hexene at 100° for 75 hr. Analysis by gas chromatography revealed 1% 4-vinylcyclohexene and 83% *cis*- and *trans*-3-ethylidenecyclohexene. The reaction mixture was quenched in water and extracted with ether. After drying of the combined ether extracts with magnesium sulfate and filtration, the ether was removed. Fractional distillation of the remaining material on a 40-plate Podbielniak column under nitrogen at 760 mm afforded 66 g (0.3 mole, 40% yield) of *cis*- and *trans*-3-ethylidenecyclohexene (bp 146–148°). Analysis by gas chromatography revealed that the purity was 99.0%.

Isomerization of Dipentene.—Analogous procedures were used for the rate studies of the base-catalyzed isomerization of dipentene. Analyses were performed by gas chromatography on a 10-ft Carbowax 20 M column at 125° and a 6-ft silver nitrate column at 50°. The three main products of the isomerization were identified in the following manner. Large samples of the reaction mixture were injected on a 12-ft Carbowax 20 M on Chromosorb P column at 125° and under these conditions good separation of the three main peaks was obtained. The three fractions (A, B, and C in increasing retention time) were collected in Dry Ice–acetone cooled traps and were checked for purity *via* analytical glpc on a 6-ft silver nitrate column at 50°.

Fraction A with the shortest retention time, *p*-mentha-2,4(8)-diene, had an infrared spectrum identical withth at reported for this compound.[12] The molecular weight as determined by mass spectrometry was 136. The ultraviolet absorption spectrum had a maximum at 246 mμ (ϵ 17,800). The nmr spectrum exhibited peaks (measured in parts per million from TMS in carbon tetrachloride) at δ 6.20–6.48, m (1 H); 5.3–5.6, m (1 H); 1.6–2.8, m (4 H); 1.70, s (6 H); 1.1–1.6, m (1 H); 1.0, d (3 H).

Fraction B with the next longest retention time, α-terpinene, had an infrared spectrum in agreement with that reported for this compound.[13] The molecular weight determined by mass spectrometry was 136. The compound exhibited an ultraviolet absorption maximum at 265 mμ (ϵ 9100). The nmr spectrum exhibited peaks (measured in parts per million from TMS in carbon tetrachloride) at δ 5.2–5.8, m (2 H); 1.8–2.5, m (1 H); 2.02, s (4 H); 1.72, s (3 H); 1.0, d (6 H).

Fraction C with the longest retention time, γ-terpinene, had an infrared spectrum that agreed with the reported spectrum for this compound.[13] The molecular weight determined by mass spectrometry was 136. The ultraviolet absorption spectrum had a maximum at 235 mμ (ϵ 3950). The nmr spectrum exhibited peaks (measured in parts per million from TMS in carbon tetrachloride) at δ 5.2–5.5, m (2 H); 2.55, s (4 H); 1.62, s (3 H); 1.6–2.2, m (1 H); 1.0, d (6 H). Some *p*-cymene and a conjugated diene was present in this fraction. The ultraviolet absorption is probably due to this latter contaminant.

Preparation of *p*-Mentha-2,4(8)-diene.—In a 3-l. flask under nitrogen, 2000 cc of dimethyl sulfoxide, 156.8 g (1.4 moles) of potassium *t*-butoxide, and 463 g (3.47 moles) of dipentene were stirred at 100° for 96 hr. The reaction mixture was quenched with water and extracted three times with *n*-pentane. The combined *n*-pentane extracts were dried (magnesium sulfate) and filtered. After evaporation of the pentane, analysis by gas chromatography showed 23.4% dipentene remaining. The material was distilled and 50.5 g (0.37 mole, 11%) of *p*-mentha-2,4(8)-diene, bp 188–193° (760 mm) (lit.[8] bp 188–189° (760 mm)), was collected. Analysis by gas chromatography on a 6-ft silver nitrate column established the purity of this material as greater than 99%.

