

as electrophiles with carbanions. We have found that they may be made directly from acrolein or methyl vinyl ketone and concentrated aqueous hydriodic acid, followed by ethylene glycol.

Previously, **1** was prepared from the corresponding chloro^{1b} or bromo^{1a} compounds, which were in turn made by using the gaseous hydrogen halides. The commonly used preparation^{2g} of **2** begins with the AlCl₃-catalyzed reaction of acetyl chloride with gaseous ethylene. The resulting chloro ketone was treated with sodium iodide and finally ketalized in 56% overall yield. Another alternative^{2h} begins with ketalization (neopentandiol) of ethyl acetate followed by lithium aluminum hydride reduction, tosylation, and iodide displacement.

Anhydrous hydrogen chloride and hydrogen bromide have been added to α,β -unsaturated carbonyl compounds while trimethylsilyl iodide³ was preferred for generating the iodo compounds via the silyl enol ethers. Although aqueous hydrobromic acid is little suited for this process,⁴ we have found that concentrated aqueous hydriodic acid gives a rapid high yield of the β -iodo compound. This may then be used without purification in the reaction with ethylene glycol. By this means we have prepared **1** in 60% yield and **2** in 56-58% yield. Although boiling points are reported for these compounds, we recommend using alumina chromatography for purification since we have found that **1** decomposes with some violence upon distillation at 55 °C and 1.2 mm.

Experimental Section

2-(2-Iodoethyl)-1,3-dioxolane (1). A solution of 5.60 g (0.100 mol) of acrolein in 100 mL of CH₂Cl₂ was vigorously stirred with 24.7 g (0.110 mol) of 57% aqueous hydriodic acid in an Enlenmeyer flask for 10 h. Ethylene glycol (12.4 g, 0.200 mol) was added, and the mixture was stirred for an additional 8 h at room temperature. Excess acid was neutralized cautiously with solid Na₂CO₃, and the CH₂Cl₂ solution was washed with three portions of dilute aqueous NaHCO₃ and dried with MgSO₄. Rotary evaporation gave an oil which was purified by being passed through a column of alumina (2 × 16 cm), eluting with hexane. This gave 13.7 g (60%) of very pale yellow oil: ¹H NMR (CDCl₃) δ 2.17 (dt, 2 H), 3.17 (t, 2 H) 3.86 (m, 4 H), 4.84 (t, 1 H).^{1b}

2-Methyl-2-(2-iodoethyl)-1,3-dioxolane (2). A solution of methyl vinyl ketone (7.00 g, 0.100 mol) in 100 mL of benzene was vigorously stirred with 45.0 g (0.200 mol) of 57% aqueous hydriodic acid for 2 h. During the first hour the reaction was slightly exothermal. The benzene solution was separated, washed with three portions of aqueous NaHCO₃ and one of aqueous NaCl, and dried with MgSO₄. Ethylene glycol (6.20 g, 0.100 mol) and *p*-toluenesulfonic acid monohydrate (0.5 g) were added to the dried solution. Azeotropic distillation for 2 h removed the product water, and then the solution was washed with saturated aqueous NaHCO₃, dried with MgSO₄, and rotary evaporated. The remaining oil was purified by being passed through a 2 × 14 cm column of neutral alumina, eluting with hexane, to afford 13.6 g (56%) of pale yellow oil. The ¹H NMR showed pure product with values identical with those reported.^{2g}

The benzene solution of the unstable intermediate iodo ketone gave the following ¹H NMR values: δ 1.56 (s, 3 H), 2.33 (t, 2 H), 2.91 (t, 2 H). In CCl₄ the values were the same as those reported.^{2g}

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Registry No. 1, 83665-55-8; 2, 53750-51-9; acrolein, 107-02-8; methyl vinyl ketone, 78-94-4.

