

with the reactivity orders of reagents that react *via* a cyclic or free-radical mechanism. These observations support the conclusion that iodine isocyanate behaves as an electrophilic reagent.

The relative reactivities also show that it is advantageous to use the *in situ* method to prepare iodine isocyanate adducts of internal olefins since the total reaction time (INCO generation plus addition) is less than that required to perform iodine isocyanate and add it to

the double bond. With terminal olefins, dienes, or alkynes, the use of performed solutions of iodine isocyanate is the method of choice.¹⁵

Registry No.—Iodine isocyanate, 3607-48-5; methyl [1-(iodomethyl)heptyl]carbamate, 16666-25-4; 4-iodo-3-aminohexane hydrochloride, 16666-26-5; 3-iodo-2-amino-2,3-dimethylbutane hydrochloride, 16666-27-6.

(15) B. Grimwood and D. Swern, *J. Org. Chem.*, **32**, 3665 (1967).

Some Rate Studies and Their Mechanistic Implications for the Reaction of 2-Methylquinoline 1-Oxide and Acetic Anhydride¹

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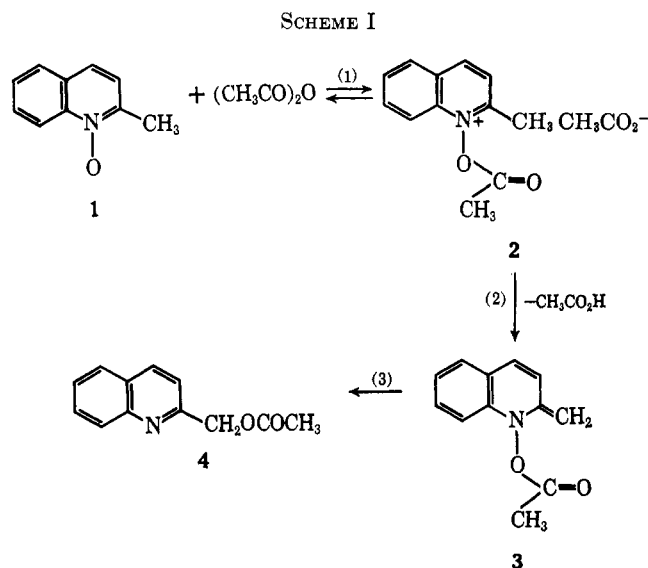
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The rate of reaction of 2-methylquinoline 1-oxide (1) with acetic anhydride has been measured by three methods which gave similar results. The rate constants are believed to be a product of the equilibrium constant for reaction of 1 with acetic anhydride to form 1-acetoxy-2-methylquinolinium acetate (2) and of a rate constant for the latter to yield 2-quinolylmethyl acetate (4). α, α, α -Trideuterio-2-methylquinoline 1-oxide was found to react one-half as rapidly as the undeuterated derivative. This, plus the fact the product (4) formed at about the same rate as the equilibrium mixture of 1 and 2 disappeared, indicates that removal of a methyl hydrogen is the rate-determining step. Also it can be seen that any intermediate between 2 and 4 must have a very fleeting existence.

The reaction of 2- and 4-alkylaromatic N-oxides has been the subject of many synthetic and mechanistic studies; however, only one report,^{3,3a} is available on the reaction kinetics of an alkylaromatic N-oxide, 2-methylquinoline 1-oxide, with acetic anhydride. Kinetic studies have been made on the reaction of pyridine N-oxide^{4,5} and of acridine N-oxide⁶ with acetic anhydride.

The following is a brief summary of some of the facts about the mechanism of the reaction of 2-alkylaromatic N-oxides and acetic anhydride. The example being cited is 2-methylquinoline 1-oxide (Scheme I) which is known to differ from 2-methylpyridine 1-oxide only in a slower rate of reaction and in more products for the latter. The first step is reversible based on C¹⁴ labeling and product studies.⁷ 1-Acetoxy-2-methylquinolinium perchlorate undergoes reaction with acetate ion, trimethylamine, or cyanide ion to yield 4.⁷ This indicates that it is possible for 2 to be an intermediate in the reaction of 1 with acetic anhydride to yield 4 and also it can be seen from the results of the reactions with trimethylamine and with cyanide that the product (4) has the same acetoxy group which 2 had. The reaction of 2 to yield 4 involves scrambling of the oxygens of the acetoxy group as



shown by O¹⁸-labeling studies.⁸ The fact that the reaction of 1-acetoxy-2-(α, α -dideuteriobenzyl)pyridinium perchlorate with sodium acetate when carried to half-completion showed no deuterium decrease in starting material⁹ indicates by analogy that any intermediate or product formed after 2 is not in equilibrium with 2. This implicates the removal of a proton as the rate-determining step. Compound 3, an anhydro base, is a reasonable intermediate which has often been postulated, but its presence has not been detected.¹⁰

