that only a very limited number of hydrocarbon substrates oxidize with major participation of intramolecular abstraction. Normal and cyclic[14] alkanes may, therefore, be the general case and explanations are required, instead, for the exceptional cases of alternately branched alkanes. We can only speculate at this time that unusual steric factors operate in the alternately branched alkanes which promote reaction 5 by a favored orientation–restricted chain rotation mechanism. Partial screening of the reactive tertiary hydrogens of the substrate from external attack (reaction 4) by the clusters of methyl groups present must also be a factor.[4]

**Acknowledgments.**—This study was supported by several chemical and petroleum companies as part of SRI's Oxidation Program.

**Registry No.**—*n*-Pentane, 109-66-0; *n*-octane, 111-65-9.

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# A Kinetic Investigation of the Configurational Isomerization of Geometrically Isomeric Nitrones[1a]

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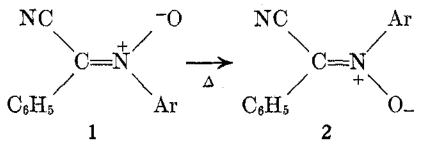
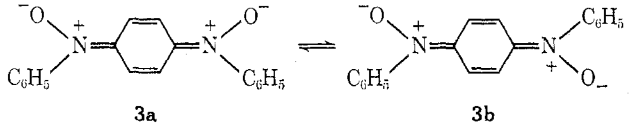
The *Z* and *E* isomers of *N*-methyl-α-(*p*-tolyl)-α-phenyl nitrone (**7a** and **8a**) and the *Z* and *E* isomers of *N*-benzyl-α-(*p*-tolyl)-α-phenyl nitrone (**9a** and **10**) were prepared. Alkylations of isomeric oxime anions and the reaction of *N*-benzylhydroxylamine (**13**) with 1,1-dichloro-4′-methyldiphenylmethane (**14**) were employed in the syntheses. The first-order rates for thermal approach to geometric equilibrium of **7a**, **8a**, **9a**, and **10** were determined in degassed *tert*-butyl alcohol solutions. Activation parameters for the isomerization of **9a** were determined in the same solvent and are $\Delta E^{\neq} = 33.6 \pm 1.4$ kcal/mol; $\Delta S^{\neq} = -4 \pm 4$ eu. The energy barrier to isomerization is substantially larger than would be anticipated from the limited data available from previous studies of geometric isomerizations of nitrones. These results are briefly discussed.

The existence of separate geometric isomers of unsymmetrical nitrones has been reported on several occasions. A modest configurational stability of α,α-diaryl-*N*-methyl nitrones has been inferred from the apparent absence of geometric isomerization during recrystallizations and upon melting.[2,3] By contrast, Barrow and Thorneycroft[4] observed that the cis isomers (**1**) of some *N*-aryl-α-phenyl nitrones slowly isomerized to the trans isomers (**2**) during melting point determinations. Koyano and Tanaka[5] investigated this isomerization in *n*-butyl alcohol. The activation energy for the cis to trans isomerization of *N*,α-diphenyl-α-cyano nitrone (**1** → **2**; Ar = $C_6H_5$) was found to be 24.6 kcal/mol. Layer and Carman[6] have reported a study of the geometric isomerization of *N*,*N*′-diphenyl-*p*-benzoquinonediimine *N*,*N*′-dioxide (**3a** and **3b**). The pmr study in deuteriochloroform provided an estimate of the energy barrier ($\Delta F^{\neq}$ below room temperature) of about 12 kcal/mol from data obtained at the coalescence temperature. More recently Boyle, Peagram, and Whitham estimated the rate constant for the "configurational exchange" of the vinyl protons for *N*-(1-ethylcyclohexyl) nitrone (**4**) by pmr methods.[7] From the first-order rate constant at 180°, a free energy of activation of 23.2 kcal/mol was calculated.

