

Table I. Luminescence Energies and Lifetimes of Ir(III) and Rh(III) Complexes of 1,10-Phenanthroline^a

Complex	Emission max ^b ν_{\max} , kK	Half- width, $\nu_{1/2}$, kK	Energy of lowest excited state, ^c kK		Lifetime (μ sec)
K[IrCl ₄ (phen)]	11.1 ^d	3.1	15.1	0.63 ± 0.05	
K[RhCl ₄ (phen)]	11.7	3.3	16.0		
K[IrCl ₄ (5-methylphen)]	11.1	3.3	15.4	0.56 ± 0.05	
K[RhCl ₄ (5-methylphen)]	11.5	3.3	15.8		
K[IrCl ₄ (5,6-methylphen)]	10.5	3.2	14.7	0.58 ± 0.04	
K[RhCl ₄ (5,6-methylphen)]	11.5	2.9	15.3		
K[IrCl ₄ (5-bromophen)]	11.9	3.3	16.2	0.65 ± 0.04	
K[RhCl ₄ (5-bromophen)]	11.7	3.4	16.1		
K[IrCl ₄ (5-chlorophen)]	11.9	3.3	16.2	0.61 ± 0.04	
K[RhCl ₄ (5-chlorophen)]	12.2	3.0	16.1		
K[IrCl ₄ (5-nitrophen)]	13.7	3.2	17.9	0.094 ± 0.005	
K[RhCl ₄ (5-nitrophen)]	11.9	3.3	16.2		
K[IrCl ₄ (4,7-phenylphen)]	13.2	2.8	16.8	2.7 ± 0.15	
K[RhCl ₄ (4,7-phenylphen)]	13.5	3.5	18.0		

^a All measurements were made on solid samples at 77°K. ^b All luminescence spectra were corrected for variations in instrumental response with wavelength in order to determine emission maxima.

^c Calculated by the method of Carstens and Crosby, see ref 7.

^d See ref 6.

On the other hand, an electron-withdrawing group would be expected to increase the π -bonding ability of the 1,10-phenanthroline ligand, which would bring about an increase in Δ . Thus the effect of ligand substituents on Δ will reflect the relative importance of σ - and π -bonding in an octahedral complex.

A complete determination of the effect of ligand substituents on Δ from the emission energies in Table I would require an analysis of electron repulsion parameters, of reduction of symmetry from O_h to C_{2v} , and of spin-orbit coupling terms. However, it is likely that the general increase in the emission energies of the Ir(III) complexes as stronger electron-withdrawing substituents are introduced on the phenanthroline ligand are indicative of an increase in Δ . This would suggest that increases in π -bonding in Ir(III) are far more important than any decrease in σ -bonding. The importance of π -bonding in Ir(III) is also evidenced by the occurrence of low-lying charge-transfer states in complexes of Ir(III) with π acceptor ligands.¹⁻³ The relative insensitivity of the emission energies of the Rh(III) complexes to ligand substituents suggests that here σ -bonding decreases are more comparable to π -bonding increases than in Ir(III). Studies of the infrared and nmr spectra of Rh(III) complexes have also led to the conclusion that π -bonding is unimportant.^{13,14}

The effects of ligand substituents on the lifetimes of the potassium salts of the Ir(III) complexes (see Table I) are also quite surprising. Although nonexponential decay curves were encountered for the phenanthroline salts of these complexes due to interfering effects of the cation, rough estimates of lifetimes from the decay curves show the same trends as those shown by the potassium salts. Thus, the lifetime trends appear to be related to intramolecular ligand substituent effects rather than to intermolecular solid state effects due to the counterion. Heavy atoms such as chlorine and

(13) R. D. Foust, Jr., and P. C. Ford, *Inorg. Chem.*, **11**, 899 (1972).

