derstanding of the conformations and intramolecular interactions in these compounds,[10] and this investigation is continuing.

Experimental Section

Materials. Trimethyl orthoacetate and trimethyl orthovalerate were commercial samples (Kodak). The remaining ortho esters were prepared as described by McElvain and Nelson.[11] Each of the ortho esters was distilled from sodium through a 25-cm glass helix packed column, collecting a middle fraction. In some cases, it was necessary to repeat the distillation. The procedure was ineffective with trimethyl orthovalerate which could only be adequately purified via distillation through a spinning band column.

The ortho esters were analyzed by IR spectroscopy, gas chromatography, and NMR spectroscopy (500 MHz). In most case, the orthoesters were found to be >99.9% pure. In three cases, an impurity (the corresponding normal methyl ester) was found. They were trimethyl orthoacetate, trimethyl orthoisobutyrate, and trimethyl ortho-2-methylbutyrate. Analyses were carried out by GC by first examining the ortho ester and then a sample of ortho ester to which a known amount of the normal ester had been added. A comparison of the normal ester peak areas for the two samples allowed the concentration of the normal ester to be determined with a precision of ±0.1 %. The observed heats of reaction were corrected to the values expected for pure ortho esters (ΔH_{corr} in Table II).

The normal esters were commercial samples. They were purified by the procedure suggested by Perrin and Perrin[12] and then distilled through a 25-cm glass helices packed column taking a middle fraction. The process was repeated if necessary until both NMR spectroscopy and GC using an SE-30 or OV-101 column showed the sample to be at least 99.9% pure.

Dioxane was distilled from benzophenone ketyl under an atmosphere of dry nitrogen. The solvent used for the calorimetric studies was 65% dioxane and 35% water (v/v) containing 0.001 N perchloric acid.

Calorimetry. The calorimetric experiments were carried out by using an automated reaction calorimeter which is similar to that previously described.[5] Some modifications were made. Instead of counting the 28-MHz signal from the quartz thermometer directly, the 28-MHz signal was mixed with a 30-MHz signal derived from the precision 10-MHz oscillator which is the master time base for the operations. The resultant 2-MHz difference frequency is more easily counted.[13] It is sent to one or the other of a pair of counters at 10-s intervals so that all of the input signal is counted, avoiding the quantization error normally encountered with counters. The heater power and timing circuits from the original LKB system were replaced. In doing so, it was found that there had been a systematic error associated with the earlier heater power circuit (it took a few seconds to reach the set voltage). It was equivalent to a heater circuit operating properly but starting 0.6 s late. All of the data from our previous studies of ketal and acetal hydrolysis were still available, and it was possible to correct for this problem. As a result, the values given in Table III are slightly different than those reported previously. Fortunately, the effect was rather small and leads to no significant change in the $\Delta\Delta H$ values resulting from changes in substituents.

The calorimeter was checked by measuring the enthalpy of reaction of TRIS (NBS standard reference material 724a) with 0.1 N hydrochloric acid. The average value for 26 runs carried out over a 3-month period was −7117 ± 5 cal/mol. The recommended value is −7116 ± 8 cal/mol.[14] The experimental uncertainties are reported as $2\bar{s}$, where $\bar{s}$ is the standard deviation from the mean ($\bar{s} = [\sum\delta^2/(n)(n-1)]^{1/2}$), in accord with the suggestion of Rossini.[15]

Acknowledgment. This investigation was supported by the Division of Basic Energy Sciences, U.S. Department of Energy.

---

[11] McElvain, S. M.; Nelson, J. W. *J. Am. Chem. Soc.* **1942**, *64*, 1826.

[12] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1980.

[13] The details of the modified calorimeter may be found in the Ph.D. thesis of E.J.M., 1984.

[14] Prosen, E. J.; Kilday, M. V. *J. Res. Natl. Bur. Stand., Sect. A* **1973**, *77A*, 581.

[15] Rossini, F. D. In "Experimental Thermochemistry"; Rossini, F. D., Ed.; Interscience, NY, 1956; Vol. 1, p 317.

[16] Hine, J.; Klueppel, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 2924.

[17] Guthrie, J. P.; Cullimore, A. C. *Can. J. Chem.* **1980**, *58*, 1281.

Electron-Transfer Substitution Reactions of Anions Derived from Malonic Esters, β-Keto Esters, and β-Diketones[1]

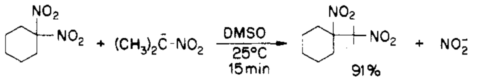
Nathan Kornblum,* William J. Kelly, and M. M. Kestner

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received June 10, 1985

Electron-transfer substitution reactions of carbanions derived from malonic esters, β-keto esters, and β-diketones with α,α-dinitro compounds are compared with oxidative coupling of these carbanions to nitroparaffin salts using potassium ferricyanide; the former routinely give better yields.

In 1970 a new reaction of α,α-dinitro compounds was described;[2] when treated with nitroparaffin salts, these compounds undergo replacement of one of the geminal nitro groups in a manner shown by the example of eq 1.