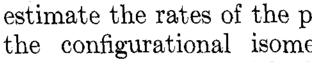


**1** **2**

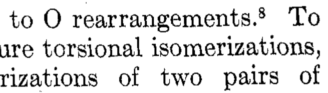


**3a** **3b**

Our interest in obtaining rates and activation energies for the geometric isomerization of certain nitrones derives from our investigation of the stereochemical course of the N to O rearrangements of (*Z*)- (**5**) and (*E*)- (**6**) *N*-benzhydryl-α-(*p*-tolyl)-α-phenyl nitrone.[8]

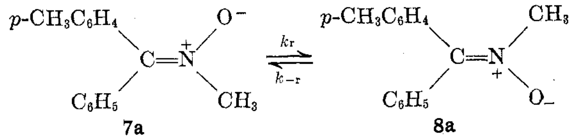


**5**



**6**

Evidence was obtained[8] that these rearrangements proceed *via* intermediate benzhydryl and rapidly interconverting iminoxy radicals. Since it was also discovered that these radicals recombine at nitrogen as well as oxygen, this provided a potential route to the geometric isomerization of **5** and **6** which was observed during the course of the N to O rearrangements.[8] To estimate the rates of the pure torsional isomerizations, the configurational isomerizations of two pairs of isomeric nitrones which do not appear to dissociate to alkyl and iminoxy radicals were investigated. The nitrones chosen for this study were the *Z* and *E* isomers of *N*-methyl-α-(*p*-tolyl)-α-phenyl nitrone (**7a** and



**7a** **8a**

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[1] (a) Taken in part from the Ph.D. Thesis of Thomas S. Dobashi, California State University, San Diego, and the University of California, San Diego, 1973. (b) NDEA Fellow, 1967–1971. (c) NSF College Teacher Reseasch Participant, summer, 1971.

[2] O. L. Brady and R. P. Mehta, *J. Chem. Soc.*, 2297 (1924).

[3] L. Semper and L. Lichtenstadt, *Chem. Ber.*, **51**, 928 (1918).

[4] F. Barrow and F. J. Thorneycroft, *J. Chem. Soc.*, 722 (1934); 769 (1939).

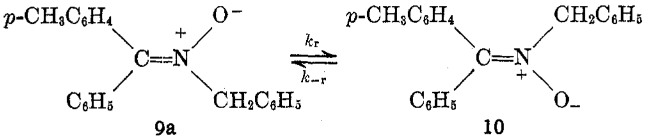
[5] K. Koyano and I. Tanaka, *J. Phys. Chem.*, **69**, 2545 (1965).

[6] R. W. Layer and C. J. Carman, *Tetrahedron Lett.*, 1285 (1968).

[7] L. W. Boyle, M. J. Peagram, and G. H. Whitham, *J. Chem. Soc. B*, 1728 (1971).

[8] T. S. Dobashi and E. J. Grubbs, *J. Amer. Chem. Soc.*, **95**, 5070 (1973).

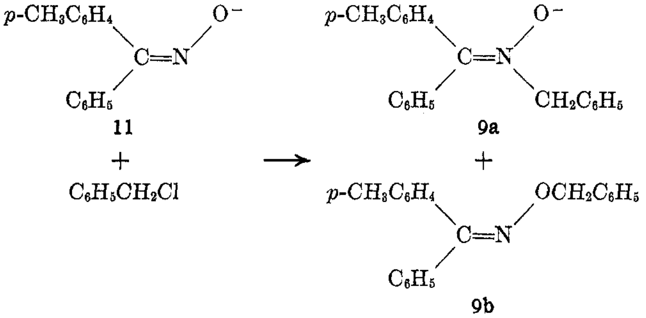
**8a**, respectively) and the corresponding isomers of *N*-benzyl-α-(*p*-tolyl)-α-phenyl nitrone (**9a** and **10**, respectively). The rates of approach to equilibrium in these systems are easily measured by use of pmr, since within each isomeric pair the chemical shifts of the methyl singlets differ sufficiently.

