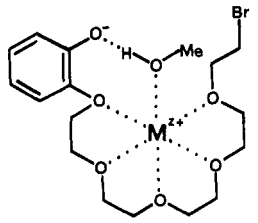

explanation for the observed insensitiveness of the P values to cation charge, we postulate a situation in which the greater loss of Coulombic energy suffered during the activation process by the ArO^-M^{2+} pairs upon dispersion of the negative charge is exactly compensated by the greater gain of Coulombic energy due to contact pairing resulting from solvent extrusion.

By a similar reasoning one would predict a substantially larger decrease of the nucleophilicity of ArO^- upon contact pairing with M^{z+} than upon solvent-separated pairing. To this end it is interesting to compare the results from the present work with those obtained in connection with a study of the template effect of alkali metal ions on the formation of B18C6 in 99% aqueous Me_2SO.[3] In the essentially aprotic 99% Me_2SO, in which contact pairing occurs in the ArO^-M^+ pairs, the nucleophilicity decrease upon cation pairing could be measured on the basis of a proper model reaction. The reactivity of the ion pair was found to be ca. $^1/_{30}$ as large as that of the free ion in the case of sodium and ca. $^1/_{15}$ in the case of the heavier metal ions. When compared with the estimated fourfold drop of nucleophilicity of ArO^- upon cation pairing with the alkali-metal ions in MeOH solution, these data strongly argue in favor of the conclusion that loss of Coulombic energy on going from initial to transition state should be larger in the case of contact pairing in the initial state than in the case of solvent-separated pairing.

Proximity Effect. An Entropy Phenomenon?

On the basis of the simple consideration that a major contribution to the standard entropy of chain molecules arises from internal rotations around single bonds and that a significant fraction of this conformational entropy is presumably lost when the chain is wrapped around a metal template, one reaches the conclusion that the metal ion associated reactant should reach the transition state with a lesser entropic penalty than the unassociated reactant. However, as it often happens with polar reactions as carried out in polar solvents, a significant contribution to the observed thermodynamic quantities is made by solvation effects,[13] which can obscure the internal thermodynamic quantities of the reaction. This is also the case with the present reaction. Although the activation parameters (Table I) are but moderately accurate since they were obtained from two temperatures only, there seems to be no doubt that the expected entropic advantage of the metal ion catalyzed cyclizations over the uncatalyzed one does not show up in the measured $\Delta S^\ddagger$ values. This is not really surprising, as a significant desolvation of the phenoxide end during the activation process is likely to produce a positive $\Delta S^\ddagger_{solv}$ term.[14] It seems also reasonable to postulate that the $\Delta S^\ddagger_{solv}$ term is more positive for the uncatalyzed reaction than for the catalyzed ones, since the free phenoxide should be more heavily solvated than the ion-paired phenoxide. If this hypothesis is correct, one must conclude that for the alkali metal ion catalyzed cyclizations the $\Delta\Delta S^\ddagger_{solv}$ and $\Delta\Delta S^\ddagger_{int}$ contributions are opposite in sign and of comparable magnitude, with the net result that the $\Delta S^\ddagger$ values are similar to that of the uncatalyzed reaction. With the alkaline-earth metal ions the $\Delta\Delta S^\ddagger_{solv}$ term predominates, thus yielding $\Delta S^\ddagger$ values appreciably more negative than the $\Delta S^\ddagger$ value for the uncatalyzed reaction. As a matter of fact, in both series the template effect turns out to be enthalpic in origin.

We may further note that also the thermodynamic macrocyclic effect related to polyether neutral ligands, which has served as a model for the template effect, might be expected to be entropic in origin as a result of the presumably smaller conformational entropy of the macrocycle as compared to the acyclic ligand. But experimental evidences not always fulfill this expectation and solvation contributions can be held responsible, at least in part, for the enthalpic origin of the effect as observed in many instances.[5]

Registry No. ArOH, 77963-49-6; B18C6, 14098-24-9; Na^+, 17341-25-2; K^+, 24203-36-9; Rb^+, 22537-38-8; Cs^+, 18459-37-5; Ca^{2+}, 14127-61-8; Sr^{2+}, 22537-39-9; Ba^{2+}, 22541-12-4.

