January, 1985] © *1985 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 58, 385—386 (1985)*

Synthesis of 2,6,8-Trinitro-4*H*-cyclopenta[*def*]phenanthren-4-one as an Electron Acceptor

Masahiro MINABE,* Masaaki YOSHIDA, and Okitoshi KIMURA

Department of Industrial Chemistry, Faculty of Engineering, Utsunomiya University, Ishiicho, Utsunomiya 321

(Received May 23, 1984)

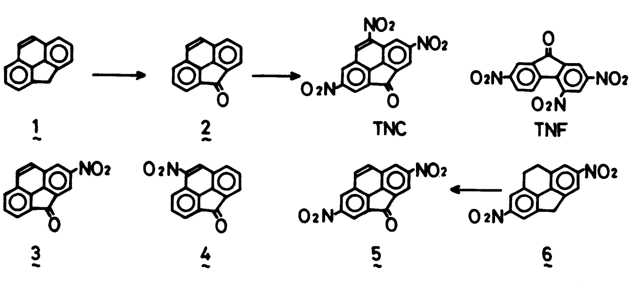
Synopsis. 2,6,8-Trinitro-4*H*-cyclopenta[*def*]phenanthren-4-one (TNC) was synthesized by the nitration of the parent ketone. TNC formed charge-transfer complexes with polycyclic aromatic hydrocarbons (PAH). The property of TNC as an electron acceptor was compared with that of 2,4,7-trinitro-9*H*-fluoren-9-one (TNF). TNC was found to be a better complexing agent than TNF.

Many mono- and disubstituted derivatives of 4*H*-cyclopenta[*def*]phenanthrene (**1**) have been synthesized by electrophilic substitution.[1] However, there are few reports relating to polysubstituted derivatives of **1**.[2] Since polynitro ketones of **1** could be expected to be good electron acceptors as 2,4,7-trinitro-9*H*-fluoren-9-one (TNF),[3] we investigated the preparation of a polynitro derivative of 4*H*-cyclopenta[*def*]phenanthren-4-one (**2**).[4]

The present paper deals with the synthesis of 2,6,8-trinitro-4*H*-cyclopenta[*def*]phenanthren-4-one (TNC) and with a comparison of the properties of TNC with those of TNF.

Nitration of **2** with nitric acid in sulfuric acid at 0—55 °C afforded TNC in 70% yield as light-yellow needles. The positions of nitro groups were confirmed by a stepwise synthesis: nitration of the 2-nitro ketone (**3**)[4] gave TNC that was also obtained by reaction of the isomeric 8-nitro ketone (**4**).[4] Moreover, TNC was obtained by the nitration of the 2,6-dinitro ketone (**5**) that was isolated by the oxidation of 2,6-dinitro-8,9-dihydro compound (**6**).[4]

Carbonyl absorption in the IR spectrum of TNC is observed at higher wavenumber than that of TNF, while absorptions of parent **2** and 9*H*-fluoren-9-one appear at the same position. The red shift of the maximum of TNC in the UV spectra from that of **1** is greater than the case between TNF[3a] and 9*H*-fluoren-9-one.



The cyclic voltammogram of TNC is very similar to that of TNF.[5—8] TNC and TNF both exhibit the first reversible one-electron reductions at −0.38 V and −0.48 V *vs.* SCE, respectively, the latter of which agrees well with the reported value.[5,6] These findings suggest that charge transfer in the case of TNC may occur easier than for the case of TNF.

The π-π charge-transfer complexes of TNC with some PAH were isolated as stable solids of 1:1 molar ratio (Table 1). The shift of the nitro absorptions to a long-wavelength region of the IR spectra of these complexes may be associated with the charge-transfer energy of each complex as the relation between TNF complexes and their transition energies.[9]

The ability of TNC to act as an electron acceptor was compared with that of TNF using the binding constant (B*) which was the reverse of the *B*-value proposed by Harvey and Halonen.[10] The *B*-value is defined as $(R_{f_I}-R_{f_{II}})\times 100/R_{f_I}$, where R_{f_I} is the R_f-value of any PAH on the usual thin-layer chromatograph, and $R_{f_{II}}$ is the R_f-value of the same PAH on a plate doped with an acceptor. The constant B^* (which is defined as $R_{f'_{II}}/R_{f_I}$) is determined by a comparison of the R_f-value ($R_{f'_{II}}$) of a given acceptor on a plate doped by a donor with the R_{f_I} of the same acceptor on the usual plate. A large B^*-value indicates a large equilibrium constant in the donor-acceptor interaction. Table 2 illustrates the comparison of the B^*-constant of TNC with that of TNF using the plate doped with 9*H*-fluorene (**7**) as an electron donor. This finding apparently suggests that TNC is superior to TNF as an electron acceptor.

