and 280 mg. of anhydrous potassium carbonate in 10 ml. of dry acetone was refluxed with stirring for 23 hr. After removal of acetone under reduced pressure, the residue was dissolved in benzene and washed with dilute hydrochloric acid; the aqueous layer was washed with three portions of benzene. The combined benzene solutions were washed with water and saturated salt solution, dried over anhydrous sodium sulfate solution, and concentrated under reduced pressure on the steam bath. The residue (524 mg., 2.8, 5.95, 6.18 and 6.28 μ) was chromatographed on 25 g. of Florisil. Elution with 150 ml. of 20% and 200 ml. of 30% benzene–petroleum ether afforded 66 mg. (10%) of **2**, identical by infrared analysis with material described above.

Elution with 200 ml. of 50% and 150 ml. of 80% benzene–petroleum ether gave 121 mg. (19%) of **6d**, m.p. 115–125°, identical by infrared analysis with authentic sample.

Finally, elution with ethyl acetate gave 146 mg. of phenanthrenequinone.

9-Methoxy-10-(*p*-methylbenzyloxy)phenanthrene (13).—A mixture of 500 mg. of **2** from Florisil chromatography, 250 mg. of methyl iodide, and 220 mg. of anhydrous potassium carbonate in 7 ml. of acetone was refluxed with stirring for 46 hr. After removal of acetone under reduced pressure, the residue was treated with dilute hydrochloric acid which was then extracted with benzene. The benzene layer was washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure on the steam bath. One crystallization of the crude product from methanol gave 460 mg. (88%) of **13**, m.p. 85–89°. Further crystallization from methanol furnished the analytical sample, m.p. 87–89°; λ_{max} (dioxane) 292 mμ (ϵ 10,000), 305 (12,000), 324 (900), 341 (1200), and 358 (1200); 6.15, 6.25, and no absorption at 2.5–3.1 μ (CH_2Cl_2). N.m.r. showed bands at τ 5.97, 6.82, 8.18, and complex absorption at 2–3.

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.75; H, 6.66.

Photoirradiation of 9,10-Dihydroxyphenanthrene Mono(*p*-methylbenzyl) Ether (2).—A solution of 132 mg. of **2** in 21 ml. of benzene was irradiated for 10 hr. at 30° in a nitrogen atmosphere. The yellow solution was then taken to dryness under reduced pressure on the steam bath and the residue chromatographed on 6 g. of Florisil. Eluion with increasing proportions of benzene in petroleum ether to pure benzene afforded a series of amorphous fractions (88-mg. total), which were analyzed from their ultraviolet spectra. The early fractions consisted predominantly of starting material **13** and the later fractions were mainly **6d**; the yields were 36 mg. (28%) of **2** and 43 mg. (33%) of **6d**.

A comparable experiment in which **13** was irradiated for 19 hr. afforded 27% of crystalline **6d**, m.p. 118–126°, identical by infrared analysis with an authentic sample. Only a trace of unreacted **13** could be detected in this experiment.

9-Dioxanyloxy-10-methoxyphenanthrene (16).—A mixture of 2.0 g. of the adduct **1**, 1.0 g. of methyl iodide, and 0.9 g. of anhydrous potassium carbonate in 20 ml. of acetone was refluxed for 26 hr. with stirring. The crude product obtained by work-up similar to that described for the preparation of **11** was chromatographed on 100 g. of Florisil. Elution with 2.5 l. of 50%, 500 ml. of 70%, and 500 ml. of 90% benzene in petroleum ether afforded 1.59 g. (76%) of crystalline **16**, m.p. 78–79°. The analytical sample of **16** was obtained by crystallization from petroleum ether and had m.p. 80–81°; λ_{max} (dioxane) 272 mμ infl. (ϵ 19,000), 281 infl. (12,000), 293 (11,000), 304 (12,000), 326 infl. (500), 341 (850), and 357 (850); 6.15, 6.25, and no absorption at 2.5–3.1 μ (CH_2Cl_2). N.m.r. showed bands at τ 4.42 (broad), 5.86–6.28 (complex), 6.00, and complex absorption 2–3.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.53; H, 5.85. Found: C, 73.64; H, 5.92.

