye, the 1-alkoxy derivatives, are reported.

2-Keto-3-azabenzanthrones with amino groups in the 6-position are red dyes. In the fifty years since their discovery the series most studied has been that containing 6-arylamino groups.[2] These have greater stability toward light than the 6-alkylamino dyes, and have an aromatic ring which can be readily sulfonated for water solubility. In an examination of lesser known derivatives of aminoanthraquinones we have made a number of 2-keto-3-azabenzanthrones with alkylamino groups in the 6-position. A few references to such materials appear in the patent literature.[3] We have used the isopropyl group as the representative alkyl group because of the known increase in light stability of alkylaminoanthraquinone dyes when primary alkyl groups on the amine are replaced by secondary alkyl groups.[4]

In the course of this work we have synthesized three members of a type of 2-keto-3-azabenzanthrone dye not previously reported, the 1-alkoxy derivatives. Three routes to their preparation, from *N*-chloracetyl-1,4-bis(*i*-propylamino)anthraquinone (IV), from 1-chloro-2-keto-3-*i*-propyl-6-*i*-propylamino-3-azabenzanthrone (V), and from 1-pyridinium-2-keto-3-*i*-propyl-6-*i*-propylamino-3-azabenzanthrone chloride (IX) were found. The 1-alkoxy dyes have much of the reactivity of simple esters (they are, in fact, vinylogous esters), being hydrolyzed by alkali or aminated by ammonia to VI and X, respectively. They are, however, resist-

Chart I



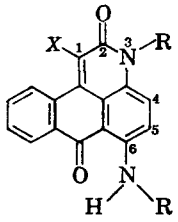
(1) These materials are probably best known as anthrapyridones, *e.g.*, "1-substituted 3-alkyl-6-alkylaminoanthrapyridones." *Chemical Abstracts* prefers "1-substituted 3-alkyl-6-alkylamino-7*H*-dibenz[*f,ij*]isoquinoline-2,7[3*H*]-diones," Ring Index No. 5168.

(2) See, *e.g.*, K. Venkataraman, *Synthetic Dyes*, Academic Press, New York, 1952, p. 99; H. A. Lubs, *The Chemistry of Synthetic Dyes and Pigments*, Reinhold, New York, 1955, p. 463.

(3) (a) Bayer, German Patent 201,904 (1907); (b) Sandoz, French Patent 975,917 (1951); (c) E. F. Elslager, U. S. Patent 2,756,234 (1956).

(4) I. G. Farbenindustrie, British Patent 490,372 (1938).

ant to concentrated hydrochloric acid, from which they are recovered unchanged after two hours at 100°.



III. X = H, R = *i*-propyl

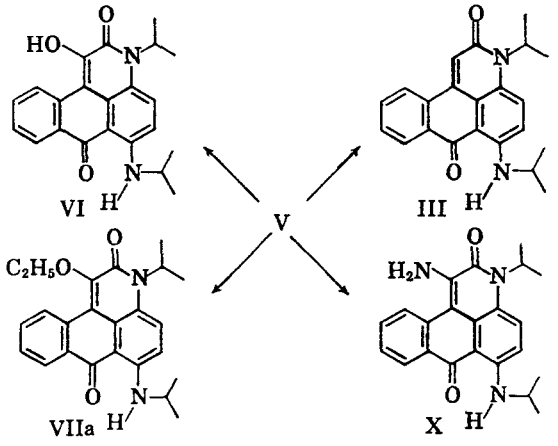
Synthetic methods for 6-amino-2-keto-3-azabenzanthrones can be divided into those routes in which the azabenzanthrone ring system is first prepared, followed by introduction of the amine group in the 6- position, usually by replacement of a halogen or nitro group,[5] and routes in which the required 1,4-diaminoanthraquinone derivative is acylated and cyclized, often in a single step.[6] The compounds described in this paper were made by the second route, using various methods for cyclization of the acylated amine as a second step in the reaction sequence. The well known method of acylating with a suitable ester and cyclizing in a single reaction[7] could not conveniently be applied to isopropylaminoanthraquinones because of their relative inertness. Thus, the reaction with ethyl malonate and sodium acetate found suitable for preparing 1-carbethoxy-2-keto-3-methyl-3-azabenzanthrone derivatives by earlier workers, using a reaction time of four hours,[8] when applied to 1-isopropylaminoanthraquinone for as long as eighteen hours, led to almost complete recovery of the starting material. Acetoacetate ester was somewhat more reactive than ethyl malonate, while ethyl cyanoacetate[9] was found to be even less reactive.

