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# Dinitromethane[1]

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Alkali salts of dinitromethane were obtained in high yields in the saponification of methyl cyanodinitroacetate or methyl dinitroacetate, prepared in the nitration of methyl cyanooximinoacetate and methyl malonate, respectively. These salts were used in the synthesis of fluorodinitromethane, fluorodinitroethanol, dinitroethanol, 2,2-dinitropropanediol, and dimethyl 4,4-dinitropimelate.

Potassium dinitromethane was first prepared by Villiers[2] in 1884 by reduction of bromodinitromethane, which was obtained[3] in low yields in the nitration of 2,4,6-tribromoaniline. Free dinitromethane,[4] an unstable pale yellow oil, decomposes readily at ambient temperatures. Dinitromethane was also obtained in low yields in the nitration of halogenated olefins, such as trichloroethylene.[5] More recently potassium dinitromethane was prepared[6] in 23% yield by the Ter Meer reaction[7] of chloronitromethane.

$$CH_3NO_2 + Cl_2 \rightarrow ClCH_2NO_2 \xrightarrow{KNO_2\text{-}KOH} K^+{}^-CH(NO_2)_2$$

Dinitromethane salts are also obtained from the alkali salts of dinitroethanol,[7] which are available in good yields in the oxidative nitration[8] of nitroethanol.

The present investigation resulted from a need for a more practical synthesis of dinitromethane salts. New routes to the compound were investigated based on methyl dinitroacetate and methyl cyanodinitroacetate.

The nitration of malonates was first investigated by Bouveault and Wahl[9] in 1903, who reported the synthesis of ethyl dinitroacetate with little experimental details. Kissinger and Ungnade[10] prepared a number of alkyl dinitroacetates in 10–20% yields in the nitration of alkyl malonates.

We obtained methyl malonate by a modification of a reported procedure;[11] yields were improved by 30% and the isolation procedure was simplified. The nitration of this monoester with nitrogen tetroxide, 100% nitric acid, nitric–sulfuric acid, and red fuming nitric acid was investigated. The best yield of methyl dinitroacetate, 55–60%, was obtained using an excess of 20% red fuming nitric acid in methylene chloride at 3–7 °C.

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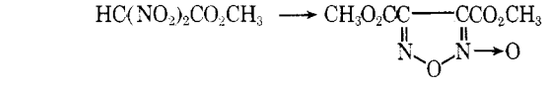
$$HO_2CCH_2CO_2CH_3 + HNO_3 \rightarrow HC(NO_2)_2CO_2CH_3$$

A side reaction product of these nitrations, 3,4-bis(carbomethoxy)furazan 2-oxide,[12] could be readily separated.

On storage at ambient temperature for several days, methyl dinitroacetate gradually decomposed to the furazan derivative.



The alkali salts of methyl dinitroacetate, however, were found to be storable at ambient temperatures. When treated with aqueous alkalies at 70–80 °C, the salts underwent saponification to give the corresponding salts of dinitromethane in 90–95% yields.

$$Na^{+-}C(NO_2)_2CO_2CH_3 + 2NaOH \xrightarrow[\Delta]{H_2O} Na^{+-}CH(NO_2)_2 + Na_2CO_3 + CH_3OH$$

Potassium dinitromethane is sparingly soluble in water, whereas the sodium salt is very soluble. Both salts can be stored without any noticeable decomposition for several weeks at ambient temperatures. These salts are sensitive to impact, and in larger scale work aqueous solutions of the sodium salt were used for safe handling.

