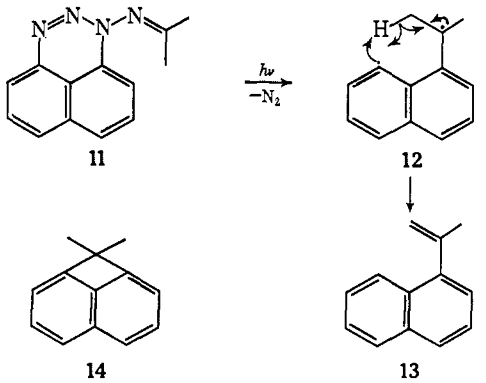
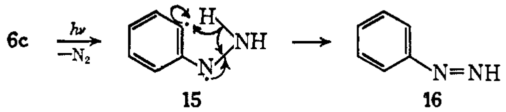
naphtho[1,8-*de*]triazine (**11**).[15] Photolysis of **11** in benzene (2×10^{-2} *M*) provided a 60% yield of 1-isopropenylnaphthalene[5] (**13**) but we were unable to isolate from this reaction the desired 1,1-dimethylcyclobut[1,8-*bc*]naphthalene, **14**.[16] Apparently the 1,4-diradical **12** encounters an insurmountable energy barrier to 1,4 cyclization and a 1,6-hydrogen transfer occurs instead.[17] The perfluoroisopropylidene of **11** upon photolysis in acetonitrile resulted in polymer formation.



In a related decomposition, the irradiation of 1-aminobenzotriazole (**6c**) in benzene (10^{-1} *M*) quantitatively produces biphenyl.[5] A mechanistic proposal for this conversion may involve a 1,5-hydrogen shift in the intermediate diradical **15** to produce phenyldiimide (**16**), whose thermal homolysis is known[18] to produce a phenyl radical which serves as a precursor to the observed product.[19]



Acknowledgment. We wish to thank the National Science Foundation (GP 6719) and the National Institutes of Health (GM 12672) for support of this investigation.

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[15] This compound was conveniently prepared by the Zn–acetic acid reduction of 1H-naphtho[1,8-*de*]triazine in the presence of acetone to afford the acetone 8-aminonaphthylhydrazone, mp 172–173°, which upon treatment with nitrous acid at 0° gave **11**, mp 115°.

[16] The only one-atom 1,8-bridged naphthalene that has been reported is thiet[1,8-*bc*]naphthalene 1,1-dioxide derived from the photolysis of 1,2,3-thiadiazino[1,8-*de*]naphthalene 1,1-dioxide: R. W. Hoffman and W. Sieber, *Angew. Chem. Intern. Ed. Engl.*, 4, 786 (1965); *Ann.*, 703, 96 (1967).

[17] A 1,3 cyclization does occur relative to a 1,4-hydrogen transfer in the photolysis of methyl 3,3-dimethylindazole-6-carboxylate to give dimethyl-3-carbomethoxybenzocyclopropene: R. Anet and F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 525 (1964).

[18] S. G. Cohen and J. Nicholson, *ibid.*, **86**, 3892 (1964); **88**, 2247 (1966); *J. Org. Chem.*, 30, 1162 (1965).

[19] The fate of the hydrogen atom released in the decomposition of **16** is unknown. No reduced reactants were detected in the reaction mixture.

[20] National Science Foundation Undergraduate Research Participant, 1966.

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Periodic Acid–Dimethyl Sulfoxide Mixtures, a Potential Hazard

Sir:

We wish to draw attention to the possibility of an explosion occurring during the preparation of concentrated solutions of periodic acid in dimethyl sulfoxide (DMSO).

In a recent paper[1] the periodic acid–dimethyl sulfoxide system was used to oxidize methyl glycopyranosides and under the conditions reported (0.15 *N* periodic acid in DMSO) there was no evidence of an exothermic reaction.[2] If, however, the periodic acid concentration is increased tenfold, a violent explosion can occur. This was first noticed when periodic acid (34.0 g) was placed in a 100-ml, aluminum-foil-wrapped flask. DMSO was added (*ca.* 70 ml) and the flask was shaken and allowed to stand. After 5–10 min an explosion occurred, shattering the flask.