(1)

The reactions occur readily at room temperature and give excellent yields of vicinal dinitro compounds. In the 1970 papers an electron-transfer chain mechanism was proposed, and evidence in its support was provided. In 1971 the displacement of one of the nitro groups of 2,2-dinitropropane by diethyl sodioethylmalonate, the sodium salt of ethyl 2-ethyl-3-ketobutyrate and sodio-3-methyl-

---

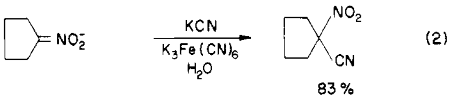
[1] This is paper 28 in the series "Substitution Reactions which Proceed via Radical Anion Intermediates". It derives, in part, from the doctoral dissertation of M. M. Kestner, Purdue University, May 1973. For the preceding paper, see: Kornblum, N.; Singh, H. K.; Boyd, S. D. *J. Org. Chem.* **1984**, *49*, 358.

[2] Kornblum, N.; Boyd, S. D.; Stuchal, F. W. *J. Am. Chem. Soc.* **1970**, *92*, 5783. Kornblum, N.; Boyd, S. D. *Ibid.* **1970**, *92*, 5784. Also see: Kornblum, N. "The Chemistry of Functional Groups, Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives"; Patai, S., Ed.; Wiley: New York, 1982; pp 380–384.

0022-3263/85/1950-4720$01.50/0

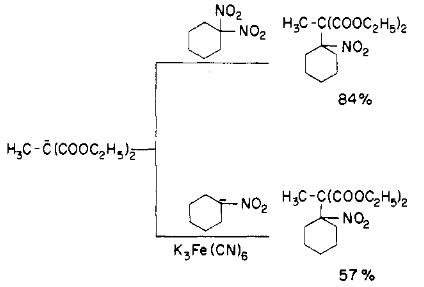
2,4-pentanedione was described; here again evidence for an electron-transfer chain mechanism was provided.[3]

Recently a related reaction, the oxidative substitution of nitroparaffin salts by the agency of potassium ferricyanide,[4] has been found to be an excellent method for coupling nitrite, benzenesulfinate, and cyanide ions to nitroparaffin salts, e.g.,



(2)

The present paper is concerned with two questions: (1) the usefulness in synthesis of the reaction of α,α-dinitro compounds with the salts of malonic esters, β-keto esters, and β-diketones and (2) how these results compare with those obtained when the ferricyanide oxidative substitution reaction is applied to the preparation of the same compounds. The results are easily summarized: although the oxidative coupling procedure is useful in some cases it is distinctly less useful than reactions employing α,α-dinitro compounds. For example,



Reactions employing α,α-dinitro compounds routinely give better yields than those employing potassium ferricyanide, and the disparity is especially great when β-diketones are used. For example, treatment of 2,2-dinitropropane with the anion of 2-methyl-1,3-cyclohexanedione results in a chain reaction (vide supra) which gives a 71% yield of the cross-coupled product (experiment X). Here, combination of the 2-nitropropyl radical with the anion of 2-methyl-1,3-cyclohexanedione gives the radical anion of the product and this, by transfer of an electron to a molecule of 2,2-dinitropropane, continues the chain and provides the cross-coupled product. In contrast, ferricyanide oxidation of a mixture of the salts of 2-nitropropane and 2-methyl-1,3-cyclohexanedione gives but a 4% yield of the cross-coupled product (experiment XVIII). In addition, an 88% yield of 2,3-dinitro-2,3-dimethylbutane (the dimer of 2-nitropropane) is isolated along with a 78% recovery of unreacted 2-methyl-1,3-cyclohexanedione. Clearly, ferricyanide oxidizes the nitroparaffin anion to the radical more rapidly than it oxidizes the β-diketone anion—a fact which is consonant with the much greater basicity of the 2-nitropropyl anion.

Since it is apparent from experiment X that combination of a 2-nitropropyl radical with the anion of 2-methyl-1,3-cyclohexanedione is a feasible process, one wonders why the yield of the cross-coupled product is only 4% in the ferricyanide reaction. The answer is clear: combination of the 2-nitropropyl radical with the anion of 2-methyl-1,3-cyclohexanedione is not as feasible as combination of a 2-nitropropyl radical with the anion of 2-nitropropane. In other words the β-diketone anion loses out in competition with the 2-nitropropyl anion; this competition does not exist in reactions which employ geminal dinitro compounds.

The failure of β-diketone anions to compete successfully for the 2-nitropropyl radical when pitted against the 2-nitropropyl anion probably derives from a combination of electronic and steric effects. The much greater basicity of the 2-nitropropyl anion must predispose it to react more rapidly than a β-diketone anion. Furthermore, it seems probable that steric effects represent yet another factor which operates against the 2-methyl-1,3-cyclohexanedione anion.

In summary, the use of potassium ferricyanide brings into play competition between the two anions in the initial oxidation step and, also, in the coupling step. These complications are avoided by the use of α,α-dinitro compounds.

Not only do the reactions which employ α,α-dinitro compounds provide higher yields but, in addition, they are more convenient to carry out. Finally, it is noteworthy that α,α-dinitro compounds are readily available.[4]

Our results are presented in Tables I and II.

Experimental Section

Infrared spectra (IR) were recorded on a Beckman IR-33 spectrometer. Nuclear magnetic resonance spectra (NMR) were obtained on a Perkin-Elmer R-32 90-MHz spectrometer.

