Alkyl Nitrate Nitration of Active Methylene Compounds. Nitration of Toluenes.[1] A Facile Preparation of Stilbenes
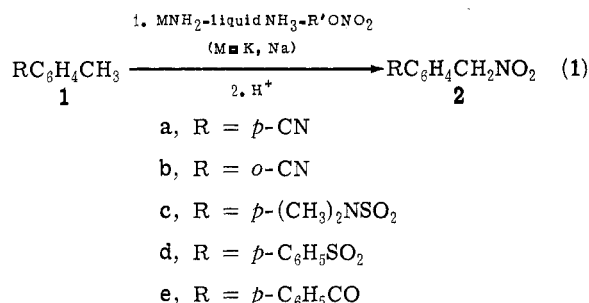
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The alkyl nitrate nitration of toluenes substituted in the ortho or para position with an electron-withdrawing group gives the corresponding α-nitrotoluenes in yields of about 40–55%. The reaction is successful with o- and p-tolunitriles, N,N-dimethyl-p-toluenesulfonamide, phenyl p-tolyl sulfone, 4-methylbenzophenone, and even such a weak acid as diphenylmethane. The reaction is unsuccessful with o- and p-N,N-dimethyltoluamides, which are converted into the corresponding o- and p-toluamides in the alkali amide–liquid ammonia system. The para-substituted α-nitrotoluenes are readily converted in good yield into the corresponding para-substituted stilbenes on treatment with catalytic amounts of potassium acetate in refluxing ethanol. However, the reaction with o-cyano-α-nitrotoluene leads to 3-oximinophthalimide.

In continuation of our studies of the alkyl nitrate nitration[2] in the alkali amide–liquid ammonia system, we now report on its application to the preparation of α-nitrotoluenes substituted in the ortho or para position with an electron-withdrawing group such as cyano, N,N-dimethylsulfonamido, phenylsulfonyl, and benzoyl (eq 1).

$$RC_6H_4CH_3 \xrightarrow[\substack{(M = K,\ Na) \\ 2.\ H^+}]{1.\ MNH_2\text{-liquid }NH_3\text{-}R'ONO_2} RC_6H_4CH_2NO_2 \quad (1)$$
$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{2}$$

a, R = p-CN

b, R = o-CN

c, R = p-(CH$_3$)$_2$NSO$_2$

d, R = p-C$_6$H$_5$SO$_2$

e, R = p-C$_6$H$_5$CO

A search of the literature indicated that the only α-nitrotoluene reported bearing an electron-withdrawing group in the ortho or para position is α-p-dinitrotoluene (3). It was prepared by Kornblum, et al.,[3] in 75% yield from p-nitrobenzyl bromide by the Victor Meyer reaction.

In order to determine optimum reaction conditions, various reaction parameters were studied with p-tolunitrile (1a). p-Cyano-α-nitrotoluene (2a) was obtained in 46% yield and 42% of 1a was recovered when nitrations were carried out in systems A (potassium amide–liquid ammonia) or B (sodium amide–liquid ammonia), and when the molar ratio of 1a to base and alkyl nitrate was 1:1.5:2. Anion formation was carried out at −33° for 15 min, and the crude nitronate salt was generally isolated and then acidified with acetic acid in absolute ether or in water.

However in the case of o-tolunitrile (1b), pure o-cyano-α-nitrotoluene (2b) (38%) was obtained only when the potassium salt of 2b was recrystallized from 95% ethanol prior to acidification with acetic acid and the crude 2b was thoroughly washed with water to remove all traces of potassium acetate. The recrystallization of 2b, contaminated with traces of potassium acetate, with 95% ethanol led exclusively to 3-oximinophthalimide (*vide infra*).
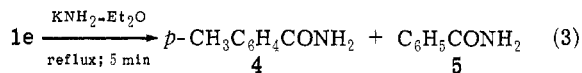
Nitrations of N,N-dimethyl-p-toluenesulfonamide (1c) and phenyl p-tolyl sulfone (1d) did not proceed equally well in systems A and B. In system B, 1c and 1d were converted into the corresponding nitro compounds 2c and 2d in yields of 39.5 and 54%, respectively, while in system A the yields were only 15 and 4%. These results are contrary to what one would expect on the basis of base strength. They were not due to side reactions because the material balances were about 80–88%. The results could be explained by the ambident nature of the anions of 1c and 1d.