We were able to repeat this result under the same conditions, in an unwrapped flask, but not when one-tenth of the quantities of reagents was mixed in a small erlenmeyer (25 ml). When the explosion did occur, dense white fumes were evolved, in addition to iodine vapors.

These results suggest great care should be taken when making up periodic acid solutions in DMSO to ensure that heat-dissipation problems do not arise, *i.e.*, by using only dilute solutions and by adding the periodic acid to DMSO in small quantities with adequate mixing and cooling.

This and other reports[3] on the explosive properties of DMSO mixtures suggest room for more work on the exothermic reactions of an otherwise impeccable reagent. The possibility of minor contaminants initiating the explosion should not be overlooked. In this report, reagent grade materials were used, and the DMSO had been purified over calcium hydride.

We are currently investigating the possibility that the heat of hydration of DMSO might, in abstracting the elements of water ($HIO_4 \cdot 2H_2O$) from periodic acid, produce concomitantly sufficiently intense local heat to initiate the explosion.

Acknowledgment. We wish to thank Dr. L. D. Hayward for useful discussions.

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(1) R. J. Yu and C. T. Bishop, *Can. J. Chem.*, **45**, 2195 (1967).

(2) Dr. C. T. Bishop, personal communication.

(3) *Chem. Eng. News*, **44**, 48 (April 11, 1966).

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Partial Rate Factors in the Nitration of 10-Methyl-10,9-Borazarophenanthrene[1]

Sir:

In a recent series of papers,[2] we described a novel series of aromatic boron heterocycles, derived from "normal" aromatic compounds by replacing pairs of adjacent carbon atoms by boron and nitrogen, or boron and oxygen. Compounds of this type are of considerable theoretical interest since they are isoelectronic with the "normal" aromatics to which they are related, and a comparison of the properties of such pairs of related structures therefore provides a very

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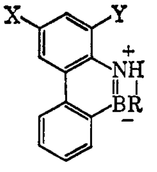
(1) This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

(2) See M. J. S. Dewar and R. Jones, *J. Am. Chem. Soc.*, **89**, 2408 (1967), and references cited there.

good test of chemical theories. We wish to report the first quantitative measurement of reactivity of such a boron-containing aromatic in a typical chemical reaction, *i.e.*, the partial rate factor (PRF) for nitration of 10,9-borazarophenanthrene (Ia) in acetic anhydride at 0°.

Previous studies[3] had shown that Ia gives a mixture of the 6- (Ib) and 8-nitro (Ic) derivatives under these conditions, together with 8-nitro-10-hydroxy-10,9-borazarophenanthrene (Id) formed[3] by secondary oxidation of Ic. Preliminary trials showed Ia to be comparable in reactivity with perylene, a hydrocarbon which gives almost exclusively the 3-nitro derivative on nitration in acetic anhydride at 0° with a partial rate factor of 77,000.[4] It was also established that nitration of a mixture of Ia and perylene, if carried to low conversions at 0°, gave only Ib, Ic, and 3-nitroperylene, formation of Id being avoided.



Ia, $R = CH_3$; $X = Y = H$
b, $R = CH_3$; $X = NO_2$; $Y = H$
c, $R = CH_3$; $X = H$; $Y = NO_2$
d, $R = OH$; $X = H$; $Y = NO_2$

The nitration product was analyzed by the spectrophotometric procedure of Dewar and Urch;[5] this has been greatly improved in these laboratories by Mr. J. Hashmall, who has written a computer program able to handle multicomponent mixtures to replace the original graphical procedure. Two independent and concordant measurements led to the following PRF's for formation of Ib and Ic: Ib, 937,000; Ic, 2,060,000.

Ia is thus a very reactive ring system; the PRF's for the corresponding positions in phenanthrene are:[4] 3 position, 300; 1 position, 360. The values for Ia are also of general interest in that they are the largest yet reported for nitration in acetic anhydride, and show that such reactions are not diffusion controlled below rates corresponding to partial rate factors of at least 2×10^6.

