CH_2Cl_2 . The organic fraction was dried (K_2CO_3) and concentrated in vacuo. The resulting oily residue was crystallized from CH_2Cl_2 /ether to yield 78 mg (55%) of azo dioxide 14: mp 115-117 °C dec; IR (KBr) 3325, 1483, 1447, 1418, 1392, 1208, 952, 777, 768 cm⁻¹; NMR (CDCl₃) & 7.33-7.05 (m, 8), 4.02 (br s, 4), 1.80 (br s, 1); mass spectrum (70 eV), m/e (relative intensity) 237 (23.9), 220 (67.6), 180 (45.1), 152 (14.85), 118 (100.0), 89 (57.0), 77 (36.0), 65 (56.5), 51 (40.3), 39 (61.8); UV max (95% C₂H₅OH) 278 nm (log € 3.98), 208 (4.26).

Anal. Calcd for C14H13N3O2: C, 65.87; H, 5.13; N, 16.46. Found: C, 66.09; H, 5.02; N, 16.18.

Trifluoroacetate salt 13 was prepared in a manner similar to that for the "free" amine. The residue after removal of the trifluoroacetic acid was taken up in THF (dry) and cooled to give white crystals: 80% yield; mp 99-100 °C; IR (KBr) 3440 (br), 1600, 1455, 1423, 1397, 1205, 1180, 1135, 955, 772, 737 cm⁻¹; NMR (DCO_2D) 7.93-7.40 (m, 8), 5.08-4.35 (A₂B₂, 4, J = 14 Hz); mass spectrum (70 eV), m/e (relative intensity) 237 (11.2), 220 (32.2), 205 (10.2), 180 (22.0), 152 (7.5), 118 (39.9), 89 (31.3), 77 (20.8), 69 (52.6), 51 (61.7), 45 (100.0).

2-(o-Nitrosobenzyl)indazole (15). A solution of 39 mg of 14 in 3 mL of CH_2Cl_2 was refluxed under N_2 for 2 h. The solution was concentrated in vacuo, and the resulting oil was taken up in a small amount of CH_2Cl_2 , placed on an alumina preparative thick-layer plate, and eluted with 75% ether/25% pentane (R_f 0.8) to give 31 mg of a green oil which was crystallized from CCl₄-pentane: pale yellow powder; mp 108.5-109 °C; IR (CHCl₃) 1632, 1505, 1437, 1312, 1170, 1159, 1140, 1087 cm⁻¹; IR (KBr) 1630,

1528, 1270, 1212, 1172, 1150, 1010, 805, 769, 760, 748 cm⁻¹; NMR $(CD_3COCD_3) \delta 8.46$ (s, 1), 7.96–7.08 (m, 7), 7.01 (s, 2), 6.46–6.26 (d, 1, J = 8, 1 Hz); mass spectrum (70 eV), m/e (relative intensity) 237 (30.4), 220 (89.6), 205 (24.1), 180 (49.8), 152 (16.1), 118 (100.0), 103 (33.3), 89 (57.2), 57 (54.5), 43 (54.2); UV max (95% $C_{24,5}OH$) 285 nm (log ϵ 4.10), 220 (4.15); UV min 240 (log ϵ 3.4); ¹³C (C-D₃COCD₃) δ 160.4,²⁴ 150.1,²⁴ 140.5,²⁴ 137.9, 131.8, 129.3, 126.4, 125.0, 122.2, 121.4, 118.3, 107.3, 53.0; high-resolution mass spectrum, m/e (relative intensity, composition, calcd m/e) 89.039 $C_7H_6N_{2}$, 118.053), 180.079 (24.4, $C_{13}H_{10}N$, 180.081), 220.084 (68.5, $C_{14}H_{10}N_3$, 220.087); calcd for $C_{14}H_{11}N_3O$ (M⁺) m/e 237.090, found m/e 237.088 (relative intensity 69.1).