The parent compound of the series, 2-keto-3-*i*-propyl-6-*i*-propylamino-3-azabenzanthrone (III), was readily prepared by acetylation of 1,4-bis(*i*-propylamino)-anthraquinone (I) with acetic anhydride and sodium acetate, followed by cyclization of II with alkali. Chloracetylation of I in benzene yielded *N*-chlor-acetyl-I (IV), the starting material for the other dyes prepared in this work (see Chart I). Treatment of IV with alkali gave several products, depending markedly on the conditions. In acetone or butanol (a two-phase system) aqueous alkali at 60° caused simple cyclization without elimination of chlorine, to the 1-chloro dye (V). Use of a water-miscible alcohol under these mild conditions caused replacement of chloride by the alkoxyl group of the alcohol, producing members of the 1-alkoxy series (VII). Elevated temperatures (*ca.* 100°) led directly to the 1-hydroxy derivatives (VI).

Treatment of IV with sodium nitrite,[10] potassium cyanide,[11] or pyridine[12,14] produced the 1-nitro compound (VIII), the 1-cyano compound (XI), and the 1-pyridinium chloride derivative (IX), respectively.

Substituents in the 1-position of 2-keto-3-azabenzanthrones are labilized by conjugation with the carbonyl group of the anthrone system. Early patents reported replacement of 1-chlorine by sulfhydryl, hydroxyl, or anilino groups,[13] and formation of the pyridinium derivative by long (two to three hours) boiling of 1-chloro-2-keto-3-azabenzanthrone.[14,17] Allen[10] found that a 1-nitro group could be displaced by anilines or hydroxyl groups. In our work we found that brief boiling of an alkaline Methyl Cellosolve solution replaced 1-chlorine with hydroxyl, while milder conditions served to replace the chlorine atom by alkoxyl (see Chart II). Reaction with ammonia in the presence of copper was complex, and from V we obtained the amino derivative (X), but also III, I, and 1-amino-4-*i*-propylaminoanthraquinone. In the absence of copper, X was the sole product, in quantitative yield.

Chart II



The 1-alkoxy group is labile toward alkali or ammonia. 1-Pyridinium salts are also active (see Chart III). Sodium ethoxide converted IX to VIIa, as well as a small amount of III. III could be formed in excellent yield by reduction of IX with

(5) Badische An. u. Sodafab., German Patent 205,095 (1907); ref. 3a. v.s.; R. Seka, G. Schreckental, and P. Heilperin, *Monatsh.*, 53–54, 471 (1929); Sandoz, German Patent 580,238 (1933); ref. 10, v.i.

(6) Bayer, German Patent 192,201 (1907); 203,752 (1908); I. G. Farbenindustrie, British Patent 412,270 (1934); F. Lodge, British Patent 525,091 (1940).

(7) *E.g.*, G. W. Seymour, V. A. Salvin, and W. D. Jones, U. S. Patent 2,501,099 (1950); ref. 3b, v.s.; Sandoz, British Patent 692,902 (1953).

(8) C. F. H. Allen, J. V. Crawford, R. H. Sprague, E. R. Webster, and C. V. Wilson, *J. Am. Chem. Soc.*, 72, 585 (1950).

(9) Private communication from Dr. S. Kasman.

(10) C. F. H. Allen and C. V. Wilson, *J. Org. Chem.*, 10, 594 (1945).

(11) I. G. Farbenindustrie, French Patent 837,591 (1939).

(12) C. Marschalk, *Bull. Soc. Chim. France*, 1952, 952.