The CT absorption spectrum of TNC with diethylamine (DEA) is illustrated along with that of TNF–

TABLE 2. BINDING CONSTANTS (B^*) OF TNC AND TNF

Compd	R_{f_I}	$R_{f'_{II}}$	B^*-value
TNC	0.37	0.46	1.24
TNF	0.42	0.47	1.12

TABLE 1. PROPERTIES OF CT COMPLEXES OF TNC WITH PAH

Donor	Yield / %	Mp θ_m/°C (dec)	Color	IR (KBr) cm^{-1} $\nu_{C=O}$	IR (KBr) cm^{-1} ν_{NO_2}
Phenanthrene	79	225—226	Yellow	1739	1537, 1530(s), 1335
7	88	211.0—211.5	Orange	1739	1537, 1335
1	89	240.0—240.5	Orange	1737	1544(s), 1530, 1337
Pyrene	87	291—292	Red	1740	1546, 1527, 1336

DEA in Fig. 1. A composit of the TNC–DEA system shows two maxima (450 and 560 nm). Also, the TNF–DEA curve has two maxima (520 and 630 nm) but the absorbance is less than that of the TNC complex. The formation constants (K) of these complexes were obtained at 25 °C by the Benesi-Hildebrand method:[11] K=1.88 l mol^{-1} for TNC at 560 nm and K=1.32 l mol^{-1} for TNF at 630 nm. The results suggest that TNC is a better complexing agent than TNF.

Experimental

All the melting points are uncorrected. The ^{1}H NMR, UV, and IR spectra were recorded on a Jeol JNM-C-60 HL, a Shimadzu UV-180, and a Jasco IRA-2 instrument, respectively. Satisfactory analytical data regarding the new compounds were obtained by elemental analyses (C, H, N, within ±0.3%) and a mass-spectra investigation.

Cyclic voltammograms were obtained with HMDE as the working electrode in aqueous dioxane (1:1 by volume) containing 50 mmol of $NaClO_4$. The solution was deoxygenated by bubbling for 30 min with dry nitrogen (99.999%).

Nitration of 2. To a solution of **2** (4.1 g, 20 mmol) in H_2SO_4 (d=1.84 g cm^{-3}, 20 ml) was added a mixed acid of HNO_3 (d=1.49 g cm^{-3}, 5 ml) and concd H_2SO_4 (5 ml) below 0 °C for 15 min. The mixture was stirred at that temperature for a period of 1 h followed by stirring at 55 °C for an additional 15 min. A precipitate, formed after adding the mixture to ice water (300 ml), was filtered and washed with water. It was then dried overnight at 60 °C and chromatographed on a Kieselguhr column (45 mmϕ, 25 cm) with benzene. The yellow eluate was concentrated to a small volume to give 4.75 g (70%) of TNC, as light-yellow needles from ethyl acetate: mp 237—239 °C (dec). IR (KBr): $\nu_{C=O}$ 1740, ν_{NO_2} 1551, 1528, 1360, and 1342 cm^{-1}. NMR (DMSO-d_6): δ= 8.62—8.68 (2H, m) and 9.36—9.45 (3H, m). UV$_{max}$ (EtOH): 207 (log ε 4.43), 266 (4.57), and 303 nm (4.23).

Oxime of TNC: mp 273.5—274.5 °C (dec). IR (KBr): ν_{OH} 3330, ν_{NO_2} 1544, 1536, and 1331 cm^{-1}. NMR (DMSO-d_6): δ=3.34 (1H, s, OH), 8.17 (1H, s), 8.42 (1H, s), 8.91 (1H, s), and 8.98—9.05 (2H, m). UV$_{max}$ ($CHCl_3$): 250 (4.51), 313 (4.37), 380 (3.72), and 403 nm (3.61). B*-value: 1.15.

Hydrazone: mp 255.5—256.5 °C (dec). IR (KBr): ν_{NH_2} 3450, 3330, 3240, ν_{NO_2} 1552, 1524, and 1336 cm^{-1}. NMR (DMSO-d_6): δ=7.69—7.84 (1H, m), 8.43—8.57 (2H, m), 8.61—8.75 (2H, m), and 9.20 (2H, s, NH_2). UV$_{max}$ ($CHCl_3$): 256 (4.41), 325 (4.34), and 416 nm (3.70). B*-value: 1.11.

Ethylene Dithioacetal: mp 310—311 °C (dec). IR (KBr): ν_{NO_2} 1543, 1529, and 1333 cm^{-1}. NMR (DMSO-d_6): δ=4.13 (4H, s), 8.95 (2H, s), 9.46 (1H, s), 9.59 (1H, s), and 9.68 (1H, s). UV$_{max}$ ($CHCl_3$): 245 (4.27) and 292 nm (4.46).

