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# Reaction of Phenanthrene-9,10-oxide with Tetracyanoethylene

The reaction of phenanthrene-9,10-oxide with tetracyanoethylene was described. The isomerization to phenanthrol was suggested and the structure of an interesting adduct with tetracyanoethylene was determined.

**Keywords**——arene oxide; charge transfer complex; rearrangement; phenanthrol; tetracyanoethylene

Arene oxides attract current chemical[1] and biological interests.[2] The acid- and thermal rearrangement of arene oxides to phenols has been studied.[3] The present paper describes a reaction of phenanthrene-9,10-oxide (**1**) which involves a rearrangement to phenanthrol catalyzed by tetracyanoethylene (TCNE), and a subsequent novel reaction with TCNE.

A benzene solution of **1** (1 mmol) and TCNE (1 mmol) was kept at room temperature in the dark for 2 days. A mixture of colored crystals was separated out in 50—80% yield. The major rubby red crystals were picked up and the composition was determined to be a 1:1 adduct of **1** and TCNE, mp 270° (darken at 150—250°). The same crystals were obtained by the recrystallization of an orange adduct (analyzed as $C_{14}H_{10}O \cdot TCNE \cdot CH_2Cl_2$) prepared in $CH_2Cl_2$ from benzene containing a trace of acetone.

The same red crystals were obtained by the reaction of 9-phenanthrol and TCNE in benzene. This suggests that the initial reaction of **1** and TCNE is an isomerization of the oxirane ring to phenol or isomeric ketone, which then reacts covalently with TCNE. The isomerization of arene oxide catalyzed by an electron deficient organic molecule is the first suggestion in the arene oxide chemistry.

The structure of the adduct was determined by an X-ray crystallographic analysis of the red crystal. The crystal belongs to the monoclinic space group $P2_1/n$ with four molecules in a unit cell of the dimensions, $a=17.375$, $b=7.107$, $c=13.312$ Å, and $\beta=103.67°$. The intensity data were collected by the $\theta$-$2\theta$ scan technique using graphite monochromated Cu K$\alpha$ radiation on Philips PW 1100 automatic four circle diffractometer. A total of 1854 independent non-zero reflections was measured out of 2370 possible reflections within $2\theta=120°$, which was then corrected for Lorenz and polarization factors. No correction was applied for either absorption or extinction.

The structure was solved by the direct method using the program MULTAN and refined by the block-diagonal least-squares method. Hydrogen atoms were located on a difference Fourier map. Successive least-squares calculations led the R-index of 0.048, assuming the anisotropic thermal parameters for non-hydrogen atoms and the isotropic ones for hydrogen atoms. The weighing scheme was $\sqrt{\omega}=1.30$, when $F_0 \leqslant 29$; $\sqrt{\omega}=(28/F_0+0.03)$ when $F_0>29$. A perspective drawing of the molecule is illustrated in Fig. 1 with the atomic numbering. The phenanthrene part of the molecule is approximately planar.

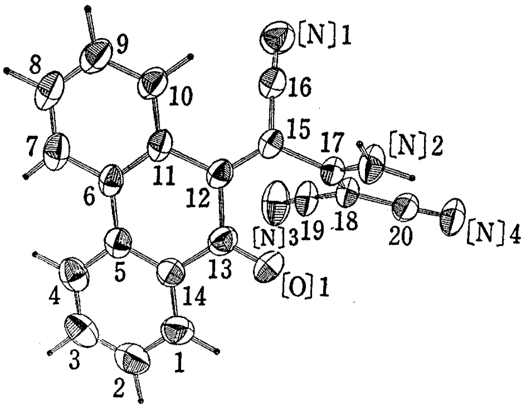

Fig. 1. A Perspective Drawing of the Structure of the Red Crystal

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The dihedral angle between the planes of the phenanthrene moiety and the dicyanoethylene moiety is about 58.4°.

A schematic mechanism of the adduct formation shown in Fig. 2 requires a rearrangement of a dicyanomethyl group to the carbon of a cyano group. This type of TCNE addition to an organic molecule presented here can not be found among currently accumulating results on the TCNE addition chemistry.[4]

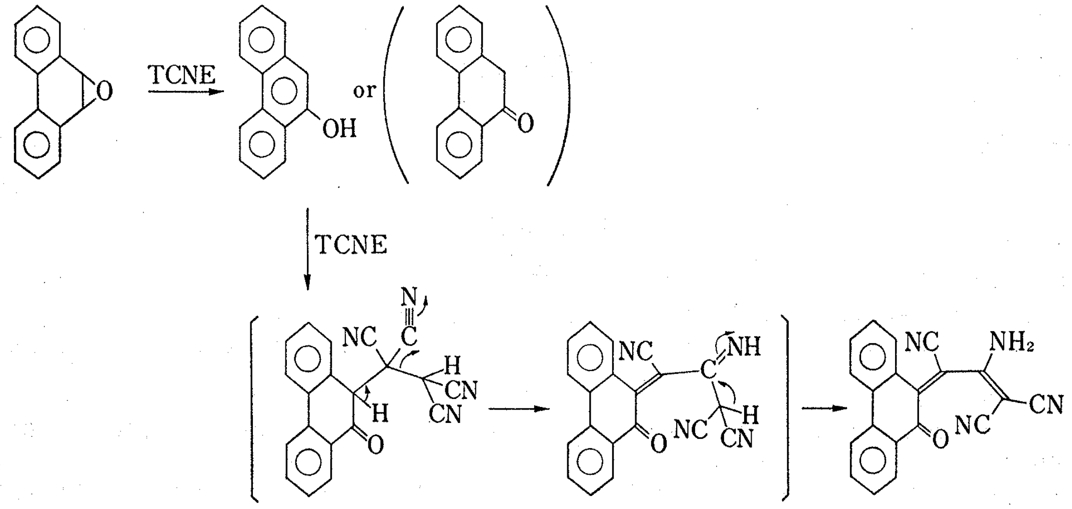

Fig. 2

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