Amine Salts using $CHCl_3$ as extracting solvent. After removal of the $CHCl_3$, the residue was chromatographed on Fischer alumina and gave 0.83 g (11%) of 2,3,5,6-tetraphenylpyridine and 2.24 g (50%) of α-hydroxymethyldeoxybenzoin.

2,3,5,6-Tetraphenylpyridine was recrystallized from dioxane–water and had mp 241–242° (lit.[19] mp 232–233°); nmr ($CDCl_3$) τ 2.75 (m); uv ($CHCl_3$) λ_{max} 248 mμ (ε 29,600), 303 (16,400).

Anal. Calcd for $C_{29}H_{21}N$: C, 90.82; H, 5.52; N, 3.65. Found: C, 90.54; H, 5.82; N, 3.55.

α-Hydroxymethyldeoxybenzoin gave an ir spectrum (neat) consistent with the assigned structure: 3430 cm^{-1} (bonded OH), 1670 (C=O), 1050 (COH).

Attempted Reaction of Acetophenone and Ammonium Chloride in Dimethyl Sulfoxide.—A solution of acetophenone (0.10 mol) and ammonium chloride (0.10 mol) in dimethyl sulfoxide (0.70 mol) was heated at 170–178° for 23 hr. Aliquots were removed periodically, processed as above, and analyzed by tlc observing the disappearance of acetophenone. After 23 hr, when all the acetophenone was gone, the reaction mixture was processed as above and gave a dark resinous residue.

(19) H. Carpenter, *Justigs Liebigs Ann. Chem.*, **302**, 234 (1898).

Registry No.—$C_6H_5CH_2NH_2$, 100-46-9; $C_6H_5CH_2NH_2 \cdot HCl$, 3287-99-8; $C_6H_5CH_2NHCH_3 \cdot HCl$, 13426-94-3; $C_6H_5CH_2N(CH_3)_2 \cdot HCl$, 1875-92-9; $C_6H_5CH_2N^+(CH_3)_3I^-$, 4525-46-6; α-hydroxymethylpropiophenone, 16735-22-1; α-hydroxymethylpropiophenone 2,4-dinitrophenylhydrazone, 24301-96-0; 2,3,5,6-tetraphenylpyridine, 24301-97-1.

Ring–Chain Tautomerism of Derivatives of 1-(α-Aminobenzyl)-2-naphthol with Aromatic Aldehydes[1]

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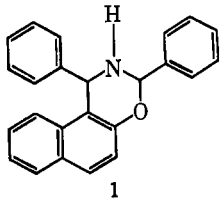
The ir spectra of the condensation products of 1-(α-aminobenzyl)-2-naphthol with benzaldehyde and substituted benzaldehydes indicate that in the crystalline state they have the 2,3-dihydro-1H-naphth[1,2-*e*][1,3]-oxazine structure. The nmr spectra show that in chloroform-*d* they equilibrate to a mixture of the *cis*- and *trans*-naphthoxazine (ring) and the corresponding Schiff base (chain) tautomers. The ring/chain ratio depends on the substituent in the benzaldehyde moiety. The greater the electron-withdrawing power of the substituent, the larger is the ring/chain ratio. In trifluoroacetic acid there is an equilibrium between *cis*- and *trans*-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazonium and the corresponding immonium ions. Electron-withdrawing substituents in the benzaldehyde moiety increase the proportion of the naphthoxazonium ions.

Betti[2] reported the condensation of 2-naphthol, benzaldehyde, and ammonia in a ratio of 1:2:1. The crystalline product was first assigned the 1,3-diphenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine structure (1).[3] Later, on the basis of its reaction in benzene with ethereal ferric chloride, which results in an intense reddish-violet color,[2a] the isomeric Schiff base structure, N-benzylidine-1-(α-aminobenzyl)-2-naphthol (2), was



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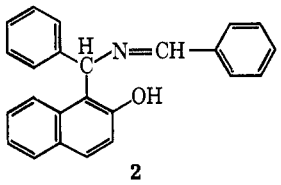


