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CHARGE-TRANSFER REACTION OF BUTATRIENE: FORMATION OF DIHYDRONAPHTHALENE DERIVATIVE

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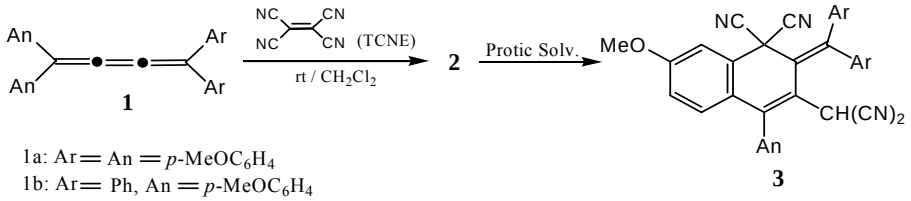
The charge-transfer reaction of tetraarylbutatriene **1** with tetracyanoethene (TCNE) in dichloromethane at room temperature was studied and we found a novel addition reaction. A red crystalline material **2** was isolated as an intermediate product which is converted slowly into dihydronaphthalene derivative **3** in dichloromethane but rapidly in protic solvent. The structure of the compounds was determined by X-ray crystallography. The detailed structure and the plausible reaction mechanism have also been discussed.

Keywords: Butatriene; charge-transfer; mechanism; tetracyanoethene

1. Introduction

Single electron transfer chemistry of C=C double bonds (both isolated and conjugated) has been studied extensively so far. By contrast, the chemistry of the congener, a cumulated C=C double bond, has not been investigated so much. Literature survey reveals very few information on the reaction of cumulated double bonds. Johnson and his coworkers[1] studied previously the photochemical electron transfer of allene-propyne system. This is likely to be the only related work of the study field. We have studied, therefore, the charge-transfer reaction of teteraarylbutatriene (**1**) with tetracyanoethene (TCNE), a strong electron accepting molecule (scheme 1). During the course of our study on exploring the new reactions of organic cation radicals[2~10], we found a novel reaction of **1**[11] with TCNE to give finally dihydronaphthalene derivative.



1a: Ar = An = *p*-$MeOC_6H_4$
1b: Ar = Ph, An = *p*-$MeOC_6H_4$
1c: Ar = *p*-ClC_6H_4, An = *p*-$MeOC_6H_4$

Scheme 1

2. Discussion

Tetraarylbutatriene **1** (**1a**; Ar = *p*-$MeOC_6H_4$) was prepared according to a known procedure[11] and TCNE was purified by sublimation. The half-wave oxidation potential of **1a** was measured in MeCN and $E_{ox.}$ of **1a** was determined to be -0.71 V (*vs*. SCE). The value showed good one-electron donating nature of **1a** in comparison with that of 1,1-di-*p*-anisylethene. At room temperature upon mixing of **1** with TCNE (2/1 molar ratio) in CH_2Cl_2 and maintaining an inert atmosphere, the color of the mixture was changed gradually from pale yellow to red.

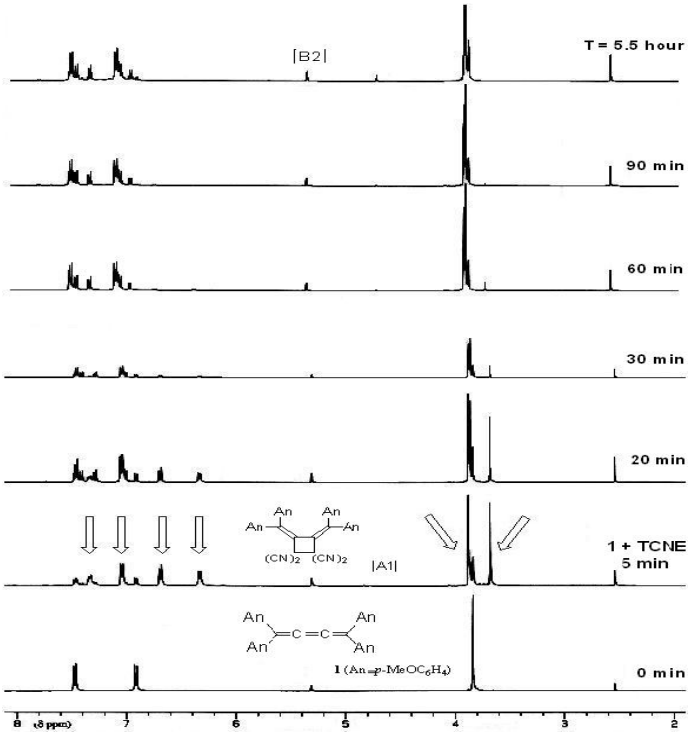


Fig. 1. Time-dependent ^{1}H NMR spectra of the reaction of **1a** with TCNE in CD_2Cl_2