Much of the recent effort in this area has been to determine whether the N–O bond undergoes homolytic or

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(2) (a) Based in part on the Ph.D. Dissertation, 1964, of R. S. Darlak who was a NDEA Fellow, 1960–1963. This assistance is gratefully acknowledged. (b) Based in part on the Ph.D. Dissertation, 1966, of M. L. DeMatte who had a West Virginia University Senate Research Grant during the summer of 1965. This assistance is also gratefully acknowledged.

(3) S. Furukawa, *Yakugaku Zasshi*, **79**, 492 (1959); *Chem. Abstr.*, **53**, 18029 (1959).

(3a) NOTE ADDED IN PROOF—See S. Oae, S. Tamagaki, T. Negoro, K. Ogino, and S. Kozuka, *Tetrahedron Lett.*, No. 8, 917 (1968), for a preliminary report on kinetic studies of 2- and 4-alkyl-substituted heteroaromatic N-oxides with acetic anhydride.

(4) J. H. Markgraf, H. B. Brown, S. C. Mohr, and R. G. Peterson, *J. Amer. Chem. Soc.*, **85**, 958 (1963).

(5) S. Oae and S. Kozuka, *Tetrahedron*, **21**, 1972 (1965).

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(8) S. Oae, T. Kitao, and Y. Kitaoka, *J. Amer. Chem. Soc.*, **84**, 3359 (1962); S. Oae and S. Kozuka, *Tetrahedron*, **20**, 2671 (1964).

(9) V. J. Traynelis and P. L. Pacini, *J. Amer. Chem. Soc.*, **86**, 4917 (1964).

(10) V. J. Traynelis, private communication. Spectral evidence for an anhydro base in the reaction of 1-acetoxy-4-benzylpyridinium perchlorate with acetate ion has been obtained.

heterolytic cleavage enroute to product.¹¹⁻¹³ The results point to heterolytic cleavage as the major pathway to product.

The present kinetic study was designed to determine whether 2 is a kinetically allowable intermediate in the foregoing reaction and to determine whether the proton abstraction in this reaction is the rate-determining step. 2-Methylquinoline 1-oxide was chosen for study rather than 2-methylpyridine 1-oxide because the former can be studied by ultraviolet spectroscopy in 100% acetic anhydride which is the solvent used in the synthesis of products such as 4.

Experimental Section

Materials.—2-Methylquinoline 1-oxide hydrate, mp 77–78° (lit.¹⁴ mp 77–78°), was distilled to yield anhydrous 2-methylquinoline 1-oxide (43% over-all yield) as a pale yellow liquid, bp 125–128° (0.2–0.3 mm). Upon standing the liquid solidified to a white solid, mp 44–45.4°. Both the hydrated and anhydrous N-oxides were stored in the dark, and the latter was stored over P₂O₅.

The nmr spectra (CDCl₃) of the hydrated and anhydrous N-oxides were the same except for the lack of a band at τ 7.0 for the anhydrous material which was present for hydrated N-oxide. The neutralization equivalent¹⁵ for 2-methylquinoline 1-oxide was found to be 159.5 (calcd, 159.2).

α, α, α -Trideuterio-2-methylquinoline 1-oxide was prepared in the following manner under an atmosphere of nitrogen. To a solution made from 0.3 g (0.013 g-atom) of sodium and 10 ml of deuterium oxide (99.7%), Merck Sharp and Dohme, Canada Ltd, was added 5.0 g (0.031 mol) of 2-methylquinoline 1-oxide. The mixture was refluxed for 24 hr. The white solid which separated on cooling was distilled to give 4.2 g of pale yellow oil. The same procedure was repeated twice to yield 2.0 g (40%) of α, α, α -trideuterio-2-methylquinoline 1-oxide as a white solid: bp 137–139° (0.8–0.9 mm); mp 43–44.5°; ir (KBr) 2250 (C–D stretch), 1060 cm⁻¹ (CD₃ bending); negligible absorption (CDCl₃) at τ 7.3 where 2-methyl hydrogens of 2-methylquinoline 1-oxide absorb.