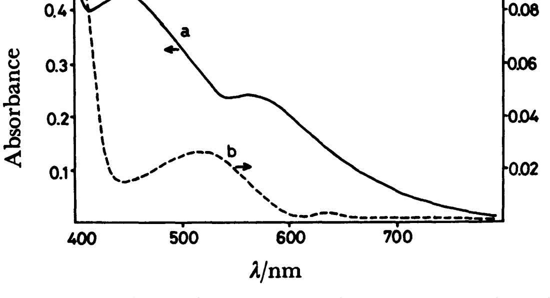


Fig. 1. CT absorption spectra of TNC and TNF with DEA in 1,2-dichloroethane at 25 °C.
(a): TNC(1.003×10^{-4} M, 1 M=1 mol dm^{-3})-DEA (4.71×10^{-1} M), (b): TNF(1.002×10^{-4} M)-DEA (4.71×10^{-1} M).

Nitration of 3. Ketone **3** (75 mg, 0.3 mmol) was nitrated with HNO_3 (0.05 ml) in H_2SO_4 (10 ml) at 55 °C for 15 min to give 65 mg (64%) of TNC.

Nitration of 4. A mixture of **4** (440 mg, 1.77 mmol), HNO_3 (0.5 ml), and H_2SO_4 (3.5 ml) was stirred at 70 °C for 1 h to afford TNC (175 mg, 28%).

Synthesis and Nitration of 5. A nitro compound **6** (564 mg, 2 mmol) in benzene (120 ml) was refluxed with MnO_2 (10 g) for 12 h, followed by chromatography on a Kieselguhr column with benzene. The yellow eluate gave 361 mg (61%) of **5**: mp 351—352 °C (dec). IR (KBr): $\nu_{C=O}$ 1724, ν_{NO_2} 1524, and 1342 cm^{-1}. UV$_{max}$ ($CHCl_3$): 262 (4.78), 312 (4.05), 322 (4.08), and 349 nm (3.74).

A mixture of **5** (60 mg, 0.2 mmol), HNO_3 (0.05 ml), and H_2SO_4 (10 ml) was maintained at 55 °C for 15 min to yield TNC (46 mg, 68%).

CT Complex of TNC with PAH. Typical Procedure. TNC (34 mg, 0.1 mmol) and **7** (17 mg, 0.1 mmol) were dissolved in a minimum quantity of HOAc with refluxing and allowed to cool to room temperature. A 45-mg (88%) of the complex was obtained as orange needles, mp 211.0—211.5 °C (dec).

Thin-layer Chromatography of Doped and Undoped Plates. TLC plates used in this experiment were purchased from E. Merck (TLC Silica gel 60; thickness 0.25 mm; 20×5 cm). The R_{f_I}-value was obtained using EtOAc/cyclohexane (1:2 by volume) as a developing solvent with the plate that was soaked in EtOAc/cyclohexane (1:2) for 5 min followed by drying at 60 °C for 20 min.

The $R_{f_{II}}$-value was determined on a plate that was soaked in a solution of EtOAc/cyclohexane (1:2) containing **7** (2%) for 5 min and dried at 60 °C for 20 min, using a developing solvent of EtOAc/cyclohexane (1:2) containing 2% of **7**. The value given in Table 2 is the average value for 10 runs.

The authors wish to thank Professor A. Yamada of the Technological University of Nagaoka for obtaining the cyclic voltammograms. Also, they thank Professor T. Toda for reading the manuscript.

References

1) For example: M. Yoshida, M. Kobayashi, M. Minabe, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **54**, 1159 (1981).

2) M. Yoshida, M. Minabe, W. Ookawa, and K. Suzuki, *Bull. Chem. Soc. Jpn.*, **56**, 1259 (1983).

3) a) M. Orchin and E. O. Woolfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946); b) M. Orchin, L. Reggel, and E. O. Woolfolk, *ibid.*, **69**, 1225 (1947).

4) M. Yoshida, S. Nagayama, M. Minabe, and K. Suzuki, *J. Org. Chem.*, **44**, 1915 (1979).

5) J. E. Kuder, J. M. Pochan, S. R. Turner, and D. F. Hinman, *J. Electrochem. Soc.*, **125**, 1750 (1978).

6) B. S. Ong, B. Keoshkerian, and T. I. Martin, *Chem. Ind. (London)*, **1984**, 110.

7) B. S. Ong, *J. Chem. Soc., Chem. Commun.*, **1984**, 266.

8) L. Ramaley and S. Gaul, *Can. J. Chem.*, **56**, 2381 (1978).

9) A. R. Lepley, *J. Am. Chem. Soc.*, **84**, 3577 (1962).

10) R. G. Harvey and M. Halonen, *J. Chromatogr.*, **25**, 294 (1966).

11) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).