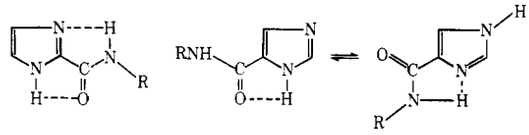
References and Notes

(1) (a) R. A. Henry and W. M. Dehn, *J. Am. Chem. Soc.*, **71**, 2297 (1949); (b) K. Schlögl and H. Woidich, *Monatsh. Chem.*, **87**, 679 (1956); (c) H. A. Staab and W. Benz, *Justus Liebigs Ann. Chem.*, **648**, 72 (1961).
(2) R. Gompper, E. Hoyer, and H. Herlinger, *Chem. Ber.*, **92**, 550 (1959).
(3) (a) M. R. Grimmett, *Adv. Heterocycl. Chem.*, **12**, 179 (1970); (b) E. Regel and K. H. Buechel, German Patent 1 926 206, 1 956 711; *Chem. Abstr.*, **74**, 31754 f (1971), **75**, 49086 v (1971); (c) C. G. Begg, M. R. Grimmett, and Lee Yu-Man, *Aust. J. Chem.*, **26**, 415 (1973).
(4) R. G. Farguer and F. L. Pyman, *J. Chem. Soc.*, **115**, 217 (1919).
(5) J. Derkosch, K. Schlögl, and H. Woidich, *Monatsh. Chem.*, **88**, 35 (1957).
(6) R. G. Jones, *J. Am. Chem. Soc.*, **71**, 383 (1949).
(7) An analogous competition has been noted for Mannich reactions of imidazoles, which lead only to N-substitution, when run in acidic medium, but to both N- (reversibly) and C-substitution (irreversibly) in basic medium. However, with imidazole itself N-substitution still predominates after 24 h, in that case, and the relative reactivity of the heterocyclic ring positions is in the order 1 > 4,5 > 2 [F. B. Stocker, J. L. Kurtz, B. L. Gilman, and D. A. Forsyth, *J. Org. Chem.*, **35**, 883 (1970)]. The greater reactivity of position 2 in the present case may be related with the possible stabilization of the 2-carboxanilide by two intramolecular hydrogen bonds simultaneously, whereas only one such bond is possible for the 4(5) product.



(8) W. Otting and H. A. Staab, *Justus Liebigs Ann. Chem.*, **622**, 23 (1959).
(9) A. A. Zalikin, L. P. Nikitenkova, and Yu. A. Strepikheev, *J. Gen. Chem. USSR (Engl. Transl.)*, **41**, 1940 (1971).
(10) It is noteworthy that reaction of 1-methylimidazole with acid chlorides, in the presence of triethylamine, also results in acylation at the 2 position (ref 3b,c). Similarly, treatment of 1-methylimidazole with formaldehyde, at 160–170 °C, yields the 2-carbinol as product [P. C. Jocelyn, *J. Chem. Soc.*, 3305 (1957)].
(11) Cf. chemical shifts of methyl protons in 2-bromo-1-methylimidazole (δ 3.64) and 5-bromo-1-methylimidazole (δ 3.63) [G. B. Barlin and T. J. Batterham, *J. Chem. Soc. B*, 516 (1967)].
(12) Cf. chemical shifts of methyl protons in 1-methyl-4-nitroimidazole (δ 3.90) and 1-methyl-5-nitroimidazole (δ 4.05) (ref 11).
(13) Cf. chemical shifts of 1-methyl protons in 1-methylimidazole (δ 3.70) and 1,2-dimethylimidazole (δ 3.52) [(a) ref 11; (b) M. R. Grimmet, *Adv. Heterocycl. Chem.*, **12**, 148 (1970)].
(14) A reviewer pointed out the fact that 1,2-dimethylimidazole has been used effectively to catalyze di- and trimerization of isocyanates [R. Richter and H. Ulrich, *Synthesis*, 463 (1975)].
(15) E. P. Papadopoulos and H. S. Habiby, *J. Org. Chem.*, **31**, 327 (1966).
(16) E. P. Papadopoulos and S. B. Bedrosian, *J. Org. Chem.*, **33**, 4551 (1968).
(17) Melting points were determined in capillaries using a Thomas-Hoover UniMelt apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer using mineral oil mulls, unless otherwise indicated. NMR spectra were obtained on a Varian EM 360 spectrometer using solutions in hexadeuteriodimethyl sulfoxide (unless otherwise specified) and tetramethylsilane as internal standard. Identification of known compounds was accomplished by comparison of IR and NMR spectra, as well as determination of mixture melting points using authentic samples.
(18) In some cases, trimerization of the isocyanate was observed when it was added to the solution of 1-methylimidazole, but not when the order of addition was reversed.
(19) In the case of **1j**, the reaction mixture was fractionally distilled under reduced pressure to yield the product.