*Anal.*¹⁶ Calcd for C₁₀H₆D₃NO: 33.3 atom % excess D. Found: 34.2 atom % excess D.

1-Acetoxy-2-methylquinolinium perchlorate was prepared as follows. To 20 ml of acetic anhydride, cooled in an ice bath, was added 4.0 g (0.024 mol) of 60% perchloric acid at such a rate that the temperature did not exceed 25°. This solution was allowed to warm to room temperature and then to stand for 0.5 hr at room temperature before use.

To 10 ml of glacial acetic acid was added 4.0 g (0.021 mol) of 2-methylquinoline 1-oxide hydrate. After this solution had been cooled to ice temperature, 5 ml of acetic anhydride was added with stirring. To the resulting solution was added the foregoing perchloric acid-acetic anhydride solution; the temperature of the reaction was maintained between 0–10°. A white precipitate formed as the perchloric acid-acetic anhydride was added and redissolved before addition was complete. The white crystals were removed by filtration under nitrogen and washed with anhydrous ether to yield 4.6 g (73%) of 1-acetoxy-2-methylquinolinium perchlorate, mp 150–152° dec (lit.¹⁵ mp 152–153°). The product was hygroscopic and was stored over phosphorus pentoxide.

Acetic anhydride (Eastman Kodak, White Label) was distilled through a 2-ft Vigreux column. The 139–139.5° fraction was used in the rate determinations.

Tetra-*n*-butylammonium acetate, mp 115–117° (lit.¹⁷ mp 118 ± 2°), was used.

(11) T. Cohen and J. H. Fager, *J. Amer. Chem. Soc.*, **87**, 5701 (1965).

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(13) R. Bodalski and A. R. Katritzky, *Tetrahedron Lett.*, No. 3, 257 (1968).

(14) I. J. Pachter, *J. Amer. Chem. Soc.*, **75**, 3026 (1953).

(15) C. W. Muth, R. S. Darlak, W. H. English, and A. T. Hammer, *Anal. Chem.*, **34**, 1163 (1962).

(16) Analysis was performed by Josef Nameth, 303 W. Washington St., Urbana, Ill. 61801.

(17) W. E. Thompson and C. A. Kraus, *J. Amer. Chem. Soc.*, **69**, 1016 (1947).

RATE DATA METHOD A

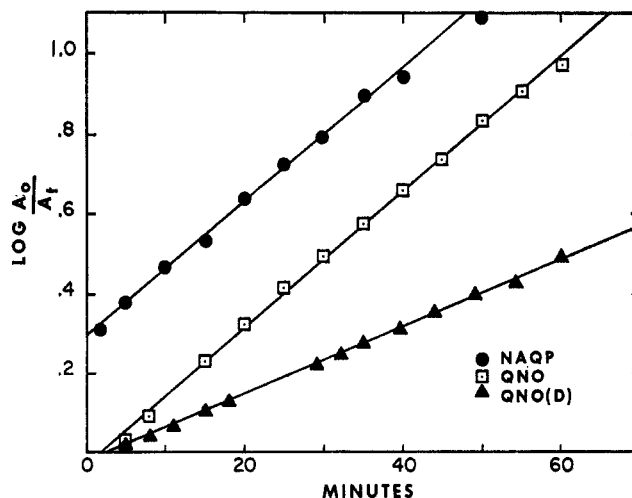


Figure 1.—Pseudo-first-order rates of reaction for (a) N-acetoxy-2-methylquinolinium perchlorate (●) with tetra-*n*-butylammonium acetate at 24.5 ± 0.1°, (b) 2-methylquinoline 1-oxide (□) at 25.1 ± 0.1°, and (c) α, α, α -trideuterio-2-methylquinoline 1-oxide at 25.2 ± 0.1 (▲) all in acetic anhydride by method A; data for a and b are from Tables I and II, respectively.

The dioxane used was purified according to the method of Wiberg.¹⁸

Methods for Determining Rates of Reaction. A. Monitoring Decrease of Absorbance of a Mixture of 2-Methylquinoline 1-Oxide and Acetic Anhydride or a Mixture of 1-Acetoxy-2-methylquinolinium Perchlorate and Acetate Ion in Acetic Anhydride. Apparatus.—A Beckman Model DU spectrophotometer, equipped with a cooling cell box which was attached to a Sargent S-84880 thermostat bath, was employed. The temperature was maintained at ±0.1° over the range 5–47°.

