Registry No.—*trans*-2-(6′-Methoxy-2′-quinolyl)-methylene-3-quinclidinone, 22058-77-1; *trans*-2-(2′-quinolyl)methylene-3-quinuclidinone, 22058-81-7; **1**, 22143-13-1; **2**, 22058-78-2; **3**, 22058-79-3; **5**, 22058-80-6; **6**, 22143-14-2; **7**, 22058-82-8.

4-(4-Nitrophenylazo)benzoic Acid. Improved Synthesis of Its Acid Chloride and Spectroscopic Properties of Its Esters[1]

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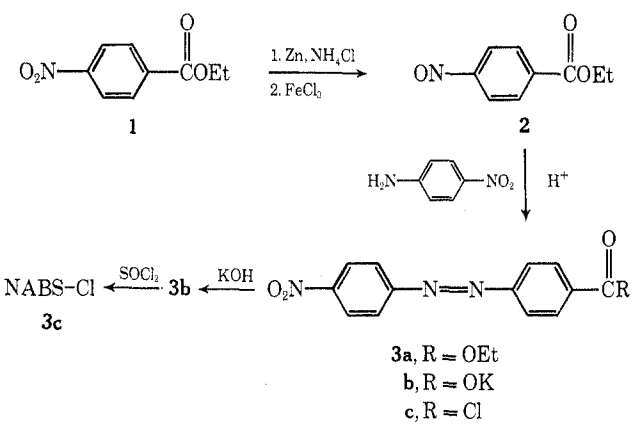
The synthesis of 4-(4-nitrophenylazo)benzoyl chloride (NABS–Cl)[2] and its use in the formation of esters was described[3] in 1955. Since then, NABS–Cl has been employed advantageously for the derivatization of other aliphatic[4] and aromatic[5] alcohols, thiols,[6] sugars,[7] amines,[8] and amino acid methyl esters;[9] NABS–hydrazide has been prepared and used to prepare derivatives of aldehydes and ketones.[10] The esters are usually solid,[11] their bright red-orange color makes them highly suitable for chromatographic purification,[4,12] and their molecular weight[13] may be determined from the ultraviolet absorption of the NABS chromophore. These properties make NABS–Cl a desirable reagent in the isolation and characterization of natural products.[12,14]

Synthesis of NABS–Cl.—In connection with work on the structure of sirenin,[14a] it became necessary to synthesize NABS–Cl in quantity as shown in Scheme I. Our attempts to obtain the 65–70% yield reported[3] for the conversion of **1** into **2** on the original 5-g scale resulted in an average yield (ten experiments) of 15%; larger scale reactions gave even lower yields. Other attempts[5a] to increase the scale of the reaction have also resulted in lower yields of **2**. A 65% yield is claimed[5a] using modified conditions, but these also failed in our hands. Consequently we examined this reaction in detail and now report conditions which reliably lead to 60–65% yields on up to a 40-g scale. In particular, vigorous stirring, closely controlled temperature, and a nitrogen atmosphere are required. Also, the use of ammonium chloride[15] in place of the originally recommended acetic acid reduced the acid-catalyzed side reactions of the intermediate ethyl *p*-hydroxylaminobenzoate, which was then oxidized to **2** using a decreased quantity of ferric chloride in the cold.

SCHEME I



No major changes were required in the subsequent steps. The crude, thoroughly dried NABS ester **3a** was purified by chromatography on alumina, and the most effect purification of the final NABS chloride (**3c**) was accomplished by vacuum sublimation.

Ultraviolet Absorption of NABS Esters.—The light-activated isomerization of substituted *trans*-azobenzenes to a photostationary equilibrium mixture of *cis* and *trans* isomers has been established.[16] In the presence of ordinary laboratory fluorescent light, solutions of *trans*-*p*-phenylazobenzoates (PAB esters) of aliphatic[17] and aromatic[5b] alcohols are isomerized, and the isomers are chromatographically separable.[17] Consequently, *trans*-4-(4-nitrophenylazo)benzoates (NABS esters) would be expected to behave similarly, and thus special precautions would be necessary to exclude light during handling of the solutions when precise chromatographic and spectroscopic determinations were being made.

About 3×10^{-3} *M* solutions of NABS ethyl ester (**3a**) were exposed to laboratory fluorescent light and the absorbance at 330 nm was noted as a function of time. A variety of solvents—benzene, ether, ethyl acetate, ethanol, and acetic acid—was used, and in each case photostationary equilibrium was reached after 2 hr with about a 5% decrease in absorbance.

