ml. benzene was stirred for 2 hr. with 9.3 g. (0.04 mol.) of commercial silver oxide. The solids were removed by filtration and the red colored filtrate evaporated in a rotary film evaporator at 15–20 mm. The dark residue was transferred with the aid of petroleum ether to a filter funnel and the solids washed with petroleum ether leaving very light lemon colored crystals, 2.8 g., m.p. 151–152° (lit.[5] m.p. 151–152°) mixed m.p. 151–152°. The filtrate was evaporated leaving 1 g. of a dark brown solid, m.p. 243°, which was identified by infrared comparison as 2,6,2′,6′-tetra-*t*-butyldiphenoquinone. This same mixture resulted when the reaction was carried out in the presence of oxygen.

b. *Alkaline ferricyanide in benzene.* The experiment reported by Kharasch and Joshi[5] was repeated in both a nitrogen atmosphere as well as in an oxygen atmosphere. In the case of the experiments with oxygen, mixing was accomplished with a Fisher "Vibro-Mixer." The reactions were worked up as described by Kharasch and Joshi and in each instance the same mixture of VI and the tetra-*t*-butyldiphenoquinone was obtained regardless of the presence or absence of oxygen. Thus oxygen appears to have no effect on this reaction.

2,6,2′,6′-Tetra-t-butyldiphenoquinone. In a typical experiment 2.06 g. (0.01 mol.) of 2,6-di-*t*-butylphenol in 200 ml. of methanol or ethanol was stirred with 4.7 g. (0.02 mol.) of silver oxide for 1 hr. The solids were removed by filtration and washed with hot benzene, the benzene being combined with the filtrate. The filtrate was then concentrated to approximately one quarter of its original volume and the red solids (2.0 g., 97%) which had separated were collected by filtration, m.p. 246° (lit.[5] for the diphenoquinone, 245°). The material was further identified by infrared comparison with an authentic sample.

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Improved Synthesis of Salts and Esters of Nitroacetic Acid

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The esters of nitroacetic acid are usually prepared from nitromethane by means of a two-step synthesis. The dipotassium salt of nitroacetic acid is made *via* the self-condensation of two molecules of nitromethane in the presence of strong, aqueous alkali[2] and the salt is then esterified directly by acidification in the presence of the appropriate alcohol.[3] The best yields reported by previous investigators were about 57% of relatively pure salt for the first step and 60% for the esterification, or an over-all yield of nitroacetate ester of 34%, based on nitromethane.[3]

In an effort to improve these yields, a study of both the salt formation and the esterification procedures was undertaken in this laboratory. The first step contains an inherent disadvantage in that the salts of nitroacetic acid are unstable in aqueous base solution, decomposing to give the alkali metal salt of nitromethane and the corresponding alkali carbonate.[4,5] Consequently, there

$$KO_2N{=}CHCOOK + KOH \longrightarrow K^+CH_2NO_2^- + K_2CO_3$$

is an upper limit to the yield of dipotassium nitroacetate which can be obtained by the self-condensation of nitromethane in aqueous potassium hydroxide. It appeared that if the amount of water in the reaction system could be minimized, the decomposition of the nitroacetate salt could be lessened and higher yields obtained.

The ultraviolet absorption spectra of nitroacetate ion and its precursors, nitromethane and methazonate ion, have been determined under a variety of conditions[5] and the effect of *p*H on the position and intensity of the methazonate absorption band has been investigated.[6] An analytical method based on the ultraviolet absorption spectra of the various entities was developed for the determination of nitroacetate in mixtures. This method is described further in the Experimental section.

Application of the optical analytical method to the study of the reaction of nitromethane with potassium hydroxide in various alcohols showed that when the condensation is carried out in *n*-butanol, yields of dipotassium nitroacetate of from 80–90% can be obtained. Results found using various solvents are listed in Table I.

TABLE I

Effect of Solvent on the Reaction of Nitromethane with Potassium Hydroxide

Mole Ratio of KOH/CH_3NO_2, 4/1

Solvent	Max. Reaction Temp.	Reflux Time, Hr.	Yield, % Nitroacetate (±2%)	Yield, % Methazonate
50% aq. KOH	118	25 min.	51	0
CH_3OH	73	38.3	0	17[a]
C_2H_5OH	95	23.25	0	81
C_4H_9OH[b]	118	20	84	3
n-Hexanol	142	20	83	0

[a] Recovered some material which had a λ_{max} of 288 mμ in 1*N* KOH. [b] When potassium butoxide was substituted for potassium hydroxide, no dipotassium nitroacetate was formed, but high yields (90–100%) of potassium methazonate were recovered.