Registry No. 1, 16968-19-7; 2, 34124-14-6; 3, 40754-26-5; 4, 74808-60-9; 6, 42467-41-4; 7, 74808-61-0; 8, 74808-62-1; 9, 74808-63-2; 10a, 74808-64-3; 10b, 74808-65-4; 11a, 74808-66-5; 11b, 74808-67-6; 12a, 74808-68-7; 12b, 74808-69-8; 13, 74808-71-2; 14, 74808-70-1; 15, 74808-72-3; o-nitrobenzyl alcohol, 612-25-9; o-nitrobenzyl iodide, 29872-21-7; o-nitrobenzylamine, 1904-78-5; o-nitrobenzaldehyde, 552-89-6; o-nitro-N-(o-nitrobenzylidene)benzylamine, 74808-73-4; methyl chloroformate, 79-22-1; 6H-5,7-dihydrodibenzo[c,h]-1,2,6triazine N-oxide, 74808-74-5; di-tert-butyl dicarbonate, 24424-99-5; nitrosocyclohexane, 2696-95-9; 1-nitroso-2,4,6-tribromobenzene, 45860-18-2; 1-nitroso-2,4,6-trimethylbenzene, 1196-12-9; p-nitrosotoluene, 623-11-0; nitrosobenzene, 586-96-9.

(24) Quaternary carbon.

Ene-Type Reaction through the Intermediacy of the 1,4-Dipolar Ion in the Reaction of Tetracyanoethylene with Nucleophilic Double Bonds in Liquid Sulfur Dioxide

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Received May 12, 1980

The expected [2 + 2] cycloadduct from the reaction of tetracyanoethylene with 1-methoxycyclohexene in liquid sulfur dioxide underwent a previously unrecognized reaction to give 1-methoxy-6-(1,1,2,2-tetracyanoethyl)cyclohexene. Further isomerization of this ene-type product with sulfur dioxide gave the isomeric 1-methoxy-2-(1,1,2,2-tetracyanoethyl)cyclohexene. The [2+2] cycloadduct is therefore a kinetic product which exists in equilibrium with the 1,4-dipolar ion precursor. Under thermodynamic conditions the dipolar ion provides a more stable ene-type product, the isomeric enol ether, and small amounts of 1,2,3,4,5,6,7,8,9,10-decahydro-8a-methoxy-9,9,10,10-tetracyanophenanthrene and 1,1-dimethoxy-2-(1,1,2,2-tetracyanoethyl)cyclohexane. The latter two products are the result of trapping of the dipolar ion with 1-methoxycyclohexene and methanol, respectively. Under similar conditions, cyclohexanone and tetracyanoethylene in liquid sulfur dioxide gave 2-(1,1,2,2-tetracyanoethyl)cyclohexanone.

Unlike typical internally stabilized heteroallyl 1,3-dipolar ions,¹ the dipolar ions in which charges are separated by an sp³-hybridized carbon atom possess electrophilic and nucleophilic ends and react with appropriate dipolarophiles with a predictable orientation.² Recently, we reported that the 1,3-dipolar ions, resulting from the electrophilic attack of nitrosonium ion on nucleophilic double bonds of trisubstituted olefins as well as of certain enols, could be trapped by a carbonyl group of ketones and aldehydes to give novel heterocyclic structures.³ A different type of 1,3-dipolar ion, generated by the reaction of sulfur dioxide with an enol ether, could be trapped by the enol ether itself.² Surprisingly, more detailed investigation of the behavior of nucleophilic double bonds in liquid sulfur dioxide revealed that the corresponding dipolar ions, although present in too low concentration to be detected spectroscopically, had a rich chemistry of their own.²⁻⁶ It became evident that the initially formed π complexes of sulfur dioxide with a typical olefin would isomerize to the dipolar σ complex (albeit short-lived) only if the positive charge in the σ complex could develop on a tertiary carbon atom.⁴ The dipolar ions were in equilibrium with the isomeric allylic sulfinic acids, formed reversibly by the abstraction of the allylic hydrogens by the negative charge of the dipolar ion. This facile intramolecular hydrogen abstraction, resembling an ene reaction, provided a basis

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for the development of a simple regiospecific deuteration of trisubstituted olefins.⁵ The allylic sulfinic acids, just as their 1,3-dipolar precursors, do not accumulate during the reaction to any spectroscopically significant concentration.⁷ Instead, once formed they undergo apparently very efficient 1,3-thiaallylic rearrangement⁸ to provide the isomeric allylic sulfinic acids. A "retro-ene" reaction generates the isomeric 1,3-dipolar ion, which after disociation of sulfur dioxide affords the isomerized olefin.⁴ The isomerization of β -pinene to α -pinene, without formation of *p*-menthadienes, illustrates the unique feature of this previously unrecognized kinetic pathway for the thermodynamic isomerization of trisubstituted olefins.⁴