In one of the resonance structures of these anions the negative charge resides on the oxygen, and it is conceivable that the electrophilic attack of the nitrate ester would be directed toward the oxygen rather than carbon. The product of such O-nitration would probably be unstable and revert to starting material (eq 2). According to the well-
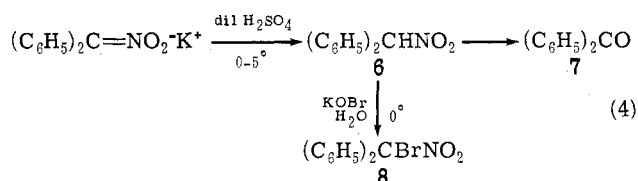

$$R = (CH_3)_2N,\ C_6H_5$$
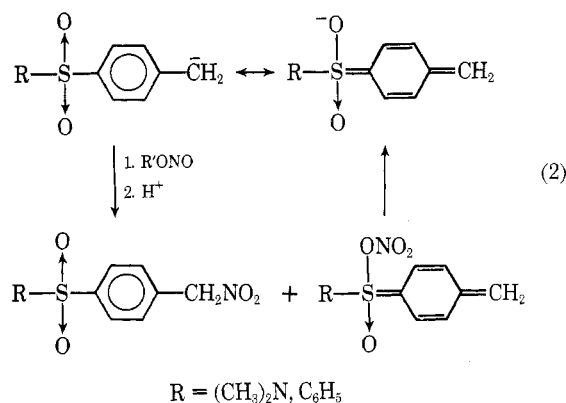
known cation effect[4] O-nitration would predominate in system A and as a consequence the yields in the nitration of 1c and 1d would be lower than in system B and C-nitration would be favored.

4-Methylbenzophenone (1e) underwent nitration only in system A. p-Benzoyl-α-nitrotoluene (2e) was obtained in 16% yield and 64% of 1e was recovered. Nitration in system B led to a quantitative recovery of 1e. Attempts to increase the yield of 2e by carrying out the anion formation with potassium amide in refluxing ether were unsuccessful. Compound 1e was cleaved in a Haller–Bauer-type reaction[5] to p-toluamide (4) in 58% yield. The other cleavage product benzamide (5) was hydrolyzed during work-up to benzoic acid (42% yield) (eq 3).

$$\mathbf{1e} \xrightarrow[\text{reflux; 5 min}]{KNH_2\text{-}Et_2O} p\text{-}CH_3C_6H_4CONH_2 + C_6H_5CONH_2 \quad (3)$$
$$\mathbf{4} \qquad\qquad \mathbf{5}$$

Diphenylmethane was converted into diphenylnitromethane[6] (6) in 40% yield. Compound 6 was found to be unstable, and even a spectroscopically pure sample decomposed to benzophenone[6b] (7) when stored at 0° (eq 4). Di-

$$(C_6H_5)_2C{=}NO_2^-K^+ \xrightarrow[0\text{-}5°]{dil\ H_2SO_4} (C_6H_5)_2CHNO_2 \longrightarrow (C_6H_5)_2CO$$
$$\mathbf{6} \qquad\qquad\qquad \mathbf{7}$$
$$\downarrow \substack{KOBr \\ H_2O}\ 0°$$
$$(C_6H_5)_2CBrNO_2 \qquad\qquad (4)$$
$$\mathbf{8}$$

phenylbromonitromethane[6b] (8), however, was found to be unchanged even after 3 years, when stored at 0°. Compound 8 was obtained in 68% yield when the bromination of 6 was performed at 0° with aqueous potassium hypobromite or with bromine in absolute ether (eq 4).

It should be mentioned that the nitration was unsuccessful with o-N,N-dimethyltoluamide (9), its para isomer (10), 2-methylbenzophenone (11), and p-nitrotoluene (12). As shown in eq 5, compounds 9 and 10 were converted in a

$$CH_3C_6H_4CON(CH_3)_2 \xrightarrow[n\text{-}C_3H_7ONO_2]{KNH_2\text{-liquid }NH_3} CH_3C_6H_4CONH_2 \quad (5)$$
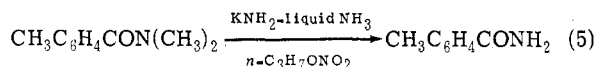
transamidation reaction into o- and p-toluamides, respectively.

The failure of compound 11 to undergo nitration is believed to be due to the lack of anion formation in systems A or B. No deuterium was incorporated when 11 was treated with potassium amide in refluxing ether and the reaction mixture quenched with deuterium oxide. Hauser[7] reported that 11 did not undergo alkylation in system B.

Nitration of compound 12 at the usual conditions in system A did not give the expected 3 but rather led to the formation of p,p'-dinitrobibenzyl (13). The conversion of compound 12 into compound 13 in basic media has been well established.[8]

The substituted α-nitrotoluenes were identified by infrared and nmr spectral data, and by conversion into the corresponding α-halo-α-nitrotoluenes.

