that of the $[Ni(diars)(triars)]^{2+}$ cation, which would suggest that, in all cases, the nickel atom is experiencing a tetragonal pyramidal field from five of the arsenics, and the sixth is either uncoordinated or else very loosely bound. If this is true, the diamagnetism presents no serious theoretical difficulties since many diamagnetic five-coordinate nickel(II) complexes are now known. However, the present system is the first example of a species with *five* arsenic donors.

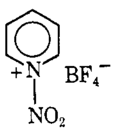
B. Bosnich, R. S. Nyholm, P. J. Pauling, M. L. Tobe
The William Ramsay and Ralph Forster Laboratories
University College, London, W.C.1. England

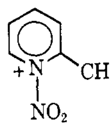
Received May 20, 1968

Transfer Nitration *via* N-Nitropyridinium Salts

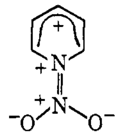
Sir:

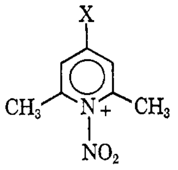
We wish to report that a variety of N-nitropyridinium tetrafluoroborates and related compounds offer a new method for effecting homogeneous nitration of aromatic substrates in organic solvents at room temperature and under essentially neutral conditions. The use of these salts as transfer nitrating agents for aromatics and other substrates offers the further possibility of designing reagents of varied reactivity by suitable choice of the heterocyclic base. The N-nitropyridinium salts are readily prepared by slow addition of the pyridine base to an equimolar suspension of nitronium tetrafluoroborate[1] in acetonitrile according to the procedure reported by Olah[2,3] for preparation of N-nitropyridinium tetrafluoroborate (1). Although the latter salt has limited solubility in acetonitrile, alkyl-substituted pyridines give salts which are quite soluble in this solvent and can be used directly without isolation.[4]


1


2

The behavior of 1 *vs.* the α-picoline salt 2 in the presence of aromatics is striking. Whereas reaction of 1 with toluene produces no nitrated product at 25°, nitration with 2 proceeds readily and quantitatively at room temperature.[5] The most reasonable explanation for these results is that in 1 the resonance structure 3 is an important contributor. Introduction of an alkyl substituent in the 2 position of the pyridine nucleus impedes the nitro group from achieving coplanarity with the pyridine ring and substantially reduces the amount of double-bond character in the N–N bond. The attendant weakening of this N–N bond in 2, due to steric inhibition of resonance, is then the major factor for allowing transfer nitration to occur.


3


4

The reactivity of various N-nitropyridinium salts can be determined by the method of competitive nitration.[6–8] Thus for 2, in the presence of equimolar quantities of toluene and benzene[9] at 25°, the observed substrate selectivity ($k_{\text{toluene}}/k_{\text{benzene}}$) = 36.5. For comparison some recently reported values for nitrating agents at 25° are: $k_T/k_B = 1.62$ for $NO_2^+PF_6^-$ in nitromethane;[10] $k_T/k_B = 28.0$ for HNO_3–H^+ in sulfolane;[11] $k_T/k_B = 26.6$ for acetyl nitrate in acetic anhydride.[12,13]

Under conditions identical with that for 2, the 2,6-lutidine salt 4 (X = H) is even more selective (k_T/k_B = 39.0). That the latter result is an inductive phenomenon and that the reactivity of N-nitropyridinium ions is a function of both the steric environment around the N–N bond and basicity of the amine are seen in the behavior of trisubstituted N-nitropyridinium ions 4 where electron-releasing 4 substituents result in increasing the selectivity even further. The substitution

Table I. Competitive Nitration of Benzene and Toluene with N-Nitro Salts in Acetonitrile at 25°

		Isomer distribution, %				Partial rate factors		
N-Nitro salts[a]	$k_{\text{toluene}}/k_{\text{benzene}}$[b]	*ortho*	*meta*	*para*	*ortho*:*para*	*ortho*	*meta*	*para*
2	36.5	63.8	3.2	33.0	1.93	69.9	3.5	72.3
4, X = H	39.0	63.9	3.0	33.1	1.93	74.7	3.5	77.4
4, X = CH_3	41.4	63.1	3.1	33.8	1.86	78.5	3.8	84.0
4, X = OCH_3	44.5	64.1	2.6	33.3	1.93	85.5	3.5	88.9
5[c]	13.2	62.1	2.1	35.8	1.73	24.6	0.8	28.4

[a] The gegenion in all cases is BF_4^-. [b] The results are the average of three independent runs and are accurate to ±2%. [c] Reaction was run using nitromethane as solvent because of limited solubility of this salt in acetonitrile.