Registry No.—Vinylcyclohexene, 100-40-3; **1**, 15094-05-0; **2**, 15094-06-1; **3**, 138-86-3; **4**, 99-86-5; **5**, 586-63-0; **6**, 99-85-4.

Acknowledgment.—The authors wish to thank Dr. Boyd M. Hudson for his nmr measurements and interpretations.

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(12) "The Sadtler Standard Spectra Catalog," Vol. XII, Midget ed, Sadtler Research Laboratories, Philadelphia, Pa., 1965, compound no. 12962.

(13) H. Westaway and J. F. Williams, *J. Appl. Chem.* (London), **9**, 443 (1959).

The Reaction of Hindered Phenols with Diazomethane

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The reaction of 2,6-di-*t*-butyl-4-nitrophenol with diazomethane yields the nitronic ester exclusively, whereas 2,6-diisopropyl-4-nitrophenol reacts with diazomethane to give a mixture of the nitronic ester and the corresponding anisole. The reaction of 10-nitro-9-anthrone with diazomethane gives the monoxime of anthraquinone and formaldehyde. Silation of 2,6-di-*t*-butyl-4-nitrophenol with bis(trimethylsilyl)acetamide gives an unstable nitronic ester which rearranges to the trimethylsilyl ether.

The methylation of hindered acids to give methyl esters is well known, but the methylation of hindered phenols does not seem to have been widely investigated. Examination of the literature failed to reveal that the methylation of picric acid, 2,4,6-tribromophenol, pentabromophenol, mesitol, or 2,4,6-triiodophenol with diazomethane had ever been attempted. In this reaction of a phenol, the oxygen atom which is methylated is attached to the aromatic ring, whereas in a hindered acid such as mesitoic acid the alkylated oxygen atom is separated from the ring by a carbon atom. Thus the hindered phenols should show greater sensitivity toward alkylation.

2,4,6-Tribromophenol, pentabromophenol, and 2,4,6-triiodophenol liberated nitrogen vigorously with diazomethane and each gave the corresponding anisole.

The next hindered phenol to be considered was 2,6-di-*t*-butylphenol, which has been shown to be so hindered that in excess it can react with only two of the hydrogen atoms in lithium aluminum hydride.[2] In addition, this phenol, unlike triiodophenol, is insoluble in sodium hydroxide. This presumably is due to the fact that the removal of a proton gives an anion which is too hindered for solvation to be an aid to solution.

Treatment of 2,6-di-*t*-butylphenol with diazomethane in ether failed to give the immediate nitrogen evolution shown by the more acidic phenols, so 2,6-di-*t*-butyl-4-nitrophenol, I, was prepared. This compound is soluble in sodium hydroxide. This may be explained by the fact that the di-*t*-butyl-nitrophenoxide ion, being a resonance hybrid (II) has the negative charge delocalized in the nitro group which is solvated. This anion, II, formed from the phenol by either triethylamine or sodium hydroxide, has the typical yellow color of a quinoid system. 2,6-Di-*t*-butyl-4-nitrophenol has been reported to be slightly more acidic than *p*-nitrophenol.[3]

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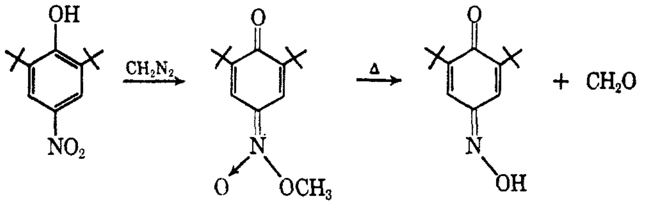
(1) (a) National Institutes of Health Predoctoral Fellow, 1966–1967; (b) National Science Foundation Summer Research Participant.

(2) J. S. Meek and C. Bouboulis, *J. Org. Chem.*, **26**, 1302 (1960).

(3) W. R. Vaughn and G. K. Finch, *ibid.*, **21**, 1201 (1956).