The equilibrium mixture, showing a yellow spot at R_f 0.14 and a red-orange spot at R_f 0.37 on silica gel–benzene thin layer chromatography, can be thermally isomerized[6a] at room temperature in the dark for 30 hr to an all-*trans* solution which shows only

(1) Supported in part by the National Science Foundation.

(2) Abbreviated from its German name, 4-nitroazobenzolcarbonsaure-4-chlorid: A. Butenandt, R. Beckmann, and D. Stamm, *Z. Physiol. Chem.*, **324**, 84 (1961).

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(17) I. Katz and M. Keeney, *Anal. Chem.*, **36**, 231 (1964).

TABLE I
SPECTROSCOPIC PROPERTIES OF NABS ESTERS

Alcohol	Registry no.	Uv ϵ_{max} at 330 nm[a]	Nmr, δ, ppm: Carbinol protons, In alcohol	Carbinol protons, In ester	=CH	=CCH$_3$	-CCH$_3$
Methanol	22428-39-3	31,300	3.47	3.95	...	...	...
1-Hexanol	22428-40-6	32,200	3.55	4.33	...	...	0.92[b]
Ethanol	22428-41-7	32,000	3.70	4.44	...	...	1.43[c]
2-Propanol	22428-38-2	32,000	3.97	5.29	...	...	1.40[d]
Cyclohexanol	222867-6-6	32,200	3.55	5.14	...	...	...
Geraniol	22286-78-8	32,200	4.12	4.90	5.14[e]	1.62	...
					5.54[e]	1.68	
						1.81	
Nerol	22286-79-9	32,500	4.10	4.82	5.09[e]	1.60	...
					5.49[e]	1.66	
						1.80	
cis-2-Methyl-2-penten-1-ol	22286-80-2	32,300	4.00	4.80	5.46[e]	1.85	1.00[e]
2-Methylenepentanol	22286-77-7	32,300	4.00	4.80	5.02	...	0.97[e]
					5.14		
trans-2-Methyl-2-penten-1-ol	22286-81-3	32,400	3.92	4.74	5.58[e]	1.76	1.00[e]

[a] All values are in 95% ethanol and are to within ±200. [b] t, $J \cong 5$ Hz. [c] t, $J \cong 7$ Hz. [d] d, $J \cong 6$ Hz. [e] $W_{1/2} = 7$ Hz.

one red-orange spot. Progress of the isomerization is followed by the increase in absorbance at 330 nm. This demonstrates the *cis–trans* light-activated equilibrium for NABS esters and provides a procedure to ensure that the spectroscopic and chromatographic measurements are being made on only the *trans* isomer.

In order to compare the ultraviolet absorption properties of the *cis* with the *trans* isomer, preparative thin layer chromatography on silica gel G–benzene was used to obtain a small sample of the *cis* isomer. However, the normal procedure used to measure an extinction coefficient involved sufficient heat and light to isomerize the sample to nearly all *trans* isomer. By immediately making the measurement at room temperature after desorption of the *cis* isomer from the silica gel at 0°, a λ_{max} of 262 nm (ϵ 13,900) in methanol–chloroform (9:1) was obtained. Isomerizing the solution of *cis*-NABS ethyl ester (**3a**) to its *trans* form allowed the concentration to be calculated from the extinction coefficient of *trans*-NABS ethyl ester (**3a**) as determined in this solvent. Within 2 hr after the measurement on *cis*-**3a** was made, tlc showed a small amount of *trans*-**3a** to be present. The *cis* extinction coefficient therefore is a minimum value and may be as high as 14,900, estimating from tlc that as much as 10% *trans*[18] isomer may have been present when the measurement was made. Using the value ϵ 13,900, the photostationary equilibrium mixture contains approximately 6% *cis* isomer. If one examines the spectra for the isomerization of *trans*-**3a** to the equilibrium mixture, the decrease in absorbance at 330 nm is accompanied by an increase in absorbance at 262 nm.

Since there is no mention[3] of any precautions to shield solutions of NABS esters from light for the extinction coefficient measurements, the high uncertainty in ϵ of ±800 in 30,880 (ethanol) could be due to some isomerized solutions, which would also lead to a lower average value for the extinction coefficient.

