with 5% sodium hydroxide and water and dried over magnesium sulfate. The ether was removed using a stream of air. The residual red oil (10 g) was analyzed by nmr and the spectrum showed that it was contaminated with solvent (16%) and that the remaining 84% was a mixture of the anisole and the nitronic ester in a ratio of 3:2. A 1.51-g sample of the red oil was chromatographed using a dry column of deactivated alumina. Elution with pentane and benzene gave orange needles. Recrystallization from methanol gave 0.35 g, mp 46–47°. The nmr spectrum of the purified nitronic ester showed a singlet at 4.0 ppm ($-OCH_3$) and two doublets for the vinyl protons centered at 7.35 and 7.55 ppm (J = 2.5 cps) in addition to signals for the isopropyl groups.

Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.81; H, 8.07. Found: C, 66.06; H, 8.11.

The remaining red oil was heated under reduced pressure until a solid began to distil. As the residue in the pot cooled, it crystallized and filtration gave 1.485 g of 2,6-diisopropylbenzoquinone monoxime, mp 156–159° (lit.[3] 158.4–159.1°). The mother liquor (6.37 g), left after filtration of the oxime, was distilled and yielded 4.67 g of a yellow liquid, bp 119–122° (1.2 mm). The nmr spectrum of this liquid showed that it was a 95:5 mixture of the oxime and the anisole which had codistilled. The addition of pentane caused the precipitation of the oxime which was filtered. Addition of methanol to the mother liquor and cooling caused the formation of colorless plates of the anisole, mp 30–31° and the analytical sample melted at 30–30.5° (methanol). The nmr spectrum of the anisole showed a singlet at 3.81 ppm ($-OCH_3$) and a singlet for the aromatic protons at 8.0 ppm in addition to signals for the isopropyl groups.

Anal. Calcd for $C_{13}H_{19}NO_3$: C, 65.81; H, 8.07. Found: C, 65.87; H, 8.20.

10-Nitro-9-anthrone (X) was prepared according to the procedure of Meyer.[13] Separation of the anthraquinone formed as a major by-product and unchanged anthrone was achieved only by successive recrystallizations from large volumes of 1:1 benzene–petroleum ether (35–60°). The purified 10-nitro-9-anthrone, obtained in 22% yield, had mp 140–141° dec (lit.[13] 140°) and $\lambda_{max}^{CH_2Cl_2}$ 5.99, 6.28, 6.42, 7.42 μ.

A solution of 3.31 g of X in 100 ml of dichloromethane was cooled to 5° and then 100 ml of ether containing 50 mmoles of diazomethane was added over a period of 15 min. The color of the solution turned to the dark orange characteristic of the nitronic ester but the color soon faded. At the end of 1 hr the solvent was carefully removed under reduced pressure. The residue was recrystallized from ethanol–chloroform and gave successive crops of anthraquinone monoxime amounting to 2.83 g. The first crop melted at 231–232° (lit. 225°,[14] 238°[15]).

Ether (10 ml) containing diazomethane (6 mmoles) was added to 0.521 g of X in 50 ml of dichloromethane at 0° and the excess diazomethane was destroyed at the end of 10 min with a drop of acetic acid. The solvent was then distilled into a flask containing 2,4-dinitrophenylhydrazine solution and the 2,4-dinitrophenylhydrazone obtained, mp 163–166°, was identified by comparison with an authentic sample. The residue from the distillation gave, after recrystallization from benzene–petroleum ether, 0.305 g of anthraquinone monoxime, mp 232–233°. The infrared spectrum of the residue obtained by evaporating the final mother liquor showed the residue to be a mixture of X and the monoxime.

Reaction of I with Bis(trimethylsilyl)acetamide.—To 0.508 g of I in 4 ml of pentane (distilled from calcium hydride) was added 0.6 ml of BSA. A bright red color of VIII developed and lasted for about 1 hr and then faded to yellow. The nmr signals of VIII have been discussed above. The pentane and by-products of the BSA were removed under vacuum leaving 0.458 g of pale yellow needles of IX, mp 111.5–113°. The nmr spectrum of this product showed three singlets at 0.45, 1.41, and 8.08 ppm in a ratio of 9:19.4:2 which indicated that 7% of I was also present. Elemental analysis was precluded by the rapid hydrolysis of the silyl ether to the original nitrophenol. This even occurred on standing in air.