Photochemistry of 2,1-Benzisoxazolium (Anthranilium) Salts

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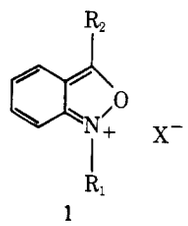
Photolysis of *N*-alkyl-2,1-benzisoxazolium perchlorates in aqueous solution results in the formation of 3-acyl- or 3-formyl-*p*-*N*-alkylaminophenols in excellent yields. Photolysis in methanol gives 3-acyl- or 3-formyl-*p*-*N*-alkylanisidines. Addition of inorganic salts to the aqueous solution leads to the introduction of the salt anion into the aromatic ring, giving 5-substituted 2-*N*-alkylaminobenzaldehydes, -acetophenones, or -benzophenones. However, photolysis of *N*-adamantyl-2,1-benzisoxazolium salts in aprotic solvents results in a ring expansion of the adamantyl moiety, yielding perhaps the first example of a stable 3-azahomoadamantyl carbenium ion.

Recent emphasis on the photochemistry of nitrogen heterocycles has prompted us to report our results on the photochemistry of N-alkylated, 2,1-benzisoxazolium salts (1).[1]

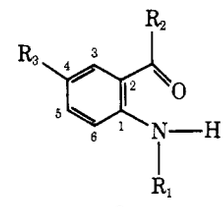


1

R_1 = Me, Et, *t*-Bu, 1-adamantyl
R_2 = H, Me, phenyl
X^- = ClO_4, FSO_3

While exploring the chemical reactivity of *N*-alkyl-3-methyl-2,1-benzisoxazolium perchlorates, we noticed that the salts acquired a dark-yellow to magenta color upon standing a few hours under normal fluorescent room light. The rate of color development as well as the hue was dependent upon both the N- and 3-substituents.[2] Since the photoreaction rate appeared to be rapid, we decided to investigate the solution photochemistry of **1** and determine the structure of the corresponding photoproducts.

Ultraviolet irradiation of an aqueous solution of **1a** (see Table I) with a 450-W Hanovia mercury lamp through a Pyrex filter quickly results in the rapid formation of a deep-yellow solution which upon basic workup yielded 82% of **2a** (see Table II). Similarly, irradiation in the presence of inorganic salts yielded photoproducts containing the inorganic anion substituted into the benzene ring of **2** instead of a hydroxyl group. Thus the addition of NaCl, NaBr, or KSCN to aqueous solutions of **1** results in the rapid formation of 4-substituted 2-acylanilines **2** (R_3 = Cl, Br, or SCN) as the major photoproducts.[3] Photolysis of **1** in methanol leads to the introduction

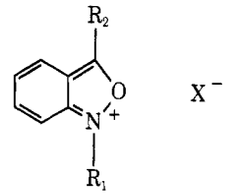


+ 10% ortho isomer

2

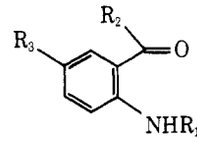
R_3 = Cl, Br, SCN, OH, OR

Table I



Registry no.	Compd	R_1	R_2	X	% yield	Mp, °C	$\lambda_{max}^{H_2O}$ (ln)
63609-41-6	1a	CH_3	CH_3	ClO_4	89	152–153	335 (3.54)
63609-42-7	b	CH_3	C_6H_5	FSO_3	87	170 dec	372 (4.04)
63609-44-9	c	CH_3CH_2	CH_3	FSO_3	56	122 dec	
31562-01-3	d	$(CH_3)_3C$	H	ClO_4	65	149 dec	278 (3.22)
63609-46-1	e	$(CH_3)_3C$	CH_3	ClO_4	70	183 dec	335 (3.72)
63609-47-2	f	$(CH_3)_3C$	C_6H_5	ClO_4	61	153 dec	373 (4.11)
63609-49-4	g	1-Adamantyl	H	ClO_4	88	195 dec	335 (3.74)
63609-51-8	h	1-Adamantyl	C_6H_5	ClO_4	70	190 dec	375 (4.19)

Table II



Compd[a]	R_1	R_2	R_3	% yield	(Para/ortho)[b]	Mp[c]	Photolysis solvent[d]	Registry no.
2a	CH_3	CH_3	HO	82		136.0	H_2O	63609-52-9
2b	CH_3	CH_3	Cl	74		52.1	H_2O + NaCl	62903-71-3
2c	CH_3	CH_3	CH_3O	100	(84/16)	66.0	CH_3OH	63609-53-0
2d	CH_3	CH_3	SCN	72		136.0	H_2O + KSCN	63609-54-1
2e	CH_3	CH_3	Br	70		66.3	H_2O + NaS	40166-68-5
2f	CH_3	C_6H_5	HO	74	(87/13)	161.4	H_2O	63609-55-2
2g	CH_3	C_6H_5	CH_3O	87	(89/11)	69.8	CH_3OH	63609-56-3
2h	CH_3CH_2	CH_3	HO	80		125.0	H_2O	63609-57-4
2i	CH_3CH_2	CH_3	CH_3O	68	(83/17)	64.2	CH_3OH	63609-58-5
2j	$(CH_3)_3C$	H	HO	78		86.3	H_2O	63609-59-6
2k	$(CH_3)_3C$	H	CH_3O	75	(88/12)	62.4	CH_3OH	63609-60-9
2l	$(CH_3)_3C$	C_6H_5	CH_3O	69	(87/13)	61.5	CH_3OH	63609-61-0
2m	$(CH_3)_3C$	CH_3	HO	63		98.0	H_2O	63609-62-1
2n	1-Adamantyl	H	CH_3O	93		153.0	CH_3OH	63609-63-2
2o	1-Adamantyl	C_6H_5	CH_3O	81		102.8	CH_3OH	63609-64-3