---

(1) S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961); S. J. Kuhn, *Can. J. Chem.*, **40**, 1660 (1962).

(2) G. A. Olah, J. A. Olah, and N. A. Overchuk, *J. Org. Chem.*, **30**, 3373 (1965).

(3) See also J. Jones and J. Jones, *Tetrahedron Letters*, 2117 (1964).

(4) In all cases thus far studied, stable crystalline salts can be isolated. The physical properties of these salts will be reported at a later time.

(5) Nitration of toluene by 1 does occur slowly at 80° (refluxing acetonitrile). However, this reaction is complicated by further reactions of 1 with solvent at this temperature.

(6) C. K. Ingold and M. S. Smith, *J. Chem. Soc.*, 905 (1938), and earlier papers.

(7) For a discussion of the competitive method of nitration, see M. J. S. Dewar, T. Mole, and E. W. T. Warford, *ibid.*, 3576 (1956).

(8) Kinetic studies are also in progress in order to determine the absolute rate constants.

(9) The competitive nitrations were carried out by the addition of a solution of the N-nitro salt in acetonitrile to a well-stirred solution of toluene and benzene in acetonitrile. The mole ratio of the combined aromatic substrate: N-nitro salt was 10:1. All reactions were run under dry nitrogen. The reaction mixtures were analyzed by gas–liquid partition chromatography on a Perkin-Elmer Model F-11 with a 150-ft polypropylene glycol capillary column.

(10) G. A. Olah and N. A. Overchuk, *Can. J. Chem.*, **43**, 3279 (1965).

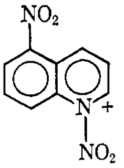
(11) G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *J. Am. Chem. Soc.*, **84**, 3687 (1962).

(12) A. K. Sparks, *J. Org. Chem.*, **31**, 2299 (1966).

(13) For a recent review of nitration, see J. H. Ridd in "Studies on Chemical Structure and Reactivity," J. H. Ridd, Ed., John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 7.

pattern, partial rate factors, and substrate selectivities for these salts are summarized in Table I.

As anticipated from our results in the pyridine series, the *peri* interaction in N-nitroquinoline sufficiently weakens the N–N bond and allows transfer nitration to occur readily. The enhanced reactivity of the N-nitroquinoline **5** (Table I) illustrates further the importance



5

of base strength in determining reactivities of N-nitro compounds.[14] Particularly noteworthy is the small but significant decrease in positional selectivity observed for **5** despite its lower substrate selectivity. The factors responsible for this behavior along with related mechanistic studies of these reactions are currently under investigation.

[14] It is tempting to ascribe the increased reactivity of **5**, in comparison with the N-nitropyridinium salts, solely to the reduced basicity of the quinoline. However, the importance of solvent in determining reactivity remains to be studied.

[15] National Defense Education Act Fellow, 1965–1968.

Chris A. Cupas, Ronald L. Pearson[15]
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received May 2, 1968

The Free-Radical Nature of Chlorotris(triphenylphosphine)rhodium-Catalyzed Autoxidations of Cyclohexene and Ethylbenzene

Sir:

Chlorotris(triphenylphosphine)rhodium [$(Ph_3P)_3RhCl$] is a well-known, potent homogeneous hydrogenation catalyst.[1] Its catalytic properties in oxidation reactions with molecular oxygen were recently reported[2–5] and postulated[2–4] to involve unique oxygen activation by coordinatively unsaturated d^8 complexes. We now wish to present evidence that autoxidations of cyclohexene and ethylbenzene catalyzed by $(Ph_3P)_3RhCl$ are free-radical chain oxidations.[6]

We compared the products and the over-all rates of oxidation[7] in the presence of $(Ph_3P)_3RhCl$ with those using rhodium acetylacetonate [$Rh(AcAc)_3$], rhodium 2-ethylhexanoate [$Rh(2\text{-}EH)_3$], and cobalt 2-ethylhexanoate [$Co(2\text{-}EH)_2$]. The results of cyclohexene autoxidations are in Table I.

