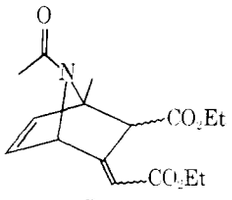

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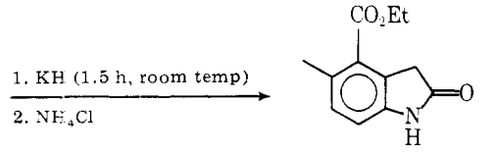
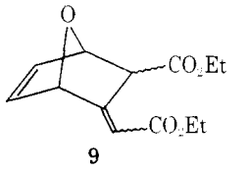


8 (55% isolated yield)



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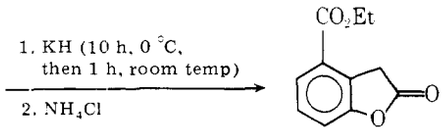
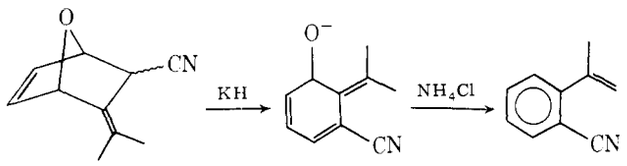


10 (45% isolated yield)

furan afforded isopropenylbenzonitrile (12) on ammonium chloride workup.



11 III 12

This product results from the acid-catalyzed dehydration of III, an intermediate which cannot aromatize in the basic milieu.

The heterolytic scission reaction reported herein thus provides a convenient method for the synthesis of fused heterocycles. This method is, however, limited to the use of allenes bearing specific electron-withdrawing groups in both the 1 and 3 positions.

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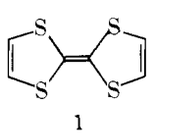
(7) TLC analysis of cycloadduct **3** reveals three separable components (two are major). Although definitive assignments of stereochemistry to these products have not been made, NMR analysis of the isomers indicates that the major components probably have the same stereochemical features as found for the cycloadducts of pentadienedioic acid and cyclopentadiene: W. C. Agosta, *J. Am. Chem. Soc.*, **86**, 2638 (1964). Also see H. Hauth, D. Stauffacher, P. Niklaus, and A. Melera, *Helv. Chim. Acta*, **48**, 1087 (1965) for the effect of the olefin geometry of an α,β-unsaturated acid on the chemical shift of neighboring protons. Since isomerization is likely to occur under these reaction conditions, the olefinic geometry of the starting materials is apparently not crucial to the success of this process.
(8) *N*-Acetyl-2-methylpyrrole, prepared from the potassium salt of 2-methylpyrrole [J. L. Rainey and H. Adkins, *J. Am. Chem. Soc.*, **61**, 1104 (1939)] and acetyl chloride, was transformed to cycloadduct **7** by refluxing with 1,3-dicarboethoxyallene in benzene for 3 days.
(9) The 4-methyl-2,3-pentadienenitrile was prepared by the method of P. M. Greaves, S. R. Landor, and D. R. J. Laws, *Chem. Commun.*, 321 (1965), and reacted with furan at 120 °C for 30 h to afford **11**. Attempts to prepare the cycloadduct of diethyl 3-methyl-1,2-butadienylphosphonate [V. Mark, *Tetrahedron Lett.*, 281 (1962)] and furan were unsuccessful.

Alan P. Kozikowski,* Michael P. Kuniak
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260
Received February 8, 1978

p-Quinobis(benzo-1,3-dithiole)

Summary: The synthesis and characterization of *p*-quinobis(benzo-1,3-dithiole) (**4**) is described. Compound **4** represents the first isolable *p*-quinodimethane derivative substituted by electron-donating groups at the *exo*-methylene groups.