(13) Bayer, German Patent 264,010 (1912).

(14) Bayer, German Patent 290,984 (1916).

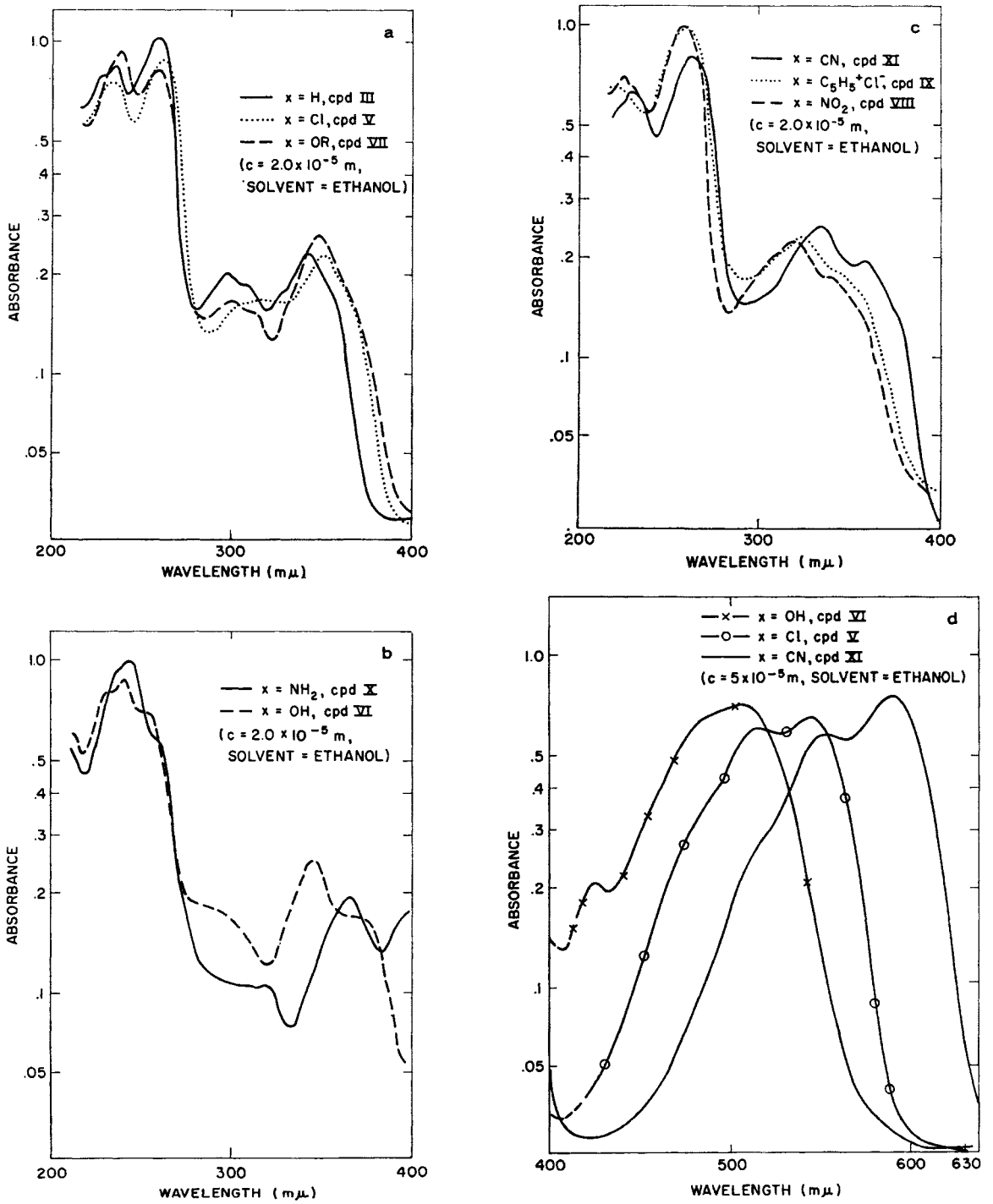


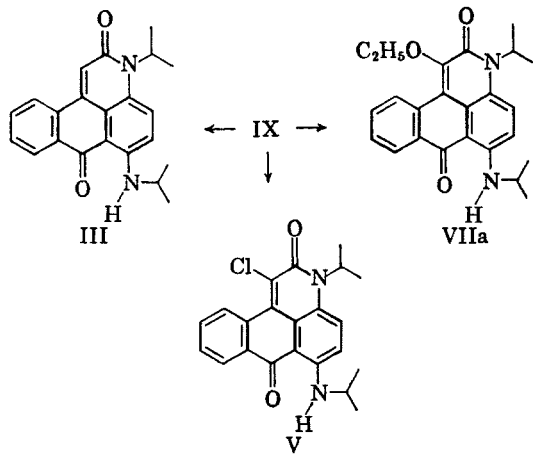
Figure 1

sodium hydrosulfite, the method of Marschalk.[15] Heating IX in nitrobenzene[12] eliminated pyridine to form V. The 1-nitro compound (VIII) was converted into VI by vigorous treatment with ethanolic potassium hydroxide, and into X by catalytic reduction.

Allen has suggested that cyclization of α-halo acetylaminoanthraquinones by sodium nitrate initially proceeds by formation of the α-nitroacetylaminoanthraquinone.[10] Results of Marschalk[12] provide more information, since he found that the transformation from 1-chloro-2-keto-3-azabenzanthrone to the 1-pyridinium salt required several hours boiling in pyridine, while the chloroacetylated aminoanthraquinone could be converted into the same salt by boiling for five minutes in pyridine. In general, replacement of the α-halogen by a more strongly electron withdrawing substituent precedes

(15) C. Marschalk, *Bull. soc. chim. France*, 1952, 955.

Chart III



