(3) On the other hand, 1-alkoxy-1,4-cyclohexadienes are readily available from aromatic ethers by dissolving metal reduction, and their subsequent conversion to cyclohexenones is well documented. For example, see (a) A. J. Birch, *J. Chem. Soc.*, 593 (1946); (b) A. L. Wilds and N. A. Nelson, *J. Am. Chem. Soc.*, **75**, 5360, 5366 (1953); and (c) H. L. Dryden, Jr., G. M. Webber, R. R. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).
(4) For related examples involving 1-alkoxy-1,3-cyclohexadienes, see (a) D. A. Evans, W. L. Scott, and L. K. Truesdale, *Tetrahedron Lett.*, 121 (1972); (b) A. J. Birch and K. P. Dastur, *ibid.*, 1009 (1974); and (c) R. G. F. Giles and G. H. P. Roos, *J. Chem. Soc., Perkin Trans. 1*, 2057 (1976).
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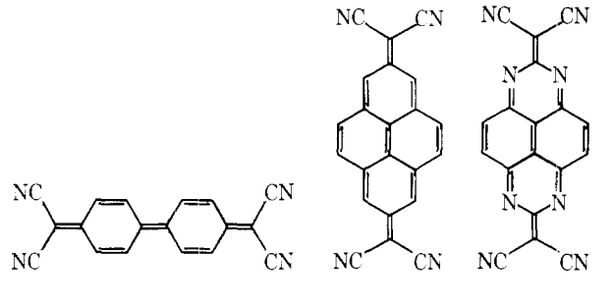
Tetracyanoquinoquinazolinoquinazoline†

Summary: The title compound was prepared as a dianionic salt whose physical properties and electrochemical behavior are reported.

Sir: Since the discovery of the unusual solid state transport properties of TTF,[1] several new donors based on the TTF skeleton have been prepared.[2-4] On the other hand, no new acceptors, except perhaps TNAP,[5] endowed with the crucial characteristic formation of stable mixed valence anionic arrays (i.e., partially filled bands) sui generis to TCNQ have appeared in the literature. For example, tetrafluoro TCNQ,[6] TCM,[7,8] TMCP,[9] and TCNDQ[10] do not appear to fulfill the above requirements.

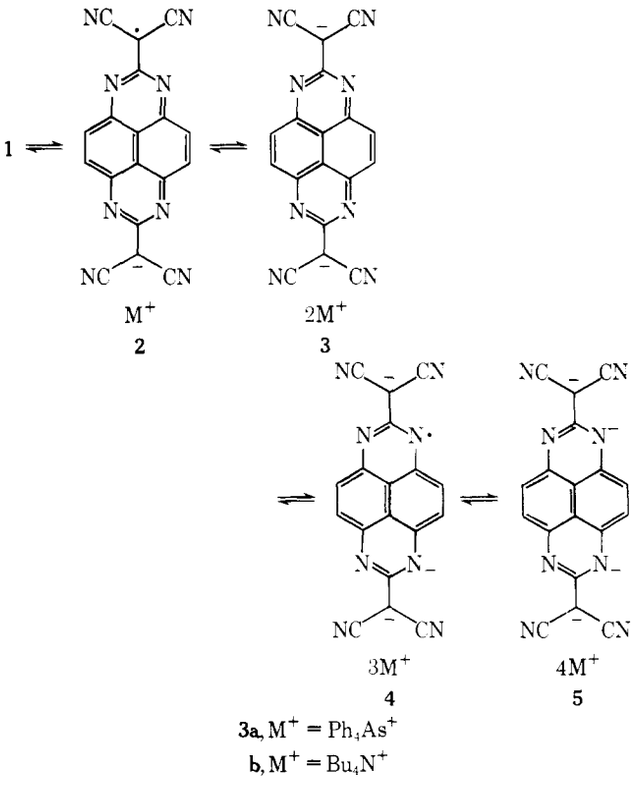
While TCNDQ tends to polymerize, a pyrene analogue (B) would be expected to be more stable because biphenyl interring hydrogen repulsions are eliminated.