[a] Satisfactory elemental analyses obtained for all compounds (±0.4%). [b] Para:ortho ratio determined from NMR integrations. [c] Melting point of para isomer. [d] Twenty grams of inorganic salt was added to the aqueous solution (200 mL).

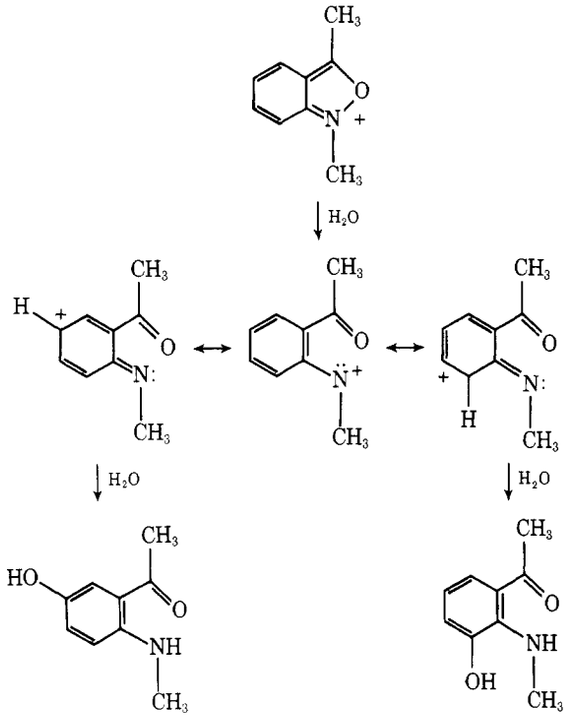
of a methoxy group para to the nitrogen atom yielding 4-alkoxyl-2-acylanilines (**2**, R_3 = OR).[5] The characterization of structure **2** rests on spectral and combustion analysis. The IR spectrum of **2** clearly shows the presence of an aryl ketone (aldehyde) and secondary amino groups. The NMR spectra of some of the crude photolysates indicated that the major product was **2**, with 10–15% impurity also present. We suspect this impurity is the ortho isomer (R_3 in position 6) based on its NMR spectrum. Recrystallization of crude **2** gave pure para isomer; however, we were not able to obtain a pure sample of the suspected ortho isomer free from the para isomer. The mass spectrum, however, was also consistent with the ortho isomer (same M^+ and similar fragmentation pattern). Tables I and II illustrate the wide variety of 2,1-benzisoxazolium salts investigated and the corresponding photoproducts obtained along with their yields.

A simple explanation for the formation of the observed photoproducts is first a heterolytic cleavage of the N–O bond of **1** in the excited state, giving rise to an intermediate arylazonium ion. This ion then undergoes a nucleophilic attack by either solvent or added salt anion at the position para (favored) or ortho to the nitrogen atom. The reaction path is illustrated in detail in Scheme I for 1,3-dimethyl-2,1-benzisoxazolium perchlorate.

This mechanism is supported by the observation by Doppler and co-workers that irradiation of 3-methyl-2,1-benzisoxazole in 98% sulfuric acid gives 2-acetyl-4-hydroxyaniline as the major photoproduct via an azonium ion.[6] In strongly acidic solution, the 3-methyl-2,1-benzisoxazole is protonated completely and thus the protonated material behaves similarly to an N-alkylated benzisoxazolium salt. A comparison of the ultraviolet spectra of 3-methyl-2,1-benzisoxazole in sulfuric acid and 1,3-dimethyl-2,1-benzisoxazolium perchlorate in water confirms their similarity. When the photolysis is monitored by ultraviolet spectroscopy, the conversion of **1a** to **2a** appears to be direct (isosbestic points at 363, 298, and 266 nm) without any absorption due to the proposed intermediate arylazonium ion. This apparent lack of absorption of intermediates might be due to an extremely fast reaction of the arylazonium ion with solvent.