Unless otherwise specified, all reactions were carried out at room temperature, under N_2, employing magnetic stirring. In all cases the reaction flask was placed under 2 20-W ordinary fluorescent lights. Dimethyl sulfoxide (Me_2SO) was dried by being refluxed for 4 h over CaH_2 (ca. 95 °C; ca 30 mm) followed by distillation at ca. 30 mm. Except as otherwise noted, the Me_2SO was purged of O_2 by passing dry N_2 through it for ca. 30 min and then used at once.

I. Reaction of 2,2-Dinitropropane with the Potassium Salt of Diethyl Methylmalonate. Approximately 1 mL of a 22.2% suspension of potassium hydride in oil[5] was placed in a 50-mL nitrogen-filled flask and washed twice with 15-20-mL portions of pentane. After removing residual pentane with a stream of N_2, the dry KH (0.207 g, 0.0052 mol) was treated with 15 mL of dry Me_2SO, and the mixture was stirred under N_2 for 15 min. To the resulting solution 0.94 g (0.0054 mol) of diethyl methylmalonate was added, and the solution was stirred for another 15 min. After placing the flask under 2 20-W ordinary fluorescent lights a solution of 2.17 g (0.0163 mol) of 2,2-dinitropropane[4] in 10 mL of dry Me_2SO was added. The reaction was allowed to proceed for 6 h at room temperature under N_2 after which the resulting yellow solution was poured into 300 mL of cold water and extracted with 3 × 100 mL of ethyl ether. The ether extracts were washed with cold water, concentrated to ca. 50 mL, and then stirred vigorously for 30 min with 50 mL of saturated aqueous sodium bicarbonate to remove any unreacted diethyl methylmalonate. The ether solution was washed once with 100 mL of cold water and dried ($MgSO_4$), and then the ether was removed. The residual yellow oil (2.61 g) was short-path distilled at ca. 0.5 mm. In this way 1.22 g (90% yield) of the pure, colorless, β-nitromalonic ester was obtained: ^1H NMR ($CDCl_3$) δ 1.28 (t, 6 H), 1.65 (s, 3 H), 1.80 (s, 6 H), 4.25 (q, 4 H); IR (neat) 1710 (C=O), 1550 cm^{-1} (NO_2). These values accord with the published values.[6]

II. Reaction of 1,1-Dinitrocyclohexane with the Potassium Salt of Diethyl Methylmalonate. With use of the procedure described in experiment I, KH (0.213 g, 0.0052 mol), diethyl methylmalonate (0.93 g, 0.0054 mol), and 1,1-dinitrocyclohexane (2.71 g, 0.0156 mol) were employed. After 6 h the product was worked up as in I. This gave 1.31 g (84% yield) of the colorless

---

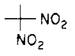
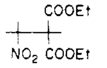
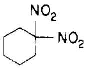
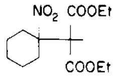
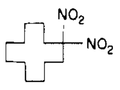
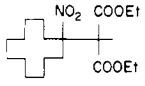
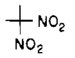
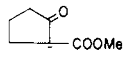
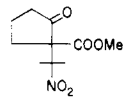
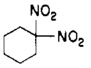
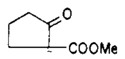
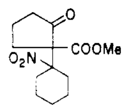
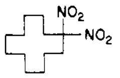
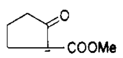
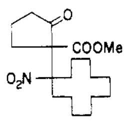
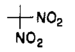
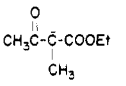
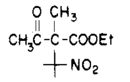
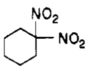
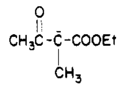
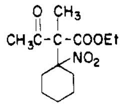
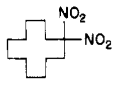
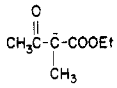
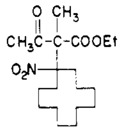
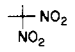
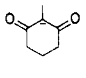
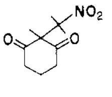
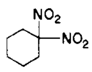
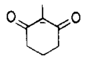
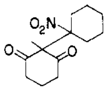
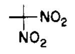
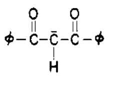
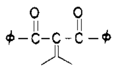
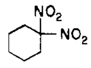
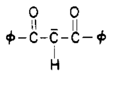
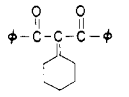
[3] Russell, G. A.; Norris, R. K.; Panek, E. J. *J. Am. Chem. Soc.* **1971**, *93*, 5839.

[4] Matacz, Z.; Piotrowska, H.; Urbanski, T. *Pol. J. Chem.* **1979**, *53*, 187. Kornblum, N.; Singh, H. K.; Kelly, W. J. *J. Org. Chem.* **1983**, *48*, 332. Garver, L. C.; Grakauskas, V.; Baum, K. *J. Org. Chem.* **1985**, *50*, 1699.

[5] Alfa Products.

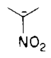
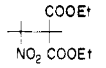
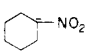
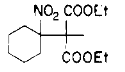
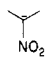
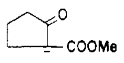
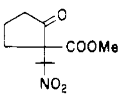
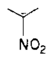
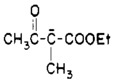
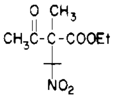
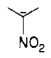
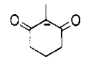
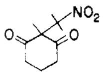
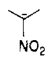
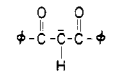
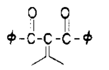
[6] Kornblum, N.; Boyd, S. D.; Ono, N. *J. Am. Chem. Soc.* **1974**, *96*, 2580.