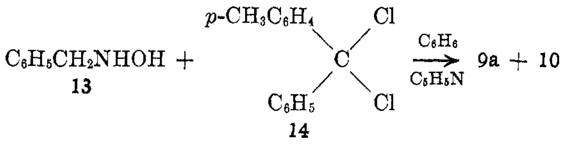


**9a** **10**

## Results and Discussion

The nitrones **7a** and **8a** (along with the corresponding *O*-methyl oximes) were obtained by the dimethyl sulfate alkylations of (*Z*)- (**11**) and (*E*)- (**12**) 4-methylbenzophenone oximates.[3] The *N*-benzyl nitrone **9a** was first prepared by the reaction of **11** with benzyl chloride in ethanol. A mixture of the two *N*-benzyl nitrones **9a** and **10** was prepared by the reaction of *N*-benzylhydroxylamine (**13**) with 1,1-dichloro-4′-methyldiphenylmethane (**14**). Geometric assignments for the pure separated nitrones were made by a pmr method based upon the multiplicity characteristics of the ortho protons of the α-aryl rings cis to the oxygen atom.[9,10]





The rate constants for approach to equilibrium (assuming a reversible first-order rate law) were determined in degassed *tert*-butyl alcohol solutions. The rate constants, $k_r$ (rotation), along with probable errors, are listed in Table I.

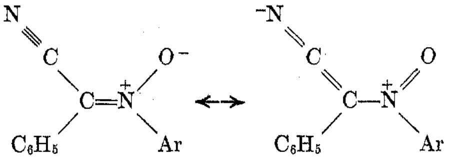
The activation parameters for the isomerization of the *N*-benzyl nitrone **9a** calculated from the last six entries of Table I are $E_a = 33.6 \pm 1.4$ kcal/mol, $\Delta S^{\ddagger} = -4 \pm 4$ eu. This energy barrier is much larger than that determined for the cis to trans isomerization of *N*,α-diphenyl-α-cyano nitrone.[5] It is also considerably larger than those which might be estimated (assuming small entropies of activation) for the **3a** to **3b** isomerization or for the "configurational exchange" of vinyl protons in **4**. The barrier for the α-cyano derivative may be low (compared with **9a**) because of the reduction of C=N double bond character through contributions of resonance forms such as **15** to the hybrid. Similar delocalization effects could account for the low rotational barriers to the **3a** ⇌ **3b** isomerization, but no such explanation appears reasonable for the relatively low barrier associated with the pmr observed rotational process in **4**. Since it was reported[7] that decomposition occurred at the elevated temperatures employed in the study, the possibility of catalysis by some by-product is a reasonable concern.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE THERMAL GEOMETRIC ISOMERIZATION OF SOME *N*-ALKYL-α-(*p*-TOLYL)-α-PHENYL NITRONES IN *tert*-BUTYL ALCOHOL

| Nitrone | Temp, °C | $k_r \times 10^6$, sec$^{-1}$ |
|---|---|---|
| **7a**$^a$ | 144 | 4.3 ± 0.4 |
| **7a**$^a$ | 144 | 3.6 ± 0.4 |
| **7a**$^b$ | 144 | 3.5 ± 0.2 |
| **7a**$^b$ | 144 | 3.1 ± 0.1 |
| **7a**$^c$ | 144 | 3.7 ± 0.7 |
| **7a**$^c$ | 144 | 3.5 ± 0.2 |
| **8a** | 144 | 3.6 ± 0.4$^d$ |
| **10** | 144 | 7.2 ± 0.3$^d$ |
| **10** | 144 | 7.2 ± 0.2$^d$ |
| **9a** | 160 | 30.1 ± 3.3 |
| **9a** | 160 | 30.3 ± 1.0 |
| **9a** | 144 | 8.8 ± 0.9 |
| **9a** | 144 | 7.4 ± 0.4 |
| **9a** | 135 | 2.4 ± 0.1 |
| **9a** | 135 | 2.9 ± 0.1 |

[a–c] Nitrone concentrations: $9.2 \times 10^{-3}$ *M*;[a] $4.6 \times 10^{-2}$ *M*;[b] $9.2 \times 10^{-2}$ *M*;[c] all other runs, $3.3 \times 10^{-2}$ *M*. [d] *E* to *Z* isomerization, $k_{-r}$.