Evidence for an azonium ion intermediate was obtained from the investigation of the photochemistry of the *N*-adamantyl-substituted benzisoxazolium salts **1g** and **1h**. On photolysis in methanol solution and basic workup, **1h** yields

Scheme I



two products in a ratio of 9:1. The major product was the expected 2-*N*-adamantylamino-5-methoxybenzophenone (**2o**); however, the minor product was shown by analysis to be a reduced derivative of **1h** having an empirical formula of $C_{23}H_{25}NO_2$. We assign structure **5** (Scheme II) to this material on the basis of the following physical data. The yellow compound exhibited two carbonyl absorptions in the IR spectrum at 1710 and 1620 cm^{-1}. Its NMR spectrum shows characteristically a two-proton doublet of doublets ($NHCH_2CH$) which collapses to a single doublet when treated with D_2O. These data along with the mass spectra and microanalytical results are consistent for structure **5**. When the photolysis was repeated in acetonitrile rather than methanol as solvent, a magenta colored isomer of **1h** was produced in quantitative yield. The magenta compound is produced directly from **1h** (isosbestic points at 422, 337, and 274 nm). The NMR spectrum of the isolated magenta isomer indicated a loss of symmetry of the adamantane skeleton with two of the adamantane protons considerably deshielded relative to the others and spin coupled to only one other proton (Figure 1). However, the magenta isomer exhibited an IR spectrum quite similar to that of **1h**. Upon hydrolysis of the magenta isomer, a yellow compound was obtained which was identical with the minor component isolated from the photolysis of **1h** in methanol. These data along with the mass spectra and microanalytical results are consistent with structures **4a**, **4b**, or **4c**, proposed for the magenta colored compound.

The formation of **4** probably occurs from the arylazonium ion as depicted in Scheme II via a ring expansion of the *N*-adamantyl group reminiscent of the known carbonium ion reactions of adamantylcarbinyl systems which form 3-homoadamantyl derivatives.[7] Compound **4** can be considered as an azahomoadamantane carbenium ion **4b**, and, as it might be expected, an adjacent nitrogen atom with its lone pair of electrons would stabilize such a homoadamantyl carbenium ion via resonance with a 3-azahomoadamantene structure such as **4a**. Since 3-homoadamantene has been predicted to be a highly strained species comparable to a trans cycloheptene, we also considered **4c** as a possible alternative structure.[8,14]

In order to differentiate between the azahomoadamantane carbenium ion **4b** and the benzoxazine **4c**, the magenta compound **4** was subjected to catalytic hydrogenation followed by acid hydrolysis. By our reasoning (Scheme III) we expected the bicyclo[3.3.1]nonan-3-one **7** from the reduction–hydrolysis of **4c** via the hemiaminal **6**. However, the reduction product **8** from **4a** or **4b** would be inert toward hydrolysis and no ketonic products would be observed. Upon completion of the above experiment (reduction and hydrolysis of **4**), only a single product was obtained which did not exhibit any carbonyl absorption in the IR spectrum. The mass spectrum, NMR, and combustion analysis of this product (see Experimental Section) are consistent only for structure **8** and not **7**. This coupled with the fact that 2 equiv of hydrogen was absorbed during the reduction (**4c** to **6** would require only 1 equiv of hydrogen) leads us to conclude that structure **4c** is not viable and the magenta compound is the first stable homoadamantane carbenium ion or perhaps a 3-homoadamantene **4a**.[9] Work is currently in progress trying to synthesize **4a** by a thermal route.[10]

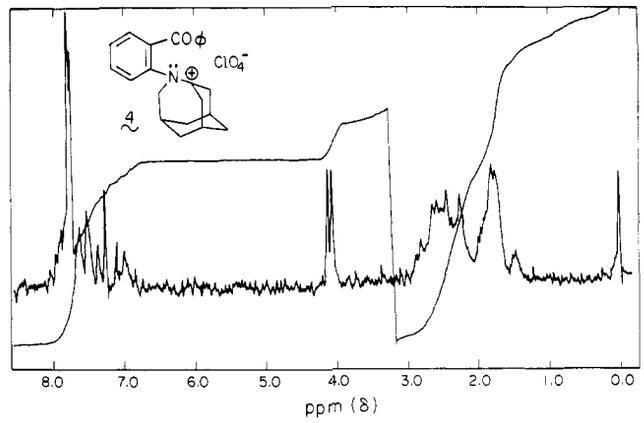


Figure 1. 60-Hz ^1H NMR spectrum of **4**.

Experimental Section[12]

***N*-Alkyl-2,1-benzisoxazolium Salts.** The following two procedures are typical. **(a) 1,3-Dimethyl-2,1-benzisoxazolium Perchlorate (1, $R_1 = R_2 = CH_3$, X = ClO_4).** To a solution of 3-methyl-2,1-benzisoxazole (13.3 g) in diethyl ether (100 mL) was added methyl fluorosulfonate (12.0 g) in one portion. The reaction mixture was stirred for 1 h at room temperature. The precipitated white solid was collected, washed with diethyl ether, and then dissolved in a minimum amount of water. To this aqueous solution was added sodium perchlorate monohydrate (15.0 g) dissolved in water (20 mL). A white crystalline solid precipitated immediately and was collected and washed with cold water. Recrystallization from hot water gave 21.9 g (89%) of 1,3-dimethyl-2,1-benzisoxazolium perchlorate, mp 152–153 °C (explodes at 154 °C): NMR (CD_3CN) δ 7.8 (m, 4 H), 4.4 (s, 3 H), 3.0 (s, 3 H); IR (KBr) 1630, 1500, 1420, 1090, 755 cm^{-1}; UV (H_2O) 335 (3.54), 201 (4.40) nm (log ε).