Further elution with pure benzene and ethyl acetate afforded 255 mg. of yellow oil (λ_{max} 2.84, 5.8, and 6.25 μ), which could not be induced to crystallize.

9,10-Dihydroxyphenanthrene Monomethyl Ether (17).—A solution of 794 mg. of **16** in 70 ml. of methanol was treated with 1 ml. of concentrated hydrochloric acid at 50° for 15 min. Work-up as described for the preparation of **13** gave 480 mg. (83%) of crystalline **17**, m.p. 106–107° (lit.[17] m.p. 103°); λ_{max} 255 mμ (ϵ 44,000), 272 infl. (13,000), 298 (7400), 308 (7200), 330 infl. (1100), 346 (1200), and 362 (1100); 2.83, 6.18, 6.28 μ (CH_2Cl_2). N.m.r. showed bands at τ 6.04 and complex absorption 2–3. This compound was considerably more stable than **2** but darkened in color after several months.

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The Separation of Ketimine Isomers[1,2]

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The separation of the geometric isomers of ketimines derived from 2-amino-5-chlorobenzophenone has been achieved by fractional crystallization. Configuration has been assigned by relating ultraviolet absorption spectra of the ketimine isomers with those of the corresponding oximes. The validity of this approach is discussed.

The separation of the geometric isomers of ketimines[3] has been claimed a number of times in the past. A review of these claims appeared in the recent paper of Curtin and Hausser[4] wherein the evidence for the presence of both *syn* and *anti* forms of some benzophenone methylimines was given. However, these authors were able to separate only one form of each imine as a stable solid. We have accomplished the preparation and separation of both forms of a number of substituted benzophenone imines. The orientation of the isomers has been established by comparison of their ultraviolet absorption spectra with those of related oximes of known configuration.[5]

The reaction between a number of *o*-aminobenzophenones and a group of primary amines led in several cases to mixtures of two products. The preparations were carried out by heating the reactants together in the presence of zinc chloride. A solvent such as xylene was used to permit azeotropic removal of the water formed as a by-product. Fractional crystallization of

(1) Presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

(2) A preliminary communication has appeared: S. C. Bell, G. L. Conklin, and S. J. Childress, *J. Am. Chem. Soc.*, **85**, 2868 (1963).

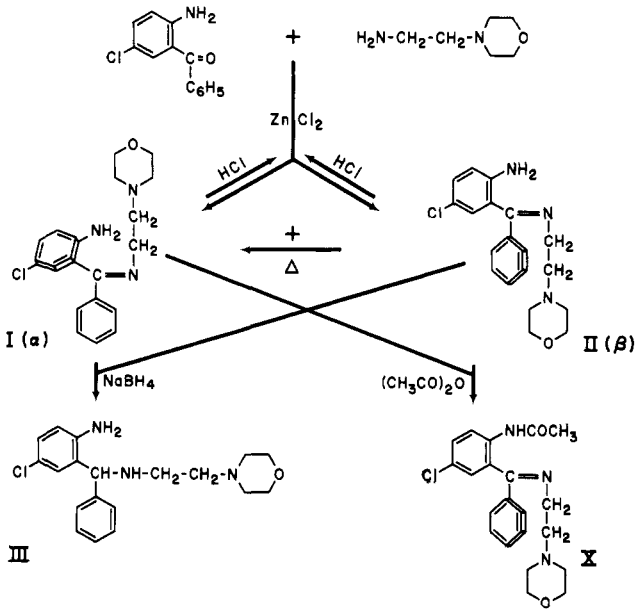
(3) A review on imines has recently been published: R. W. Layer, *Chem. Rev.*, **63**, 489 (1963).

(4) D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3474 (1961).

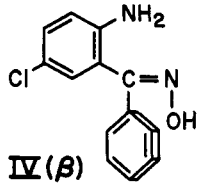
(5) After this work had been completed, a publication appeared by G. Saucy and L. H. Sternbach [*Helv. Chim. Acta*, **45**, 2226 (1962)] that described both forms of 2-methylamino-5-trifluoromethylbenzophenone methylimine. These authors attributed the longer wave-length ultraviolet absorption band of their lower melting isomer to the expanded conjugation system arising from hydrogen bonding between $NHCH_3$ and $C{=}NCH_3$. We prefer the twisted ring explanation given in the present paper since *o*-dimethylaminobenzophenone, without hydrogen bonding, has λ_{max} 385 mμ and *o*-methylaminobenzophenone is only slightly shifted to λ_{max} 392 mμ [P. Grammaticakis, *Bull. soc. chim. France*, 93 (1953)].