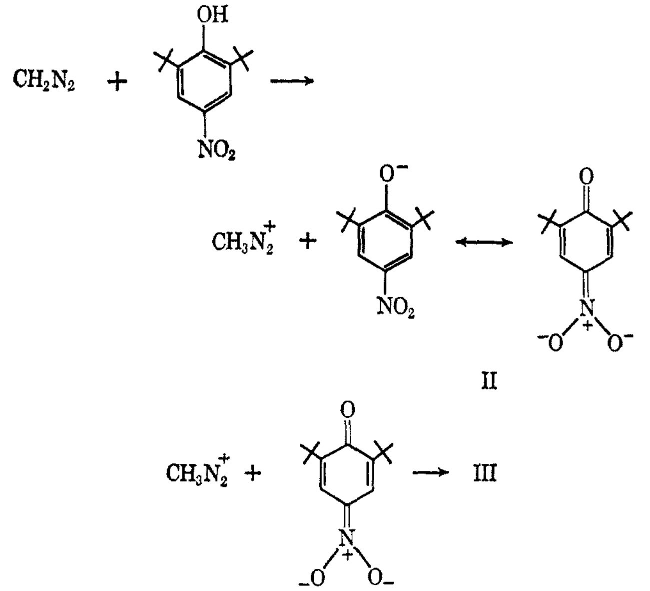
2,6-Di-*t*-butyl-4-nitrophenol and diazomethane gave a quantitative yield of an orange compound which melted at 106° and then solidified to a yellow compound which melted over 100° higher. These compounds were identified as a nitronic ester, III, and oxime, IV.[4]



I III IV

The nitronic ester III is the only one so far isolated derived from a nitro group on an aromatic ring.[5] Cohen and Jones state that "facile tautomerism is demonstrated by the quantitative methylation of the hindered nitrophenol to the stable *aci*-nitromethyl ether with diazomethane."[4] They point out that the infrared and nmr data indicated that the equilibrium between the tautomers lies overwhelmingly on the side of the phenolic form. Our data support this in that the nitrophenol is nearly colorless and the infrared spectrum in either ether or in a potassium bromide pellet shows a sharp nonhydrogen-bonded hydroxyl peak.

However, it does not seem to us that the formation of the nitronic ester proves that the *aci* tautomeric form is the one undergoing the methylation. The reaction can be broken down into two steps. The first is the abstraction of a proton by the basic diazomethane which gives the methanediazonium ion. The second step can then be an S_N2 type of reaction in which nitrogen is the leaving group and an oxygen atom of the nitro group in the ambident anion is alkylated.

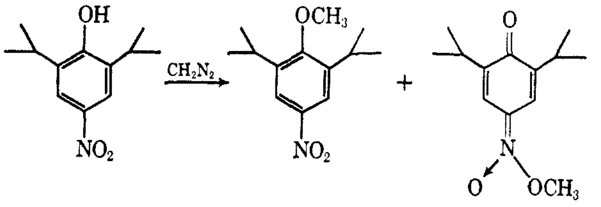


Cohen and Jones have pointed out that methylation of *p*-nitrosophenol, which in dilute carbon tetrachloride solution is mainly in the oxime form, gives exclusively *p*-nitrosoanisole. Again this methylation need not be at the site of proton removal.

Since dimethylaniline and *m*-dimethoxybenzene are easily substituted by electrophilic reagents, attempts to use these compounds to trap an intermediate methanediazonium ion were made. However, no diazo compound nor a methyl derivative of these reagents was found. It seems likely that the methanediazonium ion and the phenoxide ion do not separate from a solvent cage before alkylation occurs.

Attempts to use other diazomethanes to make nitronic esters failed. Diphenyldiazomethane did not liberate nitrogen with I but does so with picric acid. This indicated that I is not acidic enough to protonate diphenyldiazomethane. Even diazoethane in our hands was unsuccessful.