Anal. Calcd for $C_9H_{10}ClNO_5$: C, 43.7; H, 4.1; N, 5.7. Found: C, 44.1; H, 4.0; N, 5.9.

(b) *N*-*tert*-Butyl-3-methyl-2,1-benzisoxazolium Perchlorate (1e). Nitromethane (20 mL) containing 3-methyl-2,1-benzisoxazole (13 g), *tert*-butyl alcohol (8 g) and 70% perchloric acid (16 g) was stirred at room temperature for 48 h. To the solution was added diethyl ether (200 mL), and the precipitated white solid was collected and washed with diethyl ether. Recrystallization from methanol gave *N*-*tert*-butyl-3-methyl-2,1-benzisoxazolium perchlorate (20 g): mp 183 °C dec; NMR (CD_3CN) δ 8.0 (m, 3 H), 7.4 (m, 1 H), 3.0 (s, 3 H), 1.9 (s, 9 H); IR (KBr) 1625, 1450, 1090, 760 cm^{-1}; UV (H_2O) 335 (3.72), 268 (3.68), 205 (4.43) nm (log ε).

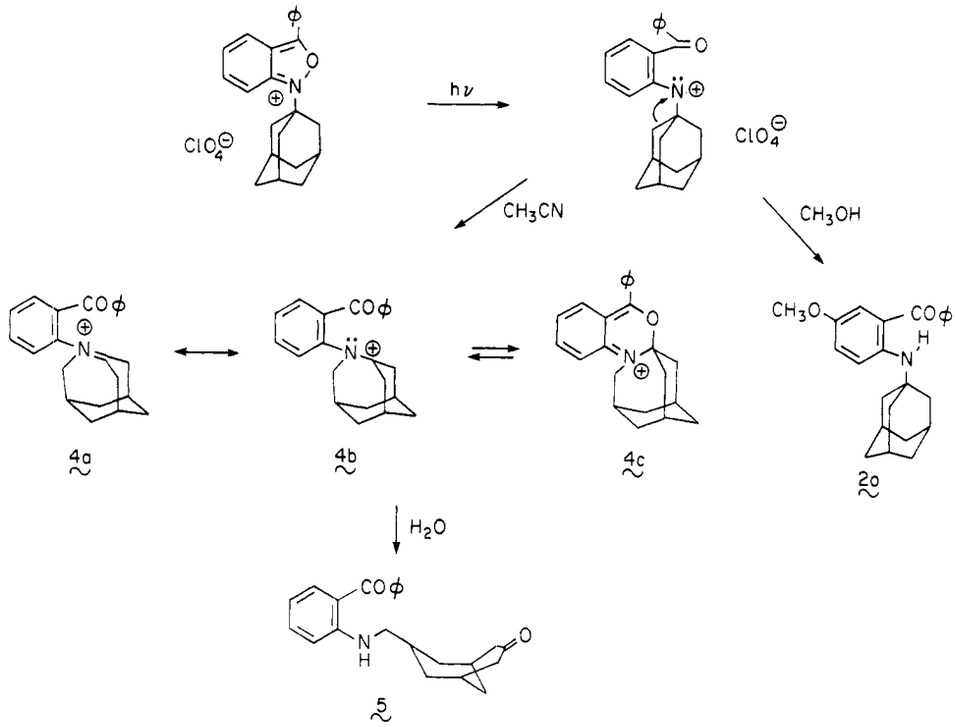
Anal. Calcd for $C_{12}H_{16}ClNO_5$; C, 49.7; H, 5.6; N, 4.8. Found: C. 49.4; H, 5.6; N, 5.1.

***N*-Methyl-3-phenyl-2,1-benzisoxazolium Fluorosulfonate (1b):** 87%; mp 170 °C dec; NMR (CD_3CN) δ 8.0 (m, 9 H), 4.5 (s, 3 H); UV (H_2O) 372 (4.04), 297 (3.65), 245 (3.70), 202 (4.40) nm (log ε).

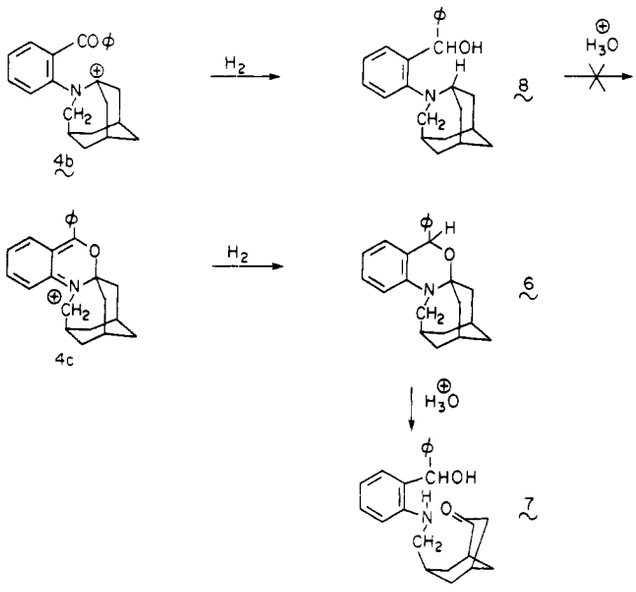
Anal. Calcd for $C_{14}H_{12}FNO_4S$: C, 54.4; H, 3.9; N, 4.5. Found: C, 54.6; H, 3.8; N, 4.4.