cyclization. On the other hand, formation of VI and VII from IV appears to go through the 1-chloro-2-keto-3-azabenzanthrone, which was isolated as the sole product of the mildest conditions by using a two-phase solvent system, but which was converted to VI and VII under the same conditions in homogeneous solution.

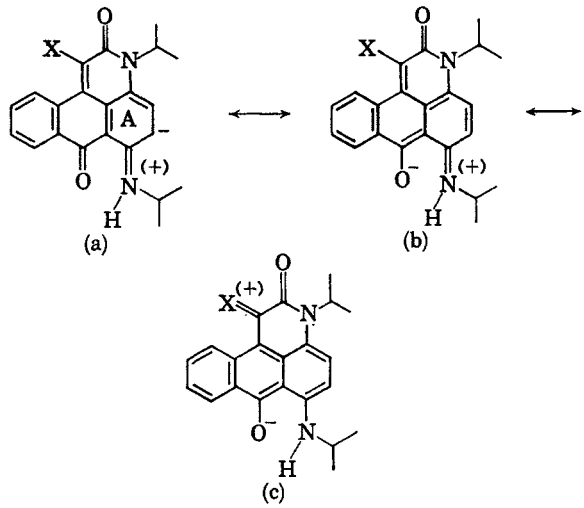


Figure 2

In contrast to dyes of the 6-arylamino series, which have a single peak in the visible spectrum, dyes with a 6-alkylamino group show the double peak characteristic of 1,4-diaminoanthraquinones. The shorter wave length peak appears to be a vibrational overtone.[16] The peaks, which are of almost equal height, with the longer wave length one of slightly greater intensity, are separated by 900 to 1100 cm.$^{-1}$ In the 1-hydroxy or 1-amino compounds these peaks are too close to be resolved, and the one at lower wave length appears as an inflection on the shoulder of the main peak. Another inflection on the short wave length side of the curves is not resolved enough to be assigned a wave length and is probably a second vibrational overtone. This band is concealed in the 1-amino or 1-hydroxy dyes by a second absorbing system around 420 mμ.

(16) Private communication from Dr. George R. Bird.