**1** **15**

In interpreting the stereochemical results of the cycloaddition of α-phenyl-*N*-methyl nitrone to norbornene, it was concluded (on the basis of the rate of "isomerization" of **4**) that at 85° the rate of geometric isomerization of this aldonitrone is reasonably rapid compared with the rate of the cycloaddition.[7] While this may be true, in light of our results it would appear that a study of the rates and interconversion barriers for aldoxime geometric isomerizations would be well justified; and the illusiveness of *E* isomers of aldonitrones may prove to be more a reflection of the difficulty in isolating them from mixtures overwhelmingly predominated by the *Z* isomers, rather than because of rapid thermal interconversion.[11]

An approximately twofold isomerization rate increase is observed when the *N*-methyl group (compounds **7a** and **8a**) is changed to *N*-benzyl (nitrones **9a** and **10**, Table I). This difference is probably due to increased ground-state energies of **9a** and **10** caused by larger nonbonded interactions between the benzyl and α-phenyl groups. The importance of such interactions in influencing electronic spectra of nitrones has been discussed.[12] Indeed, when benzyl (nitrone **9a** or **10**) is replaced by benzhydryl (nitrone **5** or **6**), the

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(9) K. Koyano and H. Suzuki, *Bull. Chem. Soc. Jap.*, **42**, 3306 (1969).

(10) E. J. Grubbs, R. J. Milligan, and M. H. Goodrow, *J. Org. Chem.*, **36**, 1780 (1971).

(11) E. Buehler, *J. Org. Chem.*, **32**, 261 (1967).

(12) T. Kubota, M. Yamakawa, and Y. Mori, *Bull. Chem. Soc. Jap.*, **36**, 1552 (1963).

observed first-order rate constant (under the same conditions) jumps to approximately $2.0 \times 10^{-5}$ sec$^{-1}$.[13] However, in this case the torsional process is, no doubt, accompanied by isomerization *via* intermediate isomerizing iminoxy radicals. Thus, this latter figure represents a maximum limiting value for the rotational rate constants for interconversion of **5** and **6**.

A comprehensive study of solvent effects upon the rates of geometric isomerization of these nitrones has not yet been conducted. However, one observation may be suggestive of the potential magnitude of such effects. The first-order rate constant for the isomerization of **10** to **9a** was determined in a degassed solution of diethylcarbitol (diethylene glycol diethyl ether) at 135°. The observed rate constant is $9.5 \pm 0.5 \times 10^{-5}$ sec$^{-1}$ (duplicate, $9.1 \pm 0.5 \times 10^{-5}$ sec$^{-1}$). A comparison of this rate constant with that for the **9a** to **10** isomerization in *tert*-butyl alcohol (approximately $2.65 \times 10^{-6}$; see Table I) at this temperature indicates that the rate is approximately 35 times slower in *tert*-butyl alcohol. Alcohols reportedly hydrogen bond to nitrones[14] (presumably at the nitrone oxygen atom). It is possible that this type of hydrogen bonding may increase the double-bond character of the α-carbon to nitrogen bond, thereby inhibiting the torsional isomerization. However, additional experimental work will be necessary to elucidate the nature of such solvent effects.

## Experimental Section

All melting points are uncorrected. The nmr spectra were obtained with a Varian Model A-60 spectrometer. Absorptions are reported in parts per million relative to internal TMS. Infrared spectra were obtained on a Perkin-Elmer 621 grating spectrophotometer, and uv spectra on a Cary Model 14 recording spectrophotometer. Analyses were performed by M. H. W. Laboratories.

(*Z*)-*N*-**Methyl-α-(*p*-tolyl)-α-phenyl Nitrone (7a)**.—This nitrone was prepared by the dimethyl sulfate methylation of (*Z*)-*p*-methylbenzophenone oxime using a method previously described by Semper and Lichtenstadt.[3] The initially obtained product is a mixture of unreacted oxime, **7a**, and the corresponding (*Z*)-*O*-methyl-*p*-methylbenzophenone oxime (**7b**). The nitrone and the *O*-methyl derivative were isolated (in low yields) by a combination of crystallization and chromatography (silica gel). The nitrone **7a** was obtained as colorless crystals, mp 90.5–91.5° (lit.[3] mp 91–92°), and showed the following spectral characteristics: pmr ($CDCl_3$) δ 7.92 (d, 2, aromatic), 6.95–7.73 (m, 7, aromatic), 3.69 (s, 3, NMe), 2.34 (s, 3, *p*-Me); uv (heptane) $\lambda_{max}$ 305 nm (ε 15,520); ir (KBr disk) 1255 cm$^{-1}$ (N → O stretch). The *O*-methyl oxime **7b** was obtained as colorless crystals, mp 70.5–71.5° (lit.[3] mp 70.5–72°), and showed the following spectral features: pmr ($CDCl_3$) δ 7.62–7.17 (m, 9, aromatic), 3.97 (s, 3, $OCH_3$), and 2.38 (s, 3, *p*-$CH_3$); uv ($C_2H_5OH$) $\lambda_{max}$ 261.5 nm (ε 11,180).