Table I. Reactions of Anions Derived from Malonic Esters, β-Keto Esters, and β-Diketones with α,α-Dinitro Compounds

expt	α,α-dinitro compd	anion	product	yield,[a] %
I		$CH_3\bar{C}(COOEt)_2$		90
II		$CH_3\bar{C}(COOEt)_2$		84
III		$CH_3\bar{C}(COOEt)_2$		80
IV				86
V				75
VI				73
VII		 $CH_3C(=O)\bar{C}(CH_3)COOEt$		84
VIII		 $CH_3C(=O)\bar{C}(CH_3)COOEt$		81
IX		 $CH_3C(=O)\bar{C}(CH_3)COOEt$		64
X				71
XI				58
XII		 $\phi\text{-}C(=O)\text{-}\bar{C}H\text{-}C(=O)\text{-}\phi$		63
XIII		 $\phi\text{-}C(=O)\text{-}\bar{C}H\text{-}C(=O)\text{-}\phi$		65

[a] Pure, isolated product.

Table II. Oxidative Coupling of Nitroparaffin Salts with Anions Derived from β-Keto Esters, β-Diketones, and a Malonic Ester

expt	nitroparaffin salt	anion	product	yield,[a] %
XIV		$CH_3\bar{C}(COOEt)_2$		68
XV		$CH_3\bar{C}(COOEt)_2$		53
XVI				70
XVII		 $CH_3C(=O)\bar{C}(CH_3)COOEt$		61
XVIII				4
XIX		 $\phi\text{-}C(=O)\text{-}\bar{C}H\text{-}C(=O)\text{-}\phi$		12

[a] Pure, isolated product.

β-nitromalonic ester: ^1H NMR ($CDCl_3$) δ 1.28 (t, 6 H), 1.65 (s, 3 H), 1.70–2.80 (m, 10 H), 4.25 (q, 4 H); IR (neat) 1710 (C=O), 1545 cm^{-1} (NO_2).[6]

III. Reaction of 1,1-Dinitrocyclododecane with the Potassium Salt of Diethyl Methylmalonate. The procedure of experiment I was followed with 0.0196 g (0.0048 mol) of KH, 0.87 g (0.0050 mol) of diethyl methylmalonate, and 3.84 g (0.0150 mol) of 1,1-dinitrocyclododecane.[4] After a 14 h reaction time, the product was poured into 300 mL of cold H_2O and extracted with three 100-mL portions of ether. The combined extracts were washed twice with 100 mL of water and dried ($MgSO_4$), and the ether was removed. The residual 3.41 g of yellow oil was flash chromatographed on a silica gel[7] column (15 × 2 cm) with pentane–benzene (3:1) for elution. This gave 2.82 g of a colorless solid, mp 58–60 °C; this when recrystallized from pentane–ether (6:1) gave 2.73 g (80% yield) of colorless crystals, mp 59.5–60.0 °C: ^1H NMR ($CDCl_3$) δ 1.26 (t, 6 H), 1.45 (br s, 16 H), 1.62 (s, 3 H), 1.80–2.80 (m, 4 H) and 4.22 (q, 4 H); IR ($CHCl_3$) 1700 (C=O), 1545 cm^{-1} (NO_2).

Anal. Calcd for $C_{20}H_{35}NO_6$: C, 62.34; H, 9.09; N, 3.64. Found: C, 62.16; H, 9.36; N, 3.88.

IV. Reaction of 2,2-Dinitropropane with the Potassium Salt of 2-Carbomethoxycyclopentanone. As in experiment I, KH (0.215 g, 0.0055 mol) was treated with 25 mL of Me_2SO for 15 min and then 0.74 g (0.0055 mol) of 2-carbomethoxycyclopentanone was added. Finally, a solution of 2,2-dinitropropane (2.11 g, 0.0160 mol) in 10 mL of Me_2SO was added, and the reaction was allowed to proceed for 6 h. The product was then poured into 300 mL of H_2O and extracted 3 times with 100-mL portions of ether; the ether extracts were washed with water and dried ($MgSO_4$), and the ether was removed. The 1.98 g of orange solid so obtained was flash chromatographed on silica gel[7] (15 × 2 cm) with benzene as the eluent. The resulting white solid was recrystallized from hexane–benzene;[6] this gave 0.98 g (86% yield) of white crystals, mp 55.5–57 °C (lit.[6] mp 56–57 °C). The IR and ^1H NMR spectra were the same as those in the literature.[6]

V. Reaction of 1,1-Dinitrocyclohexane with the Potassium Salt of 2-Carbomethoxycyclopentanone. With use of the procedure of experiment IV, 0.200 g (0.0050 mol) of KH, 0.72 g (0.0051 mol) of 2-carbomethoxycyclopentanone, and 2.61 g (0.0150 mol) of 1,1-dinitrocyclohexane were allowed to react for 6 h. After the usual workup a yellow oil was obtained and this, when flash chromatographed on silica gel[7] using pentane–benzene (1:1), gave

---

[7] Silica gel 60, 230–400 mesh (E. Merck 9385).