(13) Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969; p 313.
(14) For an estimate of this contribution in 75% ethanol see: Illuminati, G.; Mandolini, L.; Masci, B. *J. Am. Chem. Soc.* **1975**, *97*, 4960.

Communications to the Editor

Polyvalent Porphyrins. Properties of Tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin (1-P) and Its Fe^{III} and Zn^{II} Derivatives

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The peroxidases react with hydrogen peroxide to cleave the O–O bond and produce a protohemin derivative that is $2e^-$ equiv more oxidized than the resting Fe(III) porphyrin.[2,3] Recent evidence suggests that at least one of the electrons is removed from the porphyrin π system to give a cation radical that is responsible for much of the electron transfer involved in substrate oxidations.[4,5] The radical nature of the intermediates has prompted us to investigate complexes of the porphyrin **1-P**[6] in which advantage is taken of the steric protection afforded by the *tert*-butyl groups, which so effectively stabilizes species such as the tri-*tert*-butylphenoxyl radical.[7] **1-P** was synthesized by the Rothemund procedure[8,9] and purified[10] by chromatography on silica with 1:1

(1) On leave from the Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, U.K.
(2) George, P. *J. Biol. Chem.* **1953**, *201*, 413–426.
(3) Newson, W. D.; Hager, L. P. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 7, pp 295–332.
(4) Roberts, J. E.; Hoffman, B. M.; Rutter, R.; Hager, L. P. *J. Biol. Chem.* **1981**, *256*, 2118–2121.
(5) Schonbaum, G. R.; Lo, S. *J. Biol. Chem.* **1972**, *247*, 3353–3360.
(6) While this work was in progress the preparation of **1-P** and its oxidation with ferricyanide were reported by Melezhik, A. V.; Pokhodenko, V. D. *Zh. Org. Khim.* **1982**, *18*, 1054–1056. However, the oxidized forms were not purified nor characterized and some of the proposed structures (e.g., that for **2-Zn**) do not agree with our assignment.
(7) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, pp 37–112.
(8) Badger, G. M.; Jones, R. A.; Lawlett, R. L. *Aust. J. Chem.* **1964**, *17*, 1028–1035.
(9) Kim, J. B.; Adler, A. D.; Longo, F. R. in "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1, Part A, pp 85–100.
(10) The parent compounds **1-P**, **1-Zn**, and **1-Fe^{III}Cl** were characterized by elemental analysis and mass, electronic, IR, and in the first two cases NMR spectroscopies. See also: Shroyer, A. L. W.; Lorberau, C.; Eaton, S. S.; Eaton, G. R. *J. Org. Chem.* **1980**, *45*, 4296–4302.

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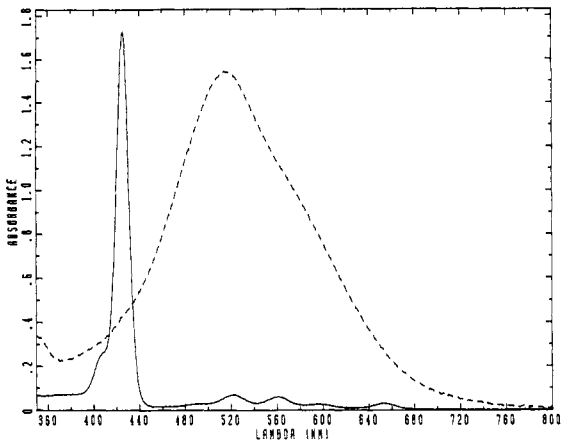


Figure 1. Visible spectra of **1-P** (continuous line) and **2-P** (broken line), the latter multiplied by 4.0, at equal concentrations (3.5×10^{-6} mol dm^{-3}) in chloroform solution. The solution of **2-P** was obtained by oxidation of a stock solution of **1-P** (5×10^{-6} mol) in chloroform (5 cm^3) using a solution of *m*-chloroperbenzoic acid (5×10^{-6} mol) in chloroform and chelated protohemin (0.3 mg) catalyst.

