

Reaction of Thiapyrylium Salts with Malononitrile

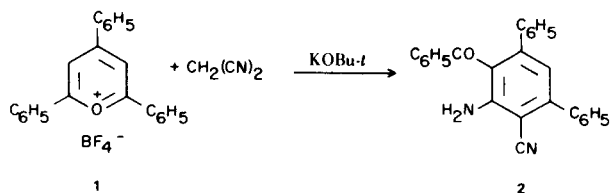
G. A. Reynolds and J. A. VanAllan

Research Laboratories, Eastman Kodak Company
Rochester, New York 14650

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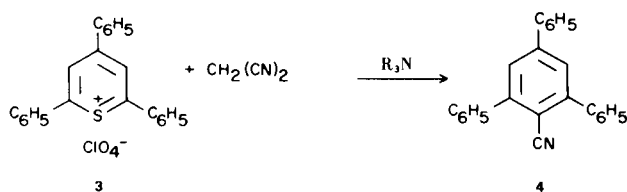
The syntheses of aromatic compounds from pyrylium salts were reviewed recently (1). One of the methods involved the reaction of a pyrylium salt with malononitrile in the presence of potassium *t*-butoxide to give a highly substituted benzophenone derivative (2), as illustrated in Scheme I for 2,4,6-triphenylpyrylium fluoroborate (1).

SCHEME I



As pointed out by Dimroth and Wolf (1), the reactions of pyrylium salts which yield aromatic compounds have scarcely been investigated with thiapyrylium salts. The present paper reports the results that were obtained when the reaction shown in Scheme I was extended to thiapyrylium salts. On the basis of the product 2, we expected to obtain the corresponding thiobenzophenone derivative, when a thiapyrylium salt was allowed to react with malononitrile. We had found previously that a tertiary amine, such as diisopropylethylamine, is an effective basic catalyst for the transformation shown in Scheme I, and therefore this base was employed for the reaction of 2,4,6-triphenylthiapyrylium perchlorate (3) with malononitrile. The product, which was isolated from this reaction in good yield, was 2,4,6-triphenylbenzophenone nitrile (4).

SCHEME II



At first this result was disappointing, since 4 is readily prepared from 1 and ethyl cyanoacetate in the presence of a tertiary amine (1). However, on further consideration, the reaction shown in Scheme II is interesting because we have never encountered a cyclization that took place through the loss of a cyano group (3).

It is interesting to speculate about the different reaction paths that pyrylium and thiapyrylium salts must take with malononitrile, and a reasonable mechanism that accounts for the products is given in Scheme III.

The cyclic four-membered transition state leading to 4 is more probable with sulfur than with oxygen owing to the greater nucleophilicity and atomic radius of sulfur. Some support was obtained for this mechanism by showing the presence of the thiocyanate ion.

EXPERIMENTAL

2,4,6-Triphenylbenzophenone nitrile (4).

A mixture of 4 g. of 3, 1 g. of malononitrile, 2 ml. of diisopropylethylamine and 25 ml. of alcohol was refluxed for 1 hour and then chilled. The white solid was collected and crystallized from alcohol giving 2.4 g. (72%) of 4, m.p. 166-167° (reported m.p. 166-167° (4)). The mother liquors were evaporated and extracted with water. The addition of ferric ion to the extract gave a red color.

The mass spectrum showed a large M^+ (331) and $\text{M}-\text{H}$ (330) with very little fragmentation.

Anal. Calcd. for $\text{C}_{25}\text{H}_{17}\text{N}$: C, 90.6; H, 5.2; N, 4.2. Found: C, 90.3; H, 5.3; N, 4.5.

2,4,6-Tri(4-methoxyphenyl)benzophenone nitrile.

