produce a solid. A crystalline product, mp 116–118°, was finally obtained when a small sample of the oily mixture of nitrones (in methanol) was seeded with a mixture of **9a** and **9b** obtained from the above oxime-alkylation reaction. This crystalline sample provided seed crystals for fractional crystallizations employing hexane and ether–hexane mixtures. In these solvents **9a** and **10** cocrystallize, but **9a** mainly as needles and **10** mainly as hemispheres. The two were separated mechanically. Two final recrystallizations of **10** from 10% ether in hexane afforded 0.345 g (15%) of **10** as nearly colorless crystals, mp 118.0–118.7°. The spectral features of **10** are as follows: pmr (CCl_4) δ 7.87–8.10 (m, 2, aromatic), 7.05–7.30 (m, 12, aromatic), 4.87 (s, 2, CH_2), 2.42 (s, 3, *p*-CH_3); uv (C_2H_5OH) λ_{max} 300 nm (ϵ 12,730).

Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 84.09; H, 6.30; N, 4.63.

Mechanically separated samples of the isomeric nitrone **9a** were combined with corresponding samples from a second preparation and recrystallized from 1:1 ether–hexane yielding pure **9a**, mp 107–108°. The yield of **9a** in the first preparation was only approximately 5%.

Kinetics of the Thermal Configurational Isomerization of Nitrones 7a, 8a, 9a, and 10 in *tert*-Butyl Alcohol.—Control experiments demonstrated that, under the conditions of the kinetic measurements, decomposition of the nitrones (to unidentified products) occurred to an extent less than 2%. Kinetic measurements were performed as follows. Samples of the nitrones in *tert*-butyl alcohol were thoroughly degassed and sealed in Pyrex tubes under reduced pressure. The sample tubes were placed in a constant-temperature bath at the appropriate temperature maintained at ±0.05° of the values cited in Table I. Samples were periodically removed, quenched at low temperature, opened, and concentrated to oils. The nmr spectra were then determined in deuteriochloroform. The isomeric composition of each sample was determined from the relative areas of the two methyl proton absorptions. In all cases, the equilibrium constant was 1.0 ± ~0.08. With the above data and assuming a first-order reversible rate law, the rate constants shown in Table I were calculated. Rate constants for the isomerization of **7a** were unaffected by a tenfold change in concentration.

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Registry No.—**7a**, 42449-48-9; **7b**, 42449-49-0; **8a**, 42449-50-3; **8b**, 42449-51-4; **9a**, 42449-52-5; **9b**, 42449-53-6; **10**, 42449-54-7; **13**, 622-30-0; **14**, 42449-55-8; (*Z*)-4-methylbenzophenone oxime, 2998-92-7; benzyl chloride, 100-44-7.

Notes

Metal-Catalyzed Electrophilic Substitution and Coupling of Naphthalene. Kinetic and Catalytic Considerations

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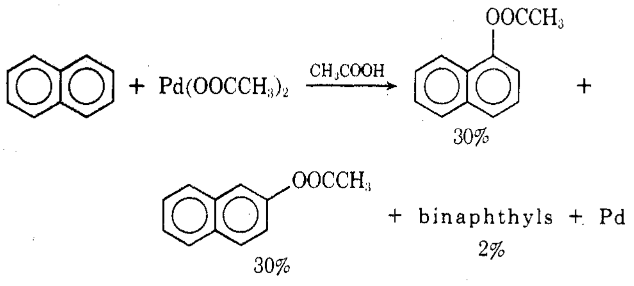
Reactions of benzene and its derivatives with palladium salts have been studied by a number of investigators in recent years.[1] Acetoxylation and/or oxidation of these aromatics in a manner analogous to the Wacker process have apparently not been developed as yet to the status of industrial processes. In that respect, little notice has been given to similar reactions of condensed aromatic ring systems. The present report concerns the results of our study of the acetoxylation of naphthalene under catalytic conditions employing $Pd(CH_3COO)_2$ and other metal salts. Of particular interest was the isomer distribution, since from the preparative standpoint a process yielding predominantly one isomer would be desirable.