2

proposed.[4] Hydrolysis of the condensation product in hydrochloric acid gives 1-(α-aminobenzyl)-2-naphthol hydrochloride which can be converted to the free base.[2b,3] The latter condenses readily with aliphatic and aromatic aldehydes, including benzaldehyde, and with aliphatic ketones.[4b] It was concluded that aliphatic aldehydes give 3-alkyl-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazines whereas aromatic aldehydes and aliphatic ketones give the Schiff bases.[4b]

In subsequent work, 1-(α-aminobenzyl)-2-naphthol was resolved,[5] and the dextrorotatory isomer was condensed with benzaldehyde and with various substituted benzaldehydes.[6] These condensation products are of substantial interest in that they show unusual differences in their rotatory powers. In benzene, they range from $[M]_D$ −990.7° for the *o*-nitrobenzaldehyde derivative to $[M]_D$ +2676.0° for the *p*-dimethylaminobenzaldehyde derivative.[7] In addition, the rotatory powers of the condensation products in benzene vary in a regular way and are correlated with the strength (pK_a) of the substituted benzoic acid corresponding to the aldehyde condensed with dextrorotatory 1-(α-aminobenzyl)-2-naphthol.[7] Inferences were drawn concerning the influence of the various substituents on the rotatory powers of these substances, all assumed to have the Schiff base structure.[7,8] More recently, the circular dichroism curves of a number of these condensation products were measured in ethyl alcohol.[9] It was assumed that the Schiff base chromophore would be dominant for all of these condensation products in ethyl alcohol.

It has been found, however, that the condensation product of 2-naphthol, benzaldehyde, and ammonia when treated in ethyl ether with nitrous acid gives a compound with the N-nitroso-1,3-diphenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine structure.[10] On this

(1) Taken from the M.S. Thesis of N. E. C., Vanderbilt University, 1969.

(2) (a) M. Betti, *Gazz. Chim. Ital.*, **30** (II), 310 (1900); *J. Chem. Soc.*, **80** (I), 81 (1901); (b) "Organic Syntheses," Coll. Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1947, p 381.

(3) M. Betti, *Gazz. Chim. Ital.*, **31** (I), 377 (1901); *J. Chem. Soc.*, **80** (I), 611 (1901).

(4) (a) M. Betti, *Gazz. Chim. Ital.*, **33** (I), 17 (1903); *J. Chem. Soc.*, **84** (I), 510 (1903); (b) M. Betti and V. Foa, *Gazz. Chim. Ital.*, **33** (I), 27 (1903); *J. Chem. Soc.*, **84** (I), 511 (1903).

(5) M. Betti, *Gazz. Chim. Ital.*, **36** (II), 392 (1906).

(6) (a) M. Betti, *ibid.*, **37** (I), 62 (1907); (b) *ibid.*, **37** (II), 5 (1907); (c) M. Betti and G. C. Conestabile, *ibid.*, **46** (I), 200 (1916).

(7) M. Betti, *Trans. Faraday Soc.*, **26**, 337 (1930).

(8) T. M. Lowry, "Optical Rotatory Power," Dover Publications, Inc., New York, N. Y., 1964, p 326.

(9) A. Bertoluzza and A. Marinangeli, *Ann. Chim.* (Rome), **59**, 295 (1969).

(10) N. Ahmed, M. G. Hemphill, and F. E. Ray, *J. Amer. Chem. Soc.*, **56**, 2403 (1934).

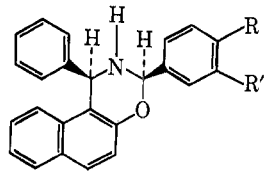
basis, the original condensation product was assigned structure **1**.

Recent quantitative studies of the ring–chain tautomerism of derivatives of *o*-hydroxybenzylamine with aldehydes and ketones[11] suggest that the reactivity of the condensation products of 1-(α-aminobenzyl)-2-naphthol with benzaldehyde and substituted benzaldehydes as well as the unusual differences in the rotatory powers of the optically active derivatives are the result of an equilibrium in solution between tautomers with the naphthoxazine (ring) (**1**) and the corresponding Schiff base (chain) (**2**) structures. The nature of the substituent on the aldehyde moiety would determine the amount of each tautomer present, electron-withdrawing substituents increasing the proportion of ring tautomer.