TABLE I

1-SUBSTITUTED 2-KETO-3-*i*-PROPYL-6-*i*-PROPYLAMINO-3-AZABENZANTHRONES, VISIBLE SPECTRA

1-Substituent	λ_{max} (mμ) (ε)	$\Delta\lambda_{max}$[a]	ν (cm.$^{-1}$)	Δν[b] (cm.$^{-1}$)
OH	507 (14,000)	−30	19,700	900
	~485 (12,600)		20,600	
	425 (4,100)			
NH_2	508 (14,800)	−29	19,600	1000
	~486 (12,600)		20,600	
	414 (9,800)			
OC_2H_5	528 (13,000)	− 9	18,900	1000
	502 (12,400)		19,900	
OC_4H_9-*n*	527 (13,000)	−10	19,000	900
	504 (12,400)		19,900	
$OC_2H_4OCH_3$	526 (13,200)	−11	19,000	900
	503 (12,800)		19,900	
H	537 (13,400)	—	18,600	1100
	507 (12,000)		19,700	
Cl	545 (12,800)	+ 8	18,300	1100
	515 (11,800)		19,400	
NO_2	557 (13,400)	+20	18,000	1100
	524 (11,000)		19,100	
$NC_5H_5^+Cl^-$	569 (13,400)	+32	17,600	1100
	535 (11,000)		18,700	
CN	590 (15,000)	+53	17,000	1100
	551 (11,400)		18,100	

[a] Difference between long wave length peak of compound and that of compound III. [b] Distance between maxima of double peak.

Allen *et al.*[8] have called attention to the influence of substituents in the 1 position on the visible spectrum. The results of our study confirm those of Allen and may be summarized by the statement: electron donating groups in the 1-position of 2-keto-3-azabenzanthrones are hypsochromic, while electron withdrawing groups are bathochromic. The peak positions range from 507 mμ for VI, with a 1-hydroxyl group, to 590 mμ for the 1-cyano derivative (XI). In Table I we have summarized the maximum absorption peaks of this series of dyes. Figure 1(d) shows absorption curves of the 1-hydroxy, 1-chloro, and 1-cyano derivatives. The hypsochromic shift with increasing electron donating nature of the 1-substituent may be rationalized by assuming that the resonance system involving forms (a) and (b) (Fig. 2) (other forms, with the negative charge elsewhere in ring A, can also be written) is associated with the visible absorption of these dyes. An electron donating group in the 1-position would be expected to raise the energy requirement needed to distribute the negative charge around ring A, in the excited state, and so shift the absorption to lower wave length. The band around 420 mμ in the 1-hydroxy and 1-amino compounds may be associated with a resonance system symbolized by form (c), which may be stabilized by hydrogen bonding with the amide carbonyl group.[17]

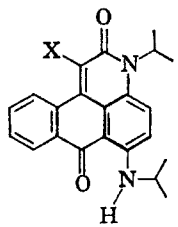
(17) R. A. A. Du Pont, *Bull. soc. chim. Belge*, 52, 7 (1943).