Dihalo derivatives of the α-nitrotoluenes were obtained when their nitronate salts were treated with aqueous solutions of potassium hypohalite (eq 6).

$$RC_6H_4CH{=}NO_2{}^-M^+ \xrightarrow[H_2O]{KOX} RC_6H_4CX_2NO_2 \quad (6)$$
$$\mathbf{2}$$

$$M = Na, K; X = Br, Cl$$
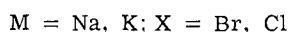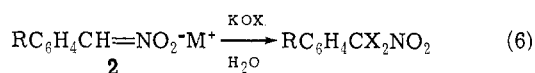
Treatment of the potassium salt of 2a with a stoichiometric amount of bromine in carbon tetrachloride afforded p-cyano-α-bromo-α-nitrotoluene (eq 7).

$$p\text{-}CNC_6H_4CH{=}NO_2{}^-K^+ \xrightarrow[CCl_4]{Br_2} p\text{-}CNC_6H_4CHBrNO_2 \quad (7)$$
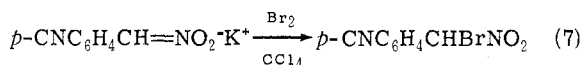
As already mentioned o-cyano-α-nitrotoluene (2b) was converted into 3-oximinophthalimide (14) in 92% yield in the presence of potassium acetate (eq 8).

$$\mathbf{2b} \xrightarrow[\Delta]{KOAc\text{-}95\% EtOH} \quad (8)$$
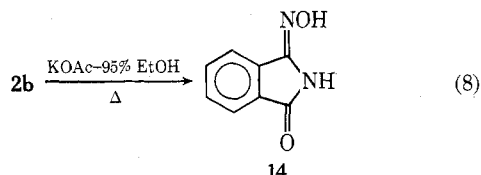
The transformation might occur by the pathway shown in Scheme I. It would account for the fact that only a catalytic amount of base is required. In step I nucleophilic attack of hydroxide ion on the nitrile group[9] of 2b which would be expected to exist to some extent in the aci form,[10] gives the enol form of amide "A." Cyclization of "A" by intramolecular nucleophilic attack in step II leads to intermediate "B." Loss of hydroxide ion in step III gives rise to nitroso compound "C" which tautomerizes to 14.
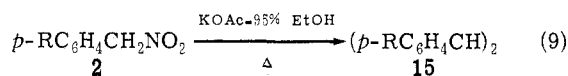
Conversion of α-Nitrotoluenes into Stilbenes. The facile conversion of o-cyano-α-nitrotoluene (2b) to 3-oximinophthalimide (14) prompted the investigation of the reaction of the α-nitrotoluenes 2 with base.

A survey of the literature revealed that Wislicenus and coworkers[11] had found that 2g and its o- and p-bromo de-

Scheme I
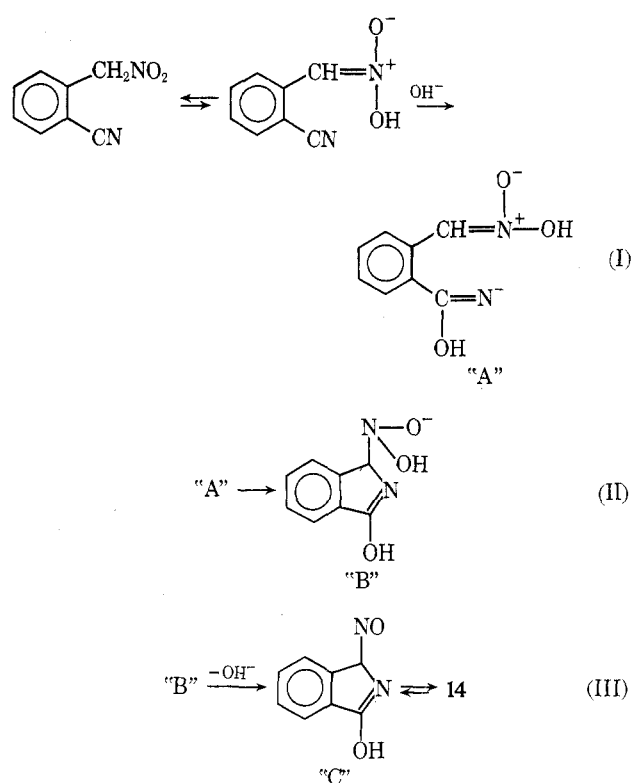
rivatives were converted into the corresponding stilbenes in yields of 85, 30, and 60% respectively, on refluxing with aqueous sodium hydroxide for several hours. Our investigation showed that even such a weak base as potassium acetate in refluxing 95% ethanol converts compounds 2 into the corresponding stilbenes 15 (eq 9). Under these mild