(*E*)-*N*-**Methyl-α-(*p*-tolyl)-α-phenyl Nitrone (8a)**.—The isomeric nitrone **8a** was prepared as described above [starting from pure (*E*)-*p*-methylbenzophenone oxime] and was isolated as colorless crystals, mp 111–112.5° (lit.[3] mp 113–114°). The spectral features of **8a** are as follows: pmr ($CDCl_3$) δ 7.82–8.20 (m, 2, aromatic), 7.06–7.68 (m, 7, aromatic), 3.73 (s, 3, NMe), 2.44 (s, 3, *p*-$CH_3$); uv ($C_2H_5OH$) $\lambda_{max}$ 303 nm (ε 14,310); ir (KBr disk) 1250 cm$^{-1}$ (N → O stretch). The corresponding *O*-methyl oxime **8b** was chromatographically separated from the reaction mixture and remained a colorless oil with the following spectral features: pmr ($CDCl_3$) δ 7.54 (m, 9, aromatic), 3.97 (s, 3, $OCH_3$), 2.34 (s, 3, *p*-$CH_3$); uv ($C_2H_5OH$) $\lambda_{max}$ 265.5 nm (ε 11,980).

(*Z*)-*N*-**Benzyl-α-phenyl-α-(*p*-tolyl) Nitrone (9a)**.—To 23 ml of absolute ethanol was added 0.490 g (0.0125 g-atom) of freshly cut potassium. Pure (*Z*)-4-methylbenzophenone oxime (2.64 g, 0.0125 mol) and then 2.14 g (0.0125 mol) of benzyl chloride were added. The mixture was stirred at room temperature for 48 hr. The reaction mixture was concentrated under dry nitrogen and the products were separated from KBr by extraction with chloroform. The chloroform extract was concentrated to a pale yellow oil. The crude product mixture (3.76 g) was chromatographed on 100 g of silica gel (60–200 mesh). Elution with hexane containing 50–75% methylene chloride afforded 2.52 g (67%) of (*Z*)-*O*-benzyl-*p*-methylbenzophenone oxime (**9b**), mp 85–86.5°. Recrystallization from hexane afforded 2.19 g of **9b** as colorless needles, mp 86–86.5°. Spectral characterization of **9b** revealed the following: pmr ($CCl_4$) δ 6.95–7.55 (m, 14, aromatic), 5.13 (s, 2, $CH_2$), 2.36 (s, 3, *p*-$CH_3$); uv ($C_2H_5OH$) $\lambda_{max}$ 263 nm (ε 12,830), 236 (16,280).

*Anal.* Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.78, 83.97; H, 6.34, 6.30; N, 4.60, 4.75.

Further elution with 10–25% ether in methylene chloride yielded approximately 10% unreacted oxime. Elution with 50% ether in methylene chloride, ether, and 2% methanol in ether afforded the crude nitrone **9a** (contaminated with approximately 6% of its geometric isomer **10**) as a white solid, mp 82–90°. Recrystallization first from 10% ether in hexane and then from hexane provided 0.56 g (15%) of **9a** as colorless crystals, mp 91.5–92.5°. The pmr spectrum (in $CCl_4$) revealed no evidence for the presence of **10** and showed the following absorptions: δ 7.88 (d, 2, aromatic), 6.85–7.50 (m, 12, aromatic), 4.83 (s, 2, $CH_2$), 2.31 (s, 3, *p*-$CH_3$).

*Anal.* Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.52, 83.71; H, 6.21, 6.28; N, 4.63, 4.63.

In a second preparation conducted as described above, the (*Z*)-*O*-benzyl oxime **9b** obtained possessed a melting point of 84–85°, but the melting point of nitrone **9a** was 106.5–108°. In all other respects (*i.e.*, spectral comparisons), this nitrone appeared identical with the lower melting sample. The source of this discrepancy in melting points is not yet clear.

