ISOMERIZATIONS OF 1,7-DIHETERADISPIRO[4.0.4.4]TETRADECA-11,13-DIENES IN THE PRESENCE OF TETRACYANOETHYLENE‡

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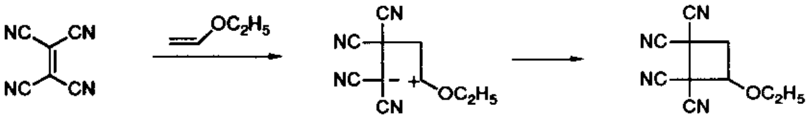
Abstract - TCNE is shown to be capable of promoting the isomerization of the title compounds to a new class of unsaturated [4.4.4]propellanes and aromatic isomers thereof.

The ability of very electron deficient olefins such as tetracyanoethylene (TCNE) to form charge-transfer complexes with electron-rich alkenes and 1,3-dienes has been recognized for some considerable time. The theoretical basis for transient color formation, formulated by Mulliken in the early 1950's,[2] rationalized the appearance of new absorption bands but did not address the mechanistic role of these species in chemical reactions. In Huisgen's elegant investigation of thermal [2+2] cycloadditions,[3] tetramethylene zwitterions such as **1** were identified as key intermediates for cyclobutane production.



However, the question of whether a charge-transfer complex precedes the generation of **1** could not be established experimentally. These difficulties carry over as well to Diels-Alder reactions.

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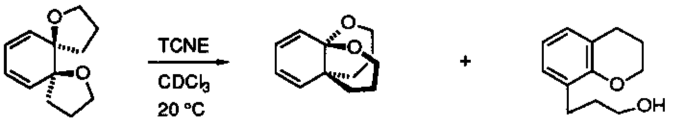
‡This paper is dedicated to Professor Rolf Huisgen on the occasion of his 75th birthday.

Despite important contributions by Kochi[4] and by Sustmann,[5] quantitative evidence for the direct mechanistic involvement of charge-transfer complexes in [4+2] cycloadditions has proven highly elusive. The same complications surface in the TCNE-promoted ring-opening reactions of cage compounds[6] and photoextrusion reactions.[7]

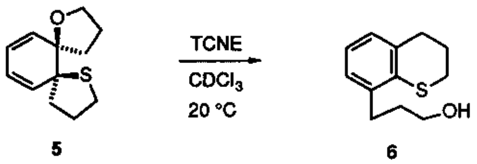
This lack of mechanistic detail has not precluded TCNE from serving as an important co-reagent in various organic processes. We describe here the discovery of a new reaction type which, while capable of proceeding under acid catalysis,[8] is also operative in the presence of TCNE.

A solution of **2** in purified $CDCl_3$ gave rise to an orange color immediately following treatment with approximately 0.5 mol equivalent of freshly sublimed TCNE. Storage of this mixture in the absence of light at room temperature was accompanied by periodic nmr analysis of the progress of reaction. After 12 days, the signals of **2** had completely disappeared. A companion control experiment showed **2** to be otherwise stable in this medium, a phenomenon that was seen throughout this study. Chromatographic purification afforded pure samples of the structurally unusual propellane (**3**) (55%) and the aromatized benzopyran (**4**) (42%).

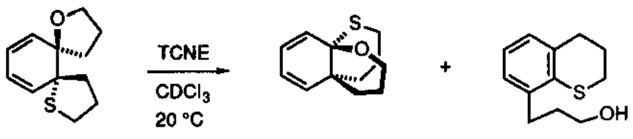


2 **3** **4**

When the oxathia system (**5**) was analogously exposed to TCNE, a deep purple hue developed immediately. This coloration persisted for approximately 18 h, at which point the reaction mixture became blue. After 35 h when **5** no longer remained, a bright green color had developed. The

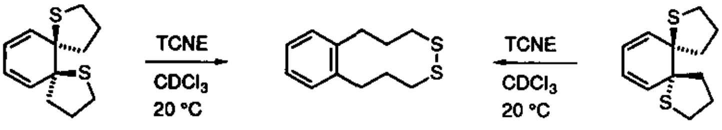


5 **6**



7 **8** **6**

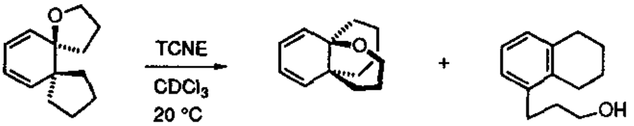
only substance produced was shown to be **6** (34% isolated). Comparable treatment of the *trans* isomer (**7**) gave rise to a significant proportion of propellane (**8**), thus providing an opportunity for the isolation of this acetal (31%) in addition to **6** (15%).



9 **11** **10**

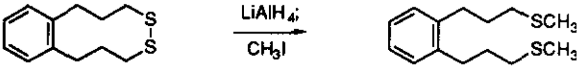
These isomerization pathways are not paralleled by the dithia analogues (**9**) and (**10**), both of which led to disulfide (**11**) (90% and 34%, respectively). In the case of **9**, the initially observed purple coloration which persisted for > 40 h gradually gave way to a gray-black shade. When reaction was complete (61 h), the solution was green. The original lavender-colored complex obtained with **10** gradually was replaced by a comparable green appearance.

There exists no requirement that two hetero atoms be present in light of the ready isomerization of **12** to a mixture of **13** (76%) and **14** (22%) after 20 h.



12 **13** **14**

The structures of the products were ascertained by ^1H and ^{13}C nmr spectroscopy, as well as chemical interconversion.[9] Thus, the 300 MHz ^1H nmr spectrum of **3** (in $CDCl_3$) exhibits four clearly distinctive olefinic protons at δ 6.72, 5.97, 5.76, and 5.63 and the expected "inner" and "outer" methylene protons as six two-proton multiplets. Its inherent symmetry was made apparent from the 9-line carbon spectrum. The characterization of **11** follows also from its symmetry (six ^{13}C signals) and its reductive alkylation to provide **15**.



11 **15**

The universal dependence of these isomerization on the presence of TCNE is compatible with the concept that the bond reorganizations proceed *via* polar charge transfer intermediates. The gradual liberation of protic acid was eliminated from consideration by pH determinations following addition of water to aliquots as reaction progressed. Notwithstanding, it has not proven possible to establish unequivocally that donor-acceptor complexes form an integral component of the transition states of these processes.[10] The inability of TCNE to enter into Diels-Alder cycloaddition with these dienes is noteworthy.

REFERENCES AND NOTES

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9. All new compounds reported herein have been fully characterized by ir, high-field ^{1}H and ^{13}C nmr, and high-resolution mass spectrometry and/or combustion analysis.
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