TABLE II

Starting Material			Reagents							
Compound	G.	Mole	Compound	G./Mole	Solvent, Ml.	Temp.	Time, Hr.	Work-up Method	Yield, %	Product
I	1.0	0.0031	Sodium acetate Acetic anhydride	0.1 20 ml.	(Acetic anhydride)	Reflux	6.5	A	84	II
I	8.0	0.025	Chloroacetyl chloride	2.5 ml./0.026	Dry benzene, 250	Reflux	16	B	76	IV
II	1.5	0.0041	Potassium hydroxide	1.5	Methyl cellosolve, 25	Reflux	0.5	C	87.5	III
IV	2.0	0.0051	Sodium hydroxide	2.0/0.05	*n*-Butyl alcohol, 100 Water, 15	60	0.75	D	100	V
IV	2.0	0.0051	Sodium hydroxide	2.0/0.05	Acetone, 80 Water, 50	60	0.75	C	89.5	V
IV	2.0	0.0051	Sodium hydroxide	2.0/0.05	Methyl Cellosolve, 50 Water, 10	Reflux	0.5	E	97	VI
IV	2.0	0.0051	Sodium (Sodium ethoxide)	1.2/0.052	Abs. ethanol, 100	60	0.5	C	65	VIIa
IV	2.0	0.0051	Sodium hydroxide	2.0/0.05	*n*-Butyl alcohol, 100	60	0.5	D	79[a]	VIIb
IV	2.0	0.0051	Sodium hydroxide	2.0/0.05	Methyl Cellosolve, 100 Water, 15	60	0.75	E	83	VIIc
IV	2.0	0.0051	Sodium nitrite	1.0/0.0145	Methyl Cellosolve, 20 Water, 1	Reflux	1	C	41	VIII
IV	2.0	0.0051	Pyridine	25 ml.	(Pyridine)	Reflux	0.5	C	76	IX
IV	2.0	0.0051	Potassium cyanide	1.1/0.0167	Ethylene glycol mono-acetate, 20 Water, 2	125	1	C	59	XI
V	0.5	0.0013	NH_3, Satd. at −78° Copper bronze	— Trace	Ethanol, 50	100 s.s. bomb	16	B, F	22	III
V	0.5	0.0013	Sodium hydroxide	0.5	Methyl Cellosolve, 20 Water, 5	Reflux	0.25	E	94.5	VI
V	0.5	0.0013	Sodium hydroxide	0.5	Ethanol, 20 Water, 5	60	0.5	E	61	VIIa
V	0.5	0.0013	NH_3, Satd. at −78° Copper bronze	— Trace	Acetone, 50	100 s.s. bomb	16	B, G, F	7 2 2	X I XII[b]
V	0.5	0.0013	NH_3, Satd. at −78°	—	Ethanol, 50	100 s.s. bomb	18	B	100[a]	X
VIIa	0.8	0.0021	Sodium hydroxide	2.0/0.05	Ethanol, 60 Water, 6	Reflux	0.5	E	53.5	VI
VIIc	1.0	0.0024	NH_3	3	Ethanol, 50	100 s.s. bomb	24	C	71.5	X
VIII	0.2	0.00051	(a) Potassium hydroxide (b) Concd. HCl	0.3 30 ml.	Ethanol, 5 (HCl)	Reflux 100	21 2	B E	96[a]	VI
VIII	1.0	0.0025	PtO_2/H_2	0.1/30 p.s.i.	Acetic acid, 40	25	1.5	H	76	X
IX	1.0	0.0022	Sodium hydrosulfite Sodium bicarbonate	1.2 1.2	Water, 60	100	0.5	C	93[a]	III
IX	1.0	0.0022	—	—	Nitrobenzene, 10	Reflux	0.4	J	54[a]	V
IX	3.7	0.008	Sodium (Sodium ethoxide)	0.38/0.016	Abs. ethanol, 200	60	1	E, F	65[a] 7[a]	VIIa III

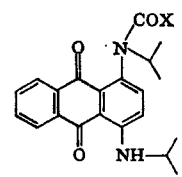
[a] Crude product. [b] XII = 1-amino-4-*i*-propylaminoanthraquinone.