A mixture of 0.09 g of the silyl ether described above (93% pure) and 4 ml of methanol was refluxed for 0.5 hr and yielded 0.054 g of I (79%), mp 156–158°.

Registry No.—I, 728-40-5; VI, 15094-00-5; VII, 15094-01-6; IX, 15094-02-7; X, 6313-44-6; diazomethane, 334-88-3; 2-*t*-butyl-4-nitrophenol, 6683-81-4; $C_{11}H_{14}N_2O_5$ (mp 78–80°), 6099-80-5; $C_{11}H_{15}NO_3$ (mp 62–62.4°), 15353-20-5; 2,6-diisopropylbenzoquinone monoxime, 15206-39-0.

(13) K. H. Meyer, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 390.

(14) E. Schunk and L. Marchlewski, *Ber.*, **27**, 2125 (1894).

(15) K. H. Meyer and H. Schlosser, *Ann.*, **420**, 132 (1920).

The Synthesis and Decomposition of Alkyl Nitronic Esters of 2,6-Di-*t*-butyl-4-nitrophenol

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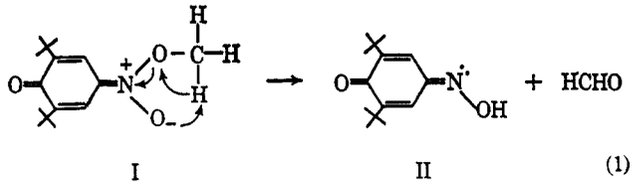
A new synthesis of nitronic esters has been developed by mixing 2,6-di-*t*-butyl-4-nitrophenol with an acrylate ester and an alkyl phosphite. The rates of thermal decomposition of methyl, ethyl, and isopropyl 3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadienenitronate to give 3,5-di-*t*-butylbenzoquinone monoxime have been measured in dimethylformamide and methylcyclohexane and activation parameters have been calculated. The rates were comparable in both solvents and consistent with a cyclic intramolecular decomposition. Saponification of the esters was found but a base-catalyzed decomposition to the oxime could not be detected even in 0.1 *N* sodium butoxide. Acid-catalyzed hydrolysis cleaved the methyl and isopropyl esters readily to give 2,6-di-*t*-butyl-4-nitrophenol.

The decomposition of nitronic esters to give an oxime and a carbonyl compound was recognized by Nef in 1894[2] before the first stable nitronic ester was isolated in 1901.[3] Nef called the decomposition an "intramolecular oxidation." Cohen and Jones have reported that the nitronic ester I decomposes at its melting point or in hot solvents to the oxime II and formaldehyde "possibly *via* a cyclic process" indicated in eq 1.[4] In addition, a base-catalyzed decomposition



I II (1)

of nitronic esters has been postulated since alkyl halides and alkali metal salts of nitroparaffins usually produce a carbonyl compound and an oxime (eq 2).[5]

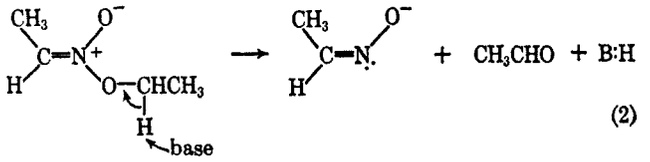
(1) National Institutes of Health Predoctoral Fellow, 1966–1967.

(2) J. U. Nef, *Ann.*, **280**, 286 (1894).

(3) E. Bamberger, *Ber.*, **34**, 574 (1901).

(4) L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963).