Rate Measurement.—As an example, 0.00309 g (1.94 × 10⁻⁵ mol) of 2-methylquinoline 1-oxide was dissolved and mixed well in 100 ml of acetic anhydride which had been thermostated to the temperature of the kinetic run. In all cases, no more than 2 min elapsed between the time of initial mixing of the reagents and the first reading which was made in a 1-cm cell. Null readings were obtained using acetic anhydride.

For studies with 1-acetoxy-2-methylquinolinium perchlorate a weighed amount of the latter was dissolved in acetic anhydride, and this solution was diluted with acetic anhydride containing the other reactants so the resulting concentration of 1-acetoxy-2-methylquinolinium perchlorate was 1–2 × 10⁻⁴ M. Each day a fresh solution was prepared.

Tetra-*n*-butylammonium acetate was dissolved in acetic anhydride and, the resulting solution was standardized by titration with perchloric acid in acetic acid.

Plots of the log of the absorbance at time zero divided by the absorbance at time *t* at 331 and 340 m μ vs. time indicated that the reaction being followed was pseudo first order. It was established that 2-quinolylmethyl acetate, the only product that has been isolated from the reaction, does not absorb appreciably at these wavelengths. With the exception of a few of the reactions conducted at lower temperatures, all reactions were followed to a minimum of 60% completion; nine or more points were plotted for each run.

Results of typical kinetic runs are given in Tables I and II and plotted in Figure 1.

Identification of 2-Methylquinolylmethyl Acetate under Conditions of the Kinetic Experiments.—The ultraviolet spectra of solutions of both 2-methylquinoline 1-oxide in acetic anhydride and 1-acetoxy-2-methylquinolinium perchlorate plus tetra-*n*-butylammonium acetate in acetic anhydride became on standing nearly superimposable on the spectrum of 2-quinolylmethyl acetate. The latter was isolated in 71% yield when the reaction was carried out on a synthetic scale and nmr analysis indicated the yield was about 90%.

(18) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 245.

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of nondeuterated acetic anhydride in order to minimize the absorption of the solvent at τ 7.3.

The pseudo-first-order rate constant (k_a) for the disappearance of the signal due to methyl hydrogens was found from the slope of the line from a plot of the log of the integration of the methyl signal vs. time. The pseudo-first-order rate constant (k_d) for the appearance of the signal for the methylene hydrogens was found from the slope of the line from a plot of $\log(a_0 - x)$ vs. time, where a_0 is two-thirds of the integration of the signal of the methyl hydrogens at time zero and x is the integration of the signal of the methylene hydrogens at time t . The slopes of the lines from which the rate constants were determined were calculated by a computer. A least-squares program was used.

2-Quinolylmethyl acetate in acetic anhydride was found to show a singlet at τ 4.65.

The results are summarized in Table IV.

TABLE IV
RATES OF REACTION OF 2-METHYLQUINOLINE 1-OXIDE
WITH HEXADEUTERIOACETIC ANHYDRIDE USING NMR
(METHOD C) AT $35 \pm 0.5^\circ$

Decay of CH ₃ , $k \times 10^4, \text{sec}^{-1}$	Growth of CH ₂ (product), $k \times 10^4, \text{sec}^{-1}$
13.1 \pm 0.7	12.2 \pm 0.7
12.5 \pm 0.6	14.5 \pm 1.0
12.7 \pm 0.6	10.1 \pm 0.7
12.0 \pm 0.7	11.3 \pm 0.7
17.9 \pm 0.4	13.1 \pm 0.9
14.7 \pm 0.9	15.3 \pm 0.2
Av 13.8 \pm 2.0	12.8 \pm 2.0

Results

The decrease of absorbance of a mixture of 2-methylquinoline 1-oxide and acetic anhydride at both 331 and 340 $m\mu$ (method A) has been found to obey pseudo-first-order kinetics at 8.2, 25.1, and 36.2°. It was determined that 2-quinolylmethyl acetate, the only product isolated, does not absorb appreciably at these wavelengths. The k values from this method (Table V) are in satisfactory agreement with those of methods B and C.