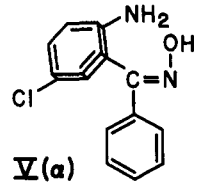
the products resulted in higher melting α-isomers and lower melting β-isomers.

2-Amino-5-chlorobenzophenone and 4-(2-aminoethyl)morpholine, for example, were treated as described. Fractional crystallization from hexane and from alcohol of the residue after evaporation of the solvent gave a less soluble, higher melting α-isomer (I) and a more soluble, lower melting β-isomer (II). Both I and II, upon treatment with aqueous acid, returned the starting materials. Both I and II, upon reduction with sodium borohydride, gave 2-amino-5-chlorobenzhydrylaminoethylmorpholine (III). Heating II without a solvent at 140–150° for 10 min. resulted in the production of I.



The infrared absorption spectra of I and II were consistent with the ketimine structures. Because of the presence of the aromatic rings, no assignment of the C=N absorption could be made. The n.m.r. spectra of I and II were also consistent with the ketimine formulations but did not reveal the geometric orientation of the isomers.





The ultraviolet absorption spectra of I and II were quite different (Fig. 1). That of II was very similar to the absorption spectrum exhibited by the β-oxime of 2-amino-5-chlorobenzophenone (IV) in which the –OH has been shown to be *syn* to the unsubstituted phenyl.[6,7] The absorption spectrum of I was closely aligned with that of the corresponding α-oxime (V). The type of curve obtained with the two sets of isomers may be explained by assuming that, because of intramolecular crowding, the imino substituent causes the aromatic

(6) L. H. Sternbach, S. Kaiser, and E. Reeder, *J. Am. Chem. Soc.*, **82**, 475 (1960).

(7) T. S. Sulkowski and S. J. Childress, *J. Org. Chem.*, **27**, 4424 (1962).

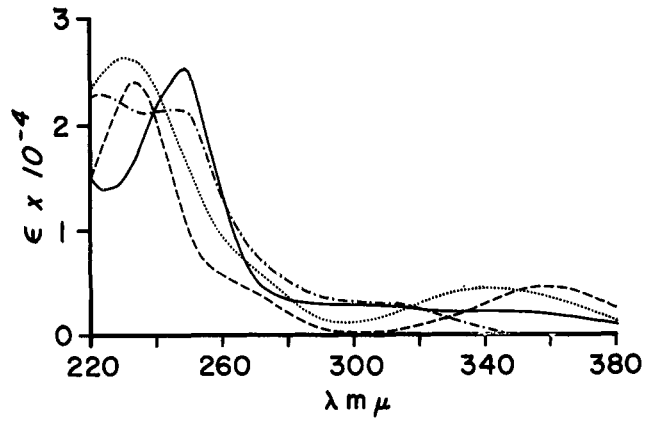
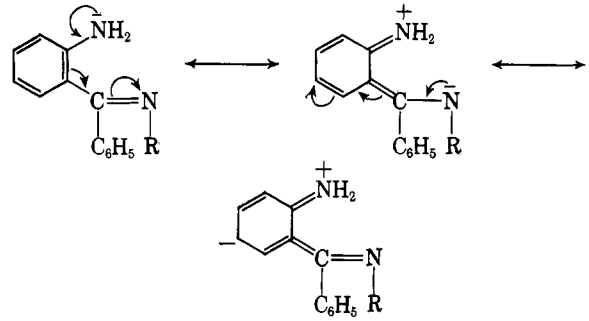
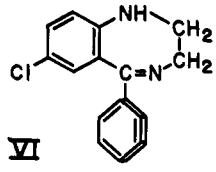


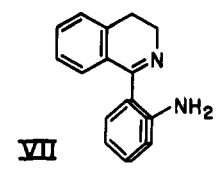
Fig. 1.—Ultraviolet absorption spectra in 95% ethanol: I, ——; II, – – – –; IV, · · · · · ·; V, –·–·–·.