Further studies of the reaction in butanolic potassium hydroxide gave the results shown in Table II.

The crude solids obtained from the reaction mixtures are always contaminated with varying amounts of alkali, alcohol, and unconverted potassium methazonate. However, they may be recrystal-

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[1] Present address: Hampden-Sydney College, Hampden-Sydney, Va.

[2] W. Steinkopf, *Ber.*, **42**, 3925 (1909).

[3] H. Feuer, H. B. Hass, and K. S. Warren, *J. Am. Chem. Soc.*, **71**, 3078 (1949).

[4] W. Steinkopf, *Ber.*, **42**, 2026 (1909).

[5] A. Hantzsch and K. Voigt, *Ber.*, **45**, 85 (1912).

[6] C. M. Drew, J. R. McNesby, and A. S. Gordon, *J. Am. Chem. Soc.*, **77**, 2622 (1955).

TABLE II

EFFECT OF REFLUX TIME ON REACTION OF NITROMETHANE AND POTASSIUM HYDROXIDE IN BUTANOL

Mole Ratio KOH/CH_3NO_2, 4/1

Reflux Time, Hr.	Yield, % Nitro-acetate (±2%)	Meth-azonate
6	63	33
9.5	71	31
12.4	80	5
15	84[a,b]	5
17	83[c]	4
20	84	3
33.25	77	0

[a] Average of three experiments. [b] For six experiments with discontinuous heating at reflux for 15 hr. (mixture allowed to stand at room temperature overnight; heating resumed next morning), the average yield of nitroacetate was 90%. [c] Average of two experiments.

lized from hot aqueous alkali to give average overall yields of relatively pure dipotassium nitroacetate of 71–77% based on nitromethane.

Preparation of methyl nitroacetate. The previously recommended procedure for the conversion of dipotassium nitroacetate to methyl nitroacetate requires reaction with concentrated sulfuric acid at from −50 to −60° for 24 hours, followed by standing at room temperature for 144 hours before isolation of the product, in order to obtain 60% yields of ester.[3] It has now been found that yields of 60–66% methyl nitroacetate can be obtained if the acidification is carried out at from −5 to −10° for 17 hours and the reaction mixture is allowed to stand at room temperature for 2 hours prior to workup. In agreement with Feuer *et al.*,[3] it was found that the omission of anhydrous sodium sulfate or use of less than 2 moles of sulfuric acid per mole of dipotassium nitroacetate gave much lower yields of ester.

In addition, the procedure used by Feuer *et al.*[3] for the isolation of methyl nitroacetate was modified. We obtained considerably better yields of the ester by extracting the excess sulfuric acid with water before distillation rather than by neutralization of the acid with aqueous sodium carbonate. This averts losses of the ester to the aqueous layer as the salt (K_a of ethyl nitroacetate is 1.4×10^{-6}).[7]

EXPERIMENTAL[8]

Spectral analysis.[9] Reference samples of dipotassium nitroacetate, methazonic acid, and nitroacetonitrile were prepared, and their absorption maxima and specific extinction coefficients were determined in water and 1*N* potassium hydroxide. The results are given in Table III. On standing in 1*N* potassium hydroxide for two weeks, the absorption maximum of nitroacetonitrile shifted from 288 mμ to 278 mμ, indicating gradual conversion to dipotassium nitroacetate. In water, no shift in the absorption maximum was observed after two weeks' standing, but the specific extinction coefficient decreased markedly. It is to be noted that the λ_{max} of methazonic acid in potassium hydroxide solution shifts from 298 mμ at a *p*H of 10 to 310 mμ in 1*N* potassium hydroxide.[10]

TABLE III

ULTRAVIOLET ABSORPTION OF DIPOTASSIUM NITROACETATE AND ITS PRECURSORS

Compound	Solvent	λ_{max}, mμ	$k = \frac{D^a}{c}$
Dipotassium nitro-acetate	Water	None[b]	—
	1*N* KOH	276	60.6
Methazonic acid	Water	298	80.0
	Dil. KOH (*p*H 10)	298	115.3
	1*N* KOH	310	197.3
	1*N* KOH	276[c]	45.0
Nitroacetonitrile (initial)	Water	288	140
	1*N* KOH	288	132
(After standing 2 weeks)	Water	288	87
	1*N* KOH	278	112

[a] Specific extinction coefficient; $D = kcl$ where l is in cm., c in g./l. [b] λ_{max} at 276 fades within seconds. [c] This value is not λ_{max} but the absorption of methazonate at this λ.

The values of the specific extinction coefficients are somewhat uncertain since they depend on the purity of the samples used for calibration.