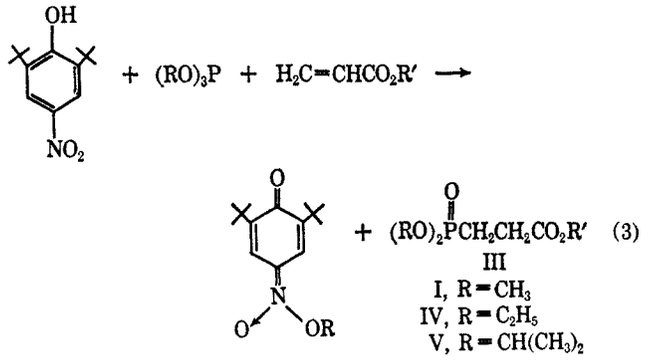
(5) N. Kornblum and R. A. Brown, *ibid.*, **86**, 2681 (1964).



(2)

In order to study the decomposition of nitronic esters to a carbonyl compound and an oxime it was decided to synthesize the unknown ethyl and isopropyl esters of *aci*-2,6-di-*t*-butyl-4-nitrophenol. The methods which have been used to prepare nitronic esters have been reviewed by Kornblum and Brown and they have developed an elegant, low-temperature synthesis using trialkyloxonium fluoroborates as alkylating agents.[5] None of these methods has as yet been shown to give an ester of a secondary alcohol.

The quantitative ethylation of phenol to phenetole at 100° in 1 day by an ethyl phosphite–ethyl acrylate mixture has been reported by Harvey and Jensen.[6] This suggested that their reaction was capable of modification to give the desired compounds. Indeed, the reaction (eq 3) proceeded readily at room temperature, usually within a week, to yield the alkyl nitronic ester of I which was easily separated from the phosphonate ester III by chromatography over alumina.



(3)

The ethyl and isopropyl nitronic esters proved to be stable at room temperature as was the case for the previously known methyl ester.[4] This allowed them to be studied with relative ease. The esters are all orange-red crystalline compounds having a single absorption maximum in the ultraviolet spectrum. The nmr spectra of the nitronic esters are completely consistent with the structures assigned.

Kinetics

The rates of decomposition of the esters were measured using the absorption maxima in the ultraviolet spectra. Ultraviolet spectral data for the nitronic esters and the oxime II are summarized in Table I. The absorption of the oxime in methylcyclohexane showed no interference with the peak of the nitronic esters. However, in dimethylformamide the anion of the oxime formed and obscured the usually sharp absorbance of the nitronic ester. This, however, did not affect concentration measurements as the yellow color of the anion could be discharged by a drop of hydrochloric acid. Rate constants at three temperatures are summarized in Table II and were determined as described in the Experimental Section. Kinetic runs were allowed to go to completion (3 days at 74.0°). Spectra of the reaction mixtures showed complete decomposition to the oxime in both solvents. In addition, the oxime was isolated from more concentrated reaction mixtures. The rates of decomposition at three different temperatures allowed the determination of enthalpy (ΔH^*) and entropy (ΔS^*) of activation (Figure 1). A summary of the activation parameters

(6) R. G. Harvey and E. V. Jensen, Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p 61M.

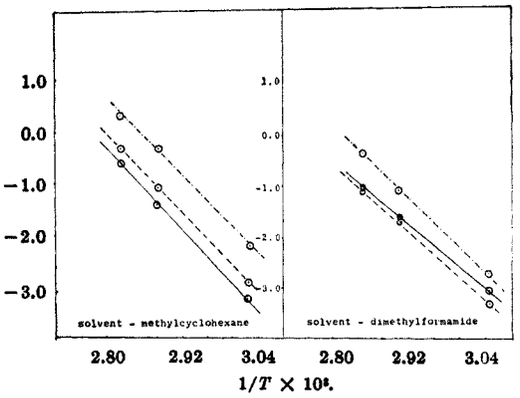


Figure 1.—Arrhenius plots for decomposition of nitronic esters in methylcyclohexane and in dimethylformamide: I, ———; IV, – – – –; V, – · – · –.