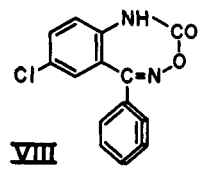
ring of the same side to be twisted out of plane.[8] The remaining chromophores are thus $C_6H_5—\underset{|}{C}=N$ for the two α-isomers (I and V) and $o\text{-}NH_2C_6H_4—\underset{|}{C}=\underset{|}{N}$ for the two β-isomers (II and IV). An extended conjugation system is possible with the latter chromophore that may account for the absorption band above 350 mμ. In agreement with this reasoning, benzophenone oxime and benzophenone morpholinoethylimine, whose chromophore must be $C_6H_5—\underset{|}{C}=N$, have ultraviolet absorption spectra closely resembling those of the α-isomers.



It is of interest to note that 7-chloro-5-phenyl-2,3-dihydro-1*H*-1,4-benzodiazepine (VI),[9] which can be considered as a cyclic imine having its imino substituent *syn* to an amino-substituted phenyl group, had an





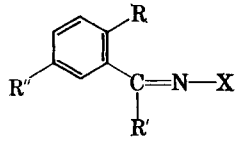


(8) An extensive discussion of this point in regard to benzophenone oximes is given by P. A. S. Smith and E. P. Antoniades, *Tetrahedron*, **9**, 210 (1960).

(9) T. S. Sulkowski and S. J. Childress, *J. Org. Chem.*, **28**, 2150 (1963).

TABLE I

GEOMETRICAL KETIMINE ISOMERS



Compound	Geometrical configuration[a]	R	X	R	R″	Method[b]	Recrystn. solvent	M.p., °C.	λ_{max}^{EtOH}, mμ (ε)	Empirical formula	Analysis, % Caled. C	H	N	Found C	H	N
I	*syn*	NH_2	$CH_2CH_2N(CH_2CH_2)O$	C_6H_5	Cl	C	C_2H_5OH	140–142	248 (25,300)	$C_{19}H_{22}ClN_3O$	66.36	6.45	12.22	66.13	6.29	12.09
II	*anti*	NH_2	$CH_2CH_2N(CH_2CH_2)O$	C_6H_5	Cl	C	C_6H_{12}	112–114	233 (24,000) 362 (4,840)	$C_{19}H_{22}ClN_3O$	66.36	6.45	12.22	66.17	6.50	12.43
XI	*syn*	NH_2	$(CH_2)_3N(CH_2CH_2)O$	C_6H_5	Cl	C	C_6H_{12}–C_2H_5OH	118–119	248 (25,400)	$C_{20}H_{24}ClN_3O$	67.12	6.76	11.74	67.36	6.79	11.85
XII	*anti*	NH_2	$(CH_2)_3N(CH_2CH_2)O$	C_6H_5	Cl	C	C_2H_5OH	91–92	230 (29,700) 359 (5,000)	$C_{20}H_{24}ClN_3O$	67.12	6.76	11.74	67.23	6.76	11.94
XIII	*syn*	$NHCH_3$	$CH_2CH_2N(CH_2CH_2)O$	C_6H_5	Cl	C	C_6H_{14}	123–125	253 (28,400)	$C_{20}H_{24}ClN_3O$	67.12	6.76	11.74	66.84	6.61	11.66
XIV	*anti*	$NHCH_3$	$CH_2CH_2N(CH_2CH_2)O$	C_6H_5	Cl	C	C_6H_{14}	100–102	230 (30,500) 378 (6,000)	$C_{20}H_{24}ClN_3O$	67.12	6.76	11.74	66.96	6.65	11.53
XV	*anti*	NH_2	CH_2CH_2OH	C_6H_5	Cl	A, B	C_6H_6–C_6H_{12}	122–124	233 (24,100) 360 (4,650)	$C_{15}H_{15}ClN_2O$	65.56	5.50	10.20	65.80	5.55	10.40
XVI	*anti*	NH_2	$(CH_2)_3OH$	C_6H_5	Cl	A, B	C_6H_{12}	106–108	234 (25,100) 358 (5,150)	$C_{16}H_{17}ClN_2O$	66.54	5.94	9.70	66.26	5.96	9.66
XVII	*anti*	NH_2	CH_2CH_2OH	*o*-ClC_6H_4	Cl	A	C_6H_{12}	123–125	231 (29,300) 363 (5,140)	$C_{15}H_{14}Cl_2N_2O$	58.27	4.56	9.06	58.54	4.62	9.25
XVIII	*anti*	$NHCOCH_3$	$(CH_2)_3OCOCH_3$	C_6H_5	Cl	D	*i*-C_3H_7OH	118–120	237 (30,500) 330 (3,040)	$C_{20}H_{21}ClN_2O_3$	64.42	5.81	7.52	64.77	5.73	7.79
XIX	*anti*	$NHCOCH_3$	$(CH_2)_2OCOCH_3$	C_6H_5	Cl	D	C_7H_{16}	99–101	237 (30,100) 329 (3,400)	$C_{19}H_{19}ClN_2O_3$	63.59	5.34	7.81	63.73	5.38	7.60
XX	*anti*	$NHCOCH_2Cl$	$(CH_2)_3N(CH_2CH_2)O$	C_6H_5	Cl	D	Aq. C_2H_5OH	107–109	237 (30,100) 323 (3,900)	$C_{22}H_{25}Cl_2N_3O_2$	60.83	5.80	9.67	60.92	5.88	9.44
X	*anti*	$NHCOCH_3$	$(CH_2)_2N(CH_2CH_2)O$	C_6H_5	Cl	D, E	CH_3CN	147–149	236 (29,000) 327 (3,180)	$C_{21}H_{24}ClN_3O_2$	65.36	6.27	10.89	65.34	6.13	10.73
XXI	*anti*	$NHCOCH_3$	CH_2CH_2OH	C_6H_5	Cl	F	CCl_4–C_6H_{12}	143–145	237 (28,000) 326 (2,900)	$C_{17}H_{17}ClN_2O_2$	64.45	5.41	8.84	64.60	5.39	8.92
XXII		H	$CH_2CH_2N(CH_2CH_2)O$	C_6H_5	H	C		180–183 (0.3)[c]	247 (14,200)	$C_{19}H_{22}N_2O$	77.51	7.53	9.52	77.74	7.54	9.23