Clearly, the entire reaction sequence owes its efficiency to the ability of intermediate 1,3-dipolar ions to undergo facile isomerization to allylic sulfinic acids. This raises an interesting possibility that even isolated "cycloadducts" in certain "cycloaddition" reactions which are known to involve a discreet dipolar intermediate could be, in fact, only products of kinetic transformation of the intermediate dipolar ions. In other words, is it possible that such dipolar ions under thermodynamic conditions could undergo a similar hydrogen abstraction to give an open-chain adduct rather than the actually observed cycloadduct?⁹ We shall present conclusive evidence that the [2 + 2] cycloadduct from the reaction of tetracvanoethylene with cyclohexanone enol ether is indeed only a product of the kinetic transformation of the initially formed 1,4-dipolar ion. Moreover, even the 1,4-dipolar ion resulting from the reaction of the cyclohexanone enol itself with tetracyanoethylene behaved in an analogous manner and provided 2-(1,1,2,2-tetracyanoethyl)cyclohexanone as a thermodynamic reaction product.

Results and Discussion

(1) Reaction of 1-Methoxycyclohexene with Tetracyanoethylene. Abundant experimental evidence indicates that the [2 + 2] cycloadducts from reaction of tetracyanoethylene with enol ethers are formed by an intramolecular cyclization of the corresponding 1,4-dipolar ion intermediates.¹⁰⁻¹⁴ The intermediate dipolar ions were successfully trapped by reactive dipolarophiles¹⁴ such as aldehydes, ketones, and Schiff bases although there was no evidence that the dipolar ion could be intercepted by the nucleophilic double bond of the enol ether itself.

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Reaction of 1-methoxycyclohexene (1) with tetracyanoethylene (TCNE) either in methylene chloride or in acetonitrile gave the expected [2 + 2] cycloadduct 1-methoxy-7,7,8,8-tetracyano[4.2.0]bicyclooctane (2) quantitatively (eq 1). While the cycloadduct 2 was completely



stable in both of these solvents, addition of methanol to either of the two solutions gave 1,1-dimethoxy-2-(1,1,2,2)tetracyanoethyl)cyclohexane (3) cleanly (eq 2). Reaction



of the enol ether 1 with TCNE in liquid sulfur dioxide at -20 °C also gave cycloadduct 2. It appears that the reaction occurred instantaneously and the product can be isolated in a quantitative yield by a simple evaporation of the solvent. However, when the reaction solution was left overnight at room temperature, the cycloadduct underwent isomerization to give 1-methoxy-6-(1,1,2,2-tetracyano-ethyl)cyclohexene (4), 1-methoxy-2-(1,1,2,2-tetracyano-ethyl)cyclohexene (5), 1,2,3,4,5,6,7,8,9,10-decahydro-8a-methoxy-9,9,10,10-tetracyanophenanthrene (6), and the ketal 3, in 30%, 60%, 5%, and 5% yields, respectively. The same results were also obtained when the isolated cycloadduct 2 was redissolved in liquid sulfur dioxide and kept at room temperature overnight (eq 3). The tetra-



cyanophenanthrene 6 was prepared independently in quantitative yield by the reaction of TCNE with diene² 7 generated in situ from sulfone² 8 in a melt with TCNE at 105 °C (eq 4). Similarly, addition of methanol to a solution of either 4 or 5 in liquid sulfur dioxide gave the ketal 3 quantitatively.



⁽⁷⁾ Recently, Raasch and Smart were able to isolate an allylic sulfinic acid that was produced by reaction of sulfur dioxide with a particular unsaturated system. M. S. Raasch and B. E. Smart, J. Am. Chem. Soc., 101, 7733 (1979).



All experimental facts indicate that the 1,4-dipolar ion A, formed by the initial reaction of TCNE with the double bond of the enol ether, is a common intermediate in all transformations (Scheme I).