TABLE V
RATES OF REACTION OF 2-METHYLQUINOLINE 1-OXIDE
AND ACETIC ANHYDRIDE BY METHOD A^a

Temp, °C	$A_0,^b M \times 10^4$	$k \times 10^4, \text{sec}^{-1}$
8.2	1.64	1.5 ^c
25.1	2.38	6.5
36.2	2.21	14

^a Rate constants from absorbances at 331 $m\mu$. ^b Average initial concentration of 2-methylquinoline 1-oxide. ^c Average of six determinations; others are the average of four determinations.

Likewise the decrease in absorbance of a mixture α, α, α -trideuterio-2-methylquinoline 1-oxide and acetic anhydride at both 331 and 340 $m\mu$ (method A) has been found to obey pseudo-first-order kinetics at three temperatures (Table VI).

TABLE VI
RATES OF REACTION OF α, α, α -TRIDEUTERIO-2-METHYLQUINOLINE
1-OXIDE AND ACETIC ANHYDRIDE BY METHOD A^a

Temp, °C	$A_0,^b M \times 10^4$	$k \times 10^4, \text{sec}^{-1}$
8.4	1.62	0.8 ^c
25.2	2.27	3.3
36.2	1.28	8.1

^a Rate constants from absorbances at 331 $m\mu$. ^b Average initial concentration of α, α, α -trideuterio-2-methylquinoline 1-oxide. ^c Average of six determinations; others are the average of four determinations.

By comparing the k values in Table V and VI it can be seen the kinetic isotope effects at approximately 8, 25, and 36° are 1.9, 2.0, and 1.7, respectively.

Method A was also used to follow the reaction of 1-acetoxy-2-methylquinolinium acetate in acetic anhydride at five temperatures. The k values (Table VII) are in good agreement with those obtained from the reaction of the N-oxide with acetic anhydride.

TABLE VII
RATES OF REACTION OF 1-ACETOXY-2-METHYLQUINOLINIUM
PERCHLORATE WITH TETRA-*n*-BUTYLAMMONIUM ACETATE
IN ACETIC ANHYDRIDE BY METHOD A

$A_0,^a M \times 10^4$	$B_0,^b M \times 10^4$	Temp, °C	$k \times 10^4, \text{sec}^{-1}$
1.45	2.57	5.5	1.6
1.52	2.57	15.2	3.9 ^c
2.00	2.57	24.5	6.7
1.49	2.57	33.6	14
1.49	2.57	47.0	34

^a Initial concentration of 1-acetoxyquinolinium perchlorate.

^b Initial concentration of tetra-*n*-butylammonium acetate.

^c Average value for three runs while remainder of values are the average value for four runs.

The change in rate caused by added substance to both 2-methylquinoline 1-oxide hydrate in acetic anhydride and to 1-acetoxy-2-methylquinolinium perchlorate plus tetra-*n*-butylammonium acetate in acetic anhydride were studied. The results are given in Tables VIII and IX. In both systems acetic acid decreased the rates and a large excess of tetra-*n*-butylammonium acetate only slightly increased the rates.

TABLE VIII
RATES OF REACTION OF 1-ACETOXY-2-METHYLQUINOLINIUM
PERCHLORATE WITH TETRA-*n*-BUTYLAMMONIUM ACETATE
IN ACETIC ANHYDRIDE WITH ADDED SUBSTANCES
AT 24.5° BY METHOD A

$A_0,^a M \times 10^4$	$B_0,^b M \times 10^4$	Added substance		$k \times 10^4, \text{sec}^{-1}$
		Identity	M	
2.00	2.57	None		6.7
2.00	2.57	HOAc	0.348	4.1
2.99	2.99	HOAc	1.374	2.1
2.00	2.57	NaClO ₄	1.99×10^{-3}	7.4
1.53	2.57	NaClO ₄	3.29×10^{-3}	9.8
1.66	23.1	None		7.5

^a Initial concentration of 1-acetoxy-2-methylquinolinium perchlorate. ^b Initial concentration of tetra-*n*-butylammonium acetate.

TABLE IX
RATES OF REACTION OF 2-METHYLQUINOLINE 1-OXIDE HYDRATE
WITH ADDED SUBSTANCES IN ACETIC ANHYDRIDE
AT 24.5° BY METHOD A

$A_0,^a M \times 10^4$	$B_0,^b M \times 10^4$	Added substance		$k \times 10^4, \text{sec}^{-1}$
		Identity	M	
2.59	None	6.4
2.99	3.11	HOAc	0.229	4.9
3.11	3.11	HOAc	0.488	4.1
3.23	2.57	NaClO ₄	3.37×10^{-3}	8.8
2.50	None	Et ₄ NClO ₄	3.29×10^{-4}	6.7
1.95	23.1	None	...	7.0

^a Initial concentration of 2-methylquinoline 1-oxide hydrate.