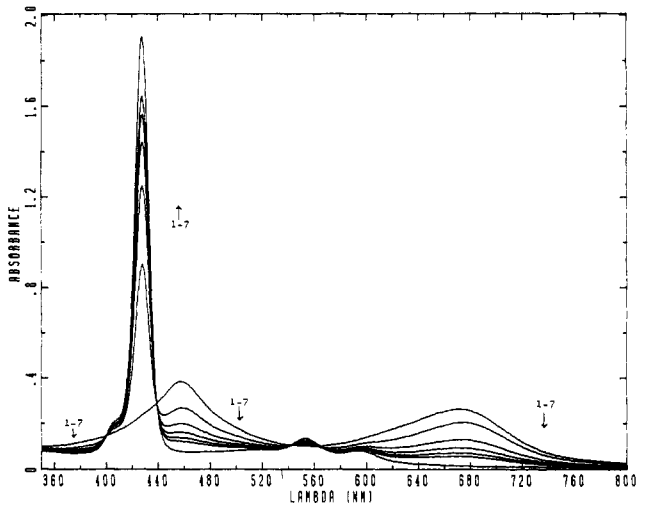
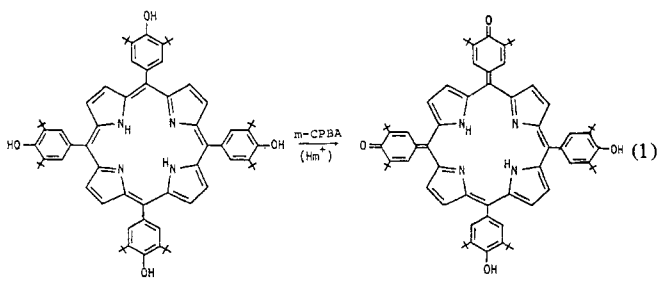


Figure 2. Spectral changes accompanying the reduction of **2-Zn** to **1-Zn** by *p*-cresol (7.9×10^{-4} mol dm^{-3}) in chloroform solution at 30 °C. Time intervals between scans 1–6 are 6.5 min each and the final spectrum, 7, was recorded after 3 h.

benzene–cyclohexane as eluent.

Treatment of **1-P** in chloroform with *m*-chloroperbenzoic acid (*m*-CPBA) in the presence of a μM concentration of chelated protohemin catalyst (Hm^+)[11] gave a purple solution (Figure 1) in a reaction shown by a spectrophotometric titration to be a 2e$^-$ oxidation (eq 1). The oxidation product **2-P** was purified[12] by



1-P **2-P** (one tautomer) (1)

(11) Traylor, T. G.; Lee, W. A.; Stynes, D. V. *Tetrahedron*, in press.

(12) The IR spectra of **2-P** in chloroform show O–H stretching bands at 3600 and 3750 cm^{-1} and a carbonyl absorption at 1560–1590 cm^{-1}. **2-P** is ESR silent. Its room-temperature NMR spectrum in CD_2Cl_2 shows signals at δ 9.25, 7.50, 6.85, and 1.55.

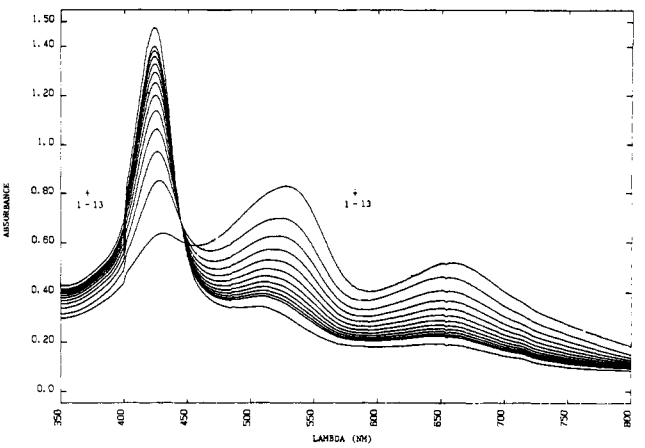
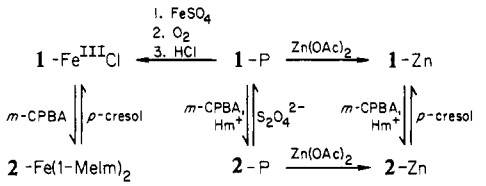


Figure 3. Spectral changes accompanying the reduction of **2-Fe** by *p*-cresol (2.0×10^{-3} mol dm^{-3}) in benzene solution containing 1-methylimidazole (0.2 mol dm^{-3}) at 30 °C. Time intervals between scans 1–12 are 2 min each and the final spectrum, 13, was recorded after 3 h.