Consequently, NABS esters of representative saturated primary and secondary alcohols as well as primary allylic alcohols were prepared to redetermine the extinction coefficients and to assess any effect of structure of the alcohol upon the extinction coefficient of the corresponding NABS ester. In particular, the difference in the reported[19] values for NABS nerol and NABS geraniol (ϵ 28,800 and 31,600, respectively) was much greater than would be expected from experimental error or from the lowering of extinction coefficient of NABS nerol owing to *trans–cis* light-activated isomerization of the NABS chromophore. This suggested a possible effect of the configuration of the allylic double bond upon the extinction coefficient of the NABS ester.

The NABS esters of primary alcohols were prepared in 85–95% yield in most cases and the reaction time was reduced from 24[3] to 0.6–1 hr. However, the 33% yield of NABS 2-propanol (0.6-hr reaction time) indicates that secondary alcohols require a longer reaction time for comparable yields. A simplified work-up was developed by directly chromatographing the crude reaction product.

The redetermined extinction coefficients of NABS esters are presented in Table I. Except for NABS methanol, an average value of 32,200 ± 400 was found. Thus there is no effect of the structure of the aliphatic alcohols upon their NABS ester chromophore. The 4% increase to 32,200 in the extinction coefficient is in accord with the 4% decrease in absorbance observed for NABS ethyl ester in ethanol solution exposed to light. The lower value of 30,880[3] is thus attributed primarily to the *cis–trans* light-activated isomerization of the NABS chromophore. Protection of the NABS ester solutions from light has not only increased the extinction coefficient but also decreased the uncertainty by 50%. The significantly smaller extinction coefficient of NABS methanol may be a true difference, since methanol is the only proton-substituted primary alcohol in the series of alkyl-substituted primary alcohols.

Nmr Properties of NABS Esters.—An additional advantage of characterizing alcohols as NABS esters has been found. The carbinol protons of alcohols, when converted into their NABS ester, fall into groups

(18) If all the absorbance at 330 nm (ϵ 6000) is due to *trans*-**3a**, as much as 19% may be present, and then *cis*-**3a** would have ϵ 17,100 and *trans*-**3a** would have ϵ 4800 at 262 nm.

(19) A. Mondon and G. Teege, *Ber.*, **91**, 1014 (1958).

in the nmr spectrum according to the type of alcohol, as shown in Tables I and II. If the chemical shift

TABLE II
NMR SIGNAL OF THE CARBINOL PROTONS OF NABS ESTERS ACCORDING TO THE TYPE OF ALCOHOL

NABS ester of alcohol	δ of carbinol proton
Primary saturated	3.95–4.44
Primary allylic	4.74–4.90
Secondary saturated	5.14–5.29

of the carbinol proton in the free alcohol is used to classify the type of alcohol, a discrepancy occurs in the case of 2-propanol and cyclohexanol. The former would be classified as a primary allylic alcohol while the latter would be regarded as a primary saturated alcohol. In contrast, conversion of the alcohols into their NABS esters allows a consistent classification according to the type of alcohol.

Experimental Section[20]

Ethyl *p*-Nitrosobenzoate (2).—After 40 g (0.21 mol) of ethyl *p*-nitrobenzoate (1) was dissolved in 560 ml of 2-methoxyethanol, a solution of 17 g of ammonium chloride in 135 ml of water was added and the solution was warmed to 30° in a nitrogen atmosphere. With vigorous stirring (Hershberg-type stirrer), 36 g (0.55 mol) of finely powdered zinc dust was added, by periodically removing the condenser, in small portions over 30 min and the temperature was held at 33–35° by cooling with an ice bath. After addition was completed, the stirring was stopped at 5-min intervals to ascertain the color[21] of the supernatant liquid. When it became colorless, the reaction mixture was suction filtered in a nitrogen atmosphere and the filter cake was washed with 30 ml of 2-methoxyethanol. The combined filtrate and washing was then added dropwise, under a nitrogen atmosphere with rapid stirring over a period of 90 min, to a solution of 84 g (0.52 mol) of anhydrous ferric chloride in 950 ml of water and 240 ml of ethanol maintained at −5° with an ice–methanol bath. After an additional 30 min of stirring, the reaction mixture was poured into 1900 ml of cold water and suction filtered. After being washed with water, the damp precipitate was steam distilled to give 28.8 g (62%) of **2**, mp 79–80.5° after recrystallization from ethanol (lit.[3] mp 83–84°).