TABLE III



1-SUBSTITUTED 2-KETO-3-ISOPROPYL-6-ISOPROPYLAMINO-3-AZABENZANTHRONES

Compound No.	X	M.P.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Cl, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
III	—H	261–263	$C_{22}H_{22}N_2O_3$	76.27	76.13	6.40	6.39	8.09	8.19	—	—
V	—Cl	184–186	$C_{22}H_{21}N_2O_3Cl$	69.38	69.62	5.55	5.59	7.35	7.36	9.31	9.02
VI	—OH	273–275	$C_{22}H_{22}N_2O_3$	72.91	72.72	6.12	6.03	7.73	7.73	—	—
VIIa	—OC_2H_5	174–175	$C_{24}H_{26}N_2O_3$	73.82	73.78	6.71	6.72	7.18	7.38	—	—
VIIb	—OC_4H_9-*n*	181–182	$C_{26}H_{30}N_2O_3$	74.61	74.85	7.23	7.23	6.69	6.97	—	—
VIIc	—$OCH_2CH_2OCH_3$	158–159	$C_{25}H_{28}N_2O_4$	71.41	71.64	6.71	6.71	6.66	6.71	—	—
VIII	—NO_2	239–239.5	$C_{22}H_{21}N_3O_4$	67.50	67.39	5.41	5.51	10.74	10.74	—	—
IX	—pyridinium$^+$ Cl^-	235–235.5	$C_{27}H_{26}N_3O_2Cl$	70.50	70.61	5.69	5.65	9.13	9.15	7.71	7.86
X	—NH_2	201–202	$C_{22}H_{23}N_3O_2$	73.10	73.14	6.41	6.24	11.63	11.55	—	—
XI	—CN	275–275.5	$C_{23}H_{21}N_3O_2$	74.37	74.55	5.70	5.89	11.31	11.61	—	—



II	CH_3—	161–162	$C_{22}H_{24}N_2O_3$	72.50	72.43	6.64	6.79	7.69	7.96	—	—
IV	$ClCH_2$—	167–168	$C_{22}H_{23}N_2O_3Cl$	66.25	66.20	5.81	5.80	7.02	6.99	8.90	9.28

TABLE IV. ULTRAVIOLET SPECTRA OF 1-SUBSTITUTED 2-KETO-3-*i*-PROPYL-6-*i*-PROPYLAMINO-3-AZABENZANTHRONES
(Ethanol solutions)

VI	max					242										346			
X = OH						(43,500)										(12,650)			
	~[a]			233			255		296								374		
				(40,000)			(34,000)		(8800)								(8200)		
		218										320						408	
	min	(26,000)										(6000)						(1000)	
X	max					244											365		
X = NH_2						(49,000)											(9650)		
	~			236			260			298–318									
				(45,000)			(28,000)			(5250)									
		220											332						384
	min	(22,500)											(4000)						(6500)
VII	max			238			257		298							347			
X = OR				(49,500)			(41,500)		(8750)							(13,700)			
	~									311									
										(7800)									
		220				246			284			322							400
	min	(26,000)				(36,000)			(8000)			(6500)							(500)
V	max			233			260									350			
X = Cl				(37,500)			(43,500)									(11,350)			
	~									305–332									
										(8250)									
		218				244			286										400
	min	(29,000)				(28,000)			(6500)										(500)
III	max			234			259		297				341						
X = H				(41,500)			(51,000)		(9700)				(11,500)						
	~		226							308							356		
			(37,500)							(9100)							(8000)		
		218				242		270				319							380
	min	(31,000)				(34,000)		(7700)				(7750)							(600)
VIII	max		224				258					320							
X = NO_2			(35,500)				(51,000)					(11,500)							
	~									306							350		
										(10,200)							(8000)		
		210		238					283										400
	min	(30,500)		(28,000)					(7000)										(1000)
IX	max						258					324							
X =							(51,000)					(11,750)							
$C_2H_5{}^+Cl^-$	~																365		
																	(8200)		
	min			236					292										400
				(28,000)					(8800)										(1000)
XI	max		228				262						332			358			
X = CN			(32,500)				(41,500)						(12,500)			(10,000)			
	~																		
						242			294							352			400
	min					(23,500)			(7500)							(9700)			(500)

[a] ~ = plateau

EXPERIMENTAL

Melting points were determined in a Mel-Temp apparatus and are not otherwise corrected. Ultraviolet and visible region spectra were taken in a Cary recording spectrophotometer, Model 10. Infrared spectra were taken on potassium bromide pressings of the compounds, in a Perkin-Elmer Model 21 spectrophotometer. The 1,4-bis(*i*-propylamino)-anthraquinone used was a commercially available dye, Waxoline Blue AS, a product of I.C.I. It was 91% pure by spectral assay. Analyses were by A. Bernhardt, Mülheim (Ruhr), Germany.

Experiments are summarized in Table II. The products were isolated by one or more of the following procedures, then recrystallized to analytical purity. The crystallization solvent was ethanol except for compound VI (acetone), IX (pyridine), and II (toluene, petroleum solvent, b.p. 90–120°).