The amount of steric hindrance required to prevent the methylation of a phenol to an anisole so that a nitronic ester can be formed instead has been partially investigated. One *t*-butyl group is not enough since 4-nitro-2-*t*-butylphenol gave the anisole. On the other hand, 2,6-diisopropyl-4-nitrophenol (V) and diazomethane gave both the anisole (VI) and the nitronic ester (VII) in a ratio of 3:2, respectively (eq 1). If the isopropyl group is in the right conformation it is sterically equivalent to a *t*-butyl group. Since one *t*-butyl group does not prevent anisole formation, the two isopropyl groups must act in concert to give the nitronic ester. In some conformations of the isopropyl group the methine hydrogen atom is near the phenolic oxygen and then the steric hindrance must be low enough to allow anisole formation.



(1)

V VI VII

The reactions of diazomethane with 2,4-dinitro-6-*t*-butylphenol and 2,6-diiodo-4-nitrophenol gave only the corresponding anisoles. This result may be due to less steric hindrance afforded by the iodo or nitro group in comparison to a *t*-butyl group, an inductive effect due to an electronegative substituent at the 2 position which results in diminished nucleophilicity at the *p*-nitro group compared to the dialkylated phenols, or to an interplay of the two factors. A space-filling model indicates an iodine atom and a *t*-butyl group offer about the same hindrance in the plane of the ring but a *t*-butyl group offers the greater hindrance to alkylation occurring perpendicularly to the plane of the ring to give an anisole. Thus the electronic and steric effects of the *t*-butyl group may both favor nitronic ester formation in comparison with iodine.

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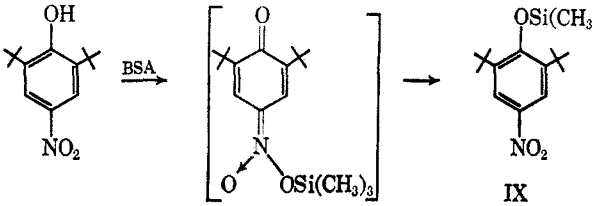
(4) These results were disclosed almost simultaneously in the Abstracts of the 149th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 59C, and in the publication of L. A. Cohen and W. M. Jones, *J. Am. Chem. Soc.*, **85**, 3397 (1963).

(5) Although the synthesis of the methyl ether of *aci*-*o*-nitrophenol and the ethyl ethers of *aci*-2,4-dinitrophenol and *aci*-picric acid has been claimed (A. Hantzsch and H. Gorke, *Ber.*, **39**, 1073 (1906)), atypical behavior of these nitronic esters was reported such as: a single blast of hydrogen chloride decolorized the *aci* ether in different media, the solution then contained the true nitro anisole; absolute alcohol isomerized the ethyl ether of *aci*-picric acid to the true ether as well as solvolyzed it to varying amounts of picric acid; the *aci* ether on standing for 2 months was almost completelyc onverted to trinitrophenetole. No mention of the decomposition to an oxime and a carbonyl compound was made and we feel the evidence given by Hantzsch and Gorke fails to substantiate the existence of the compounds claimed.

The reaction of 10-nitro-9-anthrone with diazomethane[6] was reinvestigated, but even at 0° a nitronic ester was not isolable although anthraquinone monoxime and formaldehyde were formed. The intermediate nitronic ester has steric repulsions between the *peri* hydrogen atoms and the ester moiety which forces an oxygen atom and the methyl group close together so that a facile cyclic elimination of formaldehyde occurs.