***N*-Ethyl-3-methyl-2,1-benzisoxazolium Fluorosulfonate (1c):** 56%; mp 122–3 °C dec; NMR (CD_3CN) δ 7.8 (m, 4 H), 4.8 (q, J = 7 Hz,

Scheme II



Scheme III



2 H), 3.0 (s, 3 H), 1.5 (t, J = 7 Hz, 3 H).

Anal. Calcd for $C_{10}H_{12}FNO_4S$: C, 46.0; H, 4.6; N, 5.4. Found: C, 45.8; H, 4.4; N, 5.2.

***N*-*tert*-Butyl-2,1-benzisoxazolium Perchlorate (1d):**[4] mp 149 °C dec; UV (H_2O) 278 (3.22), 242 (3.79), 210 (4.30) nm (log ϵ).

***N*-*tert*-Butyl-3-phenyl-2,1-benzisoxazolium Perchlorate (1f):** 61%; mp 153 °C dec; NMR (CD_3CN) δ 8.0 (m, 9 H), 1.9 (s, 9 H): UV (H_2O) 373 (4.11), 295 (3.85), 248 (3.90), 203 (4.41) nm (log ϵ).

Anal. Calcd for $C_{17}H_{18}ClNO_5$: C, 58.0; H, 5.2; N, 4.0. Found: C, 58.2; H, 5.2; N, 4.1.

***N*-Adamantyl-2,1-benzisoxazolium Perchlorate (1g):**[11] 88%; mp 195 °C dec; UV (CH_2Cl_2) 335 (3.74), 282 (3.52), 273 (3.63) nm (log ϵ).

***N*-Adamantyl-3-phenyl-2,1-benzisoxazolium Perchlorate (1h):** 70%; mp 190 °C dec; NMR (CD_3CN) δ 7.8 (m, 5 H), 7.4 (m, 4 H), 2.5 (m, 6 H), 2.3 (m, 3 H), 1.8 (m, 6 H); UV (CH_3CN) 375 (4.19), 295 (3.87) nm (log ϵ).

Anal. Calcd for $C_{23}H_{24}ClNO_5$: C, 64.3; H, 5.6; N, 3.3. Found: C, 64.1; H, 5.4; N, 3.2.

Photolysis of 2,1-Benzisoxazolium Salts. Typical Procedure. 5-Hydroxy-2-methylaminoacetophenone (2a). A solution of 1,3-dimethyl-2,1-benzisoxazolium perchlorate or fluorosulfonate (2.0 g) in water (200 mL) was irradiated through a Pyrex filter with a 450-W Hanovia mercury lamp for 15 min at room temperature. The solution was continuously purged with nitrogen gas during the irradiation. The photolysis solution was then neutralized by the addition of saturated sodium bicarbonate solution (20 mL), followed by extraction with diethyl ether (2 × 100 mL). The organic phase was separated and dried over anhydrous potassium carbonate. Evaporation of the solvent under vacuum followed by recrystallization from carbon tetrachloride gave 1.1 g (82%) of 5-hydroxy-2-methylaminoacetophenone: mp 137 °C; IR (KBr) 3300, 3220, 1640, 1600, 1580, 1530, 1240, 1220, 960, 915, 850, 820 cm^{-1}; NMR ($CDCl_3$) δ 8.0 (s, 1 H), 7.0 (d, 1 H), 6.8 (d of d, 1 H), 6.4 (d, 1 H), 2.8 (s, 3 H); UV (CH_3CN) 410 (3.74), 258 (3.76) nm (log ϵ).

Anal. Calcd for $C_9H_{10}NO_2$: C, 65.4; H, 6.7; N, 8.5. Found: C, 65.1; H, 6.6; N, 8.3.

Photolysis of *N*-Adamantyl-3-phenyl-2,1-benzisoxazolium Perchlorate in Acetonitrile. A solution of N-adamantyl-3-phenyl-2,1-benzisoxazolium perchlorate (2.0 g) in dry acetonitrile (300 mL) was irradiated through a Pyrex filter with 3560 Å Rayonette ultraviolet lamps for 3 h. Upon evaporation of the solvent under vacuum, a magenta colored salt was obtained (2.0 g) which was recrystallized from a mixture of methylene chloride–diethyl ether (1:1) yielding 1.9 g: mp 225 °C dec; IR (KBr) 2850, 1620, 1530, 1485, 1085, 785, 750, 715, 690 cm^{-1}; NMR (CD_2Cl_2) δ 8.0–6.9 (m, 9 H), 4.1 (d, J = 5 Hz, 2 H), 2.8–1.6 (m, 13 H); UV–vis (CH_3CN) 518 (3.77), 323 (4.15), 290 (3.84), 242 (4.20) nm (log ϵ).