TABLE I
ULTRAVIOLET SPECTRAL DATA

Compd	Solvent	λ_{max}, mμ	ε
I	Methylcyclohexane	355	29,100
IV	Methylcyclohexane	357	28,600
V	Methylcyclohexane	357	29,100
I	Dimethylformamide	362	27,500
IV	Dimethylformamide	360	29,900
V	Dimethylformamide	362	25,500
II	Dimethylformamide	420	18,600
		290	10,000
II	Methylcyclohexane	297	
		287	

TABLE II
FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF ALKYL NITRONIC ESTERS

Ester	Temp, °C	Solvent	k_1, sec⁻¹ × 10⁵ [a]
I	57.5	Methylcyclohexane	1.14 (1.16)
IV	57.5	Methylcyclohexane	3.05 (3.10)
V	57.5	Methylcyclohexane	1.53 (1.52)
I	74.0	Methylcyclohexane	7.12 (7.12)
IV	74.0	Methylcyclohexane	22.2 (21.6)
V	74.0	Methylcyclohexane	10.1 (10.2)
I	81.0	Methylcyclohexane	17.1 (17.2)
IV	81.0	Methylcyclohexane	38.4 (41.6)
V	81.0	Methylcyclohexane	22.0 (22.4)
I	57.5	Dimethylformamide	1.31 (1.36)
IV	57.5	Dimethylformamide	1.86 (1.80)
V	57.5	Dimethylformamide	1.03 (1.08)
I	74.0	Dimethylformamide	5.3 (5.6)
IV	74.0	Dimethylformamide	9.4 (9.4)
V	74.0	Dimethylformamide	5.3 (5.0)
I	81.0	Dimethylformamide	9.7 (10.8)
IV	81.0	Dimethylformamide	21.6 (20.5)
V	81.0	Dimethylformamide	9.7 (9.7)
I	81.0	*n*-Butyl alcohol	12.4 (11.4)
V	81.0	*n*-Butyl alcohol	14.9 (13.9)
V	81.0	*n*-Butyl alcohol–NaOBu (25-fold excess)	15.0 (14.5)
V	81.0	*n*-Butyl alcohol–0.1 *N* NaOBu	20.0 (22.2)

[a] Duplicate runs are given in parentheses.

appears in Table III. Maximum possible errors in ΔH^* and ΔS^* were calculated as a function of the maximum fractional error in rate constants at the highest and lowest temperature according to the method described by Peterson, Markgraf, and Ross and then averaged.[7]

TABLE III
ACTIVATION PARAMETERS

Ester	Solvent	$\Delta H^* \pm$ 2.1 kcal[a]	$\Delta S^* \pm$ 3.1 eu[b]
I	Methylcyclohexane	25	−3.2
I	Dimethylformamide	20	−22.0
IV	Methylcyclohexane	25	−2.2
IV	Dimethylformamide	24	−8.4
V	Methylcyclohexane	26	−1.3
V	Dimethylformamide	22	−15

[a] $\Delta H^* = \Delta E^* - RT$; ΔE^* was obtained from the slope of $\ln k$ *vs.* $1/T$ °K plot. [b] $\Delta S^* = 2.303R(\log k_1 - \log k_B/h - \log T + \Delta E^*/2.303RT)$. J. F. Bunnet in "Investigation of Rates and Mechanisms of Reactions," Part I, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1961, p 201.

All plots of the first-order function, $\ln (A_0/A)$ *vs.* time, t, where A_0 is the initial absorbance of the nitronic ester and A is the absorbance at time, t, gave good straight lines and thus the decomposition was determined to be first order in nitronic ester.

On the basis of statistics only, one would predict the rate to increase in the order isopropyl, ethyl, methyl due to the presence of more hydrogen atoms increasing the chance of reaction. In Table IV the first-order

TABLE IV
STATISTICAL CORRECTION FOR RATE CONSTANTS AT 74° IN METHYLCYCLOHEXANE

Ester	k_1, sec^{-1} (average)	k_1, sec^{-1} (corrected)
I	7.12	2.37
IV	21.9	10.95
V	10.15	10.15

rate constants are corrected statistically by dividing them by the number of hydrogen atoms on the oxygen-bound carbon of the alkyl group so that this factor does not obscure the trend.