Isolation procedures. (A) Excess anhydride was decomposed with water, and the product crystallized on cooling. (B). The solvent was evaporated. (C) On cooling, the product crystallized. (D) After washing with water and drying, the organic solvent was evaporated. (E) The reaction was poured into excess dilute hydrochloric acid, and the precipitated product washed with water. (F) The product was chromatographed on Florisil from benzene solution. (G) The product was dissolved in dilute hydrochloric acid and precipitated with sodium hydroxide solution. (H) The catalyst was removed by filtration, and the filtrate diluted with water. (J) Solvent was steam distilled, and the residue washed with hexane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Preparation of a Nine-Membered Cyclic Diketone, 1,2-Dicarbethoxy-3,9-diphenyl-1,2-diaza-4,8-cyclononanedione[1]

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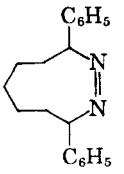
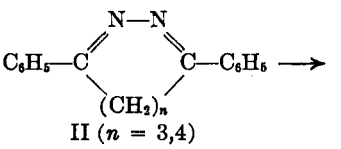
In an attempted synthesis of a nine-membered cyclic azo compound, 1,2-dibenzylidenecyclopentane was treated with ethyl azodicarboxylate to give a Diels-Alder adduct, which was hydroxylated with osmium tetroxide to give *cis*-1,6-dihydroxy-2,5-diphenyl-3,4-diazabicyclo[4.3.0]nonane. This product was cleaved to give 1,2-dicarbethoxy-3,9-diphenyl-1,2-diaza-4,8-cyclononanedione (VII). Attempts to reduce the keto groups of VII to methylene groups failed.

The synthesis of 3,9-diphenyl-1,2-diazacyclononene (I) and other medium-sized cyclic azo compounds is of particular interest as part of a continuing study of the preparation and properties of moderately active diradicals in solution.[3] Attempted synthesis of 3,9-diphenyl-1,2-diazacyclononene (I), although unsuccessful, led to several interesting compounds.

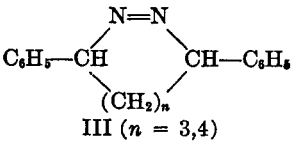


I

In previous work, the seven-[4] and eight-membered[5] cyclic azo compounds (III. n = 3,4) had been prepared from the corresponding cyclic azines (II. n = 3,4) by catalytic hydrogenation followed by oxidation of the intermediate hydrazine to give the azo compounds. Attempts to prepare the nine-, ten-, twelve-, and fourteen-membered cyclic azines



II (n = 3,4)



III (n = 3,4)

by a high dilution procedure[3] from the corresponding, α,ω-dibenzoylalkanes and hydrazine monohydrobromide, however, led to the dimeric eighteen-,[6] twenty-,[3a] twenty-four-,[3] and twenty-eight-[3] membered cyclic azines, which were converted to the corresponding azo compounds. The reaction of hydrazinium acetate and the appropriate diketone was successful in the case of eight-membered

(1) This is the 37th in a series of papers concerned with the preparation and decomposition of azo compounds. For the previous paper in this series see C. G. Overberger and N. P. Marullo, *J. Am. Chem. Soc.*, **83**, 1378 (1961).

(2) This paper comprises a portion of a thesis presented by J. Richard Hall in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) (a) C. G. Overberger, I. Tashlick, M. Bernstein, and R. G. Hiskey, *J. Am. Chem. Soc.*, **80**, 6556 (1958). (b) C. G. Overberger and M. Lapkin, *J. Am. Chem. Soc.*, **77**, 4651 (1955).

(4) C. G. Overberger and J. G. Lombardino, *J. Am. Chem. Soc.*, **80**, 3009 (1958).

(5) C. G. Overberger and I. Tashlick, *J. Am. Chem. Soc.*, **81**, 217 (1959).

(6) J. R. Hall, Ph.D. thesis, Polytechnic Institute of Brooklyn, 1961.