When it was allowed to stand for several days in CH_2Cl_2 (but rapidly in CH_3OH) the color was again changed to yellow. This unique reaction was monitored by Thin Layer Chromatography (silica gel), UV-VIS spectra and time-dependent ^{1}H NMR spectra. These techniques revealed that the reaction proceeds via multiple intermediates. Intermediate [A1] was formed at the early stage of reaction which was gradually converted to [B1]. However, intermediate [B1] was transformed to [B2; **2**]. Time-dependent ^{1}H NMR spectra of the reaction mixture measured in CD_2Cl_2 demonstrated the reaction profile (Figure 1). Upon mixing of **1a** and TCNE, the signals due to **1a** disappeared quickly and four doublets appeared at the aromatic region. Then the signals disappeared again within 30 min and instead, two equivalent and two unequivalent aromatic protons appeared. The red-colored material could

be easily obtained by evaporation of the solvent at this stage and it was recrystallized from 20% EtOAc in cyclohexane to give red needles [B2; product **2**] and the X-ray structure elucidation is now undergoing.

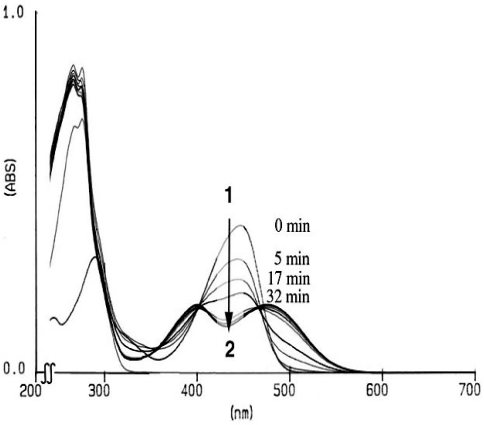


Fig. 2. Time-dependence of the UV-VIS spectral change of the reaction mixture (1a) with TCNE in CH_2Cl_2

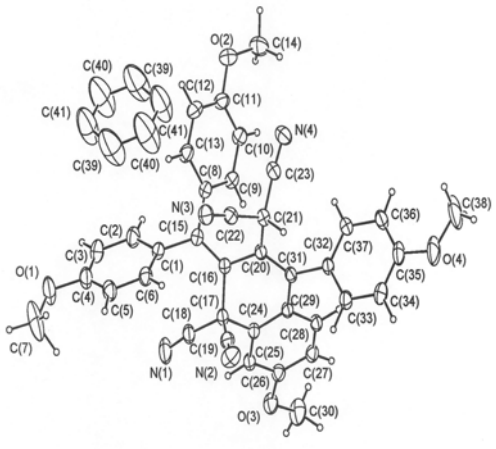
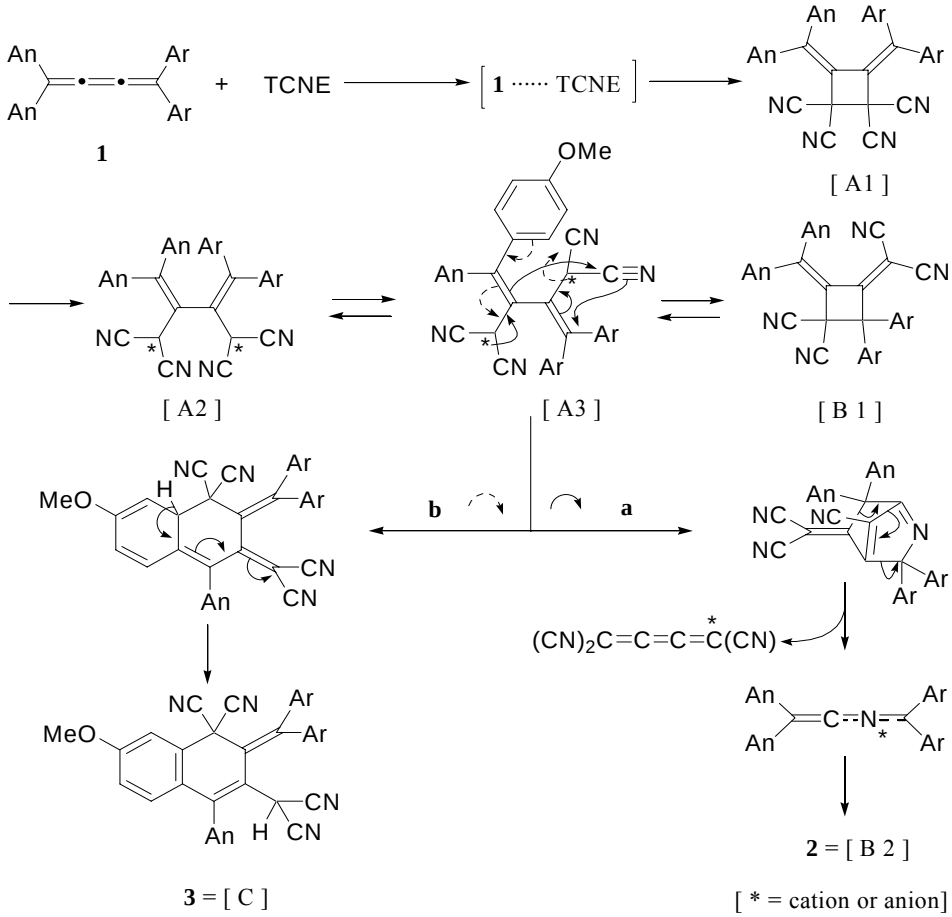