Molecular models show that the preferred conformation for the alkyl group in the nitronic esters is one in which the interaction with the ring hydrogen atom is at a minimum. In this conformation the hydrogen atom of the alkyl group, would be closer to the oxygen atom of the nitronate group, thus promoting the facile formation of the cyclic transition state. This conformation favorable to cyclic transition-state formation would probably be more populated in the ethyl and isopropyl nitronic esters than in the methyl and could account for the slight increase in rate. Also the bond strengths for primary, secondary, and tertiary hydrogen atoms bound to carbon decrease in that order, and this could account for the faster rate of the more branched alkyl groups. However, the most striking feature of the rate data is that the rates of the three esters are almost the same and do not vary appreciably as the polarity of the solvent changes. This is consistent with a concerted intramolecular cyclic mechanism.

The small decrease in rate observed in dimethylformamide relative to methylcyclohexane indicates that the ground state is more solvated than the transition state in dimethylformamide and that the rate-determining step does not involve the separation of charge. If it did, then rate enhancement in dimethylformamide would be expected. The observation that in dimethylformamide there is a slight rate decrease even though the medium is basic enough to form the anion of the oxime seems to indicate that the decomposition is not occurring through an intermolecular base-catalyzed process. It was suggested to us by Professor Nathan Kornblum that in protic solvents such as alcohols, hydrogen bonding of the O^- of the nitronate group might significantly retard the thermal decomposition. However, the rate of decomposition of the methyl ester in *n*-butyl alcohol is not significantly different from the values in methylcyclohexane and in N,N-dimethylformamide. No effect of hydrogen bonding was observed with the isopropyl ester which decomposed slightly faster in *n*-butyl alcohol than in dimethylformamide. When the butyl alcohol was 0.1 *M* in sodium butoxide, the rate of disappearance of the ester V was less than doubled. Therefore the base-catalyzed reaction (eq 2) is insignificant if it occurs at all and the slightly enhanced rate may be due to the sodium butoxide changing the dielectric constant of the reaction medium.

The values determined for the entropy of activation are all negative or near zero and this correlates with the entropies of activation observed for reactions which have five- and six-membered-ring transition states. The entropies of activation observed for reactions which have five- and six-membered-ring transition states formed from neutral species range from −2 to −17 entropy units.[8]

The entropy loss in methylcyclohexane is less than that in dimethylformamide. This suggests that the transition state is relatively nonpolar compared to the ground state and in the more polar solvent, dimethylformamide, the entropy loss is greater.

We have found that the methyl and isopropyl nitronic esters I and V are readily and quantitatively hydrolyzed in methanol acidified with hydrochloric acid to give 2,6-di-*t*-butyl-4-nitrophenol.

We have also observed that heating the methyl ester I in methanolic potassium hydroxide causeds aponification although the isopropyl nitronic ester was scarcely attacked under these conditions. This may be due to an SN2 attack on the alkyl group by the hydroxide ion which results in cleavage of the oxygen to carbon bond rather than an attack on the nitrogen atom giving a nitrogen–oxygen scission and producing alkoxide ion. This problem has been studied in other types of nitrogen esters and both types of rupture have been shown to occur in 2-octyl nitrate although 2-octyl nitrite gave only oxygen–nitrogen cleavage.[9]

(7) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

(8) C. A. Kingsbury and D. J. Cram, *ibid.*, **82**, 1810 (1960).

(9) S. J. Cristol, B. Franzus, and A. Shadan, *ibid.*, **77**, 2512 (1955).

Experimental Section

Nuclear magnetic resonance spectra were run using a Varian A-60 spectrometer with TMS as an internal standard. Ultraviolet spectra were run on a Cary 14 spectrophotometer. Melting points were taken on a Fischer-Johns melting point block and are uncorrected. Analyses of new compounds were carried out by Galbraith Laboratories, Knoxville, Tenn.