(*Z*)- (**9a**) **and** (*E*)- (**10**) *N*-**Benzyl-α-phenyl-α-(*p*-tolyl) Nitrone**. A mixture of the isomeric nitrones was prepared by the reaction of *N*-benzylhydroxylamine (**13**) with 1,1-dichloro-4′-methyl-diphenylmethane (**14**). The dichloride **14** was prepared as follows. A mixture of 4.48 g (0.0228 mol) of 4-methylbenzophenone, 4.85 g (0.0234 mol) of phosphorus pentachloride, and 25 mg of di-*tert*-butylphenol was stirred under nitrogen at 80°. The bath temperature was increased to 95–100°, whereupon the solution began to evolve gas and became darker yellow in color. The phosphorus oxychloride was removed under reduced pressure and the straw-colored product **14** (4.69 g, 82%) was obtained by a short-path distillation, bp 116–122° (0.1 mm). The pmr spectrum ($CCl_4$) exhibited the following absorptions: δ 6.9–7.7 (m, 9, aromatic), 2.35 (s, 3, *p*-$CH_3$). Weak absorption peaks in the ir spectrum characteristic of the starting ketone and a small peak at δ 2.40 in the pmr spectrum indicated the presence of approximately 3% of *p*-methylbenzophenone.

In a dry-nitrogen atmosphere, 1.2 g (0.0098 mol) of *N*-benzylhydroxylamine (**33**) (prepared by the method of Jones and Sneed[15]) was dissolved in a solution of 5 ml of benzene and 2.5 ml of pyridine. With continuous stirring, 2.4 g (0.0096 mol) of the above-described dichloride **14** was added over a 30-min period.[16] After 6 hr at room temperature, the reaction mixture had separated into two phases. The mixture was heated to 70°, but, after 15 min, considerable darkening of both layers occurred and heating was terminated. The top layer was separated and the lower phase (which had then solidified) was washed thoroughly with benzene. The combined upper phase and benzene extract was concentrated under reduced pressure to 2.70 g of a dark orange semisolid. This residue was chromatographed on 100 g of silica gel (60–80 mesh). Elution with pentane–methylene chloride mixtures and finally with 10% ether in methylene chloride removed 4-methylbenzophenone (and possibly other side products) from the column. Elution with 25–75% ether in methylene chloride, followed by concentration of the fractions, afforded 1.48 g of a mixture of the isomeric nitrones **9a** and **10** as a yellow oil. Repeated chromatography on silica gel and Florisil and repeated crystallization attempts from many common solvents failed to

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[13] T. S. Dobashi and E. J. Grubbs, unpublished data.

[14] J. Hamer and A. Macaluso, *Chem. Rev.*, **64**, 473 (1964).

[15] L. W. Jones and M. C. Sneed, *J. Amer. Chem. Soc.*, **39**, 674 (1917).

[16] During this time, the temperature of the reaction mixture increased approximately 2° (from 23–25°). However, on a fivefold scale-up, the reaction was vigorously exothermic and external cooling was required.

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 ($CCl_4$) $\delta$ 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 ($C_2H_5OH$) $\lambda_{max}$ 300 nm ($\epsilon$ 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 $\pm \sim 0.08$. 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.

**Acknowledgment.**—This investigation was supported by the National Cancer Institutes of Health, U. S. Public Health Service (Grant No. CA-10741-04).

**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.

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# *Notes*

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

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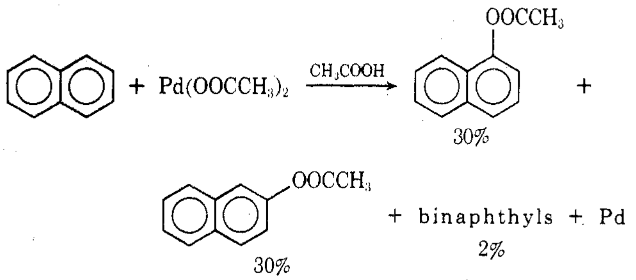
*Received May 22, 1973*

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 $\sim$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).