Anionically Activated Alumina in the Carboxyalkylation of Benzyl Halides

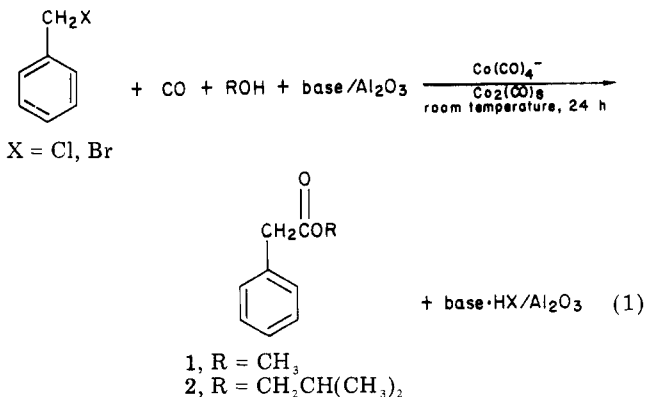
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The ability of alumina to assist in various chemical transformations is well documented.¹ The combination of alumina and base, known as anionically activated or basic alumina, has been used successfully in promoting alkylation,² condensation,³ and hydrolysis⁴ reactions. We report the use of anionically activated alumina in the carboxyalkylation of benzyl halides using the cobalt tetracarbonyl anion catalyst. This extends the use of basic alumina to include the important area of organometallic anion chemistry.

Early work⁵ on the carboxyalkylation of alkyl halides catalyzed by the cobalt tetracarbonyl anion required the use of sodium amalgam to generate the anion from the cobalt dimer. With the advent of phase-transfer catalysis,⁶ the carbonylation of benzyl halides to the corresponding acid derivatives with the cobalt anion was accomplished by using sodium hydroxide and a two-phase organic-aqueous solvent system.^{7,8} While this technique works well for the preparation of the carboxylic acids, the direct synthesis of the ester derivatives⁹ using an alcohol solvent and an organic base has proven difficult.^{5,10} Our approach (eq 1) takes advantage of the reactivity of basic alumina¹¹ in a carboxyalkylation scheme.



The reactions of benzyl halides with carbon monoxide

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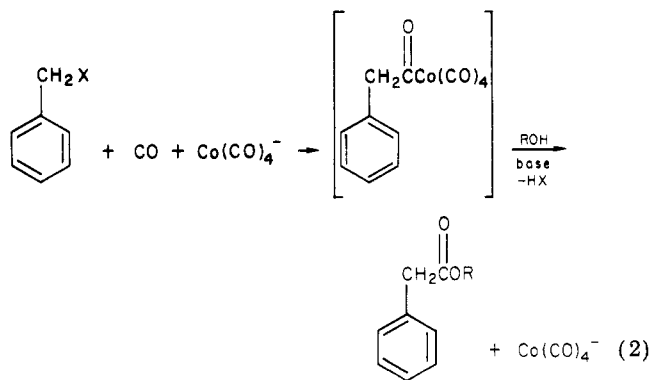
Table I. Carboxyalkylation of Benzyl Halides^a

benzyl halide	base	ROH	product ^b	yield, ^c %
PhCH ₂ Br	MeO ⁻ K ⁺	CH ₃ OH	PhCH ₂ CO ₂ CH ₃	5
PhCH ₂ Br	Al ₂ O ₃ ^d	CH ₃ OH	PhCH ₂ CO ₂ CH ₃	5
PhCH ₂ Br	MeO ⁻ K ⁺ /Al ₂ O ₃ ^e	CH ₃ OH	PhCH ₂ CO ₂ CH ₃	20
PhCH ₂ Br	MeO ⁻ K ⁺ /Al ₂ O ₃	CH ₃ OH	PhCH ₂ CO ₂ CH ₃	70 (53)
PhCH ₂ Cl	MeO ⁻ K ⁺ /Al ₂ O ₃	CH ₃ OH	PhCH ₂ CO ₂ CH ₃	57
PhCH ₂ Br	EtO ⁻ Na ⁺ /Al ₂ O ₃	CH ₃ OH	PhCH ₂ CO ₂ CH ₃	65
PhCH ₂ Br	<i>t</i> -BuO ⁻ K ⁺ /Al ₂ O ₃	CH ₃ OH	PhCH ₂ CO ₂ CH ₃	22
PhCH ₂ Br	Na ₂ CO ₃ /Al ₂ O ₃	CH ₃ OH	PhCH ₂ CO ₂ CH ₃	32 (23)
PhCH ₂ Br	<i>i</i> -BuO ⁻ Na ⁺ /Al ₂ O ₃ ^f	<i>i</i> -BuOH	PhCH ₂ CO ₂ CH ₂ CH(CH ₃) ₂	67