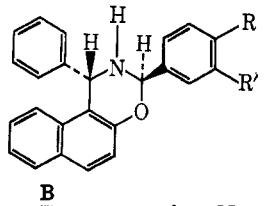
We have now prepared a number of condensation products of racemic 1-(α-aminobenzyl)-2-naphthol with benzaldehyde and substituted benzaldehydes (**3**–**9**) and have examined them spectroscopically in the solid state and as solutions in chloroform and in trifluoroacetic acid (TFA).

Results and Discussion

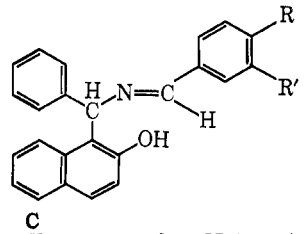
Solid State.—In the solid state, all of these condensation products have the naphthoxazine structure (**A** or **B**). The crystalline substances melt over a range of no more than 1° and do not show ir absorption (KBr disk) for the azomethine moiety. Among the absorption bands are two sharp bands at 1600–1610 and 1620–1630 cm^{-1}, except for **9** which has broad absorption from 1570 to 1630 cm^{-1}. In chloroform, an additional sharp absorption band at 1650–1660 cm^{-1} appears in the spectra of **5**–**8** while the bands at 1600–1610 and 1620–1630 cm^{-1} remain unchanged. This new band is assigned to the azomethine moiety of the Schiff base (chain) tautomer (**C**) in equilibrium with *cis*- and *trans*-naphthoxazine (ring) tautomers (**A** and **B**). A band at 1650–1660 cm^{-1} is not shown by **3** in chloroform since the concentration of the Schiff base tautomer is very small (see below). Both **4** and **9** are too insoluble in chloroform for the band to be observed.



A
D, protonated on N



B
E, protonated on N



C
F, protonated on N (*trans*)

3, R = NO_2; R′ = H
4, R = Cl; R′ = Cl
5, R = Br; R′ = H
6, R = Cl; R′ = H
7, R = H; R′ = H
8, R = $CH(CH_3)_2$; R′ = H
9, R = $N(CH_3)_2$; R′ = H

(11) A. F. McDonagh and H. E. Smith, *J. Org. Chem.*, **33**, 1 (1968).

Although there is no direct evidence for the configuration of the naphthoxazines in the solid state, they all probably have and are assigned the *cis* configuration (**A**).

Chloroform-*d* Solutions.—The nmr spectra (Table I) of the condensation products **3**–**9** in chloroform-*d* show the presence of the *cis*-naphthoxazine tautomer (**A**). In addition, in the spectra of **3** and **6**–**8**, evidence is found for the *trans*-naphthoxazine tautomer (**B**); in those of **6**–**9**, evidence is found for the Schiff base tautomer (**C**).

In each spectrum there is a singlet or a pair of singlets of equal intensity at 5.5–6.6 ppm assigned to the C-1 and C-3 protons of the *cis*-naphthoxazine tautomer (**A**).[12] For **3** and **6**–**8**, which have an appreciable solubility in chloroform-*d*, there is also a broad singlet or a pair of singlets of equal intensity at 5.7–5.9 ppm. These signals are less intense and at a slightly lower field than those assigned to the C-1 and C-3 protons of **A** and are assigned to the C-1 and C-3 protons of the *trans*-naphthoxazine tautomer (**B**). The respective assignments of the C-1 and C-3 proton signals to **A** and to **B** are made on the basis that the naphthoxazine tautomer with the *cis* configuration, for which both phenyl groups have a preferred pseudoequatorial conformation, is the more stable. Integration of the respective signals gives the *cis*/*trans* ratio as about 5 or 6 (Table I). In the spectra of **3**, **6**, and **7**, the amino proton signal is a broad hump centered at 2.3–2.6 ppm.

