Tetrahedron Letters,Vol.27,No.30,pp 3475-3478,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

π-ACCEPTOR INDUCED THERMAL REACTIONS: BOND CLEAVAGE REACTIONS

John H. Penn* and Ronald S. Smith
Department of Chemistry, West Virginia University
Morgantown, WV 26506-6045 USA

Summary: TCNQ, TCNQF4, and **DDQ** have been found to initiate unusual bond breakage reactions. Benzylphenyl sulfide (**BPS**) and benzylphenyl ether (**BPE**) undergo cleavage of their interaryl bonds while bibenzyl (**BB**) does not cleave the interaryl bond and forms only *trans*-stilbene (**TS**) when reacted under the same conditions.

The study of reactions induced by π-acceptor compounds has accelerated in recent years.[1] In our efforts to provide additional examples of this type of reactivity, we have investigated the reactions of benzylphenyl sulfide (**BPS**), benzylphenyl ether (**BPE**), and bibenzyl (**BB**) in the presence of π-acceptor compounds. **BPS, BPE,** and **BB** were chosen because of their relationship to the structure of coal which is thought to consist of a polymer of aryl groups with interconnecting alkyl chains.[2] Previous workers have used a variety of chemical techniques in order to induce bond cleavage of these compounds. Cleavage of these diaryl compounds has previously been accomplished by thermal activation at high temperatures,[3] and by reductive methods.[4] We reasoned that the charge-transfer character in electron-donor-acceptor (EDA) complexes might lead to bond weakening, and hence to thermally activated bond cleavage. In this communication, we report that bond cleavage can be induced in these diaryl compounds. The π-acceptor induced bond cleavage leads to lower molecular weight compounds at lower temperatures than those required without activation.

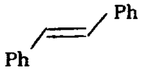
The volatile products formed by π-acceptor induced reactions are shown in equations 1-3. **BPS** reacts to form benzaldehyde (**BA**), benzyl acetamide (**BAC**), and phenyl disulfide (**PDS**). Similarly, **BPE** forms **BA**, phenol (**P**), and **BAC**. In contrast, **BB** forms only *trans*-stilbene (**TS**) under these reaction conditions. The identities of these products were established by GCMS and verified by independent HPLC analysis. In the case of **BPE** and **DDQ**, high resolution NMR was used to verify that the only products formed were those which are listed. The chemical yields of these reactions were established at low conversions to ensure that a minimum amount of secondary reactions occur (Table I). The necessity of low conversion experiments is shown by the yields for **BPE** and **TCNQF4** where the 30-45 % conversion runs give dramatically lower yields than the 8-13 % conversion runs.

In typical experiments, equimolar amounts (*ca.* 10^{-2} M) of the diaryl compound and the π-acceptor compound were dissolved together in freshly distilled acetonitrile (from CaH_2). After degassing by three freeze-pump-thaw cycles, the samples were sealed in base-washed

$$\underset{\textbf{BPS}}{PhCH_2SPh} \xrightarrow[CH_3CN]{\pi\text{-}A} \underset{\textbf{BA}}{PhCHO} + \underset{\textbf{PDS}}{PhSSPh} + \underset{\textbf{BAC}}{PhCH_2NHCOCH_3} \quad (1)$$

$$\underset{\textbf{BPE}}{PhCH_2OPh} \xrightarrow[CH_3CN]{\pi\text{-}A} \underset{\textbf{BA}}{PhCHO} + \underset{\textbf{P}}{PhOH} + \underset{\textbf{BAC}}{PhCH_2NHCOCH_3} \quad (2)$$

$$\underset{\textbf{BB}}{PhCH_2CH_2Ph} \xrightarrow[CH_3CN]{\pi\text{-}A} \quad (3)$$



