Michael Reactions of 2-Fluoro-2,2-dinitroethanol and 2,2-Dinitropropanol with Olefinic and Acetylenic Acceptors[1]

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Michael reactions of 2,2-dinitro alcohols were found to take place with or without prior deformulation, depending on the reaction conditions and the nature of the acceptor. 2-Fluoro-2,2-dinitroethanol and ethyl acrylate, methyl vinyl ketone, or acrylonitrile in aqueous alkali gave fluorodinitromethane adducts, whereas ethyl propiolate gave both fluorodinitromethane and alcohol 1:1 adducts, and dimethyl acetylenedicarboxylate gave only the 1:1 alcohol adduct. These acetylenes and 2-fluoro-2,2-dinitroethanol in pyridine gave 1:1 alcohol adducts. Ethyl propiolate and 2,2-dinitropropanol in pyridine gave 1:1 alcohol adduct, and in aqueous solution the salt of 1,1-dinitroethane gave the 1:1 adduct.

1,1-Dinitroalkanes undergo the Michael reaction with α,β-olefinic esters, nitriles, aldehydes, and ketones. 2,2-Dinitro alcohols, which are readily deformylated in the presence of base, give Michael adducts of the corresponding 1,1-dinitroalkanes.[2] Limited work has been done with acetylenic acceptors; 1:1 Michael adducts were reported for reactions of 1,1-dinitroalkanes with methyl propiolate[3] and for reactions of nitroform with propiolic acid and amide.[4] The synthesis of 2-fluoro-2,2-dinitroethanol has been reported recently,[5,6] and Michael reactions of this unusual nitro alcohol have now been examined. Because of the reported destabilization of nitronate anions by α-fluorines,[7] a significant concentration of fluorodinitroethoxide ion could be expected with the following equilibria operating in the presence of base.

$$FC(NO_2)_2CH_2OH \overset{OH^-}{\rightleftharpoons} FC(NO_2)_2CH_2O^- \rightleftharpoons FC(NO_2)_2^- + CH_2O \quad (1)$$

Inasmuch as simple alcohols have been reported to form 1,4 adducts with acrylates,[8] acrylonitrile,[9] and methyl vinyl ketone[10] in the presence of base, 2-fluoro-2,2-dinitroethanol could be expected to yield 2-fluoro-2,2-dinitroethyl ethers or fluorodinitromethane derivatives.

Ethyl acrylate, methyl vinyl ketone, and acrylonitrile were found to react with 2-fluoro-2,2-dinitroethanol in aqueous alkaline solution to give ethyl 4-fluoro-4,4-dinitrobutyrate, 5-fluoro-5,5-dinitro-2-pentanone, and 4-fluoro-4,4-dinitrobutyronitrile, respectively (Scheme I). Thus either the alkoxide ion did not react with these olefins or the addition was reversible and the fluorodinitromethane adducts were more stable under these conditions.

SCHEME I

$$C_2H_5OCCH{=}CH_2 \xrightarrow[OH^-,\,-CH_2O]{FC(NO_2)_2CH_2OH} C_2H_5OCCH_2CH_2CF(NO_2)_2$$
(O)

$$CH_3CCH{=}CH_2 \longrightarrow CH_3CCH_2CH_2CF(NO_2)_2$$
(O)

$$N{\equiv}C{-}CH{=}CH_2 \longrightarrow N{\equiv}CCH_2CH_2CF(NO_2)_2$$

Pyridine has been reported to effect the acylation of 2,2-dinitro alcohols without causing deformylation.[11] The above conjugated olefins, however, did not react with 2-fluoro-2,2-dinitroethanol in the presence of pyridine. The stronger base, triethylamine, resulted in a very slow reaction of 2-fluoro-2,2-dinitroethanol with methyl acrylate, but only with deformylation to give methyl 4-fluoro-4,4-dinitrobutyrate.

The reverse Michael reaction is most likely to occur when the forward reaction is slow.[12] Consequently, the high reactivity of activated acetylenic compounds toward nucleophiles[13] should enhance the probability of isolating the primary adducts with this class of acceptor. Therefore, reactions of 2-fluoro-2,2-dinitroethanol with ethyl propiolate and with dimethyl acetylenedicarboxylate were investigated.