(14) R. D. Foust, Jr., and P. C. Ford, *J. Amer. Chem. Soc.*, **94**, 5686 (1972).

bromine have very small effects on the lifetimes whereas the nitro and phenyl groups cause large alterations in the lifetimes but in opposing directions. This suggests that in all the Ir(III) complexes, spin-orbit coupling is dominated by the presence of the heavy metal so that heavy-atom ligand substituents have little effect. The increase in the lifetime brought about by the phenyl substituent is consistent with a decrease in the radiationless decay rate with increasing energy.⁹ However, the effect of the nitro substituent is anomalous in this respect. Although we cannot determine quantum yields for these solid state emissions, the emission from the nitro-substituted complex is quite bright relative to the parent complex. Coupled with the fact that the measured lifetime is decreased by the nitro substituent, this would indicate a large increase in the radiative decay rate. Although accurate lifetime data for the rhodium(III) complexes could not be obtained, our estimates of the luminescence lifetimes of these complexes suggest that they follow trends which are similar to those discussed for Ir(III).

Further work on the interpretation of these results and the extension of our measurements to include substituent effects on photochemical as well as photo-physical processes is currently in progress.

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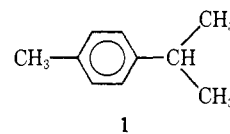
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*Ips*o Nitration. II.¹ Novel Products and True Positional Selectivities in Nitration of *p*-Cymene

Sir:

Over a hundred years has passed since nitration of *p*-cymene (**1**) first was studied.² The reaction has re-



ceived much attention in the interim, partly because of the occurrence and/or utility of **1** in commercial processes³ and partly because of mechanistic questions raised by the presence of *p*-nitrotoluene in the product mixture.⁴ Evidence for direct nitrodeisopropylation (*ipso* electrophilic attack⁵ on the isopropyl-bearing carbon) of **1** was presented in an extensive study of

(1) Part I: R. C. Hahn and M. B. Groen, *J. Amer. Chem. Soc.*, **95**, 6128 (1973).

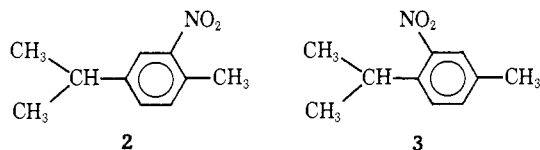
(2) J. Barlow, *Ann.*, **98**, 245 (1856).

(3) K. A. Kobe and T. F. Doumani, *Ind. Eng. Chem.*, **31**, 257 (1939), and references therein.

(4) (a) T. F. Doumani and K. A. Kobe, *J. Org. Chem.*, **7**, 1 (1942); (b) G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, **86**, 1067 (1964).

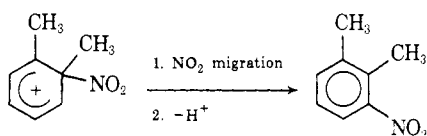
(5) C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, **93**, 3389 (1971).

nitronium fluoroborate nitration of alkylbenzenes by Olah and Kuhn.^{4b} They found *p*-nitrotoluene as 9.5% of the product mixture, essentially the same percentage as had been reported for mixed acid nitrations.³ They also were first to isolate 3-nitro-4-isopropyltoluene (**3**) from nitration of **1**, and reported a



2/3 ratio of 94:6. Thus it appeared that primary processes in nitration of *p*-cymene had been rather thoroughly elucidated.

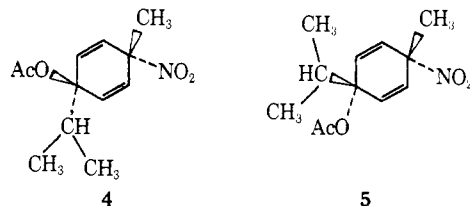
However, recently published nitration studies report extensive *ipso* attack at *methyl* positions of *o*- and *p*-alkylmethylbenzenes,⁸ in which such attack can be masked by nitro migrations.⁷ In light of these data,



we became suspicious that *p*-cymene actually undergoes significant *ipso* electrophilic attack at the *methyl* position, and that the 2/3 ratio reported by Olah and Kuhn is not an accurate representation of the relative reactivities of these positions. We report herein a re-investigation of the nitration of *p*-cymene, in which the above suspicions have been confirmed and new insight into the nature of this reaction has been obtained.