1.01 g (75% yield) of the VPC pure nitro keto ester[6] as a colorless liquid: ^{1}H NMR (CDCl$_3$) δ 1.05–2.88 (m, 16 H) and 3.75 (s, 3 H); IR (neat) 1755 cm^{-1}, 1730 cm^{-1} (C=O), 1555 cm^{-1} (NO$_2$).

Anal. Calcd for $C_{13}H_{19}NO_5$: N, 5.20. Found: N, 5.00.

VI. Reaction of 1,1-Dinitrocyclododecane with the Potassium Salt of 2-Carbomethoxycyclopentanone. With KH (0.211 g, 0.0053 mol), 2-carbomethoxycyclopentanone (0.75 g, 0.0053 mol), and 1,1-dinitrocyclododecane[4] (2.68 g, 0.011 mol) the reaction was carried out as in experiment IV except that it was allowed to proceed for 24 h. The usual workup gave 2.70 g of an orange liquid which was flash chromatographed on a silica gel[7] column (12 × 2 cm), eluting first with 200 mL of pentane–benzene (3:1) which yielded 1.18 g of 1,1-dinitrocyclododecane. Further elution with 200 mL of benzene–ether (5:1) gave 1.36 g (73% yield) of VPC pure product as a colorless oil which, on standing crystallized; mp 75–77 °C. For analysis the sample was recrystallized from pentane–ether (4:1); white crystals mp 76–77.5 °C: ^{1}H NMR (CDCl$_3$) δ 1.10–1.32 (br s, 20 H), 1.65–2.80 (m, 8 H), and 3.68 (s, 3 H); IR (CHCl$_3$) 1760, 1700 (C=O), 1540 cm^{-1} (NO$_2$).

Anal. Calcd for $C_{19}H_{31}NO_5$: C, 64.59; H, 8.78; N, 3.96. Found: C, 64.53, H, 8.97; N, 3.95.

VII. Reaction of 2,2-Dinitropropane with the Potassium Salt of Ethyl α-Methylacetoacetate. Dry Me$_2$SO (15 mL) was added, under N$_2$, to 0.228 g (0.0057 mol) KH, and after stirring for 15 min ethyl α-methylacetoacetate (0.85 g, 0.0058 mol) was introduced. The reaction mixture was stirred for another 15 min and then placed under 2 20-W ordinary fluorescent lights, and a solution of 2,2-dinitropropane (2.25 g, 0.0168 mol) in 10 mL of Me$_2$SO was added. After 6 h the product was poured into 300 mL of H$_2$O and then extracted with ether. The combined ether extracts were washed with water and dried (MgSO$_4$), and the solvent was removed. The residual 2.66 g of pale yellow oil was subjected to aspirator vacuum (ca. 30 mm) for 12 h while being warmed to 40–50 °C; this removed the excess 2,2-dinitropropane. The residue was Kugelrohr distilled at 40–50 °C at 0.10 mm; the colorless distillate weighed 1.11 g (84% yield): ^{1}H NMR (CDCl$_3$) δ 1.28 (t, 3 H), 1.58 (s, 3 H), 1.72 (s, 6 H), 2.22 (s, 3 H), 4.26 (q, 2 H); IR (neat) 1750, 1725 (C=O), 1550 cm^{-1} (NO$_2$).

Anal. Calcd for $C_{10}H_{17}NO_5$: C, 51.95; H, 7.36; N, 6.06. Found: C, 52.21; H, 7.50; N, 5.81.

VIII. Reaction of 1,1-Dinitrocyclohexane with the Potassium Salt of Ethyl α-Methylacetoacetate. As described in experiment VII, KH (0.202 g, 0.0050 mol), ethyl α-methylacetoacetate (0.72 g, 0.0051 mol), and 1,1-dinitrocyclohexane (1.91 g, 0.0126 mol) were allowed to react for 6 h. After workup as described in VII the crude product was Kugelrohr distilled at 65–75 °C (0.05 mm). This gave 1.09 g (81% yield) of a colorless oil: ^{1}H NMR (CDCl$_3$) δ 1.28 (t, 3 H), 1.50 (s, 3 H), 1.66 (m, 6 H), 2.12 (s, 3 H), 2.50 (m, 4 H) and 4.20 (q, 2 H); IR (neat) 1750, 1720 (C=O), 1550 cm^{-1} (NO$_2$).

Anal. Calcd for $C_{13}H_{21}NO_5$: C, 57.56; H, 7.75; N, 5.17. Found: C, 57.65; H, 7.97; N, 5.21.

IX. Reaction of 1,1-Dinitrocyclododecane with the Potassium Salt of Ethyl α-Methylacetoacetate. Except for a 14 h reaction time the procedure of experiment VII was employed: KH (0.21 g, 0.0052 mol), ethyl α-methylacetoacetate (0.79 g, 0.0053 mol), and 1,1-dinitrocyclododecane[4] (4.28 g, 0.0166 mol). The crude product was flash chromatographed on a silica gel[7] column (18 × 2 cm), eluting first with 200 mL of pentane–benzene (4:1)—to remove excess 1,1-dinitrocyclododecane—and then with 200 mL of benzene–ether (5:1). This gave 1.25 g (68% yield) of VPC pure nitro keto ester; pale yellow crystals mp 86.5–89 °C. Repeated recrystallization from 3:1 pentane–ether gave 1.18 g (64% yield) of white crystals, mp 88–89 °C: ^{1}H NMR (CDCl$_3$) δ 1.30 (t, 3 H), 1.38 (br s, 18 H), 1.56 (s, 3 H), 1.80 to 2.65 (m, 4 H), 2.22 (s, 3 H), and 4.26 (q, 2 H); IR (CHCl$_3$) 1740 (C=O), 1560 cm^{-1} (NO$_2$).