[a] With respect to the substituted phenyl group. [b] See Experimental section. [c] Boiling point (mm.).

absorption spectrum related to that of II (Fig. 2). This indicated that the imine bond was in resonance with the fused ring and raised the question as to whether the configuration of the noncyclic imines ought to be assigned by relation to the oximes or by relation to cyclic derivatives such as VI. It was established that the usual pattern of curves was being obtained with cyclic compounds by observing the absorption spectrum of 1-*o*-aminophenyl-3,4-dihydroisoquinoline (VII) in which the imino substituent is *syn* to a benzene ring unsubstituted by an amino group. Compound VII had a spectrum corresponding to those of I and V. The more likely choice seemed to be the relation to the oximes, explaining the contrary data from the cyclic imines by assuming that the fusion of the imino substituent to a benzene ring had brought about coplanarity where none would have existed without the ring fusion. Unfortunately, the noncyclic imines we had prepared were not susceptible of direct ring closure. However, 7-chloro-5-phenyl-3,1,4-benzoxadiazepin-2(1*H*)-one (VIII) has been prepared by direct phosgenation of V.[7] The spectrum of VIII has been found to be similar to that of 2-chloroacetamido-5-chlorobenzophenone, β-oxime (IX).[10] Despite having an imine configuration opposite to that of IX, VIII has a similar ultraviolet absorption curve, hence a similar resonating pattern. The formation of the ring in VIII has caused a switch of the aromatic ring in conjugation with the imine bond from the unsubstituted phenyl to the amide-substituted fused ring.

These results tend to confirm the use of the spectra of the oximes as a basis for assigning the configuration of the noncyclic imines.

The acetylation of II produced X and this compound had the expected type of ultraviolet curve. Mild acetylating conditions did not affect I, but more vigorous conditions afforded X. The NH_2 group is more hindered in I than in II, and the more vigorous treatment evidently causes isomerization. It is of interest that the isomerization here is from α to β, whereas heating of II caused the reverse change.