A TCNDQ B TCQQ 1

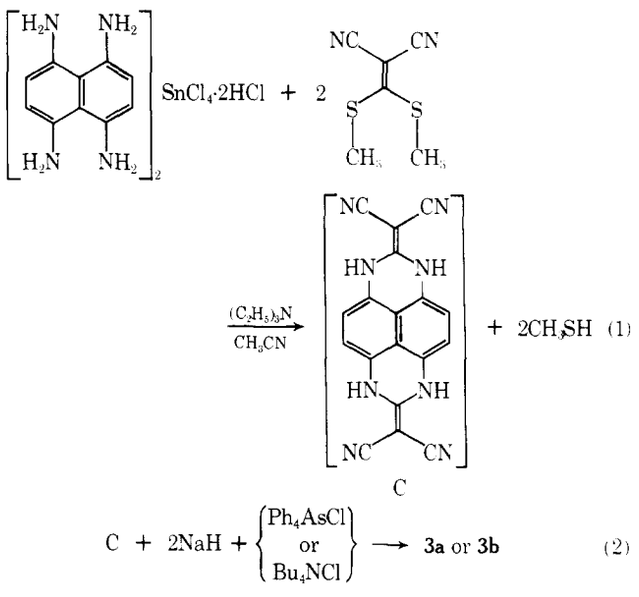
Rather than attempting a synthesis of B, we decided to prepare **1** for the following reasons: (a) projected syntheses of **1** appeared more straightforward than those of B, and (b) substitution of N for C was expected to enhance the electron affinity of the acceptor and also increase the number of available oxidation states (cf. **1-5**). Thus, by increasing the valence, we expected to enhance the probability for formation of partially filled bands.

† A systematic name would be 2,7-bisdicyanoquinomethano-2,7,*H*,*H*-quinazolino[6,5,4-*def*]quinazoline (TCQQ).



2a, $M^+ = Ph_4As^+$
b, $M^+ = Bu_4N^+$

Here we report on the preparation of **3a,b** and some of its properties. The dianion was prepared by the sequence of reactions depicted below:[11]



Since attempts to purify the crude reaction mixture obtained from reaction 1 failed, it was treated with base in acetonitrile in the presence of either tetrabutylammonium or tetraphenylarsonium chloride. Even when both reactions (1 and 2) were carried out under strictly anaerobic conditions, **3a(b)** was the only characterizable product isolated. The physical properties of **3a** are given below: **3a** UV (CH_2Cl_2) 680 nm (ϵ 690), 640 (770), 368 (1×10^5), 350 (sh, 4.8×10^4), 323 (3.6×10^4), 310 (3.8×10^4), 297 (3×10^4), 272 (2×10^4), 265 (1.8×10^4), 259 (1.6×10^4). The last three bands were due to the tetraphenylarsonium cation. For **3a**, IR (KBr) ν, 2180, 2170 (d, s), 1550 (s), 1470 (m), 1430 (m), 1380 (s), 1320 (sh), 1300 (m), 1270 (sh), 1180 (w), 1160 (w), 1080 (sh), 1070 (m), 1000 (w), 970 (w), 840 (m), 750 (s), 690 cm^{-1} (s). For **3b**, NMR (CD_3CN) δ 7.8 (s, 4 H), 3.02 (br t, 16 H), 1.4 (br m), 0.9 (s), the

last three are due to Bu_4N^+ with the expected integration ratios for the two high-field lines. We expected the chemical shift of the aromatic protons to appear at higher field than pyrene because the molecule is doubly negatively charged; instead, 7.8 ppm is precisely the chemical shift of the low field set of hydrogens in pyrene.

After several abortive trials to obtain characterizable products from attempted oxidations of **3a** to **2** or **1**, we decided to examine the solution electrochemistry of **3**. Cyclic voltammetry of **3a** in acetonitrile (0.1 M *n*-butylammonium perchlorate as supporting electrolyte and platinum bead as working electrode) revealed a one-electron reversible reduction (with peak-to-peak separation of 60 mV at a scan rate of 50–500 mV s^{-1}) at −1.55 V vs. Ag/0.01 M $AgNO_3$. No oxidation wave was observed in the range from −0.88 to +1.8 V. However, electrolysis at voltages more negative than −0.6 V produced a species which exhibited two irreversible oxidation waves at +0.16 and +0.56 V.[15] The reversible reduction at −1.55 V could be assigned to the couple **3**–**4** on the basis of ESR experiments.

Electrolysis of **3a** in CH_3CN at −1.35 V vs. SCE in an ESR cavity generated a relatively stable radical trianion (**4**) (g = 2.0033, $t_{1/2}$ ca. 2 min., $a_H = a_N$ = 2.53 G) with a 13-line spectrum.[15] From the analysis of the normalized intensities we deduced that the radical had four equivalent hydrogens and four equivalent nitrogens (calcd, 262:232:160:84:32:8:1; found, 262:235:164:82:33:8:1). There is practically no coupling to the nitrile nitrogens.