In accordance with the mechanistic scheme, the ketal 3 was formed in an equal amount with the tetracyanophenanthrene 6. Evidently, methanol eliminated in the formation of 6 is trapped by the dipolar ion A to give 3. The relative rates of disappearance and appearance of the methoxy groups signals of the cycloadduct 2 and isomeric enol ethers 4 and 5 in sulfur dioxide solution indicated that 5 is formed from 4 and not from A. The observed ratio of 4/5 probably does not reflect the thermodynamic stabilities of the two enol ethers. Earlier work has demonstrated that the isomerization of olefins in liquid sulfur dioxide was characterized by a large negative entropy of activation.⁴ As a consequence, the rates of isomerization were only slightly increased at higher temperatures.⁴ On this basis, one would expect that the relative rate of formation of the enol ether 4 from A would be more affected by higher temperature than the rate of isomerization of 4 into 5 by sulfur dioxide. Indeed, at 40 °C, a solution of 2 in liquid sulfur dioxide gave almost exclusively 4 (85-90% yield) before significant isomerization of 4 to 5 was detected. These observations notwithstanding, it should not be construed that A cannot isomerize to 5 directly; however, for the sake of simplicity in Scheme I and for conformation with the experimental observations, a direct equilibrium between 5 and A in Scheme I is omitted.

(2) Reaction of Cyclohexanone with Tetracyanoethylene in Liquid Sulfur dioxide. The efficient reaction of TCNE with cyclohexanone enol ether 1 prompted us to investigate whether TCNE could react with the double bond of cyclohexanone enol present in equilibrium with the ketone in liquid sulfur dioxide.¹⁶

A solution of equimolar quantities of cyclohexanone and tetracyanoethylene in liquid sulfur dioxide was left overnight at room temperature in a pressure bottle. Evaporation of the sulfur dioxide gave a tan solid which according to NMR and IR spectra was 2-(1,1,2,2-tetracyanoethyl)cyclohexanone (9, eq 5). When the reaction was carried



(16) A catalyzed reaction of ketones with TCNE was described by R. E. Heckert, E. L. Little, and C. G. Krespan, J. Am. Chem. Soc., 80, 2783 (1958).

out in an NMR tube, the progress of the reaction could be followed by the appearance of tertiary proton at δ 5.32 on the carbon bearing the cyano groups. Since the NMR spectrum showed no indication of formation of another product(s), it appears, perhaps not surprisingly, that the intramolecular cyclization to the bicyclic tertiary alcohol analogous to 2 is far less efficient than the intramolecular hydrogen abstraction leading to 9.

(3) Role of Liquid Sulfur Dioxide.^{15,17,18} Sulfur dioxide preferentially solvates negatively charged species, and it "reacts" even with such weak bases as ethers or olefins.⁴ This electrophilic character makes sulfur dioxide an excellent solvent for electrophilic addition reactions.^{3,17} Presumably, effective solvation of the negatively charged counterion of the electrophilic reagent leaves the electrophile itself unsolvated and therefore more reactive. It is less appreciated that sulfur dioxide also exerts the same effect on the reaction intermediates resulting from the attack of an electrophile on a double bond of a substrate. In liquid sulfur dioxide, a positive charge on such a dipolar ion intermediate would weaken the allylic C-H bonds, through an overlap of the carbon-hydrogen orbitals with the empty sp² orbital on the positive carbon, more effectively than in a nucleophilic solvent like ether. In nucleophilic solvents, a reaction of the solvent molecules with the empty sp² orbital at the positive center of the dipolar intermediates would significantly reduce the reactivity of the allylic hydrogens. Consequently, an intramolecular abstraction of these hydrogens by the negatively charged end of the dipolar intermediate should occur more readily in sulfur dioxide than in other typical organic solvents. The observed transformations of the dipolar intermediates in reactions of cyclohexanone enol ether 1, and cyclohexanone with tetracyanoethyene, provide further examples of the enhanced reactivities of these intermediates in liquid sulfur dioxide.

Conclusions

The [2 + 2] cycloadduct formed by the reaction of tetracyanoethylene and 1-methoxycyclohexene in liquid sulfur dioxide is only a kinetic product. Under thermodynamic conditions the intermediate dipolar ion undergoes an ene-type reaction to give the open-chain adduct which also can react further. In reaction of cyclohexanone with tetracyanoethylene in liquid sulfur dioxide, the corresponding dipolar ion does not give a "cycloadduct" at all. Instead, a proton rearrangement affords the 2-(1,1,2,2-

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tetracyanoethyl)cyclohexanone.