$$p\text{-}RC_6H_4CH_2NO_2 \xrightarrow[\Delta]{KOAc\text{-}95\% EtOH} (p\text{-}RC_6H_4CH)_2 \quad (9)$$
$$\mathbf{2} \qquad\qquad\qquad \mathbf{15}$$

a, R = p-CN

c, R = SO_2N(CH_3)_2

d, R = C_6H_5SO_2

e, R = C_6H_5CO

f, R = NO_2

g, R = H

conditions, groups sensitive to strong base such as sulfonamido, nitrile, and nitro were not affected during stilbene formation. It was established that only a catalytic amount of potassium acetate was required to convert 2c into stilbene 15c in 64% yield after a reaction time of 21 hr. In the absence of potassium acetate 2c was recovered unchanged after refluxing in 95% ethanol.

The results which are summarized in Table I show that the stilbenes were obtained in yields which varied from 36 to 100% and that the material balances amounted to about 80%. The low yield (36%) in the case of 2f was apparently due to a Nef reaction which gave rise to the formation of p-nitrobenzoic acid (16) in 10% yield. It is of interest that although no 16 was obtained after a reaction time of 2 hr the yield of 15f had not changed but 35% of 2f was recovered. Moreover, it should be emphasized that an electron-withdrawing group is not essential for the transformation, since α-nitrotoluene itself was converted into stilbene in high yield.

Table I
Conversion of α-Nitrotoluenes into Stilbenes[a]

$$R-\langle\bigcirc\rangle-CH_2NO_2 \xrightarrow[\Delta]{\text{KOAc–95\% EtOH}} \left[R-\langle\bigcirc\rangle-CH \right]_2$$

R	Stilbene yield, %	Mp, °C	α-Nitrotoluene recovery, %
CN	76[b]	275–277[c]	9.5
Me$_2$NSO$_2$	67[d]	254–255	7.0
C$_6$H$_5$SO$_2$	55.3[b]	324–325	26.6
C$_6$H$_5$CO	100	233–235[e]	
NO$_2$	35.7[b]	306–307[f]	g,h
H	81	123–124[i]	0

[a] Unless stated otherwise, equimolar amounts of potassium acetate were employed and the reaction time was 21 hr. [b] The yield was the same when the reaction time was 2 hr. [c] C. D. Weiss, *Helv. Chim. Acta*, **49**, 234 (1965), reports mp 272–274°. [d] The yield was 64% when a catalytic amount of potassium acetate was used. [e] G. Wittig and W. Wiener, *Justus Liebigs Ann. Chem.*, **483**, 144 (1930), report mp 234–235°. [f] C. M. Anderson, L. G. Cole, and E. C. Gilbert, *J. Amer. Chem. Soc.*, **74**, 6313 (1952), report mp 302–304°. [g] p-Nitrobenzoic acid was obtained in 10.5% yield. [h] After a reaction time of 2 hr, no p-nitrobenzoic acid was formed; however, 35% of starting material was recovered. [i] Lit.[11a] mp 124–125°.

Experimental Section

All melting points are uncorrected. All infrared spectra were taken with Perkin-Elmer recording spectrophotometer, Models 21 and 421. Nuclear magnetic resonance spectra were determined on a Varian Model A-60 analytical nmr spectrometer using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on an Aerograph A-700 using a 4-ft SF-96 on Chromosorb W column and a 6-ft SE-30 on Chromosorb P column. Solvents were evaporated on a Buchler flash-evaporator.

Reagents. Amyl nitrate was a generous gift from Ethyl Corp.; propyl nitrate, *N,N*-dimethyl-*p*-toluenesulfonamide, and *o*- and *p*-tolunitriles were of Eastman White Label grade; *o*-toluoyl chloride and diphenylmethane were obtained from Aldrich Chemical Co., 4-methylbenzophenone and *p*-nitrotoluene from J. T. Baker Chemical Co., and *p*-toluenesulfonyl chloride from Matheson Coleman and Bell. All of these compounds were used as received.