It is interesting to note that the most stable species among **1**–**5** are **3** and **4** and not **2** or **1**. This, of course, does not mean that the radical anion derived from B will also be unstable.

Current studies on the solid state structure of **3a** and the metathesis products of it with radical cations will be reported in a separate publication.

References and Notes

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(15) Copies of the cyclic voltammogram and the ESR spectrum are available from the authors upon request.

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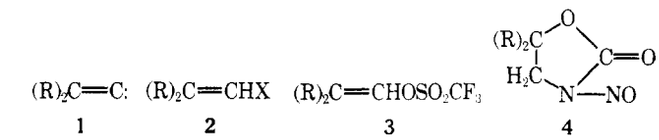
Alkylidene Carbene Generation from Tosylazoalkenes and Silylvinyl Triflates[1,2]

Summary: Thermal decomposition of tosylazoalkenes, $R_2C{=}CHN{=}NTs$, at 25 °C gave unsaturated carbene derived products in 25–40% yield; similarly fluoride ion initiated decomposition of silylvinyl triflates $R_2C{=}C(OTf)Si(CH_3)_3$ in cyclohexene or ethyl vinyl ether gave quantitative yields of carbene adducts in 1–2 h at −20 or 0 °C; these two methods represent the mildest known conditions for alkylidene carbene generation to date.

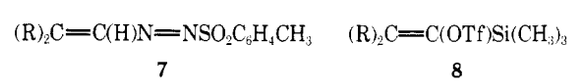
Sir: There has been considerable interest and work lately in alkylidene, **1**, and other unsaturated carbenes.[3] Such carbenes have primarily been generated by α elimination from primary vinyl halides,[4] **2**, or vinyl triflates,[5] **3**, and base-promoted decomposition of *N*-nitrosooxazolidones, **4**, or related compounds.[6] However, all of these techniques require strong bases such as RLi, *t*-BuOK or ROLi, preventing the possible interaction of **1** with base-sensitive substrates and thereby limiting the potential synthetic uses of these carbenes. Until recently, with the exception of two photochemical processes,[7,8] both in very low yield, and the nitrite deamination of certain unique vinyl amines,[9] there was no known technique for the generation of **1** in the absence of strong base analogous to the diverse nonbasic generation of saturated carbenes.[10] In early 1976 Seyferth and Dagani[11] reported the thermal generation of **1** from organomercurial **5** at 150 °C and Cunico and Han[12]



1 2 3 4

$(CH_3)_2C{=}C(Br)HgBr/(C_6H_5)_2Hg$ (5) $(CH_3)_2C{=}C(Cl)Si(CH_3)_3$ (6)

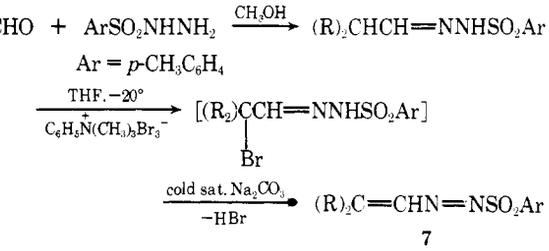
reported the formation of **1** via the fluoride promoted decomposition at 25 °C of α-chlorovinylsilane (**6**), thus providing the first useful generations of **1** under relatively mild and neutral conditions in good yields. Therefore, in this communication we wish to report two additional means of alkylidene carbene **1** generation under even milder conditions involving tosylazoethylenes **7** and silylvinyl triflates **8** as progenitors, in the latter case in quantitative yields.



7 8

Tosylazoethylenes, **7**, are known[13] and can be readily prepared in good yields according to the procedure of Rosini and coworkers[13] as shown in Scheme I. In fact, Rosini and Cacchi[14]

Scheme I



7

have shown that the tosylazoethylene derived from diphenylacetaldehyde (**7**, R = C_6H_5) decomposes in chloroform at 25 °C to give >85% diphenylacetylene via either the carbene **1** (R = C_6H_5) or vinyl cation **9**. Since ion **9** would be a primary vinyl cation,[15] and hence energetically extremely unlikely,[15] their decomposition most likely involved carbene **1**. Such diaryl carbenes (**1**, R = C_6H_5) however, cannot be successfully trapped[3,5] intermolecularly and are known[3,5] to intramolecularly rearrange to the acetylene. Therefore we prepared