The silation of I with bis(trimethylsilyl)acetamide (BSA) led to the silyl ether rather than the ester. The structure of the ether was shown by its lack of an orange color and its nmr spectrum which showed only a single aromatic peak rather than two vinyl doublets characteristic of the nitronic esters. The reaction of I with BSA in deuteriochloroform can be monitored by nmr. At the initiation of the reaction a red color appears and a broad signal can be seen at 7.34 ppm which over a period of about 20 min gradually disappears as a sharp singlet at 8.08 ppm appears. When the signal at 7.34 ppm has completely disappeared, the red color has faded to pale yellow. It appears that the signal at 7.34 ppm corresponds to the vinyl protons of the unstable trimethylsilyl nitronic ester (VIII) which rearranges to the trimethylsilyl ether (IX) (see eq 2). The red color persisted for about 2 min in acetonitrile, 20 min in chloroform, and about 1 hr in pentane. The lability of the trimethylsilyl group in the ether was shown by the fact that recrystallization of the silyl ether caused the reversion to the nitrophenol.



VIII IX (2)

Experimental Section

Nuclear magnetic resonance spectra were run using a Varian A-60 spectrometer with TMS as the internal standard. Infrared spectra were taken on a Beckman IR 5 spectrophotometer and ultraviolet spectra were run on a Cary 14 ultraviolet 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.

Preparation of Nitrophenols.—Three milliliters of a 1:1 mixture of acetic acid and nitric acid was added dropwise to a stirred solution of 5 g of 2,6-di-*t*-butylphenol in 15 ml of cyclohexane kept at 10–20°. The solid 2,6-di-*t*-butyl-4-nitrophenol was filtered, washed with water, and dried. Three recrystallizations from petroleum ether (35–60°) afforded 2.0 g of white needles, mp 154–155° (lit.[3] 153–154°). The infrared spectrum of I showed a sharp nonhydrogen-bonded hydroxyl absorption at 2.83 (KBr) and one at 2.75 μ in ether.

From 40 g of 2,6-diisopropylphenol a similar nitration gave 17 g of 2,6-diisopropyl-4-nitrophenol, mp 110–113° (lit.[3] 112°).

When 10 g of 2-*t*-butylphenol was nitrated at 0° in 30 ml of cyclohexane by 6 ml of a 1:1 acetic acid–nitric acid mixture, the reaction mixture gave a black oily semisolid which on washing with pentane gave 2.1 g of a white solid which melted with sublimation at 142–144°. Three recrystallizations from low-boiling petroleum ether afforded an analytical sample, mp 142–143°. The nmr spectrum was consistent with that expected for 2-*t*-butyl-4-nitrophenol.

Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.52; H, 6.71. Found: C, 61.57; H, 6.72.

4,6-Dinitro-2-*t*-butylphenol was prepared from 2,6-di-*t*-butylphenol according to the method of Hart and Cassis, mp 125–126° (lit.[7] 124–125°).

Reactions of Hindered Phenols with Diazomethane.—An ethereal solution of diazomethane gave no visible immediate reaction with 2,6-di-*t*-butylphenol, 2,6-diisopropylphenol, and 2,6-di-*t*-butyl-4-bromophenol.

When diazomethane in ether gave an immediate evolution of nitrogen with a phenol, the diazomethane was added until the evolution of nitrogen ceased. Evaporation of the ether deposited the corresponding anisoles in nearly quantitative yields: 2,4,6-tribromoanisole, mp 87–88° (lit.[8] 87°); pentabromoanisole, mp 170–172° (lit.[9] 173–174°); 2,4,6-triiodianisole, mp 98–99° (lit.[10] 99°); 2,6-diiodo-4-nitroanisole, mp 135–137° (lit.[11] 136.5°).

Diazomethane and 4,6-dinitro-2-*t*-butylphenol gave a product which melted at 78–80° without decomposition and it lacked the color and other spectral properties of a nitronic ester.

Anal. Calcd for $C_{11}H_{14}N_2O_5$: C, 51.98; H, 5.51; N, 11.03. Found: C, 51.80; H, 5.62; N, 10.91.