***p*-Cyano-α-nitrotoluene (2a).** The following experiment is typical of the procedure employed for the preparation of α-nitrotoluenes. Into an oven-dried 500-ml round-bottom four-necked flask equipped with Dry Ice condenser, thermometer, mechanical stirrer, and addition funnel were placed, at −33°, 250 ml of liquid ammonia, a crystal of ferric nitrate nonahydrate, and 2.95 g (0.075 g-atom) of potassium. After potassium amide had formed, a solution of 5.9 g (0.05 mol) of *p*-tolunitrile (1a) in 15 ml of ether was added dropwise within 2 min. The mixture was stirred 15 min at −33° and then 10.51 g (0.1 mol) of propyl nitrate was added in 5 min [*CAUTION!* The first drops of alkyl nitrate should be added slowly because a considerable exotherm might develop], while the temperature was kept at −33° with a Dry Ice–CHCl$_3$–CCl$_4$ bath. The mixture was stirred for an additional 30 min at −33°, and the ammonia was allowed to evaporate while replacing it with anhydrous ether. Filtering and drying the solid at 25° (0.7 mm) gave 17.8 g of crude potassium *p*-cyanophenylmethanenitronate.

To a suspension of the crude salt in 150 ml of anhydrous ether at −40° was added 15 g (0.25 mol) of glacial acetic acid. The mixture was stirred overnight in an ice–salt bath, filtered and concentrated *in vacuo* to afford 3.78 g (46.6%, based on 1a) of *p*-cyano-α-nitrotoluene, mp 94–96°. The analytically pure sample, obtained after recrystallizing the crude material from 95% ethanol and subliming at 60° (0.25 mm), gave mp 95–96°: ir (KBr) 2230 (CN) and 1558 and 1375 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 5.57 (s, 2 CH$_2$) and 7.72 (q, 4, C$_6$H$_4$).

Anal. Calcd for C$_8$H$_6$N$_2$O$_2$: C, 59.27; H, 3.73; N, 17.28. Found: C, 59.03; H, 3.54; N, 17.44.

Concentrating the filtrate from the nitration gave 2.44 g (41.5%) of recovered 1a as determined by glpc analysis.

***o*-Cyano-α-nitrotoluene (2b).** The general procedure was followed up to the isolation of the nitronate salt. From 5.9 g (0.15 mol) of potassium amide, 11.8 g (0.1 mol) of *o*-tolunitrile (1b), and 21.2 g (0.2 mol) of propyl nitrate was obtained 19.3 g of potassium *o*-cyanophenylmethanenitronate. One recrystallization from 95%

ethanol gave 12.8 g of nitronate salt, mp 220° dec. The salt was dissolved in 250 ml of water, acidified with 9 g (0.15 mol) of glacial acetic acid at room temperature, and filtered to give 6.2 g (38.3%) of *o*-cyano-α-nitrotoluene, mp 52–55°. One recrystallization from 95% ethanol gave mp 58–59°: ir (KBr) 2230 (CN) and 1555 and 1378 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 5.57 (s, 2 CH$_2$) and 7.75 (m, 4, C$_6$H$_4$).

Anal. Calcd for C$_8$H$_6$N$_2$O$_2$: C, 59.26; H, 3.73; N, 17.28. Found: C, 58.99; H, 3.78; N, 17.15.

Compound 1b (4.1 g, 35%) was recovered as determined by glpc analysis.

***p-N,N*-Dimethylsulfonamido-α-nitrotoluene (2c).** The general procedure was followed up to the isolation of the nitronate salt. From 3.46 g (0.15 mol) of sodium amide, 19.9 g (0.1 mol) of *N,N*-dimethyl-*p*-toluenesulfonamide (1c), and 21.2 g (0.2 mol) of propyl nitrate there was obtained 22.4 g of salt. It was dissolved in 400 ml of water; the solution was filtered and acidified with 9 g (0.15 mol) of glacial acetic acid to give 9.6 g (39.4%) of *p-N,N*-dimethylsulfonamido-α-nitrotoluene, mp 110–114°. Two sublimations at 95–100° (0.45 mm) gave mp 113–114°: ir (KBr) 1550 (NO$_2$) and 1340 and 1162 cm^{-1} (SO$_2$); nmr (CDCl$_3$) δ 2.72 (s, 6, NCH$_3$), 5.50 (s, 2, CH$_2$), and 7.65 (q, 4, C$_6$H$_4$); mass spectrum (75 eV) *m/e* (rel intensity) 244 (30) and 198 (100).

Anal. Calcd for C$_9$H$_{12}$N$_2$O$_4$S: C, 44.26; H, 4.92; N, 11.48; S, 13.11. Found: C, 44.51; H, 5.07; N, 11.30; S, 13.36.

Compound 1c (5.4 g, 27.1%) was recovered.

When the reaction was carried out in system A, a small amount of material remained when the crude nitronate salt was dissolved in water. It was identified as *p,p*-bis(*N,N*-dimethylsulfonamido)-stilbene (*vide infra*).