Solvents.—Methylcyclohexane was dried over calcium hydride overnight and distilled before use. Dimethylformamide was purified according to the procedure of Leader and Gormley.[10] *n*-Butyl alcohol and pentane were distilled before use.

Methyl 3,5-Di-*t*-butyl-4-oxo-2,5-cyclohexadienenitronate (I).—A mixture of 2.2 g of 2,6-di-*t*-butyl-4-nitrophenol, mp 156–158° (lit.[11] 153–154°), 1.5 g of trimethyl phosphite, and 0.76 g of methyl acrylate was allowed to react at room temperature for 2 weeks. During this time the phenol gradually went into solution and the methyl nitronic ester precipitated from solution. It was filtered and carefully washed with a small amount of chilled pentane to yield 1.3 g (56%), mp 105–109°;[4] after recrystallization from methanol, the melting point was 106–108°. Ultraviolet spectral properties are summarized in Table I.

Ethyl 3,5-Di-*t*-butyl-4-oxo-2,5-cyclohexadienenitronate (IV).—A mixture of 2.2 g of 2,6-di-*t*-butyl-4-nitrophenol, 0.75 g of ethyl acrylate, and 1.5 g of triethyl phosphite on standing for 8 days at room temperature turned red. The excess triethyl phosphite was removed using a stream of air and the product was separated by chromatography over alumina (Merck No. 71707) using pentane. The pentane was removed from the combined red fractions using a stream of air. The yield was 0.7 g (28%). Recrystallization from ethanol gave the analytical sample, mp 54.5–55.5°. The nmr spectrum showed signals at 1.35 (3 H triplet), 4.45 (2 H quartet), 1.31 (18 H singlet), 7.44 and 7.63 (2 H quartet, J = 3 cps) ppm.

Anal. Calcd for $C_{16}H_{25}NO_3$: C, 68.78; H, 9.02. Found: C, 68.59; H, 8.94.

Isopropyl 3,5-di-*t*-butyl-4-oxo-2,5-cyclohexadienenitronate (V).—A mixture of 2.2 g of 2,6-di-*t*-butyl-4-nitrophenol, 1 ml of methyl acrylate, and 1.5 ml of triisopropyl phosphite was allowed to react at room temperature for 5 days and worked up as described for the ethyl ester to yield 0.9 g (29%), mp 59–61°. Recrystallization from isopropyl alcohol yielded the analytical sample, mp 62.5–63.5°. The nmr spectrum showed signals at 1.33 (6 H, doublet), 5.22 (1 H, multiplet), 1.31 (18 H, singlet), 7.45 and 7.54 (2 H, quartet, J = 3 cps) ppm.

Anal. Calcd for $C_{17}H_{27}NO_3$: C, 69.59; H, 9.28. Found: C, 69.41; H, 9.32.

Kinetic Measurements.—The reactions were carried out in constant temperature baths (57.5, 74.0, 81.0 ± 0.05°). The solvent (*ca.* 25 ml) was prewarmed to bath temperature and not more than 0.25 ml of a stock solution of the nitronic ester was added with rapid swirling. The time was recorded after the withdrawal of the first sample and the uv absorbance of this sample was taken as the initial concentration. All runs showed good first-order plots. All reactions were sampled to at least 65% completion in dimethylformamide and to at least 75% completion in methylcyclohexane. In dimethylformamide, an error was introduced by carrying the reaction to any more than 65% due to the interference from the anion of the oxime. The absorbance readings up to 65% were confirmed by adding a drop of dilute hydrochloric acid to the sample and observing that the value did not change. Rate constants were obtained by plotting the first-order function, ln (A_0/A) against time, t, where A_0 is the initial absorbance of the nitronic ester and A is the absorbance at time, t.