The additional imines that were prepared are listed in Table I. The configurations are assigned by analogy to I and II.

Experimental

2-(2-Amino-5-chloro-α-phenylbenzylideneamino)ethanol (XV). Method A.—A solution of 3.0 g. of 2-amino-5-chlorobenzophenone and 30 ml. of ethanolamine was heated under reflux for 4 hr. After cooling, the reaction mixture was diluted with 60 ml. of water and the solid that separated was recrystallized from aqueous alcohol giving 1.0 g. of pale yellow solid, m.p. 122–124°.

Method B.—A solution of 23.0 g. of 2-amino-5-chlorobenzophenone and 40 ml. of ethanolamine was heated under reflux in 200 ml. of hexanol for 3 hr. in the presence of a small amount of zinc chloride using a Dean–Stark water separator. After the separation of water had stopped, the solvent was removed *in vacuo* and the product was washed with cyclohexane and recrystallized from isopropyl alcohol to afford 9.9 g., m.p. 122–124°.

N-[2-(2-Amino-5-chloro-α-phenylbenzylideneamino)ethyl]morpholine (I and II). Method C.—A solution of 23.1 g. of 2-amino-5-chlorobenzophenone and 45 g. of 4-[2-aminoethyl]morpholine in 100 ml. of xylene and a catalytic amount of zinc chloride was heated for 3 hr. until the theoretical amount of water had been removed azeotropically. The solvent was removed *in vacuo* and the residue was recrystallized from hexane.

(10) L. H. Sternbach and E. Reeder, *J. Org. Chem.*, **26**, 4936 (1961).

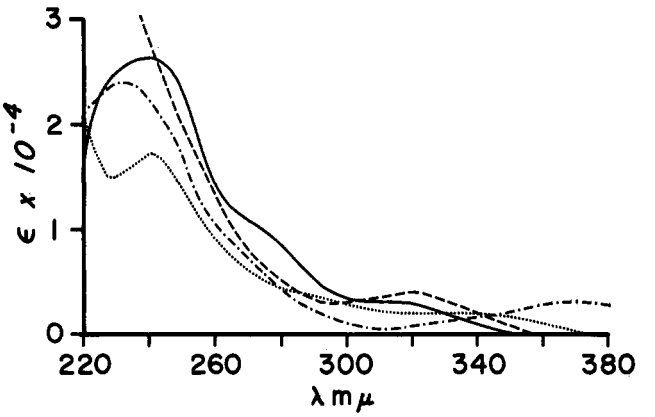


Fig. 2.—Ultraviolet absorption spectra in 95% ethanol: VI, -·-·-·; VII, ·····; VIII, - - - -; IX, ———.

There was obtained 7.8 g. of I, which was recrystallized again from ethanol, to give white plates, m.p. 140–142°.

The filtrate from the first recrystallization was concentrated to a small volume and, upon cooling, there was obtained II, m.p. 105–109°. Compound II was recrystallized from cyclohexane and then from aqueous alcohol to give 2.4 g. of pale yellow crystals, m.p. 112–114°.

Either I or II readily hydrolyzed to the starting products in an acid solution.

In the infrared (KBr), I had peaks at 3.06 and 3.15 μ (NH_2) as well as peaks at 6.08, 6.18, 6.29, and 6.40 μ (possible C=N). Compound II had peaks at 3.03 and 3.17 μ, as well as peaks at 6.23 (vs), 6.28 (sh), 6.34 (sh), and 6.49 μ.

N.m.r. spectra were determined in deuteriochloroform (tetramethylsilane standard) using a Varian A-60 spectrometer.

TABLE II

N.M.R. SPECTRA[a]

Proton	I	II
$-CH_2OCH_2-$	3.67 (m)	3.67 (t, J = 5)
$-CH_2N-CH_2-$ (ring)	2.48 (m)	2.40 (m)
$-CH_2N<$	2.75 (t, J = 7)	2.65 (t, J = 7)
$=NCH_2-$	3.56 (t, J = 7)	3.44 (t, J = 7)
Aromatic and NH_2	6.59–7.80 (m)	6.51–7.59 (m)

[a] Given in δ-values as p.p.m.; J values are in c.p.s.