Results and Discussion

A reaction stoichiometric with respect to Pd^{2+} was carried out with a mixture of $Pd(CH_3COO)_2$, $C_{10}H_8$, and CH_3COONa at a molar ratio of ~1:1.2:1 in glacial acetic acid. At the reflux temperature of the solvent the reaction appeared to proceed at a faster rate than the analogous benzene reactions. The reaction was essentially complete within 4 hr. The products and the corresponding yields based on Pd^{2+}, are shown in the following Scheme I. Decomposition of $Pd(CH_3COO)_2$ also occurs with formation of CO_2, which was detected mass spectroscopically, and partially accounts for the low overall yield. The naphthyl acetates are readily hydrolyzed in mildly alkaline solutions. Naphthols found in the products are most probably entirely formed during the work-up, which involved treatment with saturated aqueous $NaHCO_3$ and ethyl ether, but some direct production from the small amount of water present in the reaction mixture cannot be ruled out.

SCHEME I



Following completion of this work, a communication appeared[2] in which the same reaction was claimed to yield oxidation products having an isomer ratio of 1:1, in agreement with our results.

In conventional Wacker-type processes, the reoxida-

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[1] (a) O. R. Van Helden and G. Verberg, *Recl. Trav. Chim. Pays-Bas*, **84**, 1263 (1965); (b) J. M. Davidson and C. Triggs, *J. Chem. Soc. A*, 1324 (1968); (c) K. Ichikawa, S. Vemura, and T. Okada, *Nippon Kaga Ku Zasshi*, **20**, 212, (1969); (d) P. M. Henry, *J. Org. Chem.*, **36**, 1886 (1971).

[2] L. Eberson and L. Gomez-Gonzales, *Chem. Commun.*, 263 (1971).

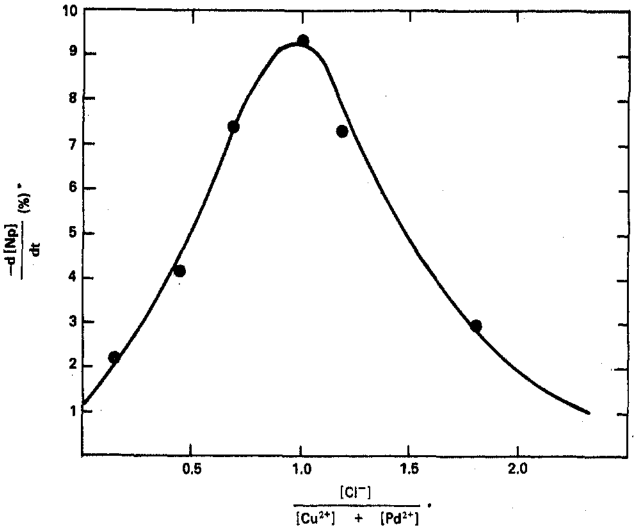


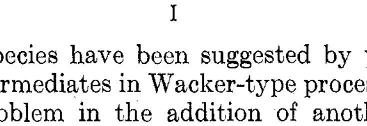
Figure 1.—Average rate of naphthalene consumption as a function of the $[Cl^-]/([Cu^{2+}] + [Pd^{2+}])$ ratio.

tion of Pd to give a catalytic reaction is accomplished by the use of redox systems such as Cu^{+2}/Cu^+ or Fe^{3+}/Fe^{2+}, *e.g.*

$$2CuX_2 + Pd \longrightarrow PdX_2 + 2CuX$$
$$2CuX + 2HX + {}^1\!/_2O_2 \longrightarrow 2CuX_2 + H_2O$$
$$\overline{Pd + 2HX + {}^1\!/_2O_2 \longrightarrow PdX_2 + H_2O}$$

A number of experiments were conducted using several redox systems to investigate the catalytic possibilities of aromatic acetoxylation. The results are presented in Table I.