Anal. Calcd for $C_{19}H_{33}NO_5$: C, 64.22; H, 9.29; N, 3.94. Found: C, 64.25; H, 9.46; N, 3.99.

X. Reaction of 2,2-Dinitropropane with the Potassium Salt of 2-Methyl-1,3-cyclohexanedione. In this experiment dry Me$_2$SO was purged of residual oxygen by the freeze–pump–thaw procedure.[8] Me$_2$SO (25 mL) was allowed to react for 15 min with 0.218 g (0.0054 mol) of KH, and then 0.72 g (0.0057 mol) of 2-methyl-1,3-cyclohexanedione in 10 mL of Me$_2$SO was introduced. After 15 min a solution of 2,2-dinitropropane (2.34 g, 0.0175 mol) in 5 mL of Me$_2$SO was added, and the reaction was allowed to proceed for 14 h. The reaction product was then poured into cold water and extracted with ether, and the ether extracts were then back-washed with water and dried (MgSO$_4$). Removal of the ether afforded a yellow oil (3.11 g) which was flash chromatographed on a silica gel[7] column (15 × 2 cm) with 300 mL of pentane–benzene (5:1) to remove excess 2,2-dinitropropane. The column was then eluted with 200 mL of ether. Removal of the ether gave a crude product from which volatile components were removed by Kugelrohr distillation at 40–50 °C (0.10 mm). The solid residue was recrystallized from pentane–ether (4:1) and, after cooling to −20 °C, 0.83 g (71% yield) of white crystals, mp 59–60 °C, were isolated: ^{1}H NMR (CDCl$_3$) δ 1.45 (s, 3 H), 1.76 (s, 6 H), 2.10 (m, 2 H), 2.75 (t, 4 H); IR (CHCl$_3$) 1700 (C=O), 1540 cm^{-1} (NO$_2$).

Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.34; H, 7.05; N, 6.55. Found: C, 56.33; H, 7.32; N, 6.44.

XI. Reaction of 1,1-Dinitrocyclohexane with the Potassium Salt of 2-Methyl-1,3-cyclohexanedione. The procedure of experiment X was followed except that, in addition to being placed under 2 20-W fluorescent lights, the reaction flask was exposed to a 150-W incandescent lamp ca. 20 cm distant. As a consequence the temperature in the vicinity of the flask was ca. 45–50 °C. KH (0.206 g, 0.0052 mol), 2-methyl-1,3-cyclohexanedione (0.72 g, 0.0057 mol), and 1,1-dinitrocyclohexane (2.67 g, 0.0150 mol) were employed; the reaction time was 48 h. Workup and purification followed the pattern of experiment X and gave 0.74 g (58% yield) of white crystals, mp 79.5–81 °C: ^{1}H NMR (CDCl$_3$) δ 1.20 (m, 2 H), 1.32 (s, 3 H), 1.50 to 2.05 (m, 8 H) and 2.30 to 2.75 (m, 6 H); IR (CHCl$_3$) 1730, 1690 (C=O), 1540 cm^{-1} (NO$_2$).

Anal. Calcd for $C_{13}H_{19}NO_4$: C, 61.66; H, 7.51; N, 5.53. Found: C, 61.60; H, 7.61; N, 5.39.

XII. Reaction of 2,2-Dinitropropane with the Potassium Salt of Dibenzoylmethane. Since the initially produced nitro diketone eliminates nitrous acid, a procedure which differs slightly from that of the preceding experiments was employed. A mixture of KH (0.20 g, 0.0050 mol) and 15 mL of Me$_2$SO was stirred for 15 min, and then a solution of dibenzoylmethane (1.24 g, 0.0055 mol) in 10 mL of Me$_2$SO was introduced; 15 min later, a solution of 2,2-dinitropropane (0.35 g, 0.0026 mol) in 5 mL of Me$_2$SO was added, and the reaction was allowed to proceed for 4 h. At the end of that time, 10 mL of a Me$_2$SO solution of dimsyl potassium (0.103 g of KH, 0.0025 mol) was introduced and, 5 min later, it was followed by a solution of 2,2-dinitropropane (1.08 g, 0.0075 mol) in 10 mL of Me$_2$SO. The reaction was then allowed to proceed for another 4 h. The usual workup gave 2.08 g of an orange solid. It was placed in a Kugelrohr apparatus and subjected to a temperature of 40–50 °C and a pressure of 0.05 mm. In this way excess 2,2-dinitropropane and any unreacted dibenzoylmethane were volatilized. The nonvolatile residue was recrystallized from pentane–ether (3:1); 0.86 g (63% yield) of white crystals, mp 74.5–76 °C, was obtained: ^{1}H NMR (CDCl$_3$) δ 1.88 (s, 6 H), 7.50 (m, 6 H), 8.00 (d of d, 4 H); IR (CHCl$_3$) 1645 cm^{-1} (C=O).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 80.95; H, 6.35. Found: C, 80.60; H, 5.99.