^b Initial concentration of tetra-*n*-butylammonium acetate.

The rate of reaction of 2-methylquinoline 1-oxide with acetic anhydride has been studied by quenching aliquots of the mixture with water and analyzing for 2-methylquinoline 1-oxide (method B). The pseudo-

first-order k values as determined from an average of three experiments at 25.2 and three experiments at 8.2° were 6.3×10^{-4} and 1.6×10^{-4} sec⁻¹, respectively. These values are in satisfactory agreement with those from method A.

From the kinetic data of Tables V and VI the thermodynamic activation parameters were calculated.¹⁹ The enthalpies of activation, ΔH^\ddagger , obtained from the slope of the line from a plot of $\log k/T$ vs. $1/T$ were 13.4 and 14.1 kcal/mol, respectively, for 2-methylquinoline 1-oxide and its α,α,α -trideuterio derivative. The entropies of activation, ΔS^\ddagger , at 25.1° were calculated to be -28.3 and -27.5 eu, respectively.

Table IV gives a summary of the results obtained by method C.

Discussion

The fact that both mixtures of 2-methylquinoline 1-oxide (1) and acetic anhydride and of N-acetoxy-2-methylquinolinium perchlorate, tetra-*n*-butylammonium acetate and acetic anhydride showed only one absorption band in the τ 7.0-7.5 region, whereas N-acetoxy-2-methylquinolinium perchlorate in acetonitrile showed singlet absorptions at both τ 7.0 and 7.2 is further support⁷ of the postulate that equilibrium for step 1 in Scheme I is rapidly obtained. It is assumed that exchange is occurring so rapidly that the nmr signal of the acetoxy methyl of N-acetoxy-2-methylquinolinium ion and of acetic anhydride are found in a weighted average which is indistinguishable from the signal for acetic anhydride.

The rate constants for the reaction of 2-methylquinoline 1-oxide (1) and acetic anhydride as determined by three methods are in satisfactory agreement. Apparently these constants are a product of the equilibrium constant for step 1 and of the rate constant for the reaction of N-acetoxy-2-methylquinolinium ion with acetate ion to form product 4. Furukawa's ultraviolet studies³ of 1 with varying amounts of acetic anhydride in dioxane can be interpreted to mean that the equilibrium constant for step 1 is important in determining the rate of formation of product 4.

A kinetic isotope effect of 1.9 for the reaction for the reactions of 1 and of 2- α,α,α -trideuterio-2-methylquinoline 1-oxide with acetic anhydride is interpreted to mean that proton abstraction from the 2-methyl group by acetate ion is the rate-determining step. Since the concentrations of the two N-oxides were about the same and since the kinetic isotope effect is believed to be the ratio of K_1k_H to K_1k_D the influence of K_1 is probably cancelled. Any secondary isotope effect on this equilibrium would be expected to be smaller than 1.9.²⁰ If the reaction of 2 to form 4 is nonreversible as is the reaction of 1-acetoxy-2-(α,α -dideuteriobenzyl)pyridinium perchlorate with sodium acetate,⁹ then the isotope effect is not on an equilibrium between 2 and a later intermediate, for example, 3. The removal of the proton in the rate-determining step probably has an early transition state.

The rate of reaction of N-acetoxy-2-methylquinolinium perchlorate with tetra-*n*-butylammonium acetate was found to be nearly the same as the rate of reaction

of 2-methylquinoline 1-oxide with acetic anhydride. This is as expected if the foregoing mixture is reacting as shown in Scheme I. The very large drop in absorbance initially after mixing N-acetoxy-2-methylquinolinium perchlorate and tetra-*n*-butylammonium acetate is believed to be due to the rapid formation of product 4 while the equilibrium of step 1 is being established.

As can be seen from Table VIII and IX the presence of acetic acid slowed both the reaction of 2-methylquinoline 1-oxide hydrate with acetic anhydride and the reaction of N-acetoxy-2-methylquinolinium perchlorate with tetra-*n*-butylammonium acetate in acetic anhydride. Acetic acid possibly reacts with N-oxide 1 to alter the position of equilibrium in step 1 of Scheme I.