Scheme I



chromatography on silica with chloroform as eluent and was obtained in green crystalline form by slow evaporation of solvent. Hence unlike tetraphenylporphyrin or hydroxyporphyrins, which undergo further redox or ring opening reactions,[13,14] **1-P** is cleanly oxidized to a stable species **2-P**. In chloroform **2-P** is reduced quantitatively to **1-P** by stannous chloride or aqueous sodium dithionite but is unaffected by *p*-cresol or other phenols.

The zinc porphyrin complex **1-Zn**, prepared from **1-P** and $Zn(OAc)_2$ in hot acetic acid solution, also gives a 2e$^-$ oxidized species, **2-Zn**, when titrated with the *m*-CPBA, chelated protohemin oxidant. The green **2-Zn** (spectrum 1, Figure 2) can also be obtained by the addition of $Zn(OAc)_2$ in methanol to a warm solution of **2-P** in chloroform. In contrast to **2-P**, **2-Zn** is rapidly and quantitatively reduced to **1-Zn** by *p*-cresol (Figure 2). Hence insertion of zinc has converted **2-P** into a species having spectroscopic and chemical similarities to peroxidase compound **1**.

Treatment of the hemin **1-Fe^{III}Cl** in benzene with *m*-CPBA in the presence of 1-methylimidazole (1-MeIm) also resulted in a 2e$^-$ oxidation to give red **2-Fe(1-MeIm)$_2$**[15] (spectrum 1, Figure 3). Like **2-Zn**, **2-Fe(1-MeIm)$_2$** is also reduced by *p*-cresol although in both cases the reactions are considerably slower than those of peroxidase compound **1** or the chelate protohemin model compound[11] with the same substrate.

The reactions of **1-P**, **2-P**, and their complexes are summarized in Scheme I. Obviously, deprotonation of any of the iron(III) forms will lead to interesting systems with possible internal redox properties.[16,17] An important property of the hemin **1-Fe^{III}Cl** is its stability toward oxidative destruction. Whereas the oxene form

(13) Clezy, P. S. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. II, Part B, pp 103–130.

(14) Furhop, J. H.; Besecke, S. *Angew. Chem., Int. Ed. Engl.* **1974**, 13, 150–151.

(15) In the absence of 1-MeIm, **1-Fe^{III}Cl** with *m*-CPBA gives a 2e$^-$-oxidation product **2-Fe** with a very similar electronic spectrum to **2-Zn**. Hence we assume that, as in **2-Zn**, the oxidation occurs on the ligand and the metal remains as Fe^{III}. **2-Fe** is reversibly converted to **2-Fe(1-MeIm)$_2$** by the addition of 1-MeIm.

(16) Sano, S. Sugiura, Y.; Maeda, Y.; Ogawa, S.; Morishima, I. *J. Am. Chem. Soc.* **1981**, *103*, 2888–2890. Observed internal reduction of iron(III) in ferric hydroxyporphyrin treated with strong base.

(17) Dioxygen in strong base also brings about the oxidation of **1-P**, **1-Zn**, and **1-Fe^{III}Cl**.

of tetraphenylhemin or other simple hemins destroys the parent compound, **1**-$Fe^{III}Cl$ is completely stable in the presence of **2**-Fe, and the redox cycle can be carried out repeatedly without hemin destruction. This makes this type of hemin particularly attractive for catalytic oxidation or dioxygen reduction.

Acknowledgment. We are grateful to the National Science Foundation, Grant CHE81-20969, for support of this research.