4-[2-(2-Acetamido-5-chloro-α-phenylbenzylideneamino)ethyl]morpholine (X). Method D.—To a solution of 3.0 g. of II in 30 ml. of pyridine was added 3.0 ml. of acetic anhydride. The solution was allowed to stand for 40 min. After chilling and diluting the reaction mixture with water, the product was extracted with ether and the extracts were washed with water, dried, and evaporated. The residue was induced to crystallize by treating with hexane. Recrystallization from acetonitrile gave 1.5 g. of white crystals of X, m.p. 147–149°.

Method E.—A solution of 13.7 g. of 2-acetamido-5-chlorobenzophenone, 30 ml. of 2-aminoethylmorpholine, 100 ml. of xylene, and a catalytic amount of zinc chloride was heated for 5 hr. until the theoretical amount of water had been removed. The solvent was removed *in vacuo*, and the product was precipitated out with heptane. Recrystallization from acetonitrile afforded 5.9 g. of X, m.p. 147–149°. This was the same as the compound prepared by method D.

4-[2-(2-Amino-5-chlorobenzhydrylamino)ethyl]morpholine (III).—To a suspension of 3.0 g. of I in 75 ml. of alcohol was added with stirring 1.0 g. of sodium borohydride in 25 ml. of water. The reaction mixture was heated at 50–60° for 20 min. After cooling, the reaction mixture was carefully acidified with acetic acid, diluted with 100 ml. of water, made alkaline with sodium hydroxide, and extracted with ether. The product was removed from the ether extract with a dilute acetic acid solution. This solution was made basic with sodium hydroxide and extracted with ether. Evaporation of the ether left 1.7 g. of residue which was taken up in acetonitrile and precipitated out as the trihydrochloride salt, m.p. 178–180°. The compound was insoluble in organic solvents and was purified by triturating with warm alco-

hol. There remained 1.3 g. of white solid (III·3HCl), m.p. 185–187°.

Anal. Calcd. for $C_{19}H_{24}ClN_3O\cdot 3HCl$: C, 50.12; H, 5.98; N, 9.73. Found: C, 49.92; H, 5.86; N, 9.37.

Compound III was also prepared as a dihydrochloride salt, m.p. 199–201°.

Anal. Calcd. for $C_{19}H_{24}ClN_3O\cdot 2HCl$: C, 54.49; H, 6.26; Cl, 25.40; N, 10.03. Found: C, 54.21; H, 6.30; Cl, 25.80; N, 9.84.

Conversion of β-Form into α-Form.—Compound II (β-form) was heated to 140–150° for a few minutes. The melt was cooled and recrystallized from alcohol giving I (α-form), m.p. 140–142°.

2-(2-Acetamido-5-chloro-α-phenylbenzylideneamino)ethanol (XXI). Method F.—Compound XIX, 3.5 g., was dissolved in a solution of 5 ml. of 4 *N* sodium hydroxide and 50 ml. of ethanol. After 5 min. the solution was diluted with water to yield 1.5 g. of XXI.

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Sulfur Heterocycles from the Ring Closure of Bisarylalkyl Disulfides[1,2]

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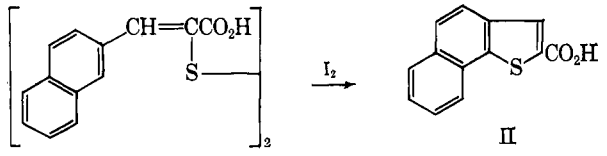
Bis(β-2-naphthylethyl) disulfide (III), bis-β-(3,4-dimethoxyphenyl)ethyl disulfide (VI), and bis(γ-2-naphthylpropyl) disulfide (X) have been synthesized. In the presence of iodine, III undergoes ring closure, giving 2,3-dihydronaphtho[1,2-*b*]thiophene (IV). An excess of iodine converts III or IV into naphtho[1,2-*b*]thiophene (V). On replacing iodine by aluminum bromide, only IV is obtained from III. Both 5,6-dimethoxybenzothiophene (VIII) and 2,3-dihydro-5,6-dimethoxybenzothiophene (VII) are obtained by the action of iodine on VI. Use of the same catalyst leads to the formation of dihydronaphtho[1,2-*b*]thiapyran (XII) from X. The identity of XII has been established by an independent synthesis. Ultraviolet spectral maxima of the products of ring closure are reported.