In the spectra of **6**–**9** in chloroform-*d* there are also two additional signals at 6.4–6.8 and 8.4–8.5 ppm. In each spectrum, these signals have equal integrated intensities and are assigned respectively to the methylidyne and the azomethine proton of the Schiff base tautomer (**C**). This tautomer presumably exists as a single stereoisomer[13] with the *trans* configuration.[14] In none of the spectra was the hydroxyl proton signal observed, and integration of the spectra indicates that it is obscured among the aromatic protons from 6.8 to 8.3 ppm. In the spectrum of **3**, the Schiff base tautomer was not detected and it is estimated that its concentration is less than 10% of that of **3A**. The Schiff base tautomer was also not detected in the nmr spectra of **4** and **5** for two reasons. First, the solubility of each in chloroform-*d* is less than that of **3** and **6**–**8** but about the same as **9**. Second, the amount of Schiff base tautomer, in comparison to the naphthoxazine tautomers, is less than that for **6**–**9**.

As shown in Table I, integration of those spectra in which both the naphthoxazine (ring) and Schiff base (chain) tautomers were detected gives the ratio of the former (*cis* and *trans* together) to the latter. Two factors limit the precision of these measuremens. First, the condensation products generally have a low solubility in chloroform-*d*, and in a variety of other solvents. Second, the relative number of nonaromatic protons is small. Nevertheless the data, of only qualitative significance, given in Table I clearly show that the greater the electron-withdrawing power of the

(12) For **9A**, the C-1 and C-3 proton signals are at an unusually low field. Also, since the ring/chain ratio is about 1, there is an ambiguity concerning the assignment of the respective signals to **9A** and to the methylidyne proton of **9C**.

(13) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, **88**, 2775 (1966).

(14) G. Wettermark, *Ark. Kemi*, **27**, 159 (1967).

TABLE I

NMR DATA AND RING–CHAIN TAUTOMER RATIOS IN CHLOROFORM-*d* FOR DERIVATIVES OF 1-(α-AMINOBENZYL)-2-NAPHTHOL WITH AROMATIC ALDEHYDES

Condensation product	Nmr[a] Naphthoxazines (ring) C-1 and C-3 protons[b] *cis*	*trans*	NH	Schiff base (chain) CH—N	N=CH	Ratios *cis/trans*	Ring/chain	Concn, g/ml, $CDCl_3$
	Chemical shifts assigned, ppm downfield from TMS = 0							
3	5.53, 5.64	5.83	2.58	...[c]	...[c]	6		0.12
4	5.63	...[c]	...[c]	...[c]	...[c]			~0.06
5	5.62	...[c]	...[c]	...[c]	...[c]			~0.06
6	5.60	5.75	2.31	6.40	8.53	5	4	0.12
7	5.57, 5.65	5.77, 5.90	2.52	6.40	8.53	5	3	0.11
8[d]	5.56, 5.65	5.75, 5.90	...[c]	6.37	8.50	5	1	0.26
9[e]	6.35,[f] 6.60[f]	...[c]	...[c]	6.75[f]	8.45		1	~0.06

[a] Singlets measured at 60 MHz and *ca.* 35°. [b] No differentiation between these protons is made or implied. [c] Not detected. [d] For $CH(CH_3)_2$, 1.22 ppm (doublet, J = 6.5 Hz); 2.90 ppm (multiplet, J = 6.5 Hz). [e] For $N(CH_3)_2$, 3.02 ppm (singlet). [f] There is some ambiguity concerning these assignments. See footnote 12.

substituent in the phenyl ring of the aldehyde moiety, the larger is the ring/chain ratio. For a given aldehyde moiety, the percentage of ring tautomer is greater for the 1-(α-aminobenzyl)-2-naphthol derivative than for the derivative of *o*-hydroxybenzylamine.[11] This difference may be related in part to the slightly greater acidity of a 2-naphthol as compared with a phenol.[15]