It appears that sulfur dioxide plays an important role in these reactions. Evidently, it prevents stabilization of positive charge in the dipolar ion intermediate through solvation, which, in effect, enhances the reactivity of the corresponding allylic hydrogens, making the observed transformations possible.

Experimental Section

Melting points are uncorrected. The ¹H NMR spectra and the infrared spectra were recorded, respectively, on Varian T-60 and Perkin-Elmer 128 spectrometers.

All the solvents were distilled prior to use. Matheson's high purity sulfur dioxide was dried over molecular sieves. Commercial TCNE was purified by recrystallization (chlorobenzene). 1-Methoxycyclohexene (1) was prepared by known methods.¹⁹

1-Methoxy-7,7,8,8-tetracyanobicyclo[4.2.0]octane (2). TCNE (1.41 g 11 mmol) dissolved in 100 mL of dry methylene chloride was treated with 1.12 g (10 mmol) of 1 at room temperature. The initial violet color of the solution persists for ~1 min. The reaction mixture was stirred for 20 min, after which it was concentrated to yield 2.5 g of a pale yellow solid. Recrystallization (1:1 methylene chloride-pentane) yielded 1.3 g (54%) of 2 as a colorless solid: mp 117-119 °C, ¹H NMR (CDCl₃) δ 3.43 (s, 3 H), 2.5 (br m, 1 H), 1.5-2.3 (br m, 8 H); mass spectrum (CI, methane), m/e 241 (MH⁺), 157, 112 (base). Anal. (C₁₃-H₁₂N₄O) C, H, N. Identical results were also obtained in acetonitrile.

1,1-Dimethoxy-2-(1,1,2,2-tetracyanoethyl)cyclohexane (3). TCNE (1.41 g, 11 mmol) dissolved in 100 mL of methylene chloride was treated with 1.12 g (10 mmol) of 1 and the mixture stirred for 1 week under nitrogen at room temperature. A 5-mL sample was withdrawn and concentrated to yield 0.12 g of pale yellow solid. The NMR and IR spectra showed that the product was 2. The remainder of the reaction mixture was treated with 0.5 mL of anhydrous methanol and stirred for 5 min. On concentration, 2.3 g of pale yellow solid was obtained. The NMR spectrum showed that 2 has been converted to the ketal 3. Recrystallization (ether) yielded colorless crystals: mp 128.5–130 °C; ¹H NMR (CDCl₃) δ 5.37 (s, 1 H), 3.37 (d, 6 H), 1.67–2.6 (br m, 9 H); mass spectrum (CI, methane), m/e 273 (MH⁺). Anal. (C₁₄H₁₆N₄O₂) C, H, N. Identical results were obtained by using acetonitrile as the solvent.

Reaction of TCNE with 1 in Liquid Sulfur Dioxide. (a) At -20 °C. TCNE (1.41 g, 11 mmol) was placed in a 100-mL three-necked flask provided with a magnetic stirrer, a condenser, and a dry ice/acetone bath maintained at -20 °C. Sulfur dioxide (50 mL) was distilled in, and after the TCNE had dissolved, 1.12 g (10 mmol) of 1 was added. A pale yellow color was observed. After being stirred for 5 min, the reaction mixture was quenched with 50 mL of anhydrous ether. Evaporation of the solvent gave 2.49 g of the cycloadduct 2.