TS

pyrex tubes,[5] and placed in an oil bath at the desired temperature, typically 200°C. The π-acceptor compounds used in this study were 7,7,8,8-tetracyanoquinodimethane (**TCNQ**), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (**TCNQF4**), and 2,3-dichloro-5,6-dicyanoquinone (**DDQ**). Several control experiments were performed to demonstrate that the reactions are due to the addition of the π-acceptor compounds and not to an external effect. The mixing of the donors and the acceptors was carefully performed in the dark in order to ensure that all reactions were thermal reactions, rather than photochemical reactions resulting from excitation of the charge-transfer absorption band. Irradiation of **TCNQ** and **TCNQF4** solutions using wavelengths suitable to excite the charge-transfer band of the complex or wavelengths suitable to excite the **TCNQ** derivative yielded no reaction of the starting material after several hours of irradiation. Photochemical reactions of the **DDQ** solutions were observed. Therefore, the analysis of the thermal reactions was corrected for the small amount (<5%) of reaction which occurred photochemically during the reaction preparation. In addition, no reaction was observed at 200°C when the π-acceptor compounds were not added to the reaction solution. Addition of stoichiometric amounts of HCl to solutions of **BB** or **BPS** gave no reactions on the time scale of the **TCNQF4** reactions. Addition of stoichiometric amounts of HCl to solutions of **BPE** yielded benzyl chloride, **P**, and **BAC** but at a rate which was ten times slower than the rate of reaction induced by **TCNQF4**.

The origin of the oxygen in the products formed from **BPE** and **BPS** was a matter of initial concern. **BA** had been identified as the product by GCMS spectroscopy and verified by HPLC retention times. This product was formed even when the tubes were opened carefully under a nitrogen atmosphere and injected directly onto the GC or GCMS. We suspect that the oxygen source is likely to be trace amounts of water in the acetonitrile, since acetonitrile is known to be hard to dry.[6] If the course of the reaction proceeds through the benzyl cation which is captured by water to yield benzyl alcohol, then benzyl alcohol would be expected as a reaction product. However, benzyl alcohol was not observed, but may react rapidly with the π-acceptor compounds. Consistent with this observation is the fact that independent

Product Yield Data[c]

Starting Material	π-Acceptor	Product			Temp (°C)	%Conv
		BA	**PDS**	**BAC**		
BPS	**DDQ**	97[a]	73[a]	<1[a]	200	60-70
	TCNQF4	96[a]	76[a]	18[b]	210	20-50
	TCNQ	92,[a] 76[b]	21,[a] 25[b]	<1,[a] 10[b]	200	7-12,[a] 10[b]
		BA	**P**	**BAC**		
BPE	**DDQ**	100[a]	85[a]	5[b]	200	20-60
	TCNQF4	28,[a] 25[b]	88,[a] 50[b]	48,[a] 5[b]	200	8-13,[a] 30-45[b]
	TCNQ	27[a]	70[a]	21[a]	200	3-22
			TS			
BB	**DDQ**		95[a]		200	10-30
	TCNQF4		98[a]		200	2-8
	TCNQ		28[a,b]		200	10-22,[a] 10[b]

a) Determined by GC Analysis Using *n*-Octyl Cyanide as an Internal Standard; b) Determined by HPLC Analysis Using Phthalide as an Internal Standard; c) Reported Yields are accurate to ± 10%.

experiments with benzyl alcohol and **TCNQF4** yielded **BA** in a very fast reaction at a temperature of 200°C.

An interesting facet of this reaction is that the rate of reaction increases as the reaction temperature increases. The reaction rates of **BPE** and **BPS** increase by a factor of 20 when the reaction temperature increases from 150-190°C. The reaction rate of **BB** increases by a factor of 10 over the same temperature range. This contrasts with expectations derived from the concentration of charge-transfer complex species present in solution. Charge-transfer complexes generally have a small negative enthalpy of formation but a large negative entropy of formation. One would anticipate that the concentration of complexed species would decrease as the temperature increases. Thus, the finding of an increased chemical reaction rate at higher temperatures is very suprising. This may imply that the thermal activation of chemical reactions by π-acceptor compounds is a very general phenomenon and not just a few isolated observations of reactivity in specially designed molecules.