Anal. Calcd for $C_{23}H_{24}ClNO_5$: C, 64.3; H, 5.6; N, 3.3; Cl, 8.2. Found: C, 64.1; H, 5.6; N, 3.2; Cl, 8.6.

Hydrolysis of Photoproduct from *N*-Adamantyl-3-phenyl-2,1-benzisoxazolium Perchlorate (4 to 5). The solution of **4** (430 mg) in methylene chloride (75 mL) was shaken with saturated sodium bicarbonate solution (25 mL) for 5 min. When the magenta color had faded to yellow, the methylene chloride layer was separated, dried (K_2CO_3), and evaporated under vacuum to yield a yellow oil (0.3 g) which refused to crystallize but was pure as determined by TLC (silica gel–chloroform): IR (liquid film) 3300, 2875, 1710, 1630, 1580, 1510, 1250, 940, 920, 750, 700 cm^{-1}; NMR ($CDCl_3$) δ 9.2 (broad singlet which disappears with D_2O, 1 H), 7.9 (m, 5 H), 7.0 (m, 4 H), 3.2 (d of d which collapses to single doublet with D_2O, J = 6 Hz, 2 H), 2.8–0.9 (m, 13 H); MS M^+ 347; UV–vis (CH_3CN) 395 (3.82) nm (log ϵ).

Anal. Calcd for $C_{23}H_{25}NO_2$: C, 79.5; H, 7.25; N, 4.0. Found: C, 79.3; H, 7.2; N, 3.8.

Reduction of Photoproduct from *N*-Adamantyl-3-phenyl-2,1-benzisoxazolium Perchlorate (4 to 8). To a well-stirred sus-

pension of prereduced platinum oxide under hydrogen gas at 1 atm pressure is injected the magenta-colored photoproduct (430 mg) dissolved in methylene chloride (50 mL). The hydrogen uptake at room temperature ceases after approximately 2 h with 2.0 equiv of gas being consumed. The catalyst was separated and the filtrate was washed repeatedly (3×) with sodium bicarbonate solution. The organic layer was separated, dried (K_2CO_3), and evaporated under vacuum. The residue was recrystallized from pentane yielding 280 mg (85%) of 8 as a slightly yellow crystalline solid: mp 145–146 °C; IR (KBr) 3400, 3000, 2850, 1600, 1490, 1440, 1320, 1080, 760, 735, 720, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (m, 5 H), 7.2–6.4 (m, 4 H), 5.8 (s, 1 H), 3.4 (m, 2 H), 2.5–1.4 (m, 15 H); MS 333 (M^+) (very weak), 332 ($M^+ - 1$) (very strong).

Anal. Calcd for $C_{23}H_{27}NO$: C, 82.8; H, 8.2; N, 4.2. Found: C, 82.6; H, 8.0; N, 4.1. Stirring a solution of the above yellow compound in 2 N hydrochloric acid at 60 °C for 48 h gave only recovered starting material with no indication of hydrolysis.

Registry No.—**4b**, 63609-66-5; **5**, 63609-67-6; **8**, 63609-68-7; 3-methyl-2,1-benzisoxazole, 4127-53-1; *tert*-butyl alcohol, 75-65-0; 3-phenyl-2,1-benzisoxazole, 5176-14-7; 2,1-benzisoxazole, 271-58-9.