(b) At Room Temperature. A 200-mL Fisher-Porter pressure bottle containing 11 mmol of TCNE (1.41 g) was cooled to -20°C. Sulfur dioxide (50 mL) was distilled in. After the TCNE had dissolved, 1.12 g (10 mmol) of 1 was added. The bottle was closed and the mixture stirred at room temperature for 16-20 h. The bottle was cooled to -20 °C and quenched with 50 mL of anhydrous ether. Evaporation of the solution gave 2.6 g of reddish semisolid. GLC analysis (3% OV-1 on Chromosorb W, 6-ft column) showed the presence of four components. One gram of the product was separated by preparative TLC (silica gel) using a 4:1 pentane-ethyl acetate solvent system. The four components were obtained in the following order. (a) 1-Methoxy-6-(1,1,2,2-tetracyanoethyl)cyclohexene (4): 0.29 g (30%); pale yellow oil (decomposes on distillation); ¹H NMR ($CDCl_3$) δ 5.43 (s, 1 H), 5.17 (t, 1 H), 3.62 (s, 3 H), 3.2 (m, 1 H), 1.33-2.67 (br d, 6 H); mass spectrum (CI, methane), m/e 241 (MH⁺) 111 (base). Anal. $(C_{13}H_{12}N_4O)$ C, H, N. (b) 1-Methoxy-2-(1,1,2,2-tetracyanoethyl)cyclohexene (5): 0.59 g (60%); colorless solid recrystallized from methylene chloride-pentane; mp 145-146 °C; ¹H NMR (CDCl₃) δ 5.11 (s, 1 H), 3.75 (s, 3 H), 1.67–2.80 (br d, 8 H); mass spectrum (CI, methane), m/e 241 (MH⁺) 175 (base). Anal. (C₁₃H₁₂N₄O) C, H, N. (c) Ketal 3 (0.06 g, 5% yield) was identical with the sample obtained earlier. (d) 1,2,3,4,5,6,7,8,9,10-Decahydro-8a-methoxy-9,9,10,10-tetracyanophenanthrene (6): white solid; 0.065 g (5%); mp 138-139 °C (ether); ¹H NMR (CDCl₃) δ 3.57 (s, 3 H), 1-3.27 (br m, 17 H); mass spectrum (CI, methane), m/e 321 (MH⁺). Anal. (C₁₉H₂₀-N₄O) Č, H, N.

Identical results were obtained when a solution of the cycloadduct 2 in liquid sulfur dioxide was kept overnight at room temperature.

Reaction of TCNE with 1 in Liquid Sulfur Dioxide at 40 °C. The experiment was carried out as described earlier in a Fischer-Porter bottle in an oil bath at 40 °C for 21 h. The bottle was then cooled to -20 °C and the contents quenched with 50 mL of anhydrous ether. Evaporation of solvents gave 2.56 g of yellow viscous liquid which accordidng to the NMR was a mixture of 2 (10-15%) and 4 (85-90%).

Heating a solution of 2 in liquid sulfur dioxide at 40 °C provided the enol ether 4 in 90% yield.

Tetracyanophenanthrene 6 from sulfone 8. A 5-mmol (1.28 g) sample of sulfone 8 (prepared according to the procedure described in ref 2) and TCNE (0.64 g, 5 mmol) were heated in a 35-mL, round-bottomed flask at 105 °C under nitrogen for 4 min. Sulfur dioxide bubbled out. Cooling provided 1.6 g of 6, mp 136.5-137.5 °C (from ether).

Reaction of 1 with TCNE in a Ratio of 2:1 in Liquid Sulfur Dioxide. TCNE (1.28 g 10 mmol) was dissolved in 50 mL of sulfur dioxide in a pressure bottle and treated with 2.2 g (20 mmol) of 1. Stirring at room temperature for 21 h yielded 3.6 g of reddish viscous liquid. The NMR spectrum of the crude product showed methoxy groups characteristic of the sulfone 8 precursor² and 3–6. From 100 mg of the product was isolated the tetracyanophenanthrene 6 in 30% yield (based on 1) by preparative TLC (silica gel) using a 4:1 pentane-ethyl acetate mixture.

2-(1,1,2,2-Tetracyanoethyl)cyclohexanone (9). TCNE (0.64 g, 5 mmol) and cyclohexanone (0.5 g, 5 mmol) were dissolved in 50 mL of sulfur dioxide in a Fisher-Porter bottle, and the mixture was stirred at room temperature overnight. A pale yellow color persisted during the course of the reaction. The reaction mixture was cooled to -20 °C and quenched with 100 mL of ether. On concentration, 1.1 g (95%) of tan compound 9 was obtained: mp 135-137 °C (acetone-hexane); IR (KBr) 1717 cm⁻¹ (C=O). ¹H NMR (CDCl₃) δ 5.32 (s, 1 H), 3.30 (br m, 1 H), 1.53-2.76 (br d, 8 H).

Registry No. 1, 931-57-7; **2**, 74966-58-8; **3**, 74966-59-9; **4**, 74966-60-2; **5**, 74966-61-3; **6**, 74966-62-4; **8**, 39190-58-4; **9**, 74966-63-5; TCNE, 670-54-2; cyclohexanone, 108-94-1.

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