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(15) Taken in part from the Ph.D. Dissertation of S. DeYoung, Bryn Mawr College, May 1976, and the work for the Ph.D. Dissertation to be submitted by S. Ehrlich.

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Variation of Stoichiometry in Tetrathiofulvalene–Tetracyanoquinodimethane Complexes

Sir:

The 1:1 charge transfer complex between tetrathiofulvalene (TTF) and tetracyanoquinodimethane (TCNQ) has metallic electrical conductivity on the order of graphite.[1,2] The percent electron transfer in such complexes could have considerable influence on final electrical conductivity since electron transfer in turn may influence the ease of a Peierls transition to an insulating state, the ability to form closely packed homogeneous stacks of cations and anions, and electronic interactions in homogeneous cation and anion stacks once formed. One way to affect electron transfer is to vary electron acceptor or donor strengths; for example, in a series of 15 substituted TTF·TCNQ's, electrical conductivity increases by at least 10^4-10^7 on going from very strong electron acceptors such as TCNQ(CN)₂ or TCNQF₄ to weaker acceptors such as TCNQEt₂ or TCNQ.[3] A second way to affect electron transfer is to alter stoichiometry: for example, the electrically conductive band contributed by TCNQ·⁻ in 1 (Et₃NH⁺TCNQ·⁻) is formally one-half full whereas the electrically conductive band contributed by (TCNQ)₂·⁻ in 2 (Et₃NH⁺(TCNQ)₂·⁻) is formally one-fourth full. Again electrical conductivity is strongly affected since 2 is ~10^9 more conductive than 1.[4]

The TTF·TCNQ system is one of the most conductive known. Attempts to increase this conductivity by changing stoichiometry from 1:1 have most often failed synthetically. For example, TTF·TCNQ itself has always been obtained as a 1:1 complex in spite of efforts to increase the proportion of

TCNQ by crystallizing from a large excess of TCNQ.[1] Reaction of TTF with 16 substituted TCNQ's in acetonitrile has given 15 1:1 complexes and just one 2:3 complex.[5] We report here synthetic techniques and substitution patterns that easily make a wide range of stoichiometries available as quite highly conductive complexes in the TTF·TCNQ family.

A low temperature metathesis technique allows preparation of new stoichiometries between the same donor and acceptor. TTF and TCNQICH₃ precipitate from acetonitrile as a highly conductive 1:1 complex.[5] However, slurrying 0.85 g of ammonium salt 3 and 0.52 g of fluoroborate salt 4 under nitrogen for 2 h at −35 to −40 °C in 50 ml of acetonitrile and filtering cold affords 0.21 g (27%) of the blue-black 2:1 salt 5. Infrared
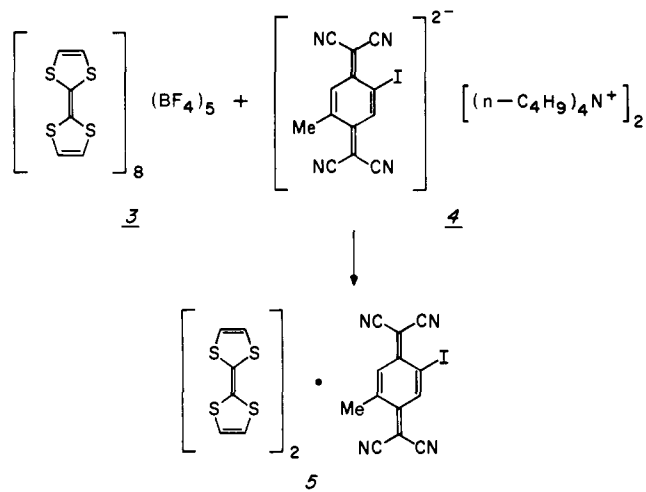
spectroscopy shows the absence of free TTF in 5, since compound 5 totally lacks the strong TTF bands at 12.6 and 12.85 μ shown by a 1:1 mixture of TTF and TTF·TCNQICH₃.