^a Procedures used were identical with those described in the Experimental Section. ^b The major identified coproducts were the corresponding alkyl benzyl ethers.¹³ All known compounds were identified by comparison with authentic samples and gave satisfactory IR and NMR spectra. ^c Yields, based on charged halide, were determined by VPC using internal standard techniques and were not optimized. Isolated distilled yields are given in parentheses. ^d The alumina (11.3 g) was dried at 175 °C for 1 h under vacuum prior to use. ^e A combination of potassium methoxide (3.7 g) and alumina^d (11.3 g) was used as the base. ^f Prepared by reaction of sodium hydroxide, isobutyl alcohol, and alumina with continuous water removal.

and alcohol solvents were carried out in the presence of excess base and catalytic amounts of dicobalt octacarbonyl. After 24 h of stirring at room temperature under approximately 1 atm of carbon monoxide, the heterogeneous mixtures were filtered and analyzed. When either potassium methoxide or alumina was used alone, the major product¹² observed was methyl benzyl ether with little methyl phenylacetate detected (<5%). This ether product may result from a simple displacement pathway.¹³ When a combination of alumina and potassium methoxide was evaluated, methyl phenylacetate was obtained but in low yield (<20%). In contrast, when potassium methoxide on alumina¹⁴ was used as the base to generate the cobalt tetracarbonyl anion, the carboxyalkylated product, methyl phenylacetate (1), was prepared in 70% yield with little ether formation. Benzyl chloride reacted similarly under these mild reaction conditions. Other alkoxide bases and sodium carbonate were used with alumina to afford the methyl ester derivative¹⁵ in 22–65% yield. The results are given in Table I. Sodium isobutoxide on alumina in isobutyl alcohol gave isobutyl phenylacetate (2) in 67% yield.

It is generally believed that the key mechanism by which inorganic metal oxides such as alumina assist in chemical reactions is by adsorption of the substrate.⁴ This phenomenon often leads to higher selectivities and milder reaction conditions.² In this system, the alkoxide- or carbonate-treated alumina surface may favor the carboxyalkylation reaction pathway shown below (eq 2).¹⁶ This



(12) Other possible side products include hydrocarbons and ketones, see ref 7.

(13) W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hart, J. H. Lamneck, Jr., and L. C. Gibbons, *J. Am. Chem. Soc.*, **69**, 2451 (1947). When a weak base such as sodium carbonate is used, methyl benzyl ether may be formed by an S_N1 mechanism.

(14) This material was prepared in a manner similar to that reported; see E. Keinan and Y. Mazur, *J. Am. Chem. Soc.*, **99**, 3861 (1977).

(15) Because transesterification occurs so quickly in the presence of base, none of the ethyl or *tert*-butyl esters were detected.

should result in higher ester yields as little of the benzyl halide would be consumed in byproduct formation. A more detailed investigation is underway to determine if the reaction selectivity observed is due to the selective adsorption of one or more of the reactants or intermediates. The use of base on alumina may represent a viable alternative to traditional phase-transfer catalysis¹⁷ in organometallic anion chemistry.¹⁸

Experimental Section

General Methods. Unless specified, all reactions were carried out by using reagent-grade materials with no prior purification. Benzyl bromide and benzyl chloride were purchased from Aldrich Chemical Co. Potassium methoxide, sodium ethoxide, and potassium *tert*-butoxide were obtained from Alfa Products. Sodium isobutoxide was prepared by reaction of isobutyl alcohol with sodium hydroxide. Neutral alumina (chromatographic grade, Aldrich) was used directly from the bottle. Dicobalt octacarbonyl (Alfa) was kept under a CO atmosphere in the freezer and weighed out rapidly under an argon atmosphere prior to each experiment. Carbon monoxide (99.5% minimum) was obtained from Matheson. Methyl benzyl ether was prepared according to a literature procedure.¹³ Methyl phenylacetate and isobutyl phenylacetate were prepared from phenylacetic acid (Fischer Scientific Co.) by esterification with either methanol or isobutyl alcohol and concentrated sulfuric acid. Infrared spectra were recorded on either a Beckman AccuLab 8 spectrometer or a Perkin-Elmer 137 Infracord spectrophotometer. NMR spectra were recorded on a Varian FT-80A spectrometer with tetramethylsilane as an internal standard. Gas chromatography was performed with a Varian Model 3700 gas chromatograph with a thermal conductivity detector on a 10% OV-101 on Chromosorb W-HP column (2 m × 1/8 in. stainless steel) with helium carrier gas. Peak integrations were obtained on a Columbia Scientific Industries Model CRS-208 automatic digital integrator using nonane as the internal standard.