The addition of a 23-fold excess of tetra-*n*-butylammonium acetate caused only a moderate increase in rates in both systems. This can be explained by assuming as is shown in Scheme I that the added acetate ion is involved in competing reactions, the formation of 1 and 4.

From method B, in which aliquots of 2-methylquinoline 1-oxide (1) in acetic anhydride were quenched with water, the amounts of 1 in the quenched aliquots were lower than would have been predicted if one assumes that all of the N-acetoxy-2-methylquinolinium acetate in the mixture before water is added is hydrolyzed to 1. Apparently water underwent reaction with N-acetoxy-2-methylquinolinium ion to form the product 4 as well as 1. The water may have served as a base to cause rearrangement to product or maybe it promoted ionization of a tight ion pair so that acetate ion could be a more effective base to cause rearrangement to product.

The pseudo-first-order rate constant for the decrease in N-oxide concentration as determined by this method was similar to that obtained by methods A and C. This agreement can be explained by assuming that any N-acetoxy-2-methylquinolinium acetate reacts with water to give a constant ratio of N-oxide and product. From a larger scale experiment in which N-acetoxy-2-methylquinolinium perchlorate was shaken with a mixture of acetic anhydride and water, the yields of N-oxide, N-acetoxy-2-methylquinolinium perchlorate, and 2-quinolylmethyl acetate isolated were 35, 14, and 25%, respectively.

By monitoring the growth of the signal at τ 4.65 of a mixture of 2-methylquinoline 1-oxide (1) in hexadeuterioacetic anhydride the rate of product formation was determined. This rate of product formation was found to be approximately the same as the rate of disappearance of the signal at τ 7.3 which was assumed to be due to 2-methyl groups of the equilibrium mixture of 1 and N-acetoxy-2-methylquinolinium acetate (see Table IV). This of course means that product is formed at about the same rate as the equilibrium mixture of the former reagents is disappearing. Consequently if N-acetoxy-2-methylquinolinium acetate is reacting to form an anhydro base (3), which in turn forms product 4, the anhydro base must have a very fleeting existence. No appreciable color was observed which one would expect from an anhydro base. Also from the nmr spectrum of the reaction mixture there was no evidence for vinyl hydrogens which the anhydro base would possess.

(19) A. Frost and R. F. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1963, p 99.

(20) E. R. Thornton, *Ann. Rev. Phys. Chem.*, **17**, 349 (1966).

The high negative entropy of activation (-28 eu) as determined from the rate constants for method A is believed to be due to both the entropy of activation for the removal of a proton from the 2-methyl group of N-acetoxy-2-methylquinolinium ion and to the entropy for the reaction which results in the formation of N-acetoxy-2-methylquinolinium acetate. Separation of these entropy factors will be necessary before their individual evaluation can be made.

Registry No.—1, 1076-28-4; acetic anhydride, 108-24-7; α,α,α -trideuterio-2-methylquinoline 1-oxide, 16649-54-0; N-acetoxy-2-methylquinolinium perchlor-

ate, 1658-39-5; tetra-*n*-butylammonium acetate, 10534-59-5; hexadeuterioacetic anhydride, 16649-49-3.

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Lead Tetraacetate Oxidation of 4,4,4-Triphenyl-1-butanol, 3,3,3-Triphenyl-1-propanol, and 4,4,4-Triphenylbutyric Acid

W. H. STARNES, JR.

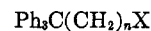
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Lead tetraacetate oxidations of 4,4,4-triphenyl-1-butanol (1), 3,3,3-triphenyl-1-propanol (2), and 4,4,4-triphenylbutyric acid (3) were carried out in benzene solution at 70°. In the absence of oxygen the major products obtained from 1 were 1,1-diphenylindan (8), 2,3,4,5-tetrahydro-5,5-diphenyl-1-benzoxepin (9), and 4,4,4-triphenyl-1-butyl acetate (4); from 2, 4,4-diphenylchroman (18) and 3,3,3-triphenyl-1-propyl acetate (5); and from 3, indan 8 exclusively. In the presence of oxygen little (if any) 8 was formed from alcohol 1 or acid 3, and in both of these cases the cyclic ether, 18, was shown to be a major product. On the basis of these results and other supporting evidence, it is argued that 3,3,3-triphenylpropyl radical (19) is a prime intermediate in the lead tetraacetate oxidations of 1 and 3, that anchimeric assistance due to phenyl participation is not involved in the oxidative deformylation of 1 or in the oxidative decarboxylation of 3, and that relief of steric compression provides a driving force for the unexpectedly facile deformylation of 1. The data are shown to be consistent with a radical chain mechanism previously proposed for the lead tetraacetate oxidation of monohydric alcohols. Possible reasons are considered for the apparent absence of carbon-oxygen phenyl migration in the lead tetraacetate oxidations of 1-3, and independent methods of synthesis for several of the possible oxidation products (including the novel cyclic ether, 9) are described.