Isolation of Products.—A solution of 0.1 g of each of the alkyl nitronic esters in methylcyclohexane as well as in N,N-dimethylformamide was heated at 80° for 3 to 4 days. The general work-up procedure for reactions in methylcyclohexane consisted of evaporation to dryness. For reactions in dimethylformamide, the reaction mixture was diluted with *ca.* 50 ml of water and extracted with *ca.* 50 ml of ether. The ether was washed with 50 ml of water, dried, and evaporated leaving a residue which was crystallized from carbon tetrachloride. Yields of the oxime ranged from 60–97%. The product was identified by melting point and infrared spectrum in each case. The methyl ester on decomposition in *n*-butyl alcohol gave a 97% yield of the oxime, mp 207–210° (lit.[11] 210.0–211.2°).

Kinetic Runs in Sodium Butoxide.—The kinetic runs with excess sodium butoxide in *n*-butyl alcohol were carried out as described above using a 25-fold excess of base. Since anion formation obscured the usually sharp nitronic ester absorption, a drop of dilute hydrochloric acid was added to each sample before running the spectrum. When 0.1 N sodium butoxide was used the solution was acidified with acetic acid, the gelatinous precipitate was centrifuged, and the spectrum was run on the supernatant liquid.

Isolation of the Product from the Decomposition of V in Sodium in *n*-Butyl Alcohol.—A solution of 0.105 g of V and 0.227 g of sodium previously dissolved in 50 ml of *n*-butyl alcohol was allowed to react for 32 hr at 80°. The reaction mixture was acidified and extracted with ether. The ether–butyl alcohol extract was dried and evaporated at reduced pressure and yielded 0.108 g of a 95:5 mixture of the oxime and nitrophenol. The ratio was determined by nmr integration. Thus thermal decomposition to the oxime was the major process and saponification occurred to a very slight extent.

Hydrolysis and Saponification of I and V.—A solution of 0.16 g of V, 3 ml of methanol, and two drops of concentrated hydrochloric acid was refluxed for 3.6 hr during which time the red color changed to yellow. The solvent was removed using a stream of air leaving 0.12 g of a yellow crystalline residue, mp 154–156°. The nmr spectrum showed the hydrolysis product was 2,6-di-*t*-butyl-4-nitrophenol.

In a similar experiment, I was hydrolyzed to the starting nitrophenol.

A solution of 0.25 g of I, 4 ml of methanol, and 0.1 g of sodium hydroxide was refluxed for 3.1 hr at 63°. The reaction mixture was acidified and extracted with ether. The ether was dried and the solvent removed using a stream of air leaving 0.254 g of an orange residue which the nmr spectrum showed to be a 1:5 mixture of the di-*t*-butyl-4-nitrophenol and I.

In a similar experiment with V no starting nitrophenol could be detected after a 3-hr reflux. The nmr spectrum of recovered V was unchanged and showed no signals for the nitrophenol. At the boiling point of methanol in Boulder not more than one-tenth of the starting ester should have decomposed thermally in the 3 hr of heating. When V was heated for 80 hr in the same concentration of alkaline methanol, about 95% of the product was the oxime and 5% was the nitrophenol.

In order to avoid the chance of acid hydrolysis, the base saponification of I was also run in the following manner. A solution of 0.1 g of I, 4 ml of methanol, and 0.09 g of sodium hydroxide was refluxed for 3.75 hr. The reaction mixture was diluted with an equal volume of water and extracted with ether three times (total volume of ether, 60 ml). The ether was dried over anhydrous magnesium sulfate, filtered, and evaporated under reduced pressure without heat to yield a yellow residue. Integration of the nmr spectrum ($CDCl_3$) of the residue showed starting material, nitrophenol, and oxime in a ratio of 6:1:1, respectively. Acidification of the water from the above extraction and extraction with ether yielded a trace of 2,6-di-*t*-butyl-4-nitrophenol.

Registry No.—I, 15052-27-4; II, 15052-28-5; IV, 15052-29-6; V, 15052-30-9; 2,6-di-*t*-butyl-4-nitrophenol, 728-40-5.

(10) G. R. Leader and J. F. Gormley, *J. Am. Chem. Soc.*, **73**, 5731 (1951).
(11) W. R. Vaughn and G. K. Finch, *J. Org. Chem.*, **21**, 1201 (1956).