References and Notes

(1) P. Claus et al., *Pure Appl. Chem.*, **33**, 339 (1973).
(2) The apparent rate difference was due to the wavelength of the longest absorption band of the salt which was found to be responsible for the photochemistry discussed. Larger groups at the N or 3 positions in **1** increased the wavelength according to the following order: phenyl > methyl > hydrogen and adamantyl > *tert*-butyl > methyl.
(3) The addition of more basic salts such as NaCN, NaN_3, or NaOAc results in a dark addition reaction yielding 3-substituted 2,1-benzisoxazolines.[4]
(4) R. A. Olofson, R. K. VanderMeer, and S. Stournas, *J. Am. Chem. Soc.*, **93**, 1543 (1971).
(5) Minor amounts of ortho substitution also occur (see Table II).
(6) Th. Doppler, H. J. Hanson, and H. Schmid, *Helv. Chim. Acta*, **55**, 1730 (1972).
(7) R. C. Bingham and P. v. R. Schleyer, *Fortschr. Chem. Forsch.*, **18**, 1 (1971).
(8) (a) P. v. R. Schleyer, E. Funke, and S. Liggero, *J. Am. Chem. Soc.*, **91**, 3965 (1969); (b) *ibid.*, **95**, 8207 (1973).
(9) The same reduction product was obtained using $NaBH_4$, indicating C–O or C–N bond hydrogenolysis was not occurring. Also, the ^{13}C NMR spectrum of **4** shows two resonances at low field, one at 211.6 (N=C^+) and 198.4 (C=O) ppm from Me_4Si. **1h**, a model for **4c**, does not exhibit any resonance below 170 ppm.
(10) If the arylazonium ion **3** is indeed a viable intermediate, then the solvolysis of *N*-chloro-*N*-phenyl-1-adamantanamine should give the 4-*N*-phenyl-3-azahomoadamantene. This route is being pursued. For analogous system, see ref 13.
(11) R. K. VanderMeer, Ph.D. Thesis, Pennsylvania State University, State College, Pa., 1972.
(12) All melting points are uncorrected. IR spectra were obtained with a Perkin-Elmer 137 spectrophotometer and NMR spectra with a Varian T-60 spectrometer using Me_4Si as internal standard. UV spectra were taken with a Cary 17 spectrophotometer.
(13) P. Kovacic, J. Liu, E. Levi, and P. Roskos, *J. Am. Chem. Soc.*, **93**, 5801 (1971).
(14) For other reports on the synthesis of 3-homoadamantene, see: B. L. Adams and P. Kovacic, *J. Am. Chem. Soc.*, **97**, 2829 (1975); H. Kwart and J. Slutsky, *J. Org. Chem.*, **41**, 1429 (1976).

A Reinvestigation of the Synthesis of *cis*-1,2,3,4,4a,10a-Hexahydro[1,4]benzodioxino[2,3-*c*]pyridine and a Synthesis of *meso*-2,3,4,5,5a,11a-Hexahydro-1*H*-[1,4]benzodioxino[2,3-*d*]azepine

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A reinvestigation of the reaction of 1-benzyl-3,4-dibromopiperidine (**2**) with the disodium salt of catechol (**1**) was made. *cis*-2-Benzyl-1,2,3,4,4a,10a-hexahydro[1,4]benzodioxino[2,3-*c*]pyridine (**5**), previously described by Coulson[2] and Berthold,[3] was formed along with a slightly greater amount of the undescribed *cis*-1-benzyl-1,2,3,3a,10,10a-hexahydro[1,5]benzodioxepino[3,2-*b*]pyrrole (**4**). A rationale in accord with previous observations on substitution reactions of 3-substituted piperidines[4] is provided for the stereospecific but not regiospecific outcome. Reaction of the disodium salt of catechol (**1**) with *cis*-hexahydro-1-methylsulfonyl-4,5-bis(methylsulfonyloxy)azepine (**12**) and removal of the *N*-methylsulfonyl group from the product **13** provided access to the previously undescribed *meso*-2,3,4,5,5a,11a-hexahydro[1,4]benzodioxino[2,3-*d*]azepine (**14**). The cis configuration of the ring junction in **14** was proven by conversion to the *d*-camphorsulfonamide **15** and demonstration that on removal of the *d*-camphorsulfonyl group the original meso compound **14** was regenerated, rather than an enantiomer.

In our search for novel drugs, we have been investigating tricyclic systems which incorporate the 2-substituted 1,4-benzodioxan moiety.[1] One system of this type had previously been reported, i.e., the 1,2,3,4,4a,10a-hexahydro[1,4]benzodioxino[2,3-*c*]pyridine (**7**).[2] This synthesis of compound **7** had been subsequently repeated by another group.[3] Nevertheless, as the formation of a single product from the reaction of 1-benzyl-3,4-dibromopiperidine and the disodium salt of catechol seemed surprising, we investigated the reaction product more closely. The distillate described by Coulson[2] behaved as a single compound under a variety of GLC conditions, yet the yield, which was described by neither of the previous workers,[2,3] of crystalline *N*-benzylbenzodioxinopyridine hydrochloride **5** was in our hands too low for this distillate to be really homogeneous.

We next examined the distillate obtained following catalytic debenzylation of the initial product. Coulson[2] reported a 92% yield of the benzodioxinopyridine **7** hydrochloride from this distillate, but did not provide a yield for the conversion of this hydrochloride to the free base **7**. Berthold,[3] who undoubtedly had prepared a pure sample of the benzodioxinopyridine **7**, based on TLC and NMR evidence, provided a yield for neither process. Examination by GLC, after silylation, of the distillate obtained from our debenzylation experiment now clearly showed that this was a 56:44 mixture, with the benzodioxinopyridine **7** being the minor product.

The main product proved to be isomeric with the benzodioxinopyridine **7** and from NMR data it was determined to be *cis*-1,2,3,3a,10,10a-hexahydro[1,5]benzodioxepino[3,2-*b*]pyrrole (**6**). The cis stereochemistry of the ring junction was assigned from the magnitude and the solvent dependency of the coupling constant of the ring-junction protons, which suggested different mixtures of rapidly inconverting conformations (see Table I). Such conformational mobility is better