TETRACYANOETHYLENE AS AN ARomatizing AGENT

Daniel T. Longone and Gary L. Smith

Department of Chemistry, The University of Michigan
Ann Arbor, Michigan

(Received 19 February 1962)

TETRACYANOETHYLENE (TCNE) has proven to be an extremely versatile chemical intermediate. The reactions of TCNE with conjugated dienes have been well delineated. In contrast to normal Diels-Alder adductions with conjugated acyclic and cisoid cyclic dienes, spiro-compounds are generated by cycloaddition of TCNE to the exocyclic double bond in transoid methylenecycloalkenes. Less commonly, the cycloaddition of TCNE to an endocyclic double bond can yield a bicyclohexane derivative. Supplementing its reactions with conjugated dienes we wish to report that TCNE functions as an efficient hydrogen acceptor in the aromatization of certain non-conjugated cycloalkadienes.

The facile addition of TCNE to norbornadiene to give the homo-Diels-Alder adduct I led us to investigate the reactions of TCNE with other non-conjugated dienes. In an attempt to generate the tricyclooctane derivative II, a solution containing equimolar amounts of 1,4-cyclohexadiene and TCNE...
in benzene-dioxane (3:2) was refluxed for 30 min. A white crystalline
product, separated from the cooled reaction mixture, had m.p. 185-190° (dec.).
Recrystallization from benzene-ethyl acetate (3:2) gave dec. 187°. This
solid, formed essentially quantitatively, proved to be tetracyanoethylene
(TCNE), identified by analysis (Found: C, 55.18; H, 1.38; N, 42.92) and by
direct comparison of its infrared spectrum with that of an authentic sample
prepared by the reduction of TCNE with hydrogen iodide. That TCNE
functioned as a hydrogen acceptor in the aromatization of the diene was
confirmed by repetition of the reaction in purified dimethylformamide as
solvent. After an arbitrary reflux time of 4 hr, the system afforded 98%
crude TCNA and 99% benzene. The above aromatization can be effected under
particularly mild reaction conditions: equimolar amounts of 1,4-cyclohexa-
\textsuperscript{a} diene and TCNE in dioxane at room temperature for three days give 98% crude
TCNA (dec. 176°) and 94% benzene. Under a variety of reaction conditions,
no evidence for the isomerization of the diene to its conjugated isomer is
observed.

\textsuperscript{8} Dr. B.C. McKusick of the du Pont Co. has informed us that his laboratory
has observed the formation of TCNA, m.p. 184-188° (see ref. 9), from the
reaction of TCNE and 1,4-cyclohexadiene.

\textsuperscript{9} The decomposition temperature of TCNA varies markedly with sample
purity and heating time. Reproducible results can be obtained by
introducing the sample into the heating bath at 170°. The previously
reported (ref. 2) decomposition temperature can be raised by ca. 20°
by this technique.

\textsuperscript{10} Determined spectrophotometrically (ultraviolet) utilizing the distillate
from the reaction filtrate and appropriate controls.

\textsuperscript{11} TCNE and 1,3-cyclohexadiene readily give a Diels-Alder adduct in high
yield (ref. 2).
In a similar manner (4 hr reflux in dioxane) 1,4-dihydronaphthalene is aromatized to naphthalene (60%, recrystallized) and 2,5-dihydrobenzoic acid gives 52% benzoic acid.

Utilizing an excess of TCNE it is possible to generate by dehydrogenation a reactive diene which subsequently undergoes Diels-Alder adduction. A dioxane solution (100 ml) of 9,10-dihydroanthracene (0.010 mole) and TCNE (0.031 mole) after 6 hr reflux affords, in 49% yield, the adduct III. The latter compound was identified by m.p., mixed-m.p., and comparison of its infrared spectrum with that of authentic III prepared in the normal manner. This example indicates that caution must be exercised in utilizing TCNE adduction as a structure probe in polycyclic systems.

It appears that TCNE is an effective dehydrogenating agent only in the aromatization of 1,4-dihydrobenzenoids. Under a variety of experimental conditions, no reaction is observed between TCNE and cyclohexene, acenaphthene, 9,10-dihydrophenanthrene, tetralin, ethylbenzene, bibenzyl and 1,5-cyclooctadiene.

Acknowledgement - This research was supported in part by the U.S. Army Research Office (Durham).