These investigations indicate that the success of this step depends on the nature of the anion, X, and on the relative concentrations of the metal ions and X in the solution. Acetates of Cu^{2+}, Fe^{3+}, and UO_2^+ were largely ineffective under atmospheric pressure of oxygen and only slightly effective under high pressures of oxygen. Similar conclusions were reached by other investigators.[3] The addition of another nucleophile, especially a halide ion, to the $Cu(CH_3COO)_2/Pd(CH_3COO)_2$ system promotes the reoxidation of Pd and makes the reaction catalytic with respect to Pd even at atmospheric pressure. The highest rate for the reoxidation of Pd, as measured by the rate of $C_{10}H_8$ consumption over the first 4 hr, occurs at a $[Cl^-]/([Cu^{2+}] + [Pd^{2+}])$ ratio equal to 1 and falls off rapidly as this ratio approaches either 0 or 2 (Figure 1). This relationship suggests that the active catalytic species may be a halide bridged complex of the form I.



I

Similar species have been suggested by various authors as intermediates in Wacker-type processes.[4] The inherent problem in the addition of another nucleophile to the system is that it functions not only to promote reoxidation of Pd, but also participates in product formation, *i.e.*, chloronaphthalene. The relative yields of naphthyl acetate and chloronaphthalene are significantly affected by changing the $[OAc^-]/[Cl^-]$ ratio. At a 2.30 ratio the highest recorded[5] yields during the course of the reaction were 21% α-naphthyl acetate and 30% α-chloronaphthalene, whereas at 3.39 the yields were 39 and 11%, respectively. In a typical run using a 7:1 molar ratio of $C_{10}H_8$ to $Pd(OOCCH_3)_2$ and under the optimum redox conditions, the highest combined yield of α-chloronaphthalene and α-acetoxynaphthalene, 25% of naphthalene consumed, is found after ~4 hr and falls over longer time periods. The bulk of naphthalene is eventually converted to binaphthyl, multisubstituted naphthalenes, and acetoxy- and chloro-substituted polynuclear products containing palladium. Water (10% in glacial acetic acid) further reduces the yield of the monomeric products.

Of the other reoxidant systems employed in conjunction with oxygen, quinones, *e.g.*, chloranil, were ineffective, but an $Fe(NO_3)_3/LiCl$ system did promote a reaction catalytic with respect to Pd.

The effects of the different $[CH_3COO^-]/[Cl^-]$ ratio on the rate is seen to be minimal. For the first 6 to 8 hr the reaction is first order in naphthalene. A control experiment was carried out without $Pd(OOCCH_3)_2$ (see Experimental Section). The rate of naphthalene consumption ($k \simeq 1.2 \times 10^{-5}$ sec^{-1}) was approximately one third that in the run with $Pd(OOCCH_3)_2$ under the same reagent concentrations and conditions. In the control experiment only traces of substituted products were found by vpc; coupling[6] and oxidation to quinonic derivatives appeared to be the predominant reaction routes. Binaphthyls were identified by vpc and the polymeric product of the reaction showed characteristic quinonic ir absorption. Acetoxy and chloro substituents appeared to be absent.

A redox system such as Cu^{2+}/Cu^+ is necessary for reoxidation of Pd under mild conditions and the achievement of a catalytic acetoxylation. However, the direct participation of Cu^{2+} in the oxidation of the organic substrate to coupled products (either of naphthalene or of the monosubstituted products) results in loss of selectivity.

An interesting effect observed in the runs incorporating both Cu and Pd and Cl^- ion is the nearly exclusive selectivity for α substitution in contrast to the 50:50% α:β substitution pattern obtained using $Pd(OOCCH_3)_2$ alone. The reason for this behavior might be electronic given the differences in structure between Cl^- bridged complexes, such as I, and $Pd(OOCCH_3)_2$.[7] The stoichiometric reaction of naphthalene with $Pd(OOCCF_3)_2$ results in exclusive α substitution.[8]

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[3] M. Tamura and T. Yasui, *Kogyo Kaga Ku Zasshi*, **71**, 1858 (1968).

[4] See, *e.g.*, R. G. Schultz and D. E. Gross in "Homogeneous Catalysis," *Advan. Chem. Series*, **70**, 97 (1968).