Ethyl 4-(4-Nitrophenylazo)benzoate (3a).—Into a flask shielded from the light and equipped with a reflux condenser, magnetic stirring bar, and nitrogen atmosphere were placed 40 g (0.22 mol) of unrecrystallized **2**, 33.6 g (0.24 mol) of *p*-nitroaniline, and a solution of 120 g of trichloroacetic acid in 800 ml of glacial acetic acid. After the solution was stirred and heated at 100° for 4 hr, it was cooled to 30° and then poured into 2400 ml of water. The suspension was filtered and the filter cake was washed with water and air dried on the filter overnight. Drying was completed by dissolving the precipitate in benzene and evaporating to dryness. The residue was then redissolved in benzene and passed through a column of 454 g of alumina (neutral, activity I) and eluted with benzene–ether (1:1) to yield, after evaporation, 58.6 g (81%) of NABS ethyl ester (**3a**), mp 164–165° (lit.[3] mp 162–165°).

Potassium 4-(4-Nitrophenylazo)benzoate (3b).—In a nitrogen atmosphere were placed 70 g (0.23 mol) of NABS ethyl ester (**3a**) dissolved in 3.5 l. of benzene and a solution of 17.3 g of potassium hydroxide in 400 ml of 2-methoxyethanol. The reaction mixture was stirred at room temperature for 15 hr and then filtered. The filter cake was washed with a small amount of 2-methoxyethanol, dried on the filter overnight, and finally placed in a vacuum oven at 120–140° for 5 hr to give 63 g (87.5%) of potassium salt **3b**.

4-(4-Nitrophenylazo)benzoyl Chloride (3c).—Using a flask shielded from light, 9.8 g (0.032 mol) of potassium salt **3b** which had been found with 5.4 g of anhydrous sodium carbonate was treated with 40 ml of thionyl chloride and 40 ml of toluene. After the reaction mixture was refluxed and magnetically stirred for 4 hr, the excess thionyl chloride and toluene were distilled at reduced pressure. The crude product was dissolved in benzene and filtered, and the filtrate was evaporated to dryness. Sublimation at 150° (0.02 mm) gave 6.35 g (69%) of acid chloride **3c**, mp 163–165° in an evacuated capillary (lit.[3] mp 162–163°).

Preparation of NABS Esters.—Geraniol was obtained from the hydrolysis of geranyl acetate (purissima, Aldrich), while the 2-methyl-2-penten-1-ols and 2-methylenepentanol were prepared as described.[22] Except for nerol, other alcohols were commercially available and were dried over Na_2SO_4 or distilled. Pyridine was distilled from *p*-toluenesulfonyl chloride and the benzene was distilled from calcium hydride.

General Procedure.—To the alcohol was added 2 mol of pyridine and sufficient benzene to dissolve 1 mol of NABS–Cl. A 1-mol excess of either the alcohol or NABS–Cl was used. After stirring for *ca.* 1 hr for primary alcohols (secondary alcohols may require 24 hr or longer) in a flask protected from light, the reaction mixture was suction filtered and the filtrate was evaporated *in vacuo*. The residue was then chromatographed on alumina (neutral, activity 2.5) with benzene to afford the NABS ester. The analytical sample was obtained by recrystallization from benzene or benzene–cyclohexane.

In addition to the ethyl ester, the following esters were prepared: **methyl ester**, mp 190–191° (lit.[3] mp 186–187°); ***n*-hexyl ester**, mp 114–115° (lit.[3] mp 110–111°); **isopropyl ester**, mp 183–184° (lit.[3] mp 178–180°); **cyclohexyl ester**, mp 163–164° (lit.[3] mp 164–165°); **geranyl ester**, mp 103–104° (lit.[3] mp 107–109°); and **neryl ester**, mp 88–89° (lit.[3] mp 90–91°). The following esters were prepared and analyzed.

***cis*-2-Methyl-2-penten-1-yl ester** had a melting point of 138–139°.

Anal. Calcd for $C_{19}H_{19}N_3O_4$: C, 64.6; H, 5.4; N, 11.9. Found: C, 64.9; H, 5.3; N, 12.2.

2-Methylenepentyl ester had a melting point of 105–106°.

Anal. Calcd for $C_{19}N_{19}N_3O_4$: C, 64.6; H, 5.4; N, 11.9. Found: C, 64.8; H, 5.1; N, 12.1.