Ammonium dinitromethane, previously reported by metathesis reaction,[4] was obtained by heating methyl dinitroacetate with ammonium hydroxide.

$$HC(NO_2)_2CO_2CH_3 + NH_4OH \xrightarrow{\Delta} NH_4^{+-}CH(NO_2)_2$$

Fluorodinitromethane was previously reported[13] by fluorination of aqueous ammonium dinitromethane. Aqueous sodium dinitromethane was fluorinated to give fluorodinitromethane in 75–80% yields.

$$Na^{+-}CH(NO_2)_2 + F_2 \xrightarrow{(H_2O)} FCH(NO_2)_2$$

Fluorodinitromethane was also obtained in ca. 60% yield in the fluorination of aqueous alkali salts of methyl dinitroacetate. Methyl fluorodinitroacetate is thus hydrolyzed under the reaction conditions.

$$K^{+-}C(NO_2)_2CO_2CH_3 + F_2 \xrightarrow{(H_2O)} [FC(NO_2)_2CO_2CH_3] \xrightarrow{H_2O} FC(NO_2)_2H + CO_2 + CH_3OH$$

The analogous fluorination of the ethyl ester,[14] however, yielded a mixture of fluorodinitromethane and ethyl fluorodinitroacetate.

Dialkyl dinitromalonates have not been previously reported,[15] but mononitromalonates are known.[16] We found that dimethyl nitromalonate undergoes slow nitration in nitric–sulfuric acid to give dimethyl dinitromalonate in 20–25% yields.

$$NO_2CH(CO_2CH_3)_2 + HNO_3\text{–}H_2SO_4 \rightarrow (NO_2)_2C(CO_2CH_3)_2$$

The compound was identified by its elemental analysis and NMR spectrum. Dimethyl dinitromalonate reacted with methanolic potassium hydroxide to give methyl potassium dinitroacetate, which on acidification yielded the previously reported methyl dinitroacetate.

$$(NO_2)_2C(CO_2CH_3)_2 + KOH \xrightarrow{CH_3OH} K^{+-}C(NO_2)_2CO_2CH_3 \xrightarrow{H_3O^+} HC(NO_2)_2CO_2CH_3$$

The second route to dinitromethane was based on cyanodinitromethide salts. The nitration of methyl cyanoacetate with the mixed acid was reported[17] to give low yields (20–30%) of the dinitro derivative. Much better yields of methyl cyanodinitroacetate, 80–85%, were reported[17] in the nitration of methyl cyanooximinoacetate, available quantitatively in the nitrosation of cyanoacetate with sodium nitrite–phosphoric acid.

$$NCCH_2CO_2CH_3 + NaNO_2 \xrightarrow{H_3PO_4} NCC(=NOH)CO_2CH_3 \xrightarrow[H_2SO_4]{HNO_3} NCC(NO_2)_2CO_2CH_3$$

Methyl cyanodinitroacetate in methylene chloride solution reacted with water at ambient temperatures to give the known[17] dinitroacetonitrile.

$$NCC(NO_2)_2CO_2CH_3 + H_2O \rightarrow NCC(NO_2)_2H + CO_2 + CH_3OH$$

When an aqueous solution of dinitroacetonitrile salts was heated with 2 mol of an alkali hydroxide, the nitrile underwent saponification to give the alkali salt of dinitromethane, the alkali carbonate, and ammonia.

$$NCC(NO_2)_2{}^-Na^+ + 2NaOH \xrightarrow[\Delta]{H_2O} Na^+CH(NO_2)_2 + Na_2CO_3 + NH_3$$

The rate of this reaction was conveniently followed by the disappearance of the nitrile UV absorption at 350 nm. The reaction was completed in ca. 2 h at 80–85 °C, and the yield of dinitromethane salts was practically quantitative. At 105 °C the saponification was completed in 15–20 min.

Sodium dinitromethane solution, obtained in this one-pot reaction, was used directly in the synthesis of other geminal dinitro compounds. Formaldehyde (1 mol) was added, and the resulting sodium dinitroethanol[18] was fluorinated according to a reported procedure[19] to give fluorodinitroethanol in 70–80% yields.

$$Na^{+-}CH(NO_2)_2 + CH_2O \rightarrow Na^{+-}C(NO_2)_2CH_2OH \xrightarrow[H_2O]{F_2} FC(NO_2)_2CH_2OH$$

Similarly, sodium dinitromethane solution was used directly in the synthesis of 2,2-dinitropropanediol. Formaldehyde (2 mol) was added, and the alkaline solution was then neutralized with acetic acid to give the diol.[6]

$$K^{+-}CH(NO_2)_2 + CH_2O \underset{\Delta}{\rightleftarrows} K^{+-}(NO_2)_2CH_2OH \underset{OH^-}{\overset{CH_2O}{\rightleftharpoons}} HOCH_2C(NO_2)_2CH_2OH$$