All three rhodium compounds catalyze autoxidation of cyclohexene and yield similar product mixtures. Furthermore, cobalt 2-ethylhexanoate catalyzed autoxidation shows an almost identical product distribution. 2-Cyclohexen-1-yl hydroperoxide, the major product from thermal autoxidation of cyclohexene,[8] was found in all metal-catalyzed oxidations. The α,β-unsaturated alcohol and ketone are secondary products which arise from the initially formed hydroperoxide. The chain nature of the reaction is demonstrated by complete inhibition of the oxidation by 2% of hydroquinone.

Table I. Products of Metal-Catalyzed Autoxidations of Cyclohexene at 60°[a]

			Yield, %			
Catalyst[b]	Time, hr	Convn, %	2-Cyclohexen-1-one[c]	2-Cyclohexen-1-ol[c,d]	Hydroperoxide[e]	Other[f]
$(Ph_3P)_3RhCl$	10	63	35	28	27	14
$Rh(AcAc)_3$	10	78	51	20	18	11
$Rh(2\text{-}EH)_3$	10	62	57	20	15	8
$Co(2\text{-}EH)_2$	10	79	48	20	21	11
$(Ph_3P)_3RhCl$[g]	10	0				
None	10	1				

[a] Oxidation reactions were 4.8 *M* in cyclohexene (Phillips 99%, silica gel treated) and 2.9×10^{-3} *M* in catalyst [$(Ph_3P)_3RhCl$ was 1.4×10^{-3} *M*] in benzene. [b] 2-Ethylhexanoates were prepared by the method of J. F. Harrod and A. J. Chalk (*J. Am. Chem. Soc.*, **86**, 1776 (1964)). Other compounds were commercial chemicals. [c] Determined by glpc after reduction with Ph_3P. Identities were confirmed by comparison of ir and mass spectra of trapped samples with reference spectra. [d] Carbinol product is total carbinol[c] minus hydroperoxide. [e] Determined iodometrically. [f] Unidentified products. [g] In the presence of 2 mol % of hydroquinone.

In the case of ethylbenzene autoxidations (Table II), the similarity in the product distribution is even more striking. Only traces of hydroperoxide were detected in these oxidations. In addition to the indicated products, small amounts of benzoic acid were formed by complete side-chain oxidation. Again, the reaction was completely inhibited by a free-radical inhibitor. With both substrates the uncatalyzed reactions were much slower than the metal-catalyzed oxidations.

Table II. Products of Metal-Catalyzed Autoxidations of Ethylbenzene at 130°[a]

			Yield, %		
Catalyst[b]	Time, hr	Convn, %	Acetophenone[c]	1-Phenylethanol[c,d]	Hydroperoxide[e]
$(Ph_3P)_3RhCl$	2	8	66	33	3
	10	34	80	19	2
$Rh(AcAc)_3$	2	10	60	40	2
	10	29	80	20	1
$Rh(2\text{-}EH)_3$	2	13	67	33	2
	10	36	82	18	1
$Co(2\text{-}EH)_2$	2	8	76	24	2
	10	63	92	8	0
$(Ph_3P)_3RhCl$[f]	10	0			
None	10	8	20	2	76

[a] Neat ethylbenzene containing 4.8×10^{-3} *M* catalyst [$Co(2\text{-}EH)_2$ was 8.2×10^{-3} *M*]. [b–e] See corresponding footnotes in Table I. [f] In the presence of 1 mol % of 6-*t*-butyl-*o*-cresol.

In separate experiments we showed that $(Ph_3P)_3RhCl$–*t*-butyl hydroperoxide system initiates rapid polymeriza-

---

[1] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1711 (1966).

[2] J. P. Collman, M. Kubota, and J. W. Hosking, *J. Am. Chem. Soc.*, **89**, 4809 (1967).

[3] J. Blum, H. Rosenman, and E. D. Bergmann, *Tetrahedron Letters*, 3665 (1967).

[4] J. Blum and H. Rosenman, *Israel J. Chem.*, **5**, 69 (1967).

[5] A. J. Birch and G. S. R. Subba Rao, *Tetrahedron Letters*, 2917 (1968).

[6] J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968), recently suggested that some oxidations catalyzed by d^8 complexes might be free-radical reactions.

[7] The oxidations were carried out in cylindrical glass vessels provided with an efficient stirrer, external heater, air-inlet tube, and reflux condenser.

[8] D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem. Soc.*, **87**, 4824 (1965).