The crude reaction products were analyzed by determining the concentration of potassium methazonate at 298 mμ in aqueous solutions having a *p*H of 10.0, followed by correcting the absorbance of the sample in 1*N* potassium hydroxide at 276 mμ for the absorbance of the methazonate and subsequent calculation of the dipotassium nitroacetate concentrations. No evidence for the presence of nitroacetonitrile was observed. Preparation of synthetic mixtures of methazonate, nitroacetonitrile, and nitroacetate and subsequent analysis indicated that the accuracy of the method was 2% for nitroacetate when the amount of methazonate present was less than 10% of the total material.

Apparatus and method. Spectral measurements were made using a Beckman Model DK recording spectrophotometer.

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[7] H. Ley and A. Hantzsch, *Ber.*, **39**, 3149 (1906).

[8] All melting and boiling points are reported uncorrected.

[9] We are indebted to Mr. C. T. Desmond of these laboratories for the development of the ultraviolet spectral method.

[10] Other investigators[6] have noted that methazonate salts exhibited only one very pronounced ultraviolet absorption peak with λ_{max} at 298 mμ, and that absorption of methazonate ion at 298 mμ obeys Beer's law only at a *p*H of 10.5 or higher. At *p*H 11 to 11.5, they found a value of ε for ammonium methazonate in sodium hydroxide of 17,840. They made no mention of a λ_{max} shift at higher *p*H values. In this laboratory, the ε value for methazonic acid in 1*N* potassium hydroxide at λ_{max} = 310 mμ was 28,086; at λ_{max} = 298, *p*H = 10, ε was 16,407. Recent evidence has shown that methazonic acid forms a disodium salt.[11] λ_{max} at 298 is undoubtedly due to the monopotassium salt (I), while that observed at 310 mμ may be due to the dipotassium salt (II).

$O_2NCH_2CH{=}NOK$ I $\qquad$ $K{-}ON{=}CH{-}CH{=}NO_2K$ II

[11] D. J. Morgan, *J. Org. Chem.*, **23**, 1069 (1958).

The *p*H values were measured with a Leeds-Northrup *p*H meter having a Leeds-Northrup Standard 1199-30 calomel reference electrode and a Leeds-Northrup Standard 1199-31 glass electrode. Measurements were referred to standards prepared from Coleman Buffer tablets.

The dilutions used were approximately 1×10^{-2} g./l. They were allowed to stand for 1 hour after preparation before the absorbance was measured to allow for complete hydrolysis of dipotassium nitroacetate in the aqueous solutions of *p*H 10. The glassware used for the sample dilutions was caustic-free.

Methazonic acid. This compound was prepared by a modification of the method of Reid and Köhler.[12] In the reaction flask were placed 40 g. (1 mole) of sodium hydroxide and 80 ml. of water. After the resulting solution had cooled to 48°, 40 g. (0.653 mole) of distilled nitromethane was added, with vigorous stirring, at a rate designed to keep the reaction temperature between 45 and 50°. The addition took 1.5 hour.

The deep amber-colored solution was then cooled to 0° and acidified by the dropwise addition of 85 ml. of concentrated hydrochloric acid. The reaction temperature was maintained at 0 to +5° throughout this addition, which took 44 min. Upon reaching an acid *p*H value, the solution changed color from amber to bright yellow, and a solid precipitated. This solid was collected by immediate filtration, pressed on a clay plate, and taken up in 200 ml. of ethyl ether. The ether solution was dried over anhydrous calcium chloride overnight, filtered, and evaporated to dryness *in vacuo* without heating. The resulting bright orange solid weighed 17.0 g., representing a 50% yield of crude methazonic acid. A portion of the solid was recrystallized from hot chloroform to give yellow needles; m.p. 70–72°.[13,14]

Anal. Calcd. for $C_2H_4O_3N_2$: N.E. 104.07. Found: N.E. 105.3.

The material is very unstable. It decomposes to a red resin within 3 days even when stored below 0°.

Nitroacetonitrile. This material was made by the procedure of Ried and Köhler,[12] using 14.7 g. (0.141 mole) of recrystallized methazonic acid, 17.1 g. (0.145 mole) of freshly distilled thionyl chloride (b.p. 75°/atm.) and 80 ml. of absolute ethyl ether. There was obtained 3.7 g. (31% yield) of pale yellow nitroacetonitrile. This liquid, which could have contained some methazonic acid as an impurity, was used as a standard for the determination of nitroacetonitrile in crude nitroacetate samples.