***trans*-2-Methyl-2-penten-1-yl ester** had a melting point of 124–125°.

Anal. Calcd for $C_{19}H_{19}N_3O_4$: C, 64.6; H, 5.4; N, 11.9. Found: C, 64.9; H, 5.1; N, 12.1,

Ultraviolet Measurements for Ethyl *trans*-4-(4-Nitrophenylazo)benzoate (3a). A. Isomerization.—*Ca.* 3×10^{-3} *M* solutions of NABS ethyl ester (**3a**) in 95% ethanol were placed 67 cm from the laboratory fluorescent light. Aliquots (1 ml) were withdrawn periodically and diluted to 100 ml with 95% ethanol before measurement in 1-cm matched cells.

B. Extinction Coefficients.—By heating at 40° in a water bath when necessary, 95% ethanol solutions of known concentration were prepared in aluminum foil covered flasks and stored in the dark at room temperature for at least 24 hr prior to measurement at λ_{max} 330 nm. The values presented in Table I are the result of at least duplicate determinations 24 hr apart on duplicate samples.

Isolation and Extinction Coefficient for Ethyl *cis*-4-(4-Nitrophenylazo)benzoate.—A 0.052 *M* solution of *trans*-NABS ethyl ester (**3a**) in benzene was exposed to laboratory fluorescent light at a distance of 67 cm for *ca.* 10 hr. The mixture was separated by preparative thin layer chromatography on silica gel G plates and developed with benzene in aluminum foil covered tanks at room temperature (*trans* ester, R_f 0.37, red-orange; *cis* ester, R_f 0.14, yellow). After cooling to 0°, the *cis*-NABS ethyl ester was desorbed in near darkness with 5 ml of absolute ethanol and 100 ml of methylene chloride, and the solution was then filtered. The filtrate was evaporated *in vacuo*, with no external heat, in the dark at 20 mm for 30 min and then for 15 min each at 2 mm and 0.020 mm. A portion of the resulting liquid was diluted to

(20) Melting points were taken in capillary tubes and are uncorrected; ultraviolet spectra were determined with a Cary Model 14 Spectrophotometer; nmr spectra were determined in deuteriochloroform on a Varian A-60 spectrometer using internal TMS (δ 0); microanalyses were performed by the Analytical Laboratory, University of California, Berkeley.

(21) The supernatant liquid was yellow at the end of the addition and beame colorless in 15–20 min. If more time is required, the stirring may not be sufficiently vigorous and the yield may be low.

(22) K. C. Chan, R. A. Jewell, W. H. Nutting, and H. Rapoport, *J. Org. Chem.*, **33**, 3382 (1968). The corresponding NABS esters were prepared by K. C. Chan.

100 ml with methanol–chloroform (9:1, v/v) and its absorbance was determined at 262 nm. After the yellow solution was exposed to laboratory fluorescent light for 2 hr, it was stored in the dark at room temperature for 65 hr. Its absorbance at 330 nm was then measured, from which the concentration of *trans* ester (and hence of the original *cis* ester) was calculated using 32,000 as the extinction coefficient.

Registry No.—3c, 22286-74-4.

Oxygen-Transfer Reactions of Amine N-Oxides. IV. The Pyridine N-Oxide–Trichloroacetic Anhydride Reaction