***p*-Phenylsulfonyl-α-nitrotoluene (2d).** From 3.46 g (0.15 mol) of sodium amide, 23.2 g (0.1 mol) of phenyl *p*-tolyl sulfone (1d), 21.2 g (0.2 mol) of propyl nitrate, and 9 g (0.15 mol) of glacial acetic acid there was obtained 7.05 g (54.7%) of *p*-phenylsulfonyl-α-nitrotoluene, mp 65–70°. Three recrystallizations from 95% ethanol gave mp 94–95°: ir (KBr) 1560 and 1380 (NO$_2$) and 1308 and 1160 cm^{-1} (SO$_2$); nmr (CDCl$_3$) δ 5.4 (s, 2, CH$_2$) and 7.6 (m, 9, C$_6$H$_5$ and C$_6$H$_4$).

Anal. Calcd for C$_{13}$H$_{11}$NO$_4$S: C, 56.32; H, 3.97; N, 5.05; S, 11.55. Found: C, 56.40; H, 3.97; N, 5.06; S, 11.51.

Compound 1d (9.1 g, 39.2%) was recovered.

***p*-Benzoyl-α-nitrotoluene (2e).** From 5.9 g (0.15 mol) of potassium amide, 19.6 g (0.1 mol) of 4-methybenzophenone (1e), 26.6 g (0.2 mol) of amyl nitrate, and 9.9 g (0.165 mol) of glacial acetic acid there was obtained 2.09 g (16%) of *p*-benzoyl-α-nitrotoluene, mp 88–89°. One sublimation at 65° (0.7 mm) gave mp 89–89.5°: ir (KBr) 1660 (CO), 1550 and 1372 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 5.70 (s, 2, CH$_2$NO$_2$) and 7.92 (m, 9, C$_6$H$_5$ and C$_6$H$_4$).

Anal. Calcd for C$_{14}$H$_{11}$NO$_3$: C, 69.70; H, 4.59; N, 5.80. Found: C, 69.46; H, 4.58; N, 5.75.

Compound 1e (12.49 g, 64%) was recovered as determined by glpc analysis.

Diphenylnitromethane (6). The general procedure was employed up to the isolation of the nitronate salt; 5.9 g (0.15 mol) of potassium amide, 16.8 g (0.1 mol) of diphenylmethane, and 21.2 g (0.2 mol) of propyl nitrate were used.

The reaction mixture was filtered and a solution of 7.2 g (0.0286 mol) of crude nitronate salt in 150 ml of water was acidified to pH 5 with 4 *M* sulfuric acid. Filtering and drying the pink solid *in vacuo* gave 2.4 g (39.5%) of diphenylnitromethane, mp 85–90° dec. One recrystallization of the crude compound from ether gave mp 90–91° dec (lit.[6b] mp 90–91° dec): ir (KBr) 1557 and 1358 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 6.8 (s, 1, CHNO$_2$) and 7.41 (m, 10, C$_6$H$_5$).

Diphenylmethane (4.91 g, 29.2%) was recovered.

***p*-Cyano-α,α-dibromo-α-nitrotoluene.** The following experiment is typical of the procedure employed for the preparation of α,α-dihalo-α-nitrotoluenes. Into a 300-ml round-bottom flask equipped with a magnetic stirring bar and thermometer were placed 26.4 g (0.47 mol) of potassium hydroxide dissolved in 100 ml of water and 26.4 g (0.165 mol) of bromine. Then a solution of 6 g (0.03 mol) of crude potassium *p*-cyanophenylmethanenitronate in 80 ml of water was added all at once by keeping the temperature at 5°. After room temperature was attained, the mixture was extracted with 6 × 50 ml portions of ether. Drying the extracts (sodium sulfate) and concentrating *in vacuo* gave 3.0 g (31.5%) of *p*-cyano-α,α-dibromo-α-nitrotoluene, mp 80–90°. Three sublimations at 50° (0.1 mm) gave mp 86–87°: ir (KBr) 2240 (CN) and 1585 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 7.89 (q, 4, C$_6$H$_4$).

Anal. Calcd for C$_8$H$_4$N$_2$O$_2$Br$_2$: C, 30.03; H, 1.26; N, 8.75; Br, 49.95. Found: C, 30.23; H, 1.29; N, 8.82; Br, 49.72.

p-Cyano-α,α-dichloro-α-nitrotoluene. A suspension of 7.5 g (0.375 mol) of crude potassium p-cyanophenylmethanenitronate in 50 ml of water at 25° was added to 58 ml of a 1.3 *M* potassium hypochlorite solution.[12]

The reaction mixture was extracted with 6 × 50 ml portions of ether and dried (sodium sulfate), and the extracts were concentrated *in vacuo* to give 3.4 g (39.6%) of p-cyano-α,α-dichloro-α-nitrotoluene, mp 72–75°. Three sublimations at 65° (3 mm) gave mp 81–82°: ir (KBr) 2240 (CN) and 1600 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 7.83 (q, 4, C$_6$H$_4$).