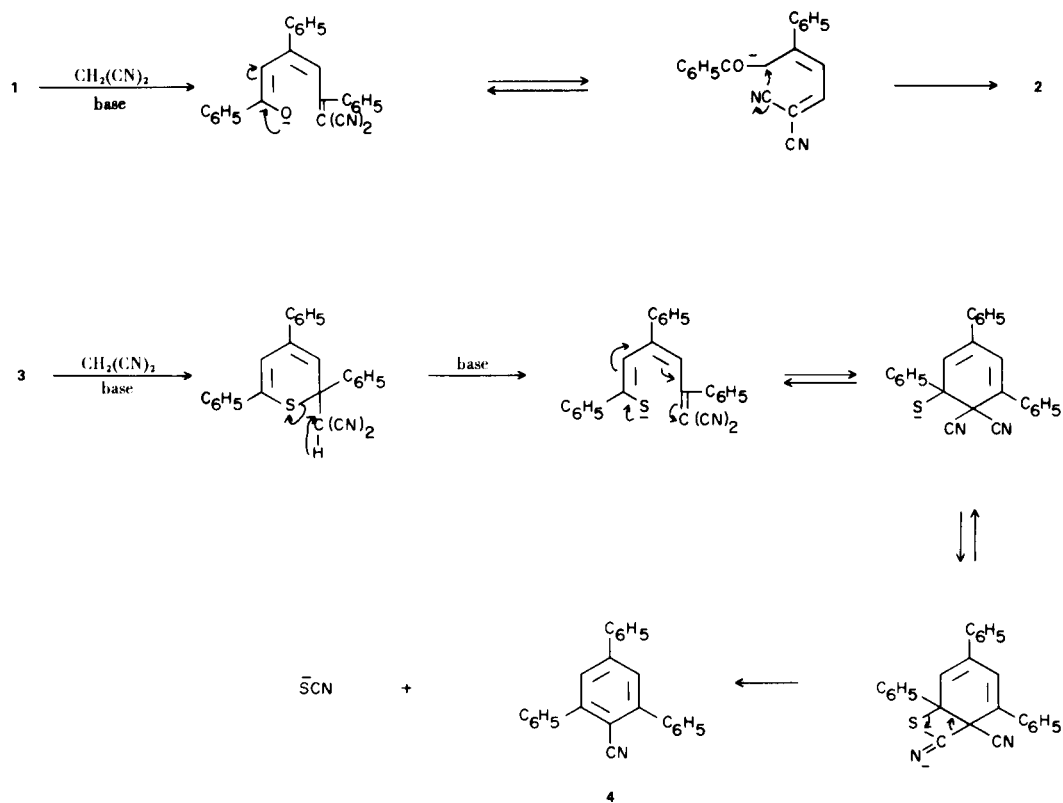
The procedure described for the preparation of 4 was repeated using 2,4,6-tri(4-methoxyphenyl)thiapyrylium perchlorate instead of 3. The yield of the benzophenone derivative was 71%, m.p. 131-132° (from alcohol). An identical product was obtained from the thiapyrylium salt and ethyl cyanoacetate by this procedure (73% yield).

Anal. Calcd. for $\text{C}_{28}\text{H}_{23}\text{NO}_3$: C, 79.8; H, 5.5; N, 3.3. Found: C, 79.5; H, 5.4; N, 3.2.

4-(4-Dimethylaminophenyl)-2,6-diphenylbenzophenone nitrile.

The method described in the preceding examples was extended

SCHEME III



REFERENCES

- (1) K. Dimroth and K. H. Wolf, "Newer Methods of Preparative Organic Chemistry," Vol. 3, Academic Press, New York, 1964, p. 357.
- (2) K. Dimroth and G. Neubauer, *Angew. Chem.*, 69, 720 (1957).
- (3) J. A. VanAllan, G. A. Reynolds and R. E. Adel, *J. Org. Chem.*, 28, 3502 (1963).
- (4) K. Dimroth and G. Neubauer, *Chem. Ber.*, 92, 2042 (1959).

to 4-(4-dimethylaminophenyl)-2,6-diphenylthiapyrylium perchlorate to give a 78% yield of the benzonitrile derivative, m.p. 147-148° (from ligroin, b.p. 100-115°).

Anal. Calcd. for $\text{C}_{27}\text{H}_{22}\text{N}_2$: C, 86.6; H, 5.9; N, 7.5. Found: C, 86.5; H, 5.8; N, 7.6.