Dinitromethane salts react with 2 mol of $\alpha,\beta$-unsaturated carbonyl compounds to give the corresponding Michael condensation products.[7] When the crude sodium dinitromethane solution above was treated with 2 mol of methyl acrylate, dimethyl 4,4-dinitropimelate[20] was obtained in 65% yield.

$$Na^{+-}CH(NO_2)_2 + 2CH_2{=}CHCO_2CH_3 \rightarrow (NO_2)_2C(CH_2CH_2CO_2CH_3)_2$$

Fluorination of sodium dinitroacetonitrile was reported[21] to give fluorodinitroacetonitrile, which was hydrolyzed to fluorodinitroacetamide. We found that fluorodinitroacetonitrile can be hydrolyzed to fluorodinitromethane in 75–80% yields. A 1,1,2-trichloro-1,2,2-trifluoroethane solution of the nitrile was stirred with concentrated hydrochloric acid at ambient temperature for 10–12 h to give fluorodini-

troacetamide. The resulting hydrochloric acid solution of the amide was heated at 80–85 °C for 2 h to give fluorodinitromethane.

$$Na^{+-}C(NO_2)_2CN + F_2 \xrightarrow{H_2O} FC(NO_2)_2CN$$

$$\xrightarrow{HCl} FC(NO_2)_2CONH_2 \xrightarrow[\Delta]{HCl} FC(NO_2)_2H$$

Fluorodinitromethane and fluorodinitroethyl methyl carbonate, rather than fluorodinitroacetonitrile, were the fluorination products of aqueous sodium dinitroacetonitrile containing small amounts of methanol.

## Experimental Section

**Caution.** Because of the explosive nature of many compounds described in this paper, safety shielding is strongly recommended in all the experimental work. Salts of dinitromethane should be handled with utmost care: remotely and in small quantities.

**Methyl Malonate.** To a stirred solution of 132 g (1.0 mol) of dimethyl malonate in 250 mL of methanol at room temperature was added dropwise (15 min) with occasional cooling a solution of 66 g (1.0 mol) of 85% potassium hydroxide in 150 mL of methanol. After 15 min, the mixture was acidified with 1 mol of concentrated hydrochloric acid and filtered. The filter cake (KCl) was washed with two 25-mL portions of methanol. The combined filtrate and washing were concentrated on a rotating evaporator, and the residual liquid was dissolved in 150 mL of methylene chloride. The solution was filtered from a small amount of salts. The filtrate was distilled to give 95 g (80% yield) of methyl malonate: bp 90 °C (0.5 mm); NMR ($CDCl_3$) $\delta$ 3.44 (s, 2 H), 3.75 (s, 3 H), and 11.1 (s, COCH).

Methyl malonate was also obtained in 85% yield when diethyl malonate instead of dimethyl malonate was used. Ethyl malonate was obtained in 85% yield from diethyl malonate followed the above procedure but using ethanol as the solvent.

**Methyl Dinitroacetate.** To a stirred and cooled solution of 80 g of 20% red fuming nitric acid in 60 mL of methylene chloride at −5 °C was added 25 g of methyl malonate. After 3 h at 5–7 °C, the reaction mixture was drowned in 150 mL of ice–water. The methylene chloride solution was washed with three 75-mL portions of ice–water, dried, and concentrated on a rotary evaporator to leave 21 g of crude methyl dinitroacetate (60% yield). An analytical sample was obtained by distillation: bp 37–38 °C (0.02 mm) [reported[17] bp 38 °C (0.02 mm)]; NMR ($CDCl_3$) $\delta$ 4.00 (s, 6 H) and 6.75 (s, 1 H).