Sir: The unusually high solid-state electrical conductivity of the charge-transfer complex of tetrathiafulvalene (TTF, **1**) with tetracyanoquinodimethane (TCNQ, **2**)[1] has provided the impetus for the synthesis of a variety of derivatives of TTF.[2] One of our recent goals has been the synthesis of derivatives of the unknown *p*-quinodimethane analogue of TTF, *p*-quinobis(1,3-dithiole) (**3**).[3] We now report the synthesis in pure crystalline form of the dibenzo derivative of **3**, namely *p*-quinobis(benzo-1,3-dithiole) (**4**), which also represents the first isolable *p*-quinodimethane substituted by electron-donating groups at C_7 and C_8.



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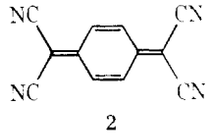

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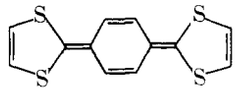

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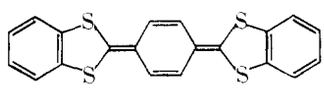

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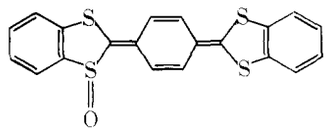
The recently described push–pull stabilized sulfoxide **5**,[4] as well as the stable bis(dithiolium)fluoborate **6**[4] should be convertible to **4** by chemical reduction; however, our attempts



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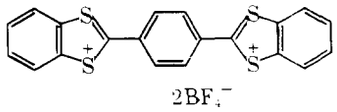
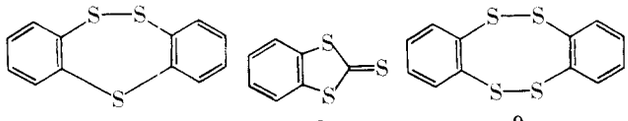


$2BF_4^-$

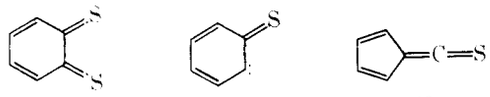
6

to effect such reductions using a variety of reagents (e.g., dithionite, silanes, thiols, phosphines, and phosphites) were unsuccessful, affording only ill-defined products.

The mass spectrum of sulfoxide **5** shows no molecular ion (*m/e* 396), but the appearance of a strong M − 16 peak (*m/e* 380) led us to investigate the pyrolysis of **5**. When **5** was heated to 300 °C under 0.01-mm pressure, three distinct zones of sublimate (A, B, and C) were collected. Chromatography of the yellow zone A on silica afforded colorless needles of trisulfide **7** (10%) [mp 149–153 °C;[5] *m/e* 248 (M^+, 17%), 216 (M − 32, 100%) and 184 (M − 64, 87%)]; a minor constituent of zone A (5%) was benzo-1,3-dithiole-2-thione (**8**), mp 165–167 °C, identical with an authentic sample. Silica chromatography of the orange zone B gave the known tetrasulfide **9** (14%) [mp 215–230 °C (lit.[6] mp 215–230 °C); *m/e* 280 (M^+, 100%)]. Products **7**, **8**, and **9** may all be considered to be derived from dithio-*o*-benzoquinone (**10**), which corresponds to the base peak (*m/e* 140) in the mass spectrum of **5**, and from the partially desulfurized intermediates **11** and **12** which can form from **10**.



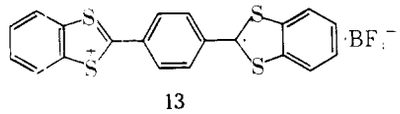
7 8 9



10 11 12

The red zone C consisted of almost pure quinodimethane **4** (38%). Recrystallization without decomposition could be achieved only from a large volume of carbon disulfide under argon, giving small crimson plates: mp 280 °C dec; *m/e* 380 (100%); IR (KBr) 3003 (w), 1527 (m), 1443 (s), 1427 (m), 1307 (m), 1285 (m), 1121 (m), 966 (m), 793 (s), 735 (s) cm^{-1}; visible λ_{max} (CS_2) (log ϵ) 478 (4.81), 503 nm (4.96). Anal. Calcd for $C_{20}H_{12}S_4$: C, 63.12; H, 3.18; S, 33.70. Found: C, 63.38; H, 2.90; S, 33.59. Proof that **4** has the unrearranged skeleton of **5** was easily obtained by treating **4** with HBF_4 in acetic anhydride, followed by crystallization from acetonitrile–HBF_4 (air present) to give an almost quantitative yield of fluoborate **6**.