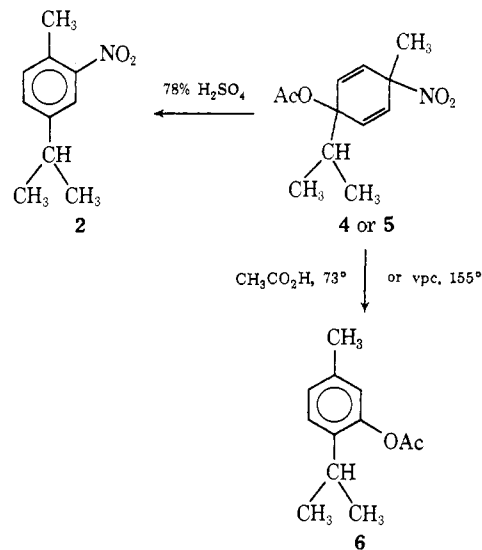
Low-temperature (0°) nitration of **1** (0.20 mol in 50 ml of acetic anhydride) with acetyl nitrate (prepared from 0.20 mol of 100% nitric acid and 30 ml of acetic anhydride) in the presence of 1.2 g of urea gave a mixture of products containing up to 41% of *ipso* adducts, 41% of **2**, 8% of **3**, and 10% of *p*-nitrotoluene, as indicated by pmr analysis.^{8,9} Careful work-up (0°) and repeated low-temperature chromatography of pentane-soluble material¹⁰ over deactivated alumina led to isolation of two noncrystalline 1,4 (nitro, acetoxy) adducts; these were assigned structures **4** and **5** on the basis of the evidence given below.

The nmr shift reagent Eu(fod)₃¹³ was added in ~10-



mg increments to separate nmr tube solutions (CDCl₃) of **4** and **5**. For both dienes, the doublet for the isopropyl methyl groups shifted downfield faster than did the ring methyl singlet; on the assumption that the preferred site of europium complexation is the acetoxy function,¹⁴ such behavior was taken to indicate that both adducts were derived from *ipso* attack on the methyl position of **1**. The *trans* and *cis* isomers (**4** and **5**, respectively) were distinguished by the faster downfield shift of the ring methyl singlet for **4** than for **5**; the ring methyl in the latter isomer should be farther away from the site of shift reagent complexation.¹⁵

Solvolysis of an 85:15 mixture of adducts **4** and **5** in 78% sulfuric acid (5 min, 25°) yielded only **2**, identical (pmr, ir, vpc) with material isolated from nitration of **1**. Thermolysis of the adducts in acetic acid (30 min, 73°) or injection on a preparative vpc column (10% QF-1, 155°) afforded only *p*-cymene (35%)¹⁶ and thymol acetate (**6**), identical (pmr, ir) with a sample inde-



pendently prepared from authentic thymol. There is ample precedent for assignment of the gross diene structures on the basis of the above-described transformations.^{6,7}

Low-temperature pmr spectra of crude nitration mixtures showed no evidence of adducts derived from *ipso* electrophilic attack at the isopropyl position of **1**, nor did nonacidic work-up procedures afford any detectable amounts of carvacrol acetate (**7**). Further, exposure of *p*-diisopropylbenzene (which undergoes 56% nitrodeisopropylation under Olah-Kuhn condi-

(14) The acetoxy methyl signal shifted downfield most rapidly; preferred acetoxy over nitro complexation was reported by (a) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971); (b) M. D. McCreary, D. W. Lewis, D. L. Wernick, and G. M. Whitesides, *ibid.*, **96**, 1038 (1974).

(15) Complete experimental details will be given in our full paper.