Mixing bis(hydroxymethyl)TTF 6 in refluxing acetonitrile with equimolar quantities of substituted TCNQ's and cooling precipitates complexes with 1:1, 3:2, and 2:1 stoichiometries.
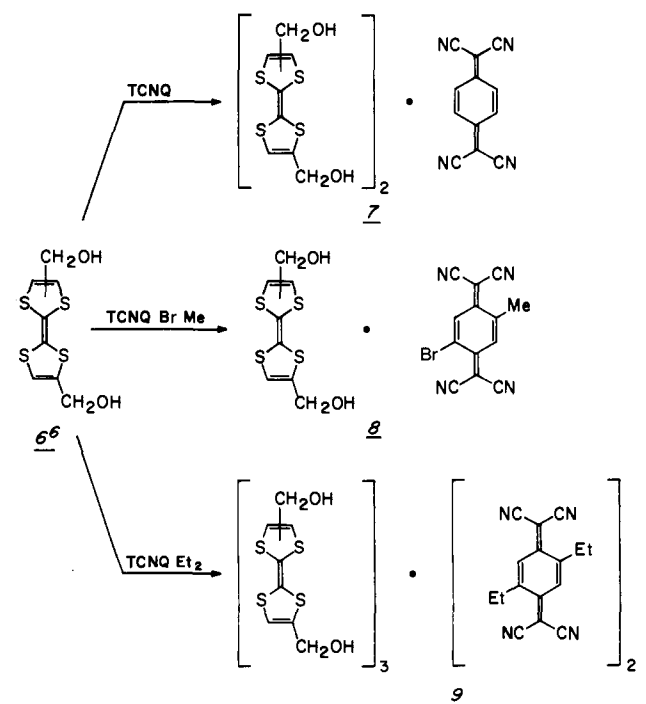
Supporting data including compaction resistivities are shown in Table I.

Table I. Complexes Prepared

Complex	Calcd C H N	Found C H N	Electrical resistivity[7]	% yield
5	39.88, 1.74, 7.44	39.72, 2.06, 7.35	0.6	2
		40.14, 1.98, 7.65	2	27
7	45.88, 2.75, 7.64	45.30, 2.82, 7.64	2	40
8	44.92, 2.33, 9.88	44.95, 2.49, 10.27	0.8	70
9	51.19, 3.68, 8.53	50.86, 3.78, 8.42	2	20

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Thermal Rearrangements of Spiro[4.4]nonapolyenes. Unusually Rapid 1,5-Vinyl Migration

Sir:

Spiro[4.4]nonatetraene (1) is a relatively unstrained hydrocarbon and of some theoretical interest,[1] yet it eluded synthesis until recently.[2] Well-precedented elimination pathways involving moderate temperatures (>150 °C) failed uniformly.[3,4] This suggestion of unexpected instability in 1 and recent interest in thermal rearrangements of unsaturated spirocycles[5] prompted us to probe the thermochemistry of 1 and the less unsaturated analogues 2, 3, and 4. These spirocycles undergo 1,5-carbon migrations when heated, producing unsaturated derivatives of the bicyclo[4.3.0]nonane skeleton. Here we report preliminary results which demonstrate the remarkably high reactivity of 1 and 2 compared to 3 and 4.

The rearrangements of 1–4 were best followed in a static gas phase reactor monitoring the disappearance of spirocycle using gas chromatography (GC).[6] In certain cases, the rearrangements have beenmonitored by increase in (product) absorption in the UV spectra, both in solution and in the gas phase, and by the disappearance of spirocycle in solution using ^{1}H NMR spectroscopy. The GC technique provided superior data which have been used to derive activation parameters as displayed in Table I.[7] The rearrangement products were isolated by gas phase flow pyrolysis over heated glass helices at ca. 0.1–1 Torr and contact times ca. 10–60 s, with collection of the product at −78 °C.

