# The Preparation and Some Reactions of a 2,1-Benzisoxazol-3-ylpyrylium Salt

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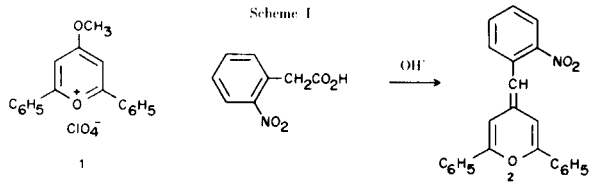
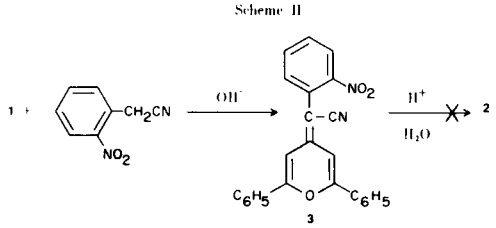
We recently described the preparation of 2,6-diphenyl-4-(2-nitrobenzylidene)-4*H*-pyran (**2**) by the route shown in Scheme I (1). Since the yield of **2** was only 30-40%, other

Scheme I



methods for the preparation of **2** were investigated, among which was the one shown in Scheme II. The condensation of **1** with the nitrile gave **3** in good yield, but hydro-

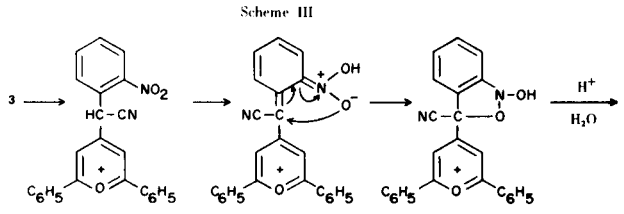
Scheme II

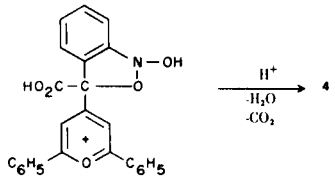


lysis of **3** with perchloric acid in acetic acid gave a product that was not **2**. The present paper deals with the structure of this product and some of its chemical reactions.

We have found that the product obtained by treatment of **3** with acid is the benzisoxazole **4**. There is precedent

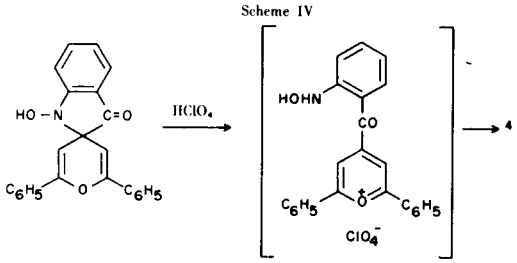
Scheme III





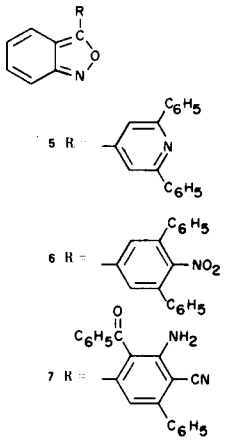
in the literature for reactions of this type, since it has been shown that heating 2,4-dinitrophenylacetic acid in sulfuric acid gave 6-nitroanthranil (2). A reasonable reaction path that leads to the formation of **4** is given in Scheme III. We later prepared **4** by the alternative route shown in Scheme IV (1).

Scheme IV

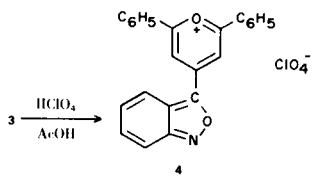


Compound **4** underwent reactions that were characteristic of a pyrylium salt as demonstrated by the formation of **5**,**6**,and **7** from ammonia, nitromethane, and malononitrile.

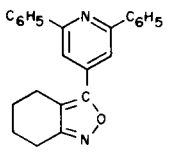
Table I



The reduction of **5** with palladium on carbon resulted in the formation of the tetrahydro derivative **8**. This result is in contrast to the report (3) that 3-phenyl-5-chloro-



anthranil was reduced under similar conditions to 2-amino-5-chlorobenzophenone. The structure **8** was established by its nmr spectrum, which in deuteriochloroform showed a



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broad multiplet centered at δ 2.65 (4H) for the protons in the 4,7-positions and at δ 1.67 (4H) for the protons in the 5,6-positions, a singlet at δ 7.58 (2H) for the protons in the pyridine ring, and the aromatic protons at δ 7.33 (M, 6H) and δ 7.92 ppm (M, 4H).

The presence of the electron-withdrawing benzisoxazole group at the 4-position of the pyrylium ring in structure **4** suggests that its electronic spectrum should resemble the spectra of other pyrylium salts with electron-withdrawing groups, and a comparison of the spectrum of **4** with that of 4-(4-nitrophenyl)-2,6-diphenylpyrylium perchlorate (**9**) showed a similarity.

TABLE II

Spectra in acetonitrile (λ max nm and $\epsilon \times 10^{-3}$)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **4** | 242 | (10.0) | 276 | (12.0) | 345 | (6.7) | 450 | (14.4) |
| **9** | 230 | (13.8) | 278 | (19.0) | | | 442 | (14.0) |

Compound **4** has been found capable of sensitizing photoconductive compositions such as those described in U. S. Patent Nos. 3,141,770 and 3,250,615.