Because of its unusually high tendency to undergo homolytic rearrangement, the trityl function has received extensive study as a neighboring group¹ in homolytic and quasihomolytic reactions.² We previously demonstrated the occurrence of trityl group rearrangements in the lead tetraacetate oxidations of 3,3,3-triarylpropionic acids^{2a} and triarylmethanols^{2t} and performed quantitative migratory aptitude measurements on these reactions. On the basis of results obtained with the latter system, a chain sequence involving the successive formation of alkoxy radicals, carbon radicals, and carbonium ions (either actual or in-cipient) was proposed as a general mechanism for the

oxidation of most types of monohydric aliphatic alcohols with lead tetraacetate.^{2t} In a continuation of our studies of the properties of trityl as a neighboring group in lead tetraacetate oxidations, we now report work dealing with the oxidation of alcohols 1 and 2 and the acid 3. These oxidations, particularly that of 1, exhibit certain unusual features that are not predictable



- 1, $n = 3$; X = OH
 2, $n = 2$; X = OH
 3, $n = 2$; X = CO₂H
 4, $n = 3$; X = OAc
 5, $n = 2$; X = OAc
 6, $n = 2$; X = CHO

(1) As used here, the term "neighboring group" does not necessarily imply the involvement of anchimeric assistance in bond-breaking processes.

(2) For representative examples, see (a) H. Wieland, *Ber.*, **44**, 2550 (1911); (b) M. A. Spielman, *J. Amer. Chem. Soc.*, **57**, 1117 (1935); (c) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950); (d) M. S. Kharasch, A. C. Poshkus, A. Fono, and W. Nudenberg, *ibid.*, **16**, 1458 (1951); (e) P. D. Bartlett and J. D. Cotman, Jr., *J. Amer. Chem. Soc.*, **72**, 3095 (1950); (f) R. M. McNeer, Ph.D. Thesis, University of Chicago, 1953; (g) S. J. Cristol and J. E. Leffer, *J. Amer. Chem. Soc.*, **76**, 4468 (1954); (h) D. Y. Curtin and T. C. Miller, *J. Org. Chem.*, **25**, 885 (1960), and earlier papers by Curtin, *et al.*; (i) L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 4531 (1966); (j) D. B. Denney and N. F. Newman, *ibid.*, **89**, 4692 (1967); (k) H. Breederveld and E. C. Kooyman, *Rec. Trav. Chim.*, **76**, 297 (1957); (l) J. W. Wilt and D. D. Oathoudt, *J. Org. Chem.*, **23**, 218 (1958); (m) J. W. Wilt and J. L. Finnerty, *ibid.*, **26**, 2173 (1961); (n) J. W. Wilt and J. A. Lundquist, *ibid.*, **29**, 921 (1964); (o) W. Rickatson and T. S. Stevens, *J. Chem. Soc.*, 3960 (1963); (p) D. B. Denney, R. L. Ellsworth, and D. Z. Denney, *J. Amer. Chem. Soc.*, **86**, 1116 (1964); (q) C. Ruchardt and R. Hecht, *Ber.*, **98**, 2460 (1965); (r) W. H. Starnes, Jr., *J. Amer. Chem. Soc.*, **85**, 3708 (1963); (s) W. H. Starnes, Jr., *ibid.*, **86**, 5603 (1964); (t) W. H. Starnes, Jr., *ibid.*, **89**, 3368 (1967), and **90**, 1807 (1968).

from the results of previous studies on related systems. Most significantly, this work has provided additional strong evidence for the involvement of radicals in the lead tetraacetate oxidation of monohydric alcohols.

Results and Discussion

Oxidation of 4,4,4-Triphenyl-1-butanol (1).—Alcohol 1 was synthesized in two ways. The preferred method involved hydroboration-oxidation of the olefin, 7,