[5] The participation of α-chloronaphthalene and α-naphthyl acetate in secondary coupling reactions under catalytic conditions results in loss of directly measurable yield of these products. This reaction sequence is shown by (a) the isolation of 1,1,-binaphthyl 4,4'-diacetate in the first 4 to 6 hr of the experiment and (b) vpc monitoring of the reaction; the yield of monosubstituted products increases gradually during the first 5 hr and then decreases exponentially. This behavior is in line with participation of the initial products in secondary reaction schemes. The pattern applies generally to all catalytic runs, with only small rate variations, attributable to the different reactant ratios.

[6] Cupric halides are well-known halogenating agents for aromatic systems and in certain occasions may act as coupling agents as well. See, *e.g.*, D. C. Nonhebel and J. A. Russel, *Tetrahedron*, **25**, 3493 (1969). $CuCl_2$ acts as an exclusive coupling agent in our reactions, as deduced by the absence of chlorinated products and the formation of coupled naphthalene derivatives.

[7] A. C. Skapski and M. L. Smart, *Chem. Commun.*, 658 (1970).

[8] G. G. Arzoumanidis, F. C. Rauch, and G. Blank, Abstracts of Papers, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, No. 73 (Inorg.).

Experimental Section

Materials.—Palladium acetate was purchased by Engelhard Industries. Absence of nitrate ions in the compound was confirmed by ir. Reagent grade chemicals were used without further purification.

Rate Studies.—The rate of naphthalene consumption and product formation was followed by vpc. A Hewlett-Packard Model 5750 research chromatograph, equipped with a flame ionization detector and a 6-ft column of 10% Apiezon L on Chromosorb W maintained at 220°, was employed. Products were identified by vpc retention time and ir comparison with authentic samples.

Acetoxylation of Naphthalene.—$Pd(OOCCH_3)_2$ [1.485 g (6.6 mmol)], $C_{10}H_8$ [1.024 g (8.0 mmol)], and CH_3COONa [0.584 g (7.1 mmol)] were dissolved in 10 ml of 99% glacial acetic acid and allowed to react at the reflux temperature of the solvent. The mixture assumed a dark color after 10 min and the reaction continued for 4 hr.

The Pd black isolated (0.725 g) indicated quantitative conversion. The acetic acid filtrate was suspended in ether–aqueous $NaHCO_3$, and the ether extract was evaporated to obtain the products. Vpc analysis of the solid products indicated the following compounds to be present (yields): α-naphthylacetate (25%), β-naphthylacetate (25%), α-naphthol (6%), β-naphthol (6%), and binaphthyls (2%).

A Typical Catalytic Reaction.—$C_{10}H_8$ [2.096 g (16.4 mmol)], $Pd(CH_3COO)_2$ [0.498 g (2.2 mmol)], $Cu(CH_3COO)_2 \cdot H_2O$ [0.890 g (4.5 mmol)], $LiOOCCH_3 \cdot 2H_2O$ [1.356 g (13.3 mmol)], and LiCl [0.291 g (6.9 mmol)] were suspended in 15 ml of CH_3COOH in a 100-ml, three-neck flask. The mixture was heated at the reflux temperature for 12 hr while oxygen was sparged through the solution. The yield (based on Pd^{2+}) of isolable[5] monomeric products was highest in about 4 hr after the start of the experiment: α-naphthylacetate (39%) and α-chloronaphthalene (11%).

Control Run.—The above reaction was repeated without $Pd(CH_3COO)_2$. Only traces of monosubstituted products could be detected *via* vpc.

Registry No.—$Pd(OOCCH_3)_2$, 3375-31-3; naphthalene, 91-20-3.

Supplementary Material Available.—A table containing 14 oxidative reactions of naphthalene in the presence of $Pd(OOCCH_3)_2$ with various redox systems and three kinetic figures depicting two of the runs will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-73-4443.