Registry No. 1-P, 74684-36-9; **1**-$Fe^{III}Cl$, 86767-72-8; **1**-Zn, 82925-38-0; **2-P**, 82934-47-2; **2**-Fe(1-MeIm)$_2$, 86784-90-9; **2**-Zn, 86767-73-9; $FeSO_4$, 7720-78-7; $Zn(OAc)_2$, 557-34-6; *m*-CPBA, 937-14-4; Hm^+, 16009-13-5; 1-MeIm, 616-47-7; $S_2O_4^{2-}$, 14844-07-6; $SnCl_2$, 7772-99-8; *p*-cresol, 106-44-5.

Thioxyallyl Ion from Allene Episulfide with Acid

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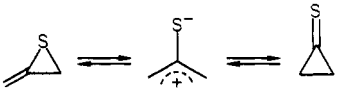
Interest has quickened over the last few years to claim the tautomeric system of cyclopropanethione–thioxyallyl ion–allene episulfide[1] in connection with analogous oxygen system.[2,3] De Boer[4] and Block[1] showed that under drastic conditions, thermodynamically stable allen episulfide (**1**) was produced presumably from cyclopropanethione (**3**) formed in situ, via thioxyallyl ion (**2**). Such an inference would be reasonable at first glance, but a closer look reveals that no definitive evidence either for thioxyallyl ion (**2**) or cyclopropanethione (**3**) is shown.[5]



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Meanwhile, chemistry associated with the cyclopropanone–oxyallyl ion–allene oxide tautomeric system has been extensively studied,[2] and even oxyallyl ion has been widely used as a versatile synthetic reagent.[6]

We have presumed that thioxyallyl ion (**2**) can serve as an intermediate in the allene episulfide–cyclopropanethione tautomerism and now present direct evidence for the formation of thioxyallyl ion from allene episulfide under acidic conditions.[7]

Tetramethylallene episulfide (**4**)[8] was treated with fluorosulfonic acid (FSO_3H) as a solvent in NMR sample tube, cooling with liquid nitrogen in glovebox. The separated solid mixture was co-warmed gradually to −70 °C to mix, affording a light yellow solution. In the ^1H NMR spectrum of the solution, only a singlet signal at 3.09 ppm appeared besides an acid proton (FSO_3H) and was assigned to four equal methyl groups of the protonated thioxyallyl ion **5**. The ^{13}C NMR chemical shifts were observed at 248.3(s), 137.8(s), and 38.4(q) ppm, which were certainly in accordance with the existence of large positive charge at carbons of **5** (Figure 1).[10] **5** shows no appreciable decomposition at −60 °C but by warming to room temperature the solution changed to dark brown and no well-identified carbonium ion was found in the NMR spectra due to the instability of the thioxyallyl ion.

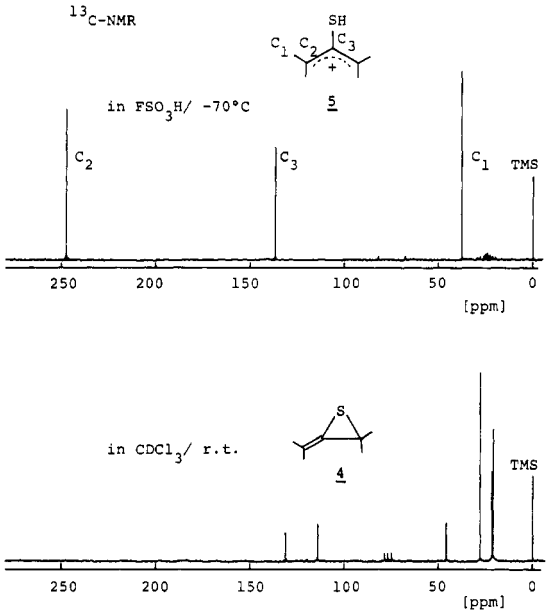


Figure 1. ^{13}C NMR spectra. Top is the protonated thioxyallyl ion **5** formed by treating **4** with FSO_3H as a solvent. Me_4Si sealed with CD_2Cl_2 in a capillary was held at the center of the NMR sample tube. Bottom is **4** in $CDCl_3$ with internal Me_4Si.