At present, the reaction mechanism is unknown. Several precedented possibilities exist, including reactions originating directly from the charge-transfer complex[1b], bond cleavage from an initially formed radical cation[7], and hydride abstraction[8] followed by hydrolysis of the resulting hemiacetal. Work is currently in progress in our laboratories to indicate which is the predominant mechanism.

In summary, we have demonstrated that π-acceptor compounds can induce bond cleavage in certain compounds by thermal activation. We believe that the ability of π-acceptor compounds to induce chemical reactions is a general phenomenon. We are presently investigating the role of both partners in chemical reactions in order to extend the scope of the reaction.

Acknowledgement: We gratefully acknowledge the generous financial support of the West Virginia Energy Research Center which allowed us to complete this work. We also acknowledge the assistance of Masako Yagyu in the preliminary stages of the work.

References:

1. a) J.H. Penn, 188th ACS National Meeting, Philadelphia, PA, August 26–31, 1984, ORGN 220; b) D.F. Eaton, *J. Amer. Chem. Soc.*, **102**, 3278 (1980); c) P. Muller and D. Joly, *Helv. Chim. Acta*, **66**, 1110 (1983); d) A.K. Colter, A.G. Parsons, K. Foohey, *Can. J. Chem.*, **63**, 2237, 1985; e) S. Fukuzumi, N. Nishizawa, T. Tanaka, *J. Org. Chem.*, **49**, 3571 (1984); f) N.J. Peacock, G.B. Schuster, *J. Org. Chem.*, **49**, 3356 (1984); g) N.J. Peacock, G.B. Schuster, *J. Am. Chem. Soc.*, **105**, 3632 (1983); h) C.J. Schlesener, C. Amatore, and J.K. Kochi, *J. Am. Chem. Soc.*, **106**, 7472 (1984).
2. W. Wiser, DOE Symposium Series on Scientific Problems Relevant to Coal Utilization, Conf. No. 770509 (West Virginia University), Oak Ridge Laboratories, TN, Nov., 1977.
3. a) F.A. Davis, T.W. Panunto, S.B. Awad, R.L. Billmers, and T.G. Squires, *J. Org. Chem.*, **49**, 1228 (1984); b) R.H. Schlosberg, W.H. Davis, Jr., and T.R. Ashe, *Fuel*, **60**, 201 (1981); c) R.E. Miller and S.E. Stein, *J. Phys. Chem.*, **85**, 580 (1981).
4 a) T. Ignasiak, A.V. Kemp-Jones, and O.P. Strausz, *J. Org. Chem.*, **42**, 312 (1977). b) K.M. Patel, R.J. Baltisberger, V.I. Stenberg, and N.F. Woolsey, *J. Org. Chem.*, **47**, 4250 (1982); c) E. Grovenstein, Jr., A.M. Bhatti, D.E. Quest, D. Sengupta, and D. VanDerveer, *J. Amer. Chem. Soc.*, **105**, 6290 (1983).
5. D.J. Pasto and S.-H. Yang, *J. Amer. Chem. Soc.*, **106**, 152 (1984).
6. D.R. Burfield, K.-H. Lee, and R.H. Smithers, *J. Org. Chem.*, **42**, 3060 (1977).
7. a) A.M. de P. Nicholas, and D.R. Arnold, *Can. J. Chem.*, **62**, 1850, 1860 (1984); b) L.W. Reichel, G.W. Griffin, A.J. Muller, P.K. Das, and S.H. Ege, *Can. J. Chem.*, **62**, 424 (1984); c) H.F. Davis, P.K. Das, L.W. Reichel, and G.W. Griffin, *J. Amer. Chem. Soc.*, **106**, 6968 (1984).
8. A.K. Colter, C.C. Lai, A.G. Parsons, N.B. Ramsey, and G. Saito, *Can. J. Chem.*, **63**, 445 (1985).

(Received in USA 25 April 1986)