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CHARGE-TRANSFER REACTION OF BUTATRIENE: FORMATION OF DIHYDRONAPHTHALENE DERIVATIVE

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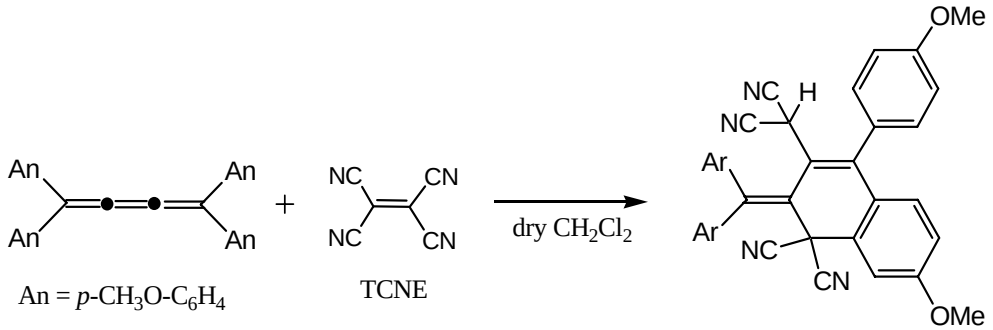
ABSTRACT

Single electron transfer chemistry of unsaturated double bonds has been studied extensively so far. By contrast, the chemistry of the congener, a cumulated C=C double bond, has been investigated less. Johnson and his coworkers studied previously the photochemical electron transfer of allene-propyne system,[1] and it is likely to be the only related work of the study titles. Since limited information on open-shell cumulated bonds is available and it is of interest to compare the reactivity of butadiene, allene, and alkyne compounds, we have studied the charge-transfer (CT; an electron transfer in an intrinsic case of CT) reactions of tetra-*p*-anisyl-1,2,3-butatriene (**1**) with tetracyanoethene (TCNE) as a strong electron accepting molecule. As a result, the reaction proceeded very smoothly in dichloromethane (CH_2Cl_2) at room temperature (rt) with intense color change, and 2-(di-*p*-anisylmethylene)-1,2-dihydrobaphthalene derivative (**2**) formed quantitatively.

Butatriene **1** was prepared by a known method.[2] Half-wave oxidation potential of **1** was measured in MeCN and the E_{ox} was determined to be -0.71 V (*vs.* SCE). The value showed good one-electron donating nature of **1** in comparison with that of di-*p*-anisylethene. Upon mixing **1** with TCNE (1/1 molar ratio) in CH_2Cl_2 at rt, the color of the mixture changed gradually from pale yellow to red. When the mixture is allowed to stand for several days, the color was changed again to pale yellow. Concentration of the reaction mixture gave colorless crystalline material (mp 164-166 ^{0}C, from cyclohexane). The structure was determined unequivocally by X-ray crystallography to be 4-*p*-anisyl-2-(di-*p*-anisylmethylene)-1,1-dicyano-7-methoxy-1,2-dihydronaphthalene (**2**). The detailed structure and the reaction mechanism will be discussed in the presentation.



An = *p*-CH_3O-C_6H_4

TCNE

1 **2**