Trifluoroacetic Acid Solutions.—All of the condensation products **3–9** have an appreciable solubility in TFA. Except for that of **8**, the nmr spectra of these solutions (Table II) show evidence for the *cis*-naphthoxazonium ion (**D**). This ion shows two singlets at 5.7–6.7 ppm of equal intensity which are assigned to the C-1 and C-3 protons. The spectra of **3**, **4**, and **9** shown an additional broad singlet at slightly lower field and of reduced intensity. This is assigned to the respective *trans*-naphthoxazonium ions (**E**). The *cis*/*trans* ratio appears to be about the same for the condensation products in TFA as in chloroform-*d*. This additional signal was not detected in the spectra of **5–7**, and it may be obscured by other signals. In the spectrum of **8** no signal for a naphthoxazonium ion was detected. It is estimated that the concentration of the *cis*-naphthoxazonium ion **8D** is less than 10% of that of the immonium ion **8F**.

TABLE II

NMR DATA AND RING–CHAIN TAUTOMER RATIOS IN TRIFLUOROACETIC ACID FOR DERIVATIVES OF 1-(α-AMINOBENZYL)-2-NAPHTHOL WITH AROMATIC ALDEHYDES

Condensation product	Nmr[a] Naphthoxazonium ions (ring) C-1 and C-3 protons[b] *cis*	*trans*	Immonium ion (chain) N=CH	Ring/chain ratio	Concn, g/ml, TFA
	Chemical shifts assigned, ppm downfield from TMS = 0				
3	6.50, 6.73	6.90	...[c]		0.25
4	6.25, 6.65	6.80	9.05	2	0.26
5	6.23, 6.65	...[c]	9.08	1	0.21
6	6.23, 6.65	...[c]	9.05	0.5	0.26
7	5.70, 6.15	...[c]	8.59[d]	0.3	0.21
8[e]	...[c]	...[c]	8.57[d]		0.25
9[f]	5.95, 6.25	6.40	...[c]		0.24

[a] Singlets, except where noted otherwise, measured at 60 MHz and *ca.* 35°. [b] No differentiation between these protons is made or implied. [c] Not detected. [d] Doublet, J = 17 Hz. [e] For $CH(CH_3)_2$, 1.37 ppm (doublet, J = 6.5 Hz); 3.12 ppm (multiplet, J = 6.5 Hz). [f] For $N^+(CH_3)_2$, 3.53 ppm (singlet).

Also seen in the spectra of **4–8** in TFA is a broad singlet or a doublet at 8.6–9.1 ppm. This is assigned to the azomethine proton of the immonium ion (**F**). In none of the spectra was the hydroxyl or NH^+ proton signal or the methylidyne proton signal detected. The latter is obscured by the aromatic proton signals. When an extremely strong electron-withdrawing group is present on the aldehyde moiety, as in **3** and **9** in TFA, the immonium ion was not detected and its concentration in TFA is less than 10% of that of the naphthoxazonium ions. For **4F–6F**, with strong electron-withdrawing groups, the basicity of the azomethine nitrogen is decreased such that coupling of the azomethine proton with the rapidly exchanging immonium proton is not observed. Without a substituent (**7F**) or with an electron-injecting group (**8F**) the azomethine proton signal appears as a doublet. The coupling constant is 17 Hz and is good evidence that the configuration of the nitrogen to carbon double bond in **4F–8F** is *trans*, as expected.[16]

Table II shows the ring/chain ratio in those solutions in which both naphthoxazonium (ring) and immonium (chain) ions were detected. Again these data are of only qualitative significance. They clearly show, however, that the greater the electron-withdrawing ability of the substituent on the aldehyde moiety, the greater is this ratio. In contrast to the condensation products of *o*-hydroxybenzylamine with benzaldehyde and substituted benzaldehydes in TFA, for which no benzoxazonium ion was detected,[16] the 1-(α-aminobenzyl)-2-naphthol derivatives, except for **8**, have substantial concentrations of the naphthoxazonium ions present in TFA. This difference may also be related to the slightly greater acidity of a 2-naphthol as compared with a phenol.[15]