No quantitative calculations of PRF's are available as yet, due to the lack of information concerning parameters for boron; indeed, the value of measurements such as these lies largely in the assistance they may give to attempts to extend existing semiempirical MO treatments. For example, the localization energies predicted[3] by the simple PMO method are: 6 position, $2.60\beta \times 1.67A$; 8 position, $2.32\beta + 1.38A$, where

$$A = (\alpha_B - \alpha_C)(\alpha_N - \alpha_C)^{-1}$$

If we assume that carbon is half way between boron and nitrogen in electronegativity, so that $A = 1$, and use the relation between PMO localization energies and PRF's established[4] for hydrocarbons, we find the values predicted for Ia to be: 6 position, 5,100,000; 8 position, 4,550,000. However, published data for valence state ionization potentials, etc.,[6] suggest that carbon is somewhat nearer to boron than to nitrogen in electronegativity, so that $A < 1$; setting $A = 0.9$ gives predicted PRF's of 903,000 and 1,130,000, respectively, in very reasonable agreement with experiment.

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[3] M. J. S. Dewar and V. P. Kubba, *Tetrahedron*, 7, 213 (1959).

[4] M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

[5] M. J. S. Dewar and D. S. Urch, *ibid.*, 3079 (1958).

[6] See, *e.g.*, J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

Nickel Tetracarbonyl. The Mechanism of Nucleophilic Substitution

Sir:

In an earlier communication[1] it was stated that the carbon monoxide exchange reaction ($L = {}^{14}CO$)[2,3] of $Ni(CO)_4$ appeared to occur by a different mechanism

$$Ni(CO)_4 + L = Ni(CO)_3L + CO$$

from other substitution reactions ($L = R_3P$, RNC, $(RO)_3P$).[1,3,4] We have remeasured the rates of these reactions. We do not confirm previous results for the CO exchange, but for ligand substitution our results fall between previous values determined in similar solvents. We now conclude that all substitutions, including exchange, proceed by the same mechanism.

In all the previous cases, a first-order rate law was observed; *i.e.*, the reaction rate was independent of the concentration of nucleophile. All nucleophiles, except CO, reacted at approximately equal rates. At 25°, the rates of CO exchange (studied using ^{14}CO and measuring radioactivity) and ligand substitution (studied by CO evolution[3] or infrared spectrophotometry[4]) were approximately equal. At lower temperatures, ligand substitution became relatively the slower process. The activation parameters for ^{14}CO exchange and triphenylphosphine (Ph_3P) substitution, obtained for reaction in heptane, were respectively: $\Delta H^{\ddagger} = 10$ and 21 kcal mole^{-1}; $\Delta S^{\ddagger} = -36$ and 1 eu.

These observations have led to speculation about the reaction mechanisms.[1,3,5] It was argued that, although the rate-determining step in each case must involve only $Ni(CO)_4$, the same activated complex could not be involved in both CO exchange and ligand substitution since the activation energies are radically different.

We have redetermined the rates of CO exchange and Ph_3P substitution, in hexane solvent, from 0 to 30°. The system is arranged so that no gas phase is present. In Table I, our rates and activation parameters are compared and are essentially the same for the two reactions.

In our experiments, $C^{18}O$ was allowed to react with $Ni(C^{16}O)_4$, and the concentrations of the five species $Ni(C^{16}O)_n(C^{18}O)_{4-n}$ ($n = 0$–4) were followed by infrared spectrophotometry. We confirm the first-order rate law, and detailed analysis of the concentration changes for the species $Ni(C^{16}O)_4$ and $Ni(C^{16}O)_3(C^{18}O)$ gave the rate constants (a discussion of the spectra of the

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[1] L. R. Kangas, R. F. Heck, P. M. Henry, S. Breitschaft, E. M. Thorsteinson, and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2334 (1966).

[2] F. Basolo and A. Wojcicki, *ibid.*, 83, 520 (1961).

[3] P. M. Henry and L. R. Kangas, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Paper O11.

[4] R. J. Angelici and B. E. Leach, *J. Organometal. Chem.* (Amsterdam), 11, 293 (1868).

[5] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 543.