XIII. Reaction of 1,1-Dinitrocyclohexane with the Potassium Salt of Dibenzoylmethane. The procedure of experiment XII was duplicated by using 0.191 g (0.0048 mol) of KH in 15 mL of Me$_2$SO, 1.18 g (0.0052 mol) of dibenzoylmethane in 10 mL of Me$_2$SO, and a solution of 0.430 g (0.0024 mol) of 1,1-dinitrocyclohexane in 10 mL Me$_2$SO in the first 4-h stage. For the second 4-stage 10 mL of Me$_2$SO in which 0.097 g of KH (0.0024 mol) had been dissolved and a solution of 1.37 g (0.0081 mol) of 1,1-dinitrocyclohexane in 10 mL of Me$_2$SO were employed. The usual workup gave 2.07 g of a brown solid which was heated at 90–110 °C in a Kugelrohr apparatus at 0.05 mm to remove excess 1,1-dinitrocyclohexane and any unreacted dibenzoylmethane. The nonvolatile residue was recrystallized from pentane to give 1.02 g (65% yield) of white crystals, mp 91–92.5 °C; ^{1}H NMR (CDCl$_3$) δ 1.60 to 2.10 (m, 8 H), 5.65 (m, 2 H), 7.50 (m, 6 H), 7.95 (d of d, 4 H); IR (CHCl$_3$) 1700, 1680 cm^{-1} (C=O).

---

(8) Kornblum, N.; Widmer, J.; Carlson, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 661.

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.89; H, 6.58. Found: C, 82.43; H, 6.73.

XIV. Oxidative Coupling of the Sodium Salts of 2-Nitropropane and Diethyl Methylmalonate. A 60% oil dispersion of NaH[5] (0.201 g, 0.0051 mol) was placed in a 1-L flask equipped with a Hershberg stirrer and, under N_2, the NaH was washed free of oil with pentane. The flask was then cooled in an ice bath and 50 mL of absolute ethanol was cautiously added. The ice bath was removed, and the mixture was stirred for 10 min; diethyl methylmalonate (0.78 g, 0.0045 mol) was introduced and, after 10 min, a mixture consisting of 25 g of sea sand and finely powdered potassium ferricyanide (32.6 g, 0.10 mol) was added. A solution prepared from 0.311 g (0.0076 mol) of 60% NaH, 50 mL of absolute ethanol, and 0.65 g (0.0074 mol) of 2-nitropropane was added dropwise in the course of 45 min to the rapidly stirred mixture. After being stirred for 3 more h, the mixture was filtered, and the solvent was removed under reduced pressure. The resulting yellow solid was leached with a total of ca. 400 mL of ethyl ether which, when removed, left 1.17 g of a yellow oil. Flash chromatography on a silica gel[7] column (16 × 2 cm) with 200 mL of pentane–benzene (4:1) gave 0.37 g of 2,3-dinitro-2,3-dimethylbutane; white crystals, mp 209–211 °C (lit.[9] mp 210–212 °C). Further elution with 200 mL of benzene–ether (10:1) afforded a pale yellow oil and this, on Kugelrohr distillation at 60–70 °C (0.05 mm), yielded 0.79 g (68% yield) of the nitromalonic ester. The ^{1}H NMR and IR spectra of this colorless liquid were identical with those recorded for the product of experiment I.

XV. Oxidative Coupling of the Sodium Salts of Nitrocyclohexane and Diethyl Methylmalonate. Following the procedure of experiment XIV 0.251 g (0.0055 mol) of 60% NaH,[5] 50 mL of absolute ethanol, 0.90 g (0.0052 mol) of diethyl methylmalonate, 35 g of sea sand, 30.0 g (0.0917 mol) of $K_3Fe(CN)_6$, 0.300 g (0.0075 mol) of 60% NaH, 50 mL of absolute ethanol, and 0.93 g (0.0072 mol) of nitrocyclohexane were employed. The crude orange oil (1.36 g) was Kugelrohr distilled at 50–60 °C (0.15 mm) to remove the dimer of nitrocyclohexane, and then the temperature was raised to 140–150 °C where 0.83 g (53% yield) of a pale yellow liquid was obtained; this had ^{1}H NMR and IR spectra which were identical with those of the product of experiment II.

XVI. Oxidative Coupling of the Sodium Salts of 2-Nitropropane and 2-Carbomethoxycyclopentanone. The procedure of experiment XIV was followed with a 60% oil dispersion of NaH[5] (0.212 g, 0.0053 mol), 50 mL of absolute ethanol, 0.710 g (0.0050 mol) of 2-carbomethoxycyclopentanone in 5 mL absolute ethanol, 35 g of sea sand, and 33.1 g (0.11 mol) of $K_3Fe(CN)_6$; a solution of the sodium salt of 2-nitropropane prepared from 0.300 g (0.0075 mol) of 60% NaH, 50 mL of absolute ethanol, and 0.633 g (0.0072 mol) of 2-nitropropane was added dropwise to the rapidly stirred reaction mixture over the course of 1 h. After another 3 h the reaction mixture was worked up as in experiment XIV. The 1.31 g of yellow solid thus obtained was flash chromatographed on silica gel[7] (15 × 3 cm) with 200 mL of 90:10 pentane–ether for elution. This gave 0.317 g of 2,3-dinitro-2,3-dimethylbutane, mp 207–209 °C. Further elution with 200 mL of 80:20 pentane–ether gave 0.81 g (70% yield) of white crystals, mp 55–57 °C; mixed melting point with the product from experiment IV was 55–57.5 °C. The ^{1}H NMR and IR spectra of the products of this experiment and experiment IV are identical.