Attempts to obtain a pure crystalline TCNQ complex of **4** have not yet succeeded, due to a combination of the great insolubility of **4** in organic solvents and by its ready decomposition in dilute solution in all solvents except carbon disulfide. Differential pulse polarography measurements of **6** in acetonitrile showed two reductions at $\epsilon_{1/2}{}^1 = 0.330$ and $\epsilon_{1/2}{}^2 = +0.057$ V, corresponding to the monothiolium radical cation **13** and the neutral compound **4**. As evidenced by the irre-



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versibility for polarographic reduction, both **13** and **4** appear highly unstable with respect to **6**. Corresponding polarographic oxidation measurements of **4** were severely hampered by the presence of oxygen even though common precautionary procedures were followed. A single, irreversible oxidation was observed for **3** at approximately −0.142 V.

Acknowledgment. This work was supported by grants from the National Science Foundation MRL program, DMR 76-00678 and CHE 76-83417.

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(7) Department of Physics.

Masaru Sato, M. V. Lakshmikantham
Michael P. Cava,* Anthony F. Garito*[7]
Departments of Chemistry and Physics
University of Pennsylvania
Philadelphia, Pennsylvania 19104
Received January 13, 1978

Deamination of 1-Methylcytosine by the Carcinogen *N*-Acetoxy-4-acetamidostilbene: Implications for Hydrocarbon Carcinogenesis[1]

Summary: Reaction of the carcinogen *N*-acetoxy-4-acetamidostilbene with 1-methylcytosine in water and acetone results in a uracil derivative, apparently 1-(4-acetamidophenyl)-1-[3-(1-methyluracilyl)]-2-hydroxy-2-phenylethane.

Sir: Upon solvolysis in water and acetone, the potent local carcinogen *N*-acetoxy-4-acetamidostilbene (*N,O*-diacetyl-*N*-(4-stilbenyl)hydroxylamine, **1**) yields α,β-dihydroxy-4-acetamidobibenzyl, while in aqueous methanol dimethoxyacetamidobibenzyl and hydroxymethoxyacetamidobibenzyl are formed.[2] Comparable products were expected in the reactions of this compound with nucleosides. In the case of 1-methylcytosine and cytidine, it appears that initial alkylation of N-3 in the pyrimidine ring is followed by neighboring group attack on the adjacent exocyclic amino group (N^4) to yield a uracil derivative (Scheme I). This appears to be the first demonstration of alteration of the CNO content of a nucleic acid base by an alkylating agent, and presents the possibility of induction of base pair transitions in DNA.

1-Methylcytosine (1 g) in water (50 mL) was treated with 1 N H_2SO_4 to reduce the pH to 7.3. **1** (300 mg) in 33 mL of acetone was added and the mixture incubated at 37 °C overnight. Acetone was evaporated under reduced pressure, the remaining mixture was extracted with four 50-mL portions of ethyl acetate, and the combined extracts were dried over sodium sulfate and evaporated. The residue was taken up in a minimal amount of 95% ethanol and applied to a dry column of silica gel (1 × 15 cm). Dihydroxyacetamidobibenzyl was eluted with CH_2Cl_2, and then adduct and some unreacted 1-methylcytosine were eluted with methanol. The residue from the methanol eluate was then applied to a 20 × 20 cm silica thin-layer plate, which was developed four times with ethyl acetate. Some residual dihydroxyacetamidobibenzyl ran close to the front, and the next major band was eluted with large volumes of methanol and evaporated and the isolated solid (31 mg) redissolved in methanol and precipitated with ether. After centrifugation and washing with ether, the product (**2**) was homogeneous on silica gel TLC: mp 252–253 °C (corr); UV absorption max at 253 nm (95% ethanol, log ϵ 4.16). Anal. Calcd for $C_{21}H_{21}N_3O_4 \cdot CH_3OH$: C, 64.23; H, 6.08; N, 10.21. Found: C, 64.30; H, 5.62; N, 10.23. Acetylation with

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