Disulfides have the ability to function as electrophilic reagents under the influence of acid catalysts. Several instances of their acid-catalyzed addition to olefinic double bonds have been reported[3,4] and a limited number of cases are known in which benzene derivatives undergo substitution reactions with disulfides to give thio ethers.[5,6] Analogous intramolecular interaction between a disulfide sulfur atom and an aromatic moiety in the same molecule leads to the formation of condensed thiophenes.[7,8] To answer the question as to whether or not formation of a thiophene ring, with its accompanying gain in stabilization energy, was a necessary conditions for cyclization, disulfides of the structure $(ArCH_2CH_2S)_2$ were sought in which Ar was the 2-naphthyl or the 3,4-dimethoxyphenyl radical. Results of studies on the cyclization of α,α′-dithiobis-β-arylacrylic acids support earlier evidence[5] of the electrophilic nature of the ring-closure reaction, and these groups are known to be active toward electrophilic attack.



I II

The ring closure of disulfide I proceeded smoothly, giving II in excellent yield using iodine as the catalyst in dioxane at 50° (see Table I).[7] When the same conditions were employed for the cyclization of bis(β-2-naphthylethyl) disulfide (III), the starting material was recovered. Clearly then, unsaturation in the side chain facilitates the cyclization. Boron trifluoride in benzene also failed to bring about the ring closure of III. However, when the reaction was conducted in refluxing ethylene glycol, using an equimolar quantity of iodine, although more than half of the disulfide remained unchanged, an oil was obtained in 32% yield which was identified as 2,3-dihydronaphthol[1,2-*b*]thiophene (IV).[9] No IV was detected after refluxing III for 12 hr. in ethylene glycol alone.

The same product (IV) was formed when III was treated with aluminum bromide in benzene. Oxidation of IV with hydrogen peroxide gave 2,3-dihydronaphtho[1,2-*b*]thiophene 1,1-dioxide.[10] The ultraviolet spectral maxima of IV are recorded in Table II. A by-product of the reaction employing aluminum bromide was found to be β-2-naphthylethanethiol which, if it were formed also during the cyclization reaction with iodine as the catalyst, would immediately be oxidized to disulfide, thereby increasing the yield of IV.

With excess iodine, III was converted to naphtho[1,2-*b*]thiophene (V) in 60% yield and no disulfide was recovered. V was identified by oxidation to the corresponding sulfone[9] and comparison of the compound and its derivatives with authentic samples. Evidently, initially formed IV was dehydrogenated by iodine to give V, since a sample of IV, treated under similar conditions with an excess of iodine, was converted wholly to V.

Employing iodine in dioxane at 60°, a large proportion of bis-β-(3,4-dimethoxyphenyl)ethyl disulfide (VI) was recovered and less than 5% of an impure product, m.p. 65–75°, was isolated. Here again, the effect of

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(2) A preliminary communication of a portion of this work: E. Campaigne and B. G. Heaton, *Chem. Ind.* (London), 96 (1962).

(3) B. Holmberg, *Arkiv Kemi Mineral. Geol.*, **13B**, 6 (1939); *Chem. Abstr.*, **34**, 2341 (1940).

(4) D. McCaulay and A. P. Lien, U. S. Patent 2,519,586 (Aug. 22, 1950); *Chem. Abstr.*, **44**, 10,728 (1950).

(5) S. Archer and C. M. Suter, *J. Am. Chem. Soc.*, **74**, 4296 (1952).

(6) H. Behringer and K. Kuchinka, *Angew. Chem.*, **72**, 348 (1960).

(7) E. Campaigne and R. E. Cline, *J. Org. Chem.*, **21**, 39 (1956).

(8) E. Campaigne and W. E. Kreighbaum, *ibid.*, **26**, 1326 (1961).

(9) J. E. Banfield, *et al.*, *J. Chem. Soc.*, 2603 (1956).

(10) W. Davies and Q. N. Porter, *ibid.*, 2609 (1956).