Excess diazomethane was allowed to react overnight at room temperature with 0.5 g of 2-*t*-butyl-4-nitrophenol. The ether was washed with water, dried over anhydrous magnesium sulfate, and then removed under reduced pressure which left 0.44 g of a yellow oil whose nmr spectrum showed only the anisole. Only one O–CH_3 peak at 3.95 ppm was observed and no vinyl hydrogen peaks characteristic of either a quinone–oxime or a nitronic ester were visible. The yellow oil was taken up in ether and washed with 1 *N* sodium hydroxide until the alkaline washes were colorless. The ether was dried and removed as before and the pale yellow oil remaining crystallized on cooling and melted at 57–59°. Three recrystallizations from methanol raised the melting point to 62–62.4°.

Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23. Found: 62.98; H, 7.14.

Methyl 3,4-Di-*t*-butyl-4-oxo-2,5-cyclohexadienenitronate.—Diazomethane converted I quantitatively into the nitronic ester III which decomposed at 106° to give the oxime IV and formaldehyde. The spectral properties of III and IV and the identification of IV and formaldehyde were almost identical in detail with the experimental data of Cohen and Jones.[4]

Diazoethane and diphenyldiazomethane did not give a visible orange color with I. Picric acid liberated nitrogen from diphenyldiazomethane and tetraphenylethylene crystallized upon evaporation of the ether solution. A similar production of tetraphenylethylene has been reported.[12]

Methyl 3,5-Diisopropyl-4-oxo-2,5-cyclohexadienenitronate.—To a diazomethane solution prepared from 24 g of nitrosomethylurea in 1 l. of ether, dried over sodium hydroxide pellets, was added 15 g of 2,6-diisopropyl-4-nitrophenol dissolved in 150 ml of ether. After the solution had stood overnight it was washed

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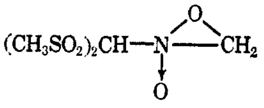
(6) W. G. H. Edwards, *Chem. Ind.* (London), 112 (1951). Edwards reported that 10-nitro-9-anthrone reacted with diazomethane in ether and benzene to give a 60% yield of anthraquinone monoxime and that 4-nitro-1-naphthol similarly gave a 16% yield of 1,4-naphthoquinone monoxime. He did not suggest that a nitronic ester was involved in what he called a "novel reaction." However, he did refer to the work of H. J. Backer (*Rec. Trav. Chem.*, **69**, 610 (1950)) in which bis(dimethanesulfonyl)nitromethane was converted by diazomethane into a compound which on decomposition gave formaldehyde and "bis(methylsulfonyl)isonitrosomethane." Backer considered a nitronic ester as an intermediate but decided that his compound was XI. Today an nmr spectrum would undoubtedly rule out structure XI.



XI

Since Edwards reported neither the formation of formaldehyde nor the temperature reached in removing the solvent from his reaction and apparently was unaware of the course of the reaction, it was felt advisable to try to isolate the intermediate nitronic ester.

(7) H. Hart and F. A. Cassis, Jr., *J. Am. Chem. Soc.*, **73**, 3179 (1951).

(8) A. Hantzsch and G. Scholtz, *Ber.*, **40**, 4875 (1907).

(9) M. Kohn and A. Fink, *Monatsh. Chem.*, **44**, 183 (1923).

(10) M. Kohn and A. Rosenfeld, *ibid.*, **46**, 101 (1925).

(11) P. Block and R. G. Powell, *J. Am. Chem. Soc.*, **64**, 1070 (1942).

(12) J. D. Roberts and W. Watanabe, *ibid.*, **72**, 4869 (1950).

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.[8] 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.

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[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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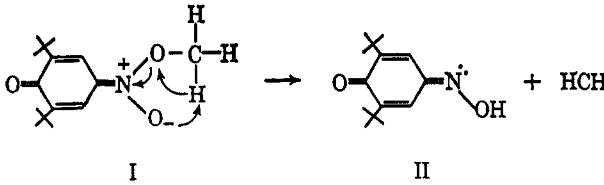
Received September 21, 1967

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 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]



I II (1)

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[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).