Experimental Section

Melting points were taken in open capillary tubes and are corrected. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared absorption spectra were obtained with a Beckman Model IR-10 spectrophotometer. Ir spectra of solids were obtained in potassium bromide disks and of chloroform solutions using matched 0.1-mm sodium chloride cells. Nmr spectra were determined at *ca.* 35° with a Varian A-60 spectrometer operating at 60 MHz. In all spectra, tetramethylsilane (TMS) was used as an internal standard, and chemical shifts are reported in parts per million downfield from the standard. Solutions in TFA were prepared by adding the acid (Baker Analyzed Reagent) to a known weight of sample in an

(15) A. Bryson and R. W. Matthews, *Aust. J. Chem.*, **16**, 401 (1963).

(16) A. F. McDonagh and H. E. Smith, *J. Org. Chem.*, **33**, 8 (1968).

nmr tube. The spectra were then run immediately. Tautomer ratios were estimated by integration of the respective spectra.

cis-**1,3-Diphenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (7A).**—As described previously,[2b] 2-naphthol was condensed with ammonia and benzaldehyde in 95% ethanol. After recrystallization from 95% ethanol, **7A** (71%) had mp 144–145°, ir $\nu_{max}^{CHCl_3}$ 1650 cm^{-1} (lit.[2b] mp 148–150°).

1-(α-Aminobenzyl)-2-naphthol.—Using the reported procedure,[2b] **7** was hydrolyzed with 20% hydrochloric acid. After recrystallization from ether–methanol 1-(α-aminobenzyl)-2-naphthol hydrochloride (85%) had mp 196–198° dec (lit.[2b] mp 190–220° dec).

The hydrochloride was decomposed in the usual way.[2b] The free base (98%) had mp 120–122°; nmr 5.68 (broad hump, 2 H, NH_2), 5.87 ppm (singlet, 1 H, methylidyne proton) (lit.[2b] mp 124–125°).

Condensation of 1-(α-Aminobenzyl)-2-naphthol with Aldehydes.—To *ca.* 0.03 mol of the free base in 75 ml of warm 95% ethanol was added a 10% molar excess of the aldehyde in 50 ml of warm 95% ethanol. The mixture was allowed to stand at room temperature overnight. The crystals which separated were collected by filtration and recrystallized to a constant melting point from an appropriate solvent. The reported yield was calculated on the basis of the weight of material with the constant melting point. A sample for elemental analysis was dried overnight at 56° (0.02 mm).

cis-**3-(*p*-Nitrophenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (3A)** resulted: light yellow needles (88%) from 95% ethanol, mp 174–175° (lit.[6b] mp 196° for an optically active isomer).

Anal. Calcd for $C_{24}H_{18}N_2O_3$: C, 75.38; H, 4.74. Found: C, 75.24; H, 5.10.

cis-**3-(3,4-Dichlorophenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (4A)** resulted: microscopic, white needles (48%) from benzene, mp 193°.

Anal. Calcd for $C_{24}H_{17}Cl_2NO$: C, 70.94; H, 4.22. Found: C, 71.34; H, 4.20.

cis-**3-(*p*-Bromophenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (5A)** resulted: microscopic, white needles (68%) from benzene, mp 181–182°, ir $\nu_{max}^{CHCl_3}$ 1650 cm^{-1}.

Anal. Calcd for $C_{24}H_{18}BrNO$; C, 69.24; H, 4.36. Found: C, 69.47; H, 4.50.

cis-**3-(*p*-Chlorophenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (6A)** resulted: microscopic, white needles (64%) from benzene, mp 173°, ir $\nu_{max}^{CHCl_3}$ 1660 cm^{-1} (lit.[6c] mp 158° for an optically active isomer).