XVII. Oxidative Coupling of the Sodium Salts of 2-Nitropropane and Ethyl α-Methylacetoacetate. The procedure of experiment XIV was followed with a solution of ethyl sodio-α-methylacetoacetate prepared from 0.282 g (0.0070 mol) of 60% NaH,[5] 50 mL of absolute ethanol, and 0.950 g (0.0066 mol) of the β-keto ester. To this was added 30 g of sea sand and 30.0 g (0.092 mol) of $K_3Fe(CN)_6$, and this was followed by the dropwise addition, over the course of 1 h, of a solution prepared from 0.320 g (0.0081 mol) of 60% NaH, 50 mL of absolute ethanol, and 0.667 g (0:0075 mol) of 2-nitropropane. After another 3 h the reaction mixture was worked up as in experiment XIV. The 1.53 g of orange-yellow solid thus obtained when recrystallized from ether yielded 0.246 g of 2,3-dinitro-2,3-dimethylbutane, mp 207–209 °C. Removal of the ether from the mother liquor, followed by flash chromatography on silica gel[7] (15 × 2 cm) with 80:20 pentane–ether for elution, afforded 0.924 g (61% yield) of a colorless oil whose ^{1}H NMR and IR are identical with those of the product of experiment VII.

XVIII. Oxidative Coupling of the Sodium Salts of 2-Nitropropane and 2-Methyl-1,3-cyclohexanedione. As in experiment XIV, a solution of the sodium salt of the β-diketone was prepared from 60% NaH[5] (0.212 g, 0.0053 mol), 50 mL of absolute ethanol, and 0.630 g (0.0050 mol) of 2-methyl-1,3-cyclohexanedione. To this was added a mixture of 32 g of sea sand and finely powdered $K_3Fe(CN)_6$ (23.0 g, 0.070 mol). To the vigorously stirred mixture was added, dropwise, over the course of 40 min a solution of the sodium salt of 2-nitropropane made from 0.283 g, (0.0070 mol) of 60% NaH, 50 mL of absolute ethanol, and 2-nitropropane (0.578 g, 0.0065 mol). After 3 h of stirring under N_2 the usual workup afforded 1.13 g of a yellow oil. Flash chromatography on a silica gel[7] column (15 × 2 cm) with 200 mL of pentane–ether (90:10) afforded 0.55 g (88% yield) of 2,3-dinitro-2,3-dimethylbutane, white crystals mp 207–209 °C. Further elution with 200 mL of pentane–ether (80:20) gave 0.54 g of a white solid which, when rechromatographed on silica gel (15 × 2 cm) with 150 mL of pentane–ether (85:15) for elution, gave 0.49 g of 2-methyl-1,3-cyclohexanedione, mp 205–209 °C. The IR spectrum of this material was identical with that of the starting β-diketone, and both had identical VPC retention times. Further elution with 100 mL of pentane–ether (80:20) yielded 0.042 g (4% yield) of the nitro diketone; mp 57.5–59.5 °C. The mixed melting point with the product of experiment 10 was 57.5–60 °C. The IR spectra of these two samples were identical.

XIX. Oxidative Coupling of the Sodium Salts of 2-Nitropropane and Dibenzoylmethane. This reaction was run exactly as described for experiment XVIII with 0.255 g (0.0064 mol) of 60% NaH, 1.344 g (0.0060 mol) of dibenzoylmethane, 50 mL of absolute ethanol, 30 g of sea sand, and 32.0 g (0.010 mol) of $K_3Fe(CN)_6$. To this mixture was added a solution prepared from 0.312 g (0.0078 mol) of 60% NaH, 50 mL of absolute ethanol, and 0.665 g (0.0074 mol) of 2-nitropropane dropwise in the course of 1 h, and then the reaction was allowed to proceed for an additional 3 h. The usual workup produced 1.91 g of an orange solid which, when flash chromatographed on a silica gel[7] column (15 × 2 cm) with 90:10 pentane–ether for elution, gave 1.85 g of a white solid. Recrystallization from ether yielded 0.391 g (64%) of 2,3-dinitro-2,3-dimethylbutane; white crystals, mp 207–209 °C. After removal of ether, the mother liquor was Kugelrohr distilled at 40–50 °C (0.05 mm), and the nonvolatile residue was recrystallized from 3:1 pentane–ether. In this way 0.190 g (12% yield) of the olefinic diketone was isolated, white crystals, mp 74–76 °C. The mixed melting point with the product of experiment XII was 74–76 °C. The IR and ^{1}H NMR spectra of the two products were identical.

Acknowledgment. We are indebted to the National Science Foundation for support of this work.

---

[9] Zeldin, L.; Shechter, H. *J. Am. Chem. Soc.* **1957**, *79*, 4708.