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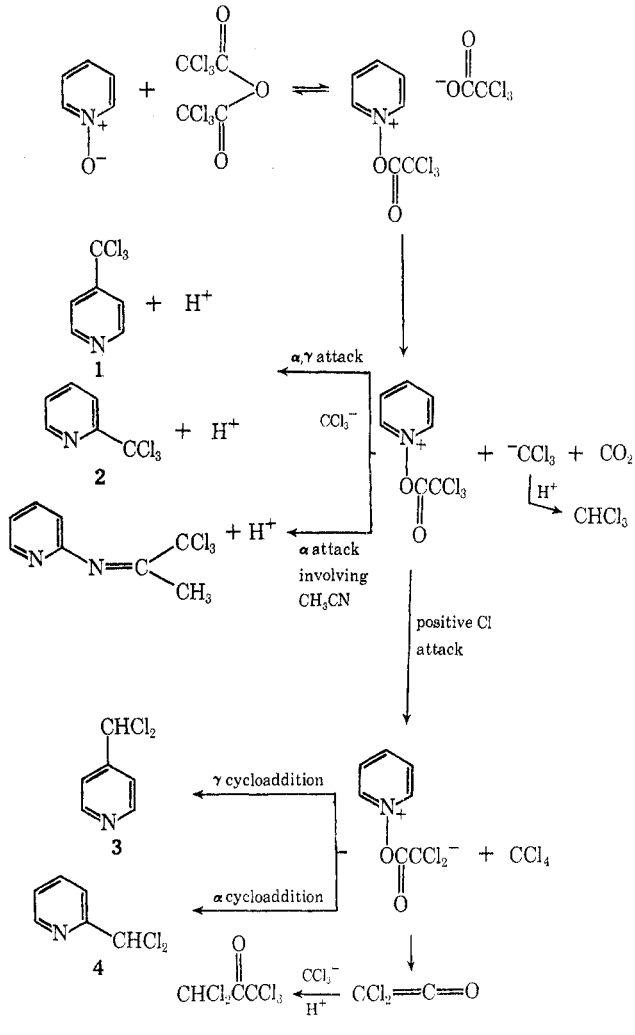
During the course of our general studies[2] on the reactions of N-oxides with acylating agents, we observed[3] a rather unusual reaction between trichloroacetyl chloride and picoline N-oxides which gives picolyl chlorides and carbon dioxide in fairly high yields after a few hours in refluxing chloroform. The chloride product was found to be a result of the high susceptibility of trichloroacetate esters to displacement by chloride ion, and the carbon dioxide was found to be a result of the unexpectedly fast rate of decarboxylation of ammonium trichloroacetate salts in solutions at high concentration. The present report deals with an additional manifestation of the rapid decarboxylation rate of the trichloroacetate ion in the reaction of pyridine N-oxide with trichloroacetic anhydride.

When pyridine N-oxide is refluxed in chloroform in the presence of trichloroacetic anhydride, no appreciable reaction is evident even after several hours. The N-oxide can be largely recovered after such a period. However, when the two reagents are mixed in acetonitrile solvent even at 0°, an exothermic reaction is immediately evident and carbon dioxide evolution begins at once. If the temperature is maintained at 0°, the gas evolution levels off at *ca.* 30%. When the reaction is carried out at 20–30°, 1 equiv of gas is evolved after *ca.* 5 hr.

The resulting product solution contains an exceedingly complex mixture of substituted pyridine derivatives. The products isolated and identified after the complicated work-up procedure, summarized in the Experimental Section, are carbon tetrachloride (40%), chloroform (20%), pentachloroacetone (20%), α-trichloromethylpyridine (10–20%), γ-trichloromethylpyridine (1–4%), α-dichloromethylpyridine (present), γ-dichloromethylpyridine (5%), and α-aminopyridine (4%). These yields are based on amount of N-oxide present initially, since 2 equiv of the anhydride were used in the runs in which quantitative analyses were attempted. No detectable amount of α-trichloroacetoxypyridine, which was synthesized independently, was observed by nmr or infrared. This product is the expected one based on analogy with the acetic anhydride–pyridine N-oxide reaction.[4]

The reaction at hand is apparently not a result of homolytic cleavage of the N–O bond of the acylated N-oxide, since very little carbon dioxide is obtained when the N-oxide is treated with trichloroacetyl chloride. A more likely explanation is that the driving force for the reaction is the exothermic loss of carbon dioxide from free trichloroacetate ion, which is not complexed with its counterion. Scheme I uses this idea in *rationalizing* the products observed.

SCHEME I



That the observation of any reaction at all is definitely coupled to the polarity of the medium was evidenced by slow addition of acetonitrile to a refluxing solution of the reagents in chloroform. Only when the solvent mixture contains *ca.* 50% acetonitrile does carbon dioxide evolution occur at an appreciable rate. The spectral properties of the product residues from

(1) Fellow of the Kosciusko Foundation on leave from Politechnika Wroclawska, Poland, 1966–1967.

(2) T. Koenig and T. Barklow, *Tetrahedron*, in press; T. Koenig, *J. Amer. Chem. Soc.*, **88**, 4045 (1966); T. Koenig, *Tetrahedron Lett.*, No. 29, 2751 (1967); T. Koenig, *ibid.*, No. 35, 3127 (1965).

(3) T. Koenig and J. Wieczorek, *J. Org. Chem.*, **33**, 1530 (1968).

(4) M. Katada, *J. Pharm. Soc., Jap.*, **67**, 51 (1947); J. H. Markgraf, H. B. Brown, S. C. Mohr, and R. G. Peterson, *J. Amer. Chem. Soc.*, **85**, 958 (1963).