**3,4-Bis(methoxycarbonyl)furazan 2-Oxide.** The title compound was isolated from crude methyl malonate nitration mixtures from which methyl dinitroacetate was removed by extraction with aqueous sodium bicarbonate. The crude 3,4-bis(methoxycarbonyl)furazan 2-oxide was distilled to give a pale yellow liquid: bp 93 °C (0.25 mm); NMR ($CDCl_3$) $\delta$ 3.96 (s) and 4.02 (s). Anal. Calcd for $C_6H_5N_2O_6$: C, 35.65; H, 2.99; N, 13.86. Found: C, 35.40; H, 2.81; N, 13.61.

**Potassium Dinitromethane. A. From Methyl Potassium Dinitroacetate.** To a stirred solution of 1.5 g of potassium hydroxide in 15 mL of water was added 4.05 g (0.02 mol) of methyl potassium dinitroacetate, and the mixture was heated at 65–70 °C for a few minutes. The deep orange-red solution turned turbid and began to deposit some yellow solid. The mixture was cooled to 0–5 °C. The yellow crystalline solid was collected and washed with two 5-mL portions of ice–water. Air-dried solid amounted to 2.6 g (90% yield), mp 220 °C (expl) (reported[4] mp 216 °C dec).

**B. From Potassium Dinitroacetonitrile.** A stirred suspension of 3.4 g (0.02 mol) of potassium cyanodinitromethide in 15 mL of 10% aqueous potassium hydroxide was heated at 90–95 °C for 2 h. Ammonia odor, strong at the beginning, gradually faded away. The yellow solution was cooled to 0–5 °C. The yellow crystalline solid was collected and washed with two 5-mL portions of ice–water: 2.5 g (85% yield); mp 220 °C (expl).

**Ammonium Dinitromethane.** To a stirred suspension of 4.1 g (0.025 mol) of methyl dinitroacetate in 10 mL of water was added 10 mL of 14% ammonium hydroxide, and the mixture was heated in an open Erlenmeyer flask at 85–90 °C for 1.5 h. The solution was cooled in a refrigerator overnight, and a yellow crystalline solid was collected. The filter cake was washed with 2 mL of ice–water. The air-dried yellow solid weighed 2.4 g (77% yield): mp 110 °C dec (reported[4] mp 105 °C); IR (Nujol mull) no C=O.

**Potassium Dinitroethanol.** A suspension of 1.0 g of potassium dinitromethane obtained from methyl potassium dinitroacetate in 5 mL of 10% aqueous formaldehyde was heated at 90–95 °C for a few minutes, and the solution was cooled to 0–5 °C. A yellow solid was collected and washed with ice–water. The air-dried material weighed 0.9 g, mp 152 °C dec alone or when mixed with an authentic sample of potassium dinitroethanol.[6]

In another experiment, a suspension of potassium dinitroethanol obtained from potassium dinitromethane was fluorinated at 0–5 °C with elementary fluorine. The aqueous fluorination mixture was extracted with methylene chloride. Fluorodinitroethanol, bp 33–34 °C (0.1 mm), was isolated from the extract and identified by its published[19] physical properties.

**Fluorodinitromethane. A. From Potassium Dinitromethane.** A stirred suspension of 3.1 g (0.02 mol) of potassium dinitromethane in 25 mL of water was fluorinated with elemental fluorine following a previously described technique.[19] When all of the yellow potassium salt was consumed, the fluorination mixture was extracted with five 10-mL portions of methylene chloride. The combined extracts were dried and distilled to give 2.0 g of fluorodinitromethane, bp 36–37 °C (20 mm) [reported[13] bp 35–38 °C (20 mm)].

**B. From Methyl Dinitroacetate.** A suspension of potassium salt of methyl dinitroacetate (150 g, 0.75 mol) in 1400 mL of water was fluorinated at 0–5 °C with 0.65 mol of fluorine over a 7-h period. The aqueous reaction mixture was extracted with ten 150-mL portions of methylene chloride. The combined extracts were dried with anhydrous sodium sulfate and concentrated using an 18 in Vigreux column. The amount of product present in the distillation residue was determined by fluorine NMR spectroscopy using benzotrifluoride as the standard. There was obtained 60 g of fluorodinitromethane, 65% yield based on methyl potassium dinitroacetate.