In the flow pyrolysis apparatus, 1 rearranged to indene at 260 °C (eq 1); no additional products were observed at lower temperature (partial conversion). Isoindene 5, an unknown compound which is presumed to be important in the formation
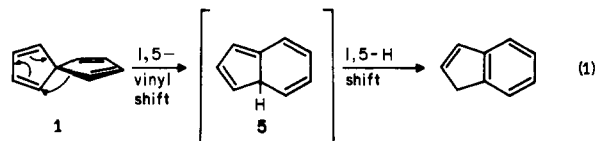
of indene, has not been detected. Repeated scanning of the UV spectrum during pyrolysis demonstrated the presence of isobestic points at 220 and 258 nm; intermediate 5, if present, remains at very low concentration. Reaction in solution occurred four–fivefold faster than in the gas phase (Table I, entries 1 and 4), but the polarity of the solvent and the presence of sulfuric acid (entry 3, acid:spirocycle = 10:1) had little effect on the rate.

Spiro[4.4]nona-1,3-diene (4)[8] is stable indefinitely at 25 °C, but is converted to a mixture of 6, 7, and 8 upon heating (eq 2), with an activation barrier previously measured in a "micro
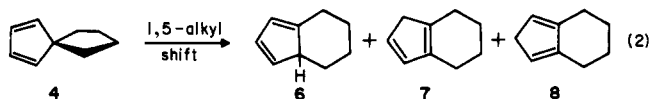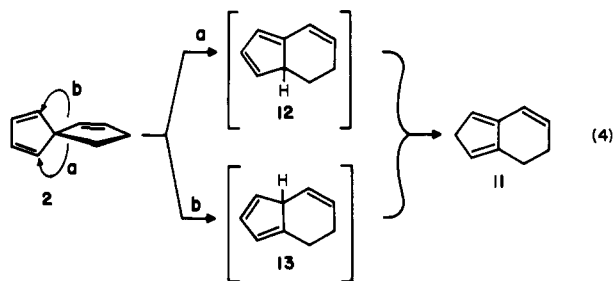

flow reactor" by Kloosterzeil[5b] (Table, entry 9). Using GC monitoring, in a static gas phase system, we find rates and activation parameters in good agreement with Kloosterzeil's data (Table I, entry 10).

Spiro[4.4]nona-1,3,7-triene (3)[2,3b] rearranges during flow pyrolysis (370 °C/0.05 Torr) to a single product, isoindane 9, presumably via the hydrogen-shift isomer, 10 (eq 3).[9] At higher reaction temperatures, indane begins to appear and is the only product in flow pyrolysis at 450 °C. Only small changes in UV absorption occur during the reaction, so kinetic data were obtained by GC monitoring (entry 8, Table I).
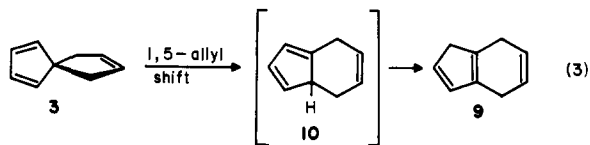
Spiro[4.4]nona-1,3,6-triene (2), previously an unknown compound, was prepared from spiro[4.4]nona-1,6-diene[10] by allylic bromination (N-bromosuccinimide) followed by dehydrohalogenation (potassium *tert*-butoxide/tetraglyme) under conditions (0.2 Torr) where 2 distilled as it formed at 25 °C.[11] The UV and PES spectra of 2 are perturbed compared to those of 3 and 4, showing the effects of spiroconjugation, as in 1.[12] The chemical reactivity of 2 is also more similar to 1 than to 3 or 4. Flow pyrolysis at 305 °C/2.0 Torr caused rearrangement of 2 to a single product, isoindane 11.[13] Presumably, the rearrangement occurs through a 1,5-alkyl shift (to give 12, path a, eq 4) or a 1,5-vinyl shift (to give 13, path b, eq 4), followed by 1,5-hydrogen shift to produce 11. No in-

termediates have been detected. No data are available to suggest which path, a or b, is operating. The disappearance of 2 was monitored by GC; smooh first-order kinetics were observed but no products were detected (Table I, entry 6).