Dipotassium nitroacetate. The analytical standard was prepared by the method of Feuer, Hass, and Warren.[3] A yield of 47.5% of fairly high purity material was obtained in two crops. A sample was recrystallized from the minimum amount of hot 50% aqueous potassium hydroxide, washed with methanol, and dried *in vacuo* at 100°.

Anal. Calcd. for $C_2HNO_4K_2$: K, 43.15; N, 7.73. Found: K, 42.8; N, 7.29.

Reactions in alcoholic potassium hydroxide. The studies of the effect of various conditions on the reaction of nitromethane with potassium hydroxide were carried out using similar procedures. Generally, the reactions were carried out in 1-, 2-, or 5-l. flasks fitted with air-driven, high speed stirrers. The reaction flasks were also fitted with reflux condensers, dropping funnels, and thermowells.

Potassium butoxide was prepared by adding freshly cut slivers of potassium to an excess of distilled *n*-butanol with vigorous stirring under a nitrogen purge. The resulting solutions were heated at 96° for 2 hours to insure complete reaction, and the reaction with nitromethane was carried out in the same system.

A representative reaction procedure is described below. Results of the various studies are given in the tables.

In a 2-l. creased flask was placed 705 g. of a 15.9% solution of potassium hydroxide in *n*-butanol. Nitromethane (31 g., 0.5 mole) was added dropwise with vigorous stirring over a 25-minute period. The temperature rose from 30 to 49° during the addition. The mixture was then warmed to reflux in a 58-minute period and heated at reflux (117 to 120°) for 15 hours.

The reaction mixture was cooled, and the pale yellow solid product was removed by filtration (sintered glass filter) washed with methanol, crushed, and dried in a vacuum desiccator for 8 hr. The material was powdered and dried in a vacuum oven at 60°/1 mm. for 7.5 hr. The dried material (66.3 g.) was off-white, and contained 62% (by ultraviolet analysis; 41.1 g., 0.226 mole) of dipotassium nitroacetate and 1% (0.66 g., 0.006 mole) of potassium methazonate, corresponding to yields of 91% and 2%, respectively, based on nitromethane.

Recrystallization of crude dipotassium nitroacetate. There was dissolved 472 g. of crude reaction product, which contained 319 g. of dipotassium nitroacetate, in hot 50% aqueous potassium hydroxide. The mixture was cooled in an ice bath to yield two crops of silky white needles. The solid was collected by filtration, washed with methanol, and dried in the vacuum oven at 90°/1 mm. for 5 hours. The crops weighed 230 g. and 41 g., respectively, and had purities of 100% and 98% as dipotassium nitroacetate. This represented a recovery of 85%.

Methyl nitroacetate. To 90.5 g. (0.5 mole) of 100% pure dipotassium nitroacetate in a jacketed kettle there were added 600 ml. (471 g., 14.69 moles) of methanol and 15 g. (0.11 mole) of anhydrous sodium sulfate. The flask contents were cooled to −11° by circulating brine through the outer jacket while stirring the cream-colored slurry. One hundred g. of 98% sulfuric acid was added dropwise to the stirred mixture over a period of 2.1 hours. The resulting white slurry was stirred at −5 to −11° for 17 hours, then for 2.3 hours at room temperature. The precipitated white solid was filtered, washed with methanol, and discarded. The excess methanol was stripped at room temperature from the amber-colored filtrate at reduced pressure. The oily residue was shaken with 150 ml. of methylene chloride and 100 ml. of water. The resulting layers (a light yellow, organic layer, and a deep amber water layer) were separated and the organic layer was washed with 100 ml. of water. The aqueous washings were combined, extracted with 50 ml. of ether, and discarded. The combined organic layers were dried over anhydrous sodium sulfate and the solvent was distilled through a 30 × 180 mm., glass ring-packed column at atmospheric pressure. Vacuum distillation of the residue from a smaller flask *via* the same column (heated) gave 39.3 g. (0.33 mole, 66% yield) of methyl nitroacetate, boiling at 46–47°/0.8 mm.; n_D^{20} 1.4260 (lit.[3] gives b.p. 93–94°/15 mm., n_D^{20} 1.4245).

Anal. Calcd. for $C_3H_5O_4N$: N, 11.77; neut. equiv. 119. Found: N, 11.98; neut. equiv. 119.

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(12) W. Reid and E. Köhler, *Ann.*, **598**, 145 (1956).

(13) Melting point taken in sealed, evacuated capillary.

(14) O. Schultze, *Ber.*, **29**, 2287 (1896) reported a m.p. of 78–80° for methazonic acid; W. Dunstan and E. Goulding, *J. Chem. Soc.*, **77**, 1264 (1900) reported a m.p. between 60 and 70°, depending on the rate of heating.