(16) P. C. Myhre (private communication) has found that gas chromatographic thermolysis of pure *ipso* (nitro, acetoxy) dienes from *o*-xylene and hemimellitene yields 30–85% of parent hydrocarbon. We are indebted to Professor Myhre for these data and the suggestion of the generality of this reaction.

(6) Cf. D. J. Blackstock, J. R. Cretney, A. Fischer, M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *Tetrahedron Lett.*, 2793 (1970).

(7) P. C. Myhre, *J. Amer. Chem. Soc.*, **94**, 7921 (1972).

(8) Cf. (a) ref 1; (b) A. Fischer and J. N. Ramsay, *J. Chem. Soc., Perkin Trans. 2*, 237 (1973), and references therein.

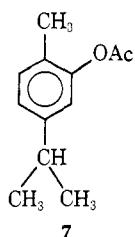
(9) Curiously, to our knowledge, the only previous workers³ to use nitric acid (fuming) and acetic anhydride on *p*-cymene reported "little effect."

(10) After unreacted *p*-cymene had been removed from the crude mixture by slow distillation (30–35°, 0.05 mm), multiple pentane extractions (0°) left ca. 25% of insoluble residue. This residue may be derived from diene decomposition products, in which case the percentage of diene formed from *p*-cymene would be even greater than 41%.¹¹ No evidence (pmr) was found for the presence of side-chain products, which often occur on *ipso* nitration of *p*-dialkylbenzenes;¹² however, such products cannot be excluded and are being sought.

(11) Nitration of *p*-cymene at –15° (AcONO₂, Ac₂O) gives *ipso* dienes as ca. 55% of identifiable products; A. Fischer, private communication. We are indebted to Professor Fischer for providing this information.

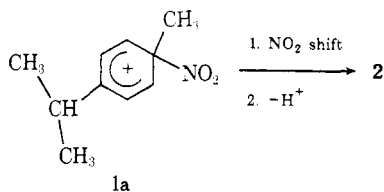
(12) Cf. A. Fischer and J. N. Ramsay, *J. Amer. Chem. Soc.*, **96**, 1614 (1974), and references therein.

(13) R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).



tions^{4b}) to acetyl nitrate under the mildest conditions so far devised gave no evidence (pmr) of *ipso* adduct formation. It is concluded that nitrodeisopropylation is an extremely facile process, and that the *p*-nitrotoluene formed in nitration of *p*-cymene is an accurate indication of the extent of *ipso* attack occurring at the isopropyl position of this substrate. By the same token, the extent of direct nitrodeprotonation of **1** to give nitro derivative **3** can be assumed to be reflected accurately by the relative amount of this product obtained from a wide variety of nitration procedures.

In contrast, *ipso* attack at the methyl position of *p*-cymene (and attack at the positions *ortho* to the methyl) can be assessed only under conditions amenable to nucleophilic trapping of the *ipso* nitroarenium ion (**1a**); otherwise, nitro migration and deprotonation mask the



ipso process and falsely enhance the reactivity of the *ortho* positions. Product distributions from nitration of **1** by three different reagents (Table I) provide nearly

Table I. Product Distributions (%) from Nitration of *p*-Cymene by Various Reagents

Reagent	Products		
	2	3	<i>p</i> -Nitro-toluene Dienes
NO ₂ ⁺ BF ₄ ^{-a}	85.2	5.3	9.5
HNO ₃ -H ₂ SO ₄ , 25 ^{ob}	82	7	11
AcONO ₂ -Ac ₂ O, 0 ^{ob}	41	8	41

^a In tetramethylene sulfone at 25° (ref 4b). ^b This work.

quantitative support for the above assertions. These data indicate that the true ratio of reactivities of the 2- and 3-positions of *p*-cymene is only 5:1 instead of the *ca.* 16:1 previously reported;^{4b} the additivity principle¹⁷ (using data from acetyl nitrate nitration (0°) of toluene and cumene)¹⁸ predicts a 6.2:1 ratio. It is noteworthy that the previously unsuspected 1-position of *p*-cymene is the most reactive position in the molecule toward nitronium ion.

