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TETRACYANOETHYLENE AS AN AROMATIZING AGENT

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TETRACYANOETHYLENE (TCNE) has proven to be an extremely versatile chemical intermediate.[1] The reactions of TCNE with conjugated dienes have been well delineated. In contrast to normal Diels-Alder adductions[2,3] with conjugated acyclic and cisoid cyclic dienes, spiro-compounds[4-6] 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.[5] 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[4] 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[7] to generate the tricyloöctane derivative II, a solution containing equimolar amounts of 1,4-cyclohexadiene and TCNE

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[1] T.L. Cairns *et al.*, *J. Amer. Chem. Soc.* **80**, 2775 (1958).

[2] W.J. Middleton, R.E. Heckert, E.L. Little and C.G. Krespan, *J. Amer. Chem. Soc.* **80**, 2783 (1958).

[3] A.T. Blomquist and Y.C. Meinwald, *J. Amer. Chem. Soc.* **82**, 3619 (1960).

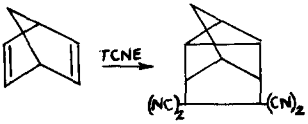
[4] A.T. Blomquist and Y.C. Meinwald, *J. Amer. Chem. Soc.* **81**, 667 (1959).

[5] J.K. Williams, *J. Amer. Chem. Soc.* **81**, 4013 (1959).

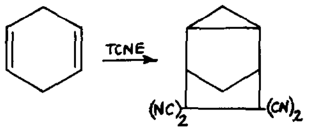
[6] D.S. Matteson, J.J. Drysdale and W.H. Sharkey, *J. Amer. Chem. Soc.* **82**, 2853 (1960).

[7] We are indebted to Dr. P. Scheiner for carrying out this reaction.

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.);



I



II

recrystallization from benzene-ethyl acetate (3:2) gave dec. 187°. This solid, formed essentially quantitatively, proved to be tetracyanoethane (TCNA), 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.[2] That TCNE functioned as a hydrogen acceptor in the aromatization of the diene was confirmed[8] 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.[10] The above aromatization can be effected under particularly mild reaction conditions: equimolar amounts of 1,4-cyclohexadiene and TCNE in dioxane at room temperature for three days give 98% crude TCNA (dec. 176°) and 94% benzene.[10] Under a variety of reaction conditions, no evidence for the isomerization of the diene to its conjugated isomer is observed.[11]

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[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.

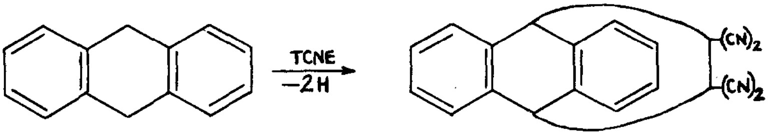
[9] The decomposition temperature of TCNA varies markedly with sample purity and heating time. Reproducible results can be obtained by introducing the sample into the heating bath at 170°. The previously reported (ref. 2) decomposition temperature can be raised by ca. 20° by this technique.

[10] Determined spectrophotometrically (ultraviolet) utilizing the distillate from the reaction filtrate and appropriate controls.

[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.[2] This example indicates that caution must be exercised in utilizing TCNE adduction as a structure probe in polycyclic systems.



III

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.

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