Fig. 3. ORTEP Drawing of the compound **3a**

Time-dependent UV-VIS spectroscopy demonstrated the clear transformation profile with isobestic points in CH_2Cl_2 (Figure 2). The final spectrum is that of the compound **2**. Although the compound **2** is stable under usual laboratory conditions, a solution of **2** (especially in a protic solvent like MeOH) turned to another product **3** within a few hours. The structure of **3** was determined unequivocally by X-ray crystallography study. The single crystal obtained by recrystallization from 20% EtOAc in cyclohexane showed a unique structure shown in Figure 3. The name of the compound **3a** is 4-*p*-anisyl-2-(di-*p*-anisylmethylene)-1,1-dicyano-3-dicyanomethyl-7-methoxy-1,2-dihydronaphthalene.

3. Reaction Mechanism

A plausible reaction mechanism is proposed here on the basis of the products and the reaction intermediates afforded by the reaction of **1** with TCNE. Scheme 2 summarizes the mechanism in which intermediate [A1] is formed after addition of TCNE to **1** which can be converted to [A2] and then to [A3] by rotation of the central C-C bonding. The zwitterionic species [A3] after facing intramolecular nucleophilic attack (path **a**) at the cyano carbon (C≡N) and simultaneously to alkenic carbon by nitrogen, can further be possibly converted to bicyclic compound.



Scheme 2

As a result, a bicyclic compound is expected to be formed. After elimination of $(CN)_2C{=}C{=}C{=}{*}C(CN)$ and subsequent dimerization afforded to the compound **2**. In presence of protic solvent the zwitterionic species [A3] can be further transformed to **3** by another pathway (path **b**) with concomitant hydrogen migration.

4. Experimental Section

To a CH_2Cl_2 solution (20 ml) containing 55 mg (0.12 mmol) of tetraanisylbutatriene **1a**, was added at once 16 mg (0.12 mmol) of TCNE in the same solvent (10 ml) at room temperature. The mixture was allowed to stir magnetically for 3.5 hrs and the color of the mixture turned from pale yellow to red. Evaporation of the solvent afforded 79 mg of red crystals. The materials were purified by recrystallization from EtOAc—cyclohexane (1/4 vol. ratio) to give red needles (**2a**, mp 142-143^{0}C). Then **2a** was further converted to dihydronaphthalene derivative **3a** by dissolving **2a** in MeOH. The structures of the compounds were determined by the extensive use of X-ray crystallography data and herein the data of **3a** are shown.

Compound **3a**: mp. 164 -166^{0}C (decomp.).
X-ray data: Triclinic; $C_{38}H_{28}O_4N_4$, Space group P-1 (#2); V = 1801.1(3) Å^3; Z = 2; D_{calcd} = 1.10 g cm^{-3}; R = 0.0622; R_w = 0.0636.
Yield: 82% (recrystallized from cyclohexane)
Anal. Calcd for $C_{38}H_{28}O_4N_4$: C, 75.69; H, 4.57; N, 9.02%; Found: C, 75.48; H, 4.67; N, 9.27%.
UV λ_{max} nm (MeCN, log ε): 199 (4.87), 229 (4.49), 275 (4.14), 367 (4.10).
MS (70 eV) m/e (%): 604 (M^+, 67), 578 (M^+-CN, 100), 552 (M^+-2CN, 11), 496 (M^+-3CN-OCH_2, 27), 469 (M^+-4CN-OMe, 54), 446 (M^+-TCNE-OMe, 4).
^{1}H NMR (400 MHz, $CDCl_3$) δ_{ppm}: 6.8—7.4 (m, 16H), 3.91 (s, 1H), 3.90 (s, 3H, OMe), 3.87 (s, 3H, OMe), 3.86 (s, 3H, OMe), 3.85 (s, 3H, OMe).
^{13}C NMR (100 MHz , $CDCl_3$) δ_{ppm}: 27.57, 55.37 (2 OMe), 55.55 (OMe), 55.71 (OMe), 112.77, 114.27, 114.45, 114.55, 114.77, 115.26, 115.44, 117.51, 117.97, 126.27, 126.36, 128.21, 130.53, 130.79, 131.08, 132.45, 132.83, 133.09, 134.10, 145.89, 152.58, 160.61, 161.60, 161.88, 163.08.

5. Conclusion

We found a novel addition reaction of tetraarylbutatriene **1** with tetracyanoethene (TCNE) to give **2** and it is converted to dihydronaphthalene derivative **3** especially in a protic media. The reaction is unique because of the presence of multiple intermediates. One of the intermediates was isolated and the structure elucidation of that colored material is now in progress. Exploration of the chemistry of charge transfer reaction of cumulated double bond (*e.g.* allene) is also continuing.

Acknowledgments

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