Partial rate factors for nitration of all *o*- and *p*-alkyltoluenes^{4b} now clearly are suspect; a general re-

(17) Cf. L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963), and references therein.

(18) *I.e.*, $o_t^{\text{CH}_3} = 49.7$, $m_t^{\text{CH}_3} = 2.4$; $o_t^{\text{CH}_3} = 14.8$, $m_t^{\text{CH}_3} = 1.3$; J. R. Knowles, R. O. C. Norman, and G. K. Radda, *J. Chem. Soc.*, 4885 (1960).

investigation of these substrates is under way.¹⁹ The present work suggests that nitrodealkylation of any secondary alkyl group (*e.g.*, isopropyl) may be difficult to avoid; that this is *not* true is shown in the accompanying communication.²⁰ Finally, this work makes feasible a novel, essentially one-pot synthesis of the commercially useful thymol.²¹

Acknowledgment. Partial support of this research by donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(19) Preliminary study of *o*-cymene has yielded nitro, acetoxy *ipso* dienes which produce almost exclusively *o*-nitrotoluene on strong acid solvolysis; details will be included in our full paper.

(20) M. W. Galley and R. C. Hahn, *J. Amer. Chem. Soc.*, **96**, 4337 (1974).

(21) Thymol is a constituent of oil of thyme, and is used (*e.g.*) as an antiseptic mouthwash ingredient.

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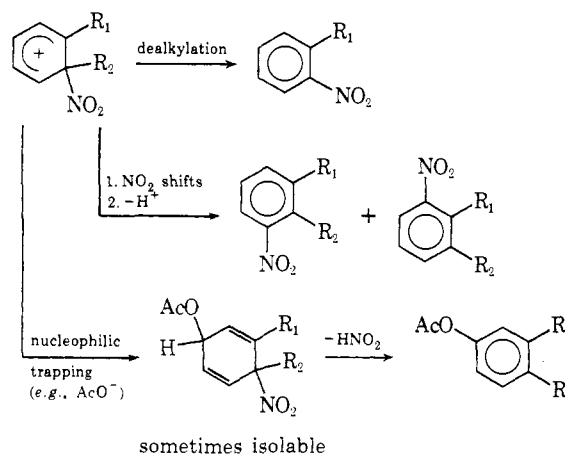
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Ipso Nitration. III.¹ Steric Effects on Extent and Consequences

Sir:

Ipso electrophilic aromatic substitution (electrophilic displacement of a substituent other than hydrogen)² is a long-known³ but long-neglected phenomenon. However, extensive *ipso* attack on many aromatic substrates in reaction with nitrating agents has been implicated only in recent years. It now is established that a nitroarenium ion derived from *ipso* attack can undergo (*inter alia*) dealkylation,⁴ nitro group migration^{1,5} (followed by deprotonation), or nucleophilic trapping⁶ (which may be followed by HNO₂ elimination) (Scheme I).

Scheme I



(1) Part II: R. C. Hahn and D. L. Strack, *J. Amer. Chem. Soc.*, **96**, 4335 (1974).

(2) C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, **93**, 3389 (1971).

(3) (a) R. Piria, *Ann.*, **56**, 35 (1845); (b) E. M. Arnett and G. B. Klingsmith, *J. Amer. Chem. Soc.*, **87**, 1023 (1965), and references therein.

(4) G. A. Olah and S. J. Kuhn, *J. Amer. Chem. Soc.*, **86**, 1067 (1964).

(5) (a) P. C. Myhre, *J. Amer. Chem. Soc.*, **94**, 7921 (1972); (b) R. C. Hahn and M. B. Groen, *ibid.*, **95**, 6128 (1973).

(6) D. J. Blackstock, A. Fischer, K. E. Richards, and G. J. Wright, *Aust. J. Chem.*, **26**, 775 (1973), and references therein.