Anal. Calcd for C$_8$H$_4$N$_2$O$_2$Cl$_2$: C, 41.60; H, 1.75; N, 12.13; Cl, 30.73. Found: C, 41.63; H, 1.88; N, 11.94; Cl, 30.57.

o-Cyano-α,α-dibromo-α-nitrotoluene. Crude potassium o-cyanophenylmethanenitronate (10.1 g, 0.0505 mol) gave 4.34 g (27%) of yellowish o-cyano-α,α-dibromo-α-nitrotoluene, mp 100–101°. One sublimation at 50–55° (0.05 mm) gave mp 101–102°: ir (KBr) 2225 (CN) and 1570 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 7.85 (m, 4, C$_6$H$_4$).

Anal. Calcd for C$_8$H$_4$N$_2$O$_2$Br$_2$: C, 30.03; H, 1.26; N, 8.75; Br, 49.95. Found: C, 30.32; H, 1.50; N, 8.45; Br, 50.16.

p-N,N-Dimethylsulfonamido-α,α-dibromo-α-nitrotoluene. Crude sodium p-N,N-dimethylsulfonamidophenylmethanenitronate (7.3 g, 0.0274 mol) gave 8.6 g (78.2%) of p-N,N-dimethylsulfonamido-α,α-dibromo-α-nitrotoluene, mp 158–160°. One recrystallization from 95% ethanol gave mp 163–164°: ir (KBr) 1572 (NO$_2$) and 1325 and 1162 cm^{-1} (SO$_2$); nmr (CDCl$_3$) δ 2.72 (s, 6, NCH$_3$) and 7.80 (q, 4, C$_6$H$_4$); mass spectrum (75 eV) *m/e* (rel intensity) 356 (100).

Anal. Calcd for C$_9$H$_{10}$N$_2$O$_4$Br$_2$S: C, 26.87; H, 2.47; N, 6.97; Br, 39.80; S, 7.96. Found: C, 26.62; H, 2.45; N, 6.75; Br, 39.57; S, 8.24.

p-Phenylsulfonyl-α,α-dibromo-α-nitrotoluene. Crude sodium p-phenylsulfonylphenylmethanenitronate (8.65 g, 0.0289 mol) gave 11.27 g (90%) of p-phenylsulfonyl-α,α-dibromo-α-nitrotoluene, mp 121–124°. Recrystallizing three times from 95% ethanol gave mp 130–131°: ir (KBr) 1580 (NO$_2$) and 1310 and 1151 cm^{-1} (SO$_2$); nmr (CDCl$_3$) δ 7.64 (m, 9, C$_6$H$_5$ and C$_6$H$_4$).

Anal. Calcd for C$_{13}$H$_9$NO$_4$Br$_2$S: C, 35.86; H, 2.07; N, 3.22; Br, 36.78; S, 7.38. Found: C, 36.03; H, 2.20; N, 3.20; Br, 36.00; S, 7.80.

p-Benzoyl-α,α-dibromo-α-nitrotoluene. Crude potassium p-benzoylphenylmethanenitronate (7 g, 0.025 mol) gave 2.5 g (54%) of p-benzoyl-α,α-dibromo-α-nitrotoluene, mp 90–93°. One recrystallization from absolute ethanol gave mp 99–99.5°: ir (KBr) 1668 (CO) and 1580 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 7.78 (m, 9, C$_6$H$_5$ and C$_6$H$_4$).

Anal. Calcd for C$_{14}$H$_9$NO$_3$Br$_2$: C, 42.15; H, 2.27; N, 3.51; Br, 40.04. Found: C, 42.28; H, 2.42; N, 3.46; Br, 40.05.

α-Bromo-α-nitro-α-phenyltoluene. Crude potassium diphenylmethanenitronate (7.6 g, 0.0303 mol) gave, after one recrystallization from 95% ethanol, 6.8 g (67.5%) of α-bromo-α-nitro-α-phenyltoluene: mp 47–49° (lit.[6b] mp 44°); ir (KBr) 1562 and 1331 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 7.44 (s, 10, C$_6$H$_5$).