## EXPERIMENTAL

2,6-Diphenyl-4-(α-cyano-2-nitrobenzylidene)-4*H*-pyran (**3**).

A mixture of 6.9 g. of 4-methoxy-2,6-diphenylpyrylium perchlorate and 3.2 g. of *o*-nitrobenzacetonitrile was dissolved in 100 ml. of hot methanol; 40 ml. of 10% methanolic potassium hydroxide was added; and after being refluxed for 10 minutes, the mixture was chilled and the solid collected; yield 7 g. (recrystallized from pyridine and methanol), m.p. 203-204°.

*Anal.* Calcd. for $C_{25}H_{16}N_2O_3$: C, 76.5; H, 4.1; N, 7.1. Found: C, 76.2; H, 4.2; N, 7.0.

4-(2,1-Benzisoxazol-3-yl)-2,6-diphenylpyrylium Perchlorate (**4**).

A mixture of 3 g. of **3**, 4 ml. of 70% perchloric acid, and 20 ml. of acetic acid was refluxed for 1/2 hour, cooled, and the solid was collected and crystallized from formic acid giving 1.8 g. of **4**, m.p. 253-254°.

*Anal.* Calcd. for $C_{24}H_{16}ClNO_6$: C, 64.1; H, 3.6; Cl, 7.9; N, 3.1. Found: C, 64.0; H, 3.5; Cl, 7.9; N, 3.2.

3-(2,6-Diphenyl-4-pyridyl)-2,1-benzisoxazole (**5**).

A solution of 10 g. of **4** in 100 ml. of nitromethane was mixed with 10 ml. of ammonium hydroxide and the mixture was refluxed for 15 minutes and chilled. The solid was collected and crystallized from nitromethane yielding 7 g. of **5**; m.p. 145-150°; λ max ($\epsilon \times 10^{-3}$) in acetonitrile 250 (78.5) and 345 (52.6).

*Anal.* Calcd. for $C_{24}H_{16}N_2O$: C, 82.7; H, 4.6; N, 8.0. Found: C, 82.6; H, 4.8; N, 8.1.

3-(3,5-Diphenyl-4-nitrophenyl)-2,1-benzisoxazole (**6**).

A mixture of 1.2 g. of **4**, 3 ml. of nitromethane, and 2 ml. of diisopropylethylamine was heated on a steam bath for 2 hours, and concentrated under vacuum. The residue was triturated with alcohol and recrystallized from acetonitrile giving 0.8 g. of **6**, m.p. 199-200°. The mass spectral cracking pattern showed peaks at *m/e* 392 $M^+$ (100%); 376 M-O (5%); 363 M-HCO (3%); 362 M-NO (2.8%); 346 M-$NO_2$ (42%); 345 (16%); 317 (12%) and other peaks at lower mass which were below 5%.

*Anal.* Calcd. for $C_{25}H_{16}N_2O_3$: C, 76.5; H, 4.1; N, 7.1. Found: C, 76.4; H, 4.0; N, 7.1.

3-(3-Amino-2-benzoyl-4-cyano-5-phenylphenyl)-2,1-benzisoxazole (**7**).

A mixture of 2.3 g. of **4**, 2 g. of malononitrile, 3 ml. of diisopropylethylamine, and 15 ml. of acetonitrile was heated on a steam bath for 1 hour and chilled. The solid was collected and crystallized from nitromethane yielding 1.5 g. of **7**, m.p. 200-201°. The mass spectrum showed peaks at *m/e* 415 $M^+$ (100%); 414 M-1 (21%); 399 (4.5%); 398 (9%); 387 (8%); 386 (13%); 371 M-$CO_2$ (85%); 370 (36%); 355 (18%); 338 (36%); 312 (24%); 294 (10%); and 105 $C_6H_5CO$ (60%).

*Anal.* Calcd. for $C_{27}H_{17}N_3O_2$: C, 78.1; H, 4.1; N, 10.1. Found: C, 78.4; H, 4.1; N, 10.3.

3-(2,6-Diphenyl-4-pyridyl)-4,5,6,7-tetrahydro-2,1-benzisoxazole (**8**).

A mixture of 1 g. of **5** and 0.5 g. of 10% Pd/C in 100 ml. of tetrahydrofuran was shaken under an initial pressure of 50 lb. of hydrogen at room temperature for 3 hours. After the catalyst had been filtered off, the solution was evaporated to dryness under vacuum and methanol was added to the oily residue. The solid was collected and crystallized from alcohol yielding 0.7 g. of **8**, m.p. 146-147°. The mass spectrum showed peaks at m/e 352 $M^+$ (100%); 351 (13%); 323 M-$C_2H_5$ (28%); 309 (6%); and 296 M-$C_4H_8$ (25%).

*Anal.* Calcd. for $C_{24}H_{20}N_2O$: C, 81.8; H, 5.7; N, 7.9. Found: C, 81.8; H, 5.6; N, 8.1.

Acknowledgments.

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## REFERENCES

(1) J. A. Van Allan, S. Farid, G. A. Reynolds, and S. C. Chang, *J. Org. Chem.*, 38, 2834 (1973).
(2) H. G. Garg, *ibid.*, 27, 3683 (1962).
(3) G. N. Walker, *ibid.*, 27, 1930 (1962).