Anal. Calcd for $C_{24}H_{18}ClNO$: C, 77.52; H, 4.88. Found: C, 77.49; H, 4.56.

cis-**3-(*p*-Isopropylphenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (8A)** resulted: white needles (57%) from 95% ethanol, mp 134–135°, ir $\nu_{max}^{CHCl_3}$ 1650 cm^{-1} (lit.[6a] mp 155–156° for an optically active isomer).

Anal. Calcd for $C_{27}H_{25}NO$: C, 85.45; H, 6.64. Found: C, 84.96; H, 6.69.

cis-**3-(*p*-Dimethylaminophenyl)-1-phenyl-2,3-dihydro-1H-naphth[1,2-*e*][1,3]oxazine (9A)** resulted: yellow needles (58%) from ethylene chloride, mp 192–193° (lit.[6c] mp 219–220° for an optically active isomer).

Anal. Calcd for $C_{26}H_{24}N_2O$: C, 82.07; H, 6.36. Found: C, 81.57; H, 6.06.

Registry No.—**3A**, 24609-72-1; **3B**, 24609-73-2; **4A**, 24609-74-3; **5A**, 24609-75-4; **6A**, 24609-76-5; **6B**, 24609-77-6; **6C**, 24605-71-8; **7A**, 24609-78-7; **7B**, 24609-79-8; **7C**, 24609-80-1; **8A**, 24609-81-2; **8B**, 24609-82-3; **8C**, 24609-84-5; **9A**, 24609-85-6; **9C**, 24609-86-7.

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Isolation of Primary Decomposition Products of Azides. II. Azidopyrazoles[1]

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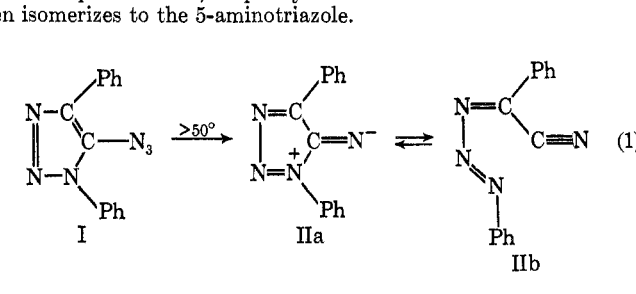
Variously substituted 5-aminopyrazoles have been converted into the azides, which lose nitrogen above room temperature to form red, monomeric products analogous to those from 5-azidotriazoles. The same or isomeric substances are formed by oxidations of 5-aminopyrazoles, along with variable quantities of 5,5′-azopyrazoles. Both are converted back into 5-aminopyrazoles by reducing agents, in some instances through an isolable open-chain β-hydrazono nitrile. The overall behavior of the fragmentation products of 5-azidopyrazoles indicates a β-azoacrylonitrile structure, which may equilibrate with a kinetically significant concentration of a cyclic form. Whereas some of them are identical with the β-azoacrylonitriles obtained by oxidizing the hydrazones of β-ketopropionitriles, many are geometrical isomers, such as the product from 1-phenyl-3-methyl-5-azidopyrazole, which is distinct from the known β-phenylazocrotononitrile, into which it can be converted by acid, and from the "azipyrazole" of Michaelis and Schäfer. The fragmentation product of 1,4-diphenyl-5-azidotriazole can be reduced to 1-phenyl-3-(α-cyanobenzyl)triazene, which then isomerizes to the 5-aminotriazole.

We recently reported[2] the fragmentation of 5-azido-1,4-diphenyltriazole, which loses 1 mol of nitrogen at temperatures above about 50° to form a deep red, monomeric compound (II), whose chemical and physical characteristics suggested a mobile equilibrium in solution between an open-chain and a cyclic structure (eq 1). Most of the reactions of this substance involved further loss of nitrogen, which added complications to the investigation although at the same time giving



(1)

interesting information. In order to reduce such complications and to gain further information about fragmentation products of heterocyclic azides, we have now investigated the analogous pyrazole systems.

(1) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., March 1967. Address correspondence to P. A. S. S.

(2) P. A. S. Smith, L. O. Krbechek, and W. Resemann, *J. Amer. Chem. Soc.*, **86**, 2025 (1964).