**C. From Fluorodinitroacetonitrile.** A mixture of 13.4 g (0.09 mol) of fluorodinitroacetonitrile in 50 mL of 1,1,2-trichloro-1,2,2-trifluoroethane and 15 mL of concentrated hydrochloric acid was stirred for 10 h at room temperature. The fluorine NMR signal at $\phi$ 91.4 for fluorodinitroacetonitrile disappeared, and a strong signal for fluorodinitroacetamide at $\phi$ 101 appeared in the hydrochloric acid phase. The phases were separated, and the hydrochloric acid solution was heated at 80–85 °C for 1.5 h. During this time, carbon dioxide was evolved and some water-insoluble liquid was formed. The reaction mixture was allowed to cool and was extracted with five 15-mL portions of methylene chloride. The combined dried extracts were distilled to give 9.9 g (90% yield) of fluorodinitromethane.

**Dimethyl Dinitromalonate.** To a stirred solution of 4 g of 100% nitric acid in 15 mL of concentrated sulfuric acid at room temperature was added 2.7 g of dimethyl nitromalonate.[22] After 30 min the reaction mixture was drowned on ice and an insoluble oil was extracted with 20 mL of methylene chloride. The dried extract was distilled in a microdistillation apparatus to give 0.7 g of a colorless liquid: bp 85–87 °C (0.1 mm); NMR ($CDCl_3$) $\delta$ 4.04 (s). Anal. Calcd for $C_5H_6N_2O_8$: C, 27.04; H, 2.72; N, 12.61. Found: C, 27.35; H, 2.75; N, 11.82.

A 2.22-g (0.01 mol) sample of dimethyl dinitromalonate was treated at ambient temperature with an excess of methanolic potassium hydroxide. A yellow potassium salt of methyl dinitroacetate was collected and washed with methanol: 1.8 g (90% yield); mp 216 °C dec (reported[17] mp 213–214 °C).

A suspension of the methyl potassium dinitroacetate above in 5 mL of ice–water was acidified with 2 mL of 20% hydrochloric acid. The water-insoluble liquid which separated on acidification was extracted with 10 mL of methylene chloride. The extract was dried and distilled to give 1.1 g (76% yield) of methyl dinitroacetate.

**Fluorodinitroethyl Methyl Carbonate.** Methyl cyanodinitroacetate (120 g, 0.635 mol) was stirred with 250 mL of water at 25–30 °C with occasional ice–water cooling until a clear solution resulted (45 min). The acidic solution was neutralized (pH 7–8) with 10% aqueous sodium hydroxide, 400 mL of 1,1,2-trichloro-1,2,2-trifluoroethane was added, and the mixture was fluorinated (5.5 h) with 0.6 mol of elemental fluorine at 5–8 °C. The phases were separated, and the aqueous phase was extracted with three 50-mL portions of methylene chloride. The 1,1,2-trichloro-1,2,2-trifluoroethane solution was combined with the methylene chloride extracts. The combined solutions were dried and concentrated to remove the solvents. The residue, 40 g of a pale yellow liquid, analyzed by fluorine and proton NMR spectroscopy, contained ca. 15% of fluorodinitroacetonitrile, 30% of fluorodinitromethane, and 55% of fluorodinitroethyl methyl carbonate. This mixture was fractionated, and after removal of the two volatile components, 20 g of the carbonate, bp 60 °C (0.5 mm), was obtained: NMR ($CDCl_3$) $\delta$ 3.84 (s, $CH_3$) and 5.18 (d, $J_{HF}$ = 16 Hz, $CH_2$).[23] Anal. Calcd for $C_4H_5N_2FO_7$: C, 22.65; H, 2.38; N, 13.21. Found: C, 22.41; H, 2.20; N, 12.98.