By treating **4** with slightly weaker acids such as $HClO_4$ as a Brønsted acid and BF_3 etherate as a Lewis acid under mild conditions, a few interesting dimerization products were obtained in good yields.[11]

4 (1.6 mmol) reacted with excess BF_3 etherate (4.8 mmol) or 70% perchloric acid ($HClO_4$, 0.6 mL)[12] in ether to give in a few minutes thioketone **6** and 1,4-dithiane **7**,[13] whereas in CH_2Cl_2, 1,3-dithiolane **8** as well as **6** and **7** were obtained (eq 1).[14] The structures of these products were fully determined by elemental analyses and spectroscopic data.[15] The light red color of **6** is well associated with the very low ^{13}C NMR chemical shift (276.2 ppm) assigned for the thioketone carbon. The quartet signal of the isopropyl methyl groups in the ^1H NMR spectrum of **8** is clearly consistent with a structure in which the isopropyl group is attached to an asymmetric carbon.

The formation of these products is well explained by assuming the thioxyallyl ion **9** as a reactive intermediate that possibly

(1) Block, E.; Penn, R. E.; Ennis, M. D.; Owens, T. A.; Yu, S.-L. *J. Am. Chem. Soc.* **1978**, *100*, 7436–7437.

(2) (a) Chan, T. H.; Ong, B. S. *Tetrahedron* **1980**, *36*, 2269–2289. (b) Turro, N. J. *Acc. Chem. Res.* **1969**, *2*, 25–32.

(3) Block et al. reported that allene episulfide (**1**) is 7 kcal/mol more stable than cyclopropanethione (**3**).[1] This situation is reverse for the cyclopropanone–allene oxide system.[2]

(4) Longejan, E.; Buys, Th. S. V.; Steinberg, H.; De Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 214–218.

(5) Recently, Saalfrank et al. postulated the intermediacy of thioxyallyl ion in the reaction of elemental sulfur with substituted allene produced in situ by thermolysis of oxaphosphetane. However, they did not isolate either allene episulfide or cyclopropanthione: Saalfrank, R. W.; Paul, W.; Schierling, P.; Schüler, H.; Wilhelm, E. *Chem. Ber.* **1982**, *115*, 57–64.

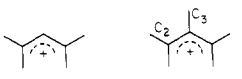
(6) Noyori, R. *Acc. Chem. Res.* **1979**, *12*, 61–66.

(7) Ring-opening reaction of thiiranes with C–S bond cleavage by acid is known to proceed via an opened cationic species by kinetic study: Odden, A.; Wylde, J. *Bull. Soc. Chim. Fr.* **1967**, 1607–1612.

(8) Tetramethylallene episulfide (**4**) was prepared by bulk vacuum pyrolysis of the lithium salt of tosylhydrazone of tetramethyl-3-thietanone, as reported by Hortmann et al.[9]

(9) Hortmann, A. G.; Bhattacharjya, A. *J. Chem. Soc.* **1976**, *98*, 7081–7082.

(10) These shifts are approximately consistent with those for allyl cations by Olah et al. i: ^1H NMR 2.91 ppm (CH_3). ((a) Olah, G. A.; Calin, M. *J. Am. Chem. Soc.* **1968**, *90*, 938–943). ü: ^{13}C NMR C_2: 234.7 (s) and C_3: 142.7 (s). ((b) Olah, G. A.; Bollinger, J. M. *Ibid.* **1968**, *90*, 6082–6091).



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(11) The yields of the products in acid-catalyzed dimerization of **4** were exceptionally high and no polymer was observed. Generally, yields of dimers from other thiiranes are low enough due to the formation of much polymer (e.g., 15% of dimer for styrene sulfide[12]).

(12) Noshay, A.; Price, C. C. *J. Polymer Sci.* **1961**, *54*, 533–541.

(13) The formation of dimer **7** has been reported by Hortmann et al. in the reaction of **4** with $HClO_4$; however, physical and spectroscopic data and even the yield were not given.[9]

(14) All yields are those isolated by column chromatography.

(15) Supplementary material available.

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