Anionically Activated Alumina. The base on alumina reagents (4.0 mmol of base per g alumina) were prepared in a manner similar to that reported by Mazur¹⁴ using either alcohol (alkoxide) or water (carbonate) solvent. The resulting powders were dried under vacuum for 1 h at 175 °C.

General Procedure for Carboxyalkylation Reactions. Procedures similar to that described below were followed for all reactions reported in Table I. Into a 100-mL ice-cooled three-neck flask fitted with a magnetic stirrer, reflux condenser, and addition funnel was added 50 mL of methanol, 15 g (50 mmol) of potassium methoxide/alumina base, and 0.316 g (0.92 mmol) of dicobalt octacarbonyl. The system was evacuated and the atmosphere replaced with carbon monoxide. A solution containing 4.3 g (25 mmol) of benzyl bromide in 25 mL of methanol was added slowly

(16) An alternate mechanism cannot be ruled out without further study of the solution-surface phenomena.

(17) R. A. Sawicki, *Tetrahedron Lett.*, **23**, 2249 (1982).

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over 1 h. After complete addition the heterogeneous mixture was stirred rapidly at room temperature for 24 h under approximately 1 atm of carbon monoxide. After being filtered, the resulting crude product mixture was analyzed by gas chromatography using nonane as the internal standard.

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Registry No. PhCH₂Br, 100-39-0; PhCH₂Cl, 100-44-7; MeO⁻·K⁺, 865-33-8; EtO⁻·Na⁺, 141-52-6; *t*-BuO⁻·K⁺, 865-47-4; Na₂CO₃, 497-19-8; *i*-BuO⁻·Na⁺, 13259-29-5; Al₂O₃, 1344-28-1; CH₃OH, 67-56-1; *i*-BuOH, 78-83-1; PhCH₂CO₂CH₃, 101-41-7; PhCH₂CO₂CH₂CH(CH₃)₂, 102-13-6; methyl benzyl ether, 538-86-3; benzyl isobutyl ether, 940-49-8; carbon monoxide, 630-08-0; dicobalt octacarbonyl, 10210-68-1.

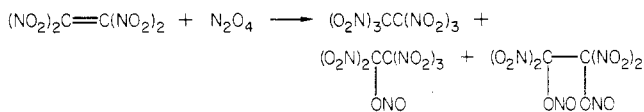
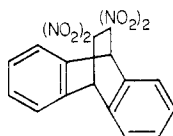
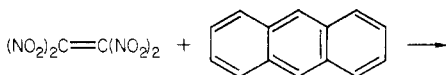
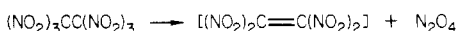
Reactions of Hexanitroethane with Alcohols¹

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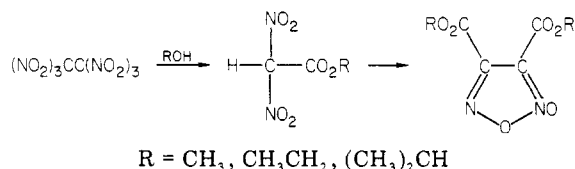
Olefins highly substituted with electron-withdrawing substituents are of general interest, and tetranitroethylene, an extreme example of this class, remains a challenge in that its isolation has not been reported. We reported recently that hexanitroethane undergoes extrusion of dinitrogen tetroxide in refluxing benzene, and in the presence of a diene or anthracene, the Diels-Alder adduct derived from tetranitroethylene is obtained.² Other geminal tetranitro compounds also underwent this extrusion to give stable *vic*-dinitro olefins.³ In the absence of a trapping agent, however, only gaseous decomposition products were obtained from hexanitroethane. The results were rationalized on the basis of readdition to tetranitroethylene of the ambident NO₂ radical at its oxygen center to give unstable dinitro-nitrite structures. To explore