Anal. Calcd for C$_{13}$H$_{10}$NO$_2$Br: C, 55.44; H, 3.45; N, 4.80. Found: C, 53.51; H, 3.43; N, 4.55.

p-Cyano-α-bromo-α-nitrotoluene. Into a 300-ml round-bottom flask equipped with a magnetic stirring bar, dropping funnel, and thermometer were placed 150 ml of dry carbon tetrachloride and thermometer were placed 150 ml of dry carbon tetrachloride and 10.0 g (0.05 mol) of crude potassium p-cyanophenylmethanenitronate. The suspension was cooled to 0–5°, a solution of 8 g (0.05 mol) of bromine in 10 ml of carbon tetrachloride added, and the mixture stirred an additional 1.25 hr at 0–5°. The filtrate was concentrated *in vacuo* to give a yellow oil which deposited white crystals upon storage in the freezer. Two recrystallizations from 95% ethanol gave 3.0 g (32%) of p-cyano-α-bromo-α-nitrotoluene: mp 44–45°; ir (KBr) 2250 (CN) and 1562 cm^{-1} (NO$_2$); nmr (CDCl$_3$) δ 5.58 (s, 1, CHNO$_2$Br) and 7.82 (m, 4, C$_6$H$_4$).

Anal. Calcd for C$_8$H$_5$N$_2$O$_2$Br: C, 39.85; H, 2.09; N, 11.62; Br, 33.14. Found: C, 40.02; H, 2.33; N, 11.62; Br, 33.13.

p,p′-Bis(N,N-dimethysulfonamido)stilbene (15c). The following experiment is typical of the procedure employed for preparing disubstituted stilbenes. Into a 50-ml round-bottom flask equipped with a magnetic stirring bar and reflux condenser were placed 0.267 g (1.09 mmol) of p-(N,N-dimethylsulfonamido)-α-nitrotoluene (2c), 0.107 g (1.09 mmol) of potassium acetate, and 20 ml of 95% ethanol. The mixture was refluxed for 21 hr, cooled, and filtered to give 0.1431 g (67.5%) of p,p′-bis(N,N-dimethylsulfonamido)stilbene, mp 245–250°. One recrystallization from trifluoroacetic acid and water (1:1) gave mp 254–255°; ir (KBr) 1600 (C=C) and 1340 and 1162 cm^{-1} (SO$_2$); nmr (CF$_3$CO$_2$H) δ 2.83 [s, 12, N(CH$_3$)$_2$], 7.30 (s, 2, CH), and 7.78 (s, 8, C$_6$H$_4$).

Anal. Calcd for C$_{18}$H$_{22}$N$_2$O$_4$S$_2$: C, 54.82; H, 5.58; N, 7.16; S, 16.24. Found: C, 54.67; H, 5.77; N, 7.31; S, 16.19.

Concentrating the filtrate *in vacuo* gave 0.019 g (7%) of unreacted **2c.**

p,p′-Diphenylsulfonylstilbene (15d). Similarly, 0.84 g (3.06 mmol) of p-phenylsulfonyl-α-nitrotoluene (2d) gave 0.36 g (52%) of p,p′-diphenylsulfonylstilbene: mp 324–325° [CF$_3$CO$_2$H–H$_2$O (1:1)]; ir (KBr) 1600 (C=C) and 1308 and 1158 cm^{-1} (SO$_2$); mass spectrum (75 eV) *m/e* (rel intensity) 460 (100).

*Anal.* Calcd for C$_{26}$H$_{20}$O$_4$S$_2$: C, 67.83; H, 4.35; S, 13.91. Found: C, 67.85; H, 4.13; S, 13.65.

3-Oximinophthalimide (14). o-Cyano-α-nitrotoluene (2b) (0.54 g, 2.1 mmol), potassium acetate (0.023 g, 0.2 mmol) and 25 ml of 95% ethanol were refluxed 3 hr. The solution was placed in the freezer to give 0.495 g (92%) of 3-oximinophthalimide, mp 220–225°. Two recrystallizations from 95% ethanol gave mp 255–256° (lit.[13] mp 256.5°); ir (KBr) 2800–3500 (NH and OH), 1715 (CO), and 1695 cm^{-1} (C=N); nmr (DMSO-d$_6$) δ 7.68 (s, 4, C$_6$H$_4$), and 11.12 (s, 2, NH and OH); mass spectrum (75 eV) *m/e* (rel intensity) 162 (100).

References and Notes

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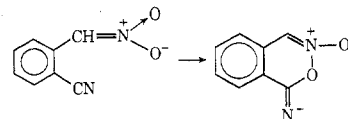
when the potassium salt of **2b** was recrystallized from 95% ethanol does not support this suggestion.

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