**Registry No.**—Dimethyl malonate, 108-59-8; methyl malonate, 16695-14-0; ethyl malonate, 1071-46-1; diethyl malonate, 105-53-3; methyl dinitroacetete, 25160-76-3; 3,4-bis(methoxycarbonyl)furazan 2-oxide, 18322-90-2; potassium dinitromethane, 32617-22-4;

methyl potassium dinitroacetate, 33717-84-9; potassium dinitroacetonitrile, 6928-22-9; ammonium dinitromethane, 12373-04-5; potassium dinitroethanol, 6928-29-6; fluorodinitroethanol, 17003-75-7; fluorodinitromethane, 7182-87-8; fluorodinitroacetonitrile, 15562-09-1; fluorodinitroacetamide, 15562-10-4; dimethyl dinitromalonate, 66901-53-9; dimethyl nitromalonate, 5437-67-2; fluorodinitroethyl methyl carbonate, 66901-54-0; methyl cyanodinitroacetate, 66901-55-1; diethyl nitromalonate, 603-67-8; dinitromethane, 625-76-3.

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# Competitive Processes in the Hydration of Dicarbonyl $\eta^5$-(Cyclopentadienyl)alleneiron Cations


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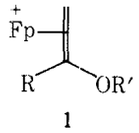
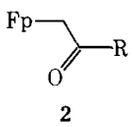
Hydration of the allene complex [**3**, Fp = $CpFe(CO)_2$], under acidic conditions, gives a mixture of ketone and aldehyde complexes (**4** and **5**). The aldehyde complex is shown to be derived by acid catalyzed rearrangement of the allyl alcohol complex (**6**) in a process involving the metal-stabilized cation (**7**). Rearrangement occurs at an appreciable rate even at pH 3.3, reflecting the unusually high stability of **7**. Hydration of *syn*-3-methylallene and *syn*-3-phenylallene complexes (**13a,b**) proceeds in a manner closely paralleling the parent complex, but the isomeric *anti*-3-methylallene and *anti*-3-phenylallene complexes (**14a,b**) behave differently. These undergo hydration principally through the less stable tautomeric 1-methylallene and 1-phenylallene complexes (**15a,b**) due to steric effects associated with the anti substituent.


Recently, our interest in the use of complexes such as **1** as organometallic synthons prompted us to examine the preparation of the precursor ketones (**2**) by routes other than those previously employed[1] [Fp ≡ $\eta^5$-$C_5H_5Fe(CO)_2$].



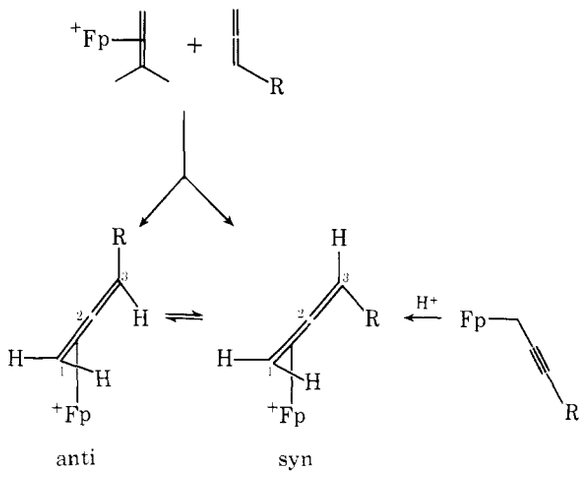
1



2

Since it is well known that coordinated olefins in Fp(olefin) cations readily add a number of carbon and heteronuclear nucleophiles,[2] we considered the prospect that Fp(allene) cations might serve as useful precursors of **2**. The allene complexes are readily available either through an exchange reaction involving the Fp(isobutylene) cation and an allene[3] or by protonation of a ($\sigma$-propargyl)Fp complex.[4] The latter are conveniently obtained by metalation with Fp anion of either 1-halo- or 1-tosyloxy-2-alkynes.[5] While the exchange reaction with monosubstituted allenes may be expected to afford mixtures of syn- and anti-3-substituted allene complexes,[3] protonation of ($\sigma$-progargyl)Fp complexes has been observed to proceed stereospecifically to give the syn stereoisomers exclusively.[6,7] Furthermore, syn and anti stereoisomers have been shown to be thermally interconvertible through a succession of 1,2 shifts by the Fp group[3] (Scheme I).

**Scheme I**




## Results

**Hydration of the Fp(allene) Cation.** In general, the addition of nucleophiles, including hydroxide ion, to Fp(allene)

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