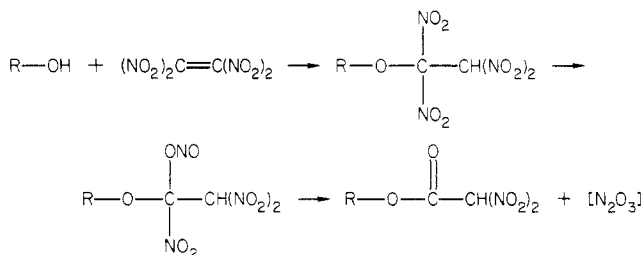
whether tetranitroethylene can be trapped by other reagents, we investigated reactions of hexanitroethane with alcohols.

Heating a solution of hexanitroethane in refluxing methanol for 3 h resulted in the isolation of methyl dinitroacetate in 48% yield. The material was identified by its spectral properties⁴ and by its quantitative transformation on standing at room temperature to give 3,4-bis-(methoxycarbonyl)furan 2-oxide.⁴⁻⁶ Ethyl dinitroacetate

and isopropyl dinitroacetate were obtained similarly from hexanitroethane with ethanol and 2-propanol, in 53% and 52% yield, respectively, and were likewise converted to the furazan oxides.



The conditions at which these reactions take place are similar to those under which the tetranitroethylene Diels-Alder adducts are obtained from hexanitroethane.² The dinitroacetate esters might be formed by the addition of alcohols to tetranitroethylene to give the unstable 1-alkoxy-1,1,2,2-tetranitroethane structures. The formation of the carbonyl group could take place by the inversion of a nitro group to a nitrite group, followed by the loss of the elements of N₂O₃. Other examples of the isomerization



of nitro groups to nitrites have been reported.⁷ Alternatively, the nitro groups adjacent to the alkoxy could be hydrolyzed by trace amounts of water in the system, and equilibration of the resulting nitrous acid to oxides of nitrogen would regenerate the water. The formation of dinitroacetates from hexanitroethane and alcohols provides additional evidence for the transitory existence of tetranitroethylene.

Experimental Section

NMR spectra were obtained with a Varian T-60 spectrometer, with tetramethylsilane as an internal reference. Infrared spectra were recorded with a Perkin-Elmer 700 spectrophotometer and mass spectra with an AEI MS-9 instrument at a potential of 70 eV. Elemental analysis was carried out by Galbraith Laboratories, Inc. Knoxville, TN.

Caution: Because of the explosive nature of many polynitro compounds, experimental manipulations should be performed behind safety shielding.

Methyl Dinitroacetate. A mixture of 1.50 g (5.0 mmol) of hexanitroethane and 100 mL of methanol was heated at reflux with stirring for 3 h. Methanol was removed at reduced pressure with a rotary evaporator. The residue was dissolved in 15 mL of methylene chloride and was extracted with 20 mL of 0.2 N aqueous sodium hydroxide, and the aqueous layer was washed with two 10-mL portions of methylene chloride. The aqueous layer was acidified to pH 2-4 and was extracted with three 15-mL portions of methylene chloride. These three organic layers were combined, dried over sodium sulfate, and stripped of solvent to give 0.39 g (48%) of methyl dinitroacetate. NMR and IR spectral data were identical with reported⁴ values.

Ethyl dinitroacetate was obtained in 53% yield by the above procedure: NMR (CDCl₃) δ 6.65 (s, 1 H), 4.43 (q, 2 H, *J* = 7 Hz), 1.40 (t, 3 H, *J* = 7 Hz); IR (CCl₄) 1765 (C=O), 1580 (NO₂) cm⁻¹.

Isopropyl dinitroacetate was obtained in 52% yield by the above procedure: NMR (CDCl₃) δ 6.57 (s, 1 H), 5.20 (sept, 1 H,

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