Kinetics and Mechanism of the Reactions of Allyl Halides with Silver Nitrate in Acetonitrile

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Kinetic studies of the reactions of methyl, primary, and secondary alkyl halides with acetonitrile solutions of silver nitrate have indicated a mechanism in which electrophilic assistance by the silver ion is accompanied, in the rate-determining step, by nucleophilic attack by nitrate ion.[1,2] Alkyl halides found to exhibit these characteristics include methyl,[1] ethyl,[1,3] neopentyl,[1] and isopropyl[1] iodides, 1-octyl and 2-octyl bromides,[2] and 2-octyl chloride.[2] For concentrations of silver salt within the range 0.002–0.2 *M* the overall kinetic order approximates 2.5, first order in alkyl halide, first order in silver ion, and one-half order in nitrate ion.[2]

If the reasonably nucleophilic nitrate ion is replaced by the weakly nucleophilic perchlorate ion, the rate of precipitation of silver halide is considerably reduced; for example, with 0.03 *M* silver salt at 44.6°, silver nitrate reacts with 2-octyl bromide 80 times faster than silver perchlorate.[4] Additional evidence for SN2 character in the rate-determining step comes from a considerably slower reaction for the appreciably sterically hindered neopentyl iodide than for the considerably less hindered, but also primary, ethyl iodide.[1]

A reconsideration[1,2] of product data obtained for reactions of silver nitrate with ethyl iodide in ethanol[5,6] suggested that an ion pair containing the carbonium ion and the nitrate ion is formed, which then either collapses to product or undergoes solvolysis. A recent study of the reactions of 1-adamantyl halides with silver nitrate in ethanol[7] also implicated such an ion pair. The complex kinetics and the variation observed for the product partitioning between solvolysis and anion exchange with changing identity of the halogen suggested that, in the product-determining step, the halide ion is still in the vicinity of the carbonium ion. They may well be contained within an ion quadruplet or an even more complex aggregate.[7]

While it is reasonable to suppose that the scheme postulated for reactions in ethanol[1,2,7] can also be extended to reactions in other solvents, it should be emphasized that there is no *direct* evidence for formation of ion pairs between a carbonium ion and the anion of the silver salt during reactions in acetonitrile. An argument developed earlier[1] in favor of such an ion pair within reactions of alkyl iodides with silver perchlorate was based on the assumption that covalent alkyl perchlorates would not be solvolyzed by acetonitrile. It has, however, been shown that 2-octyl perchlorate has, in acetonitrile at 25.0°, a half-life of less than 1 min.[8] Nucleophilic attack within the rate-determining step and intermediate ion-pair formation has also been suggested for the reaction in acetonitrile between *tert*-butyl bromide and silver *p*-toluenesulfonate.[9]

A study of the reactions of the tertiary α-halogenated ketone, α-bromo-*p*-phenylisobutyrophenone, with silver salts in acetonitrile[10] also suggested nucleophilic participation by nitrate ion within the rate-determining step of the reaction with silver nitrate.

Previous studies of silver ion assisted reactions of allylic halides have usually been interpreted (in the Hughes–Ingold terminology[11]) as SN1 Ag^+ reactions, involving in the rate-determining step an electrophili-

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[1] G. S. Hammond, M. F. Hawthorne, J. H. Waters, and B. M. Graybill, *J. Amer. Chem. Soc.*, **82**, 704 (1960).

[2] Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.*, **87**, 4760 (1965).

[3] F. G. Donnan and H. E. Potts, *J. Chem. Soc.*, **97**, 882 (1910); for a reassessment of these data see ref 2.

[4] Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.*, **87**, 4771 (1965).

[5] A. K. Burke and F. G. Donnan, *J. Chem. Soc.*, **85**, 555 (1904).

[6] F. G. Donnan and A. K. Burke, *Z. Phys. Chem. (Leipzig)*, **69**, 148 (1909).

[7] D. N. Kevill and V. M. Horvath, *Tetrahedron Lett.*, 711 (1971).

[8] Y. Pocker and D. N. Kevill, *J. Amer. Chem. Soc.*, **87**, 5060 (1965).

[9] H. M. R. Hoffmann, *J. Chem. Soc.*, 6748 (1965).

[10] D. N. Kevill and N. H. Cromwell, *J. Org. Chem.*, **29**, 499 (1964).

[11] See, for example, C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, pp 479–483.