The reaction of 2-fluoro-2,2-dinitroethanol with ethyl propiolate in methylene chloride solution catalyzed by pyridine, gave ethyl β-(2-fluoro-2,2-dinitroethoxy)acrylate in 76% yield. Nmr spectra showed that the product was a mixture of *trans* and *cis* isomers in the ratio 5.3:1. The olefinic hydrogen chemical shifts and coupling constants (J_{cis} = 7.5 cps, J_{trans} = 12.6 cps) corresponded with those reported for other β-alkoxyacrylates[14] (J_{cis} = 7 cps, J_{trans} = 12.5 cps). Details of the spectra are given in the Experimental Section.

When the reaction of ethyl propiolate with 2-fluoro-2,2-dinitroethanol was carried out in aqueous alkaline solution, both ethyl β-(2-fluoro-2,2-dinitroethoxy)-acrylate and ethyl 3-fluoro-3,3-dinitrocrotonate were isolated. The latter product was also prepared from fluorodinitromethane and ethyl propiolate under the

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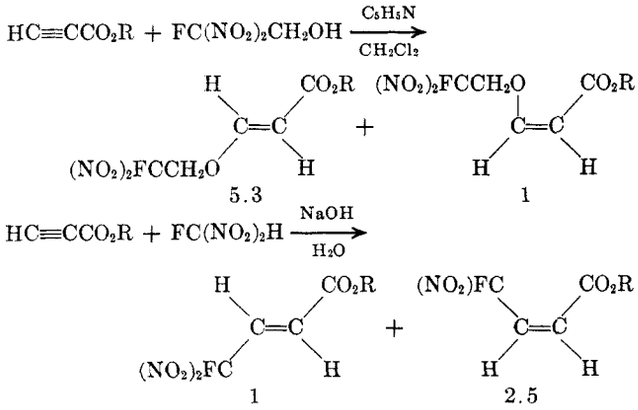
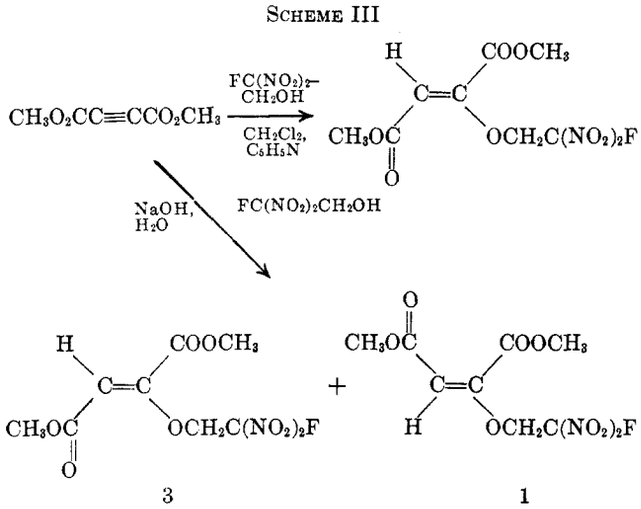
same conditions, and the ratio of *trans* to *cis* isomers was 1:2.5 (Scheme II).

SCHEME II



With dimethyl acetylenedicarboxylate, only alkoxide addition without deformylation was observed. The reaction with 2-fluoro-2,2-dinitroethanol in methylene chloride catalyzed by pyridine gave an 88% yield of dimethyl 2-fluoro-2,2-dinitroethoxyfumarate, and the maleate was not detected. When this reaction was conducted in aqueous sodium hydroxide, both isomers were obtained in the ratio 3:1, respectively (Scheme III). In this case, the combined yield was only 11%, and the major product was a nonvolatile oil with elemental analysis identical with that of the above esters. Comparison of the chemical shifts of the olefinic protons (δ 6.41 for the fumarate, 5.6 for the maleate) with values reported[14] for other alkoxyfumarates (δ 6.1–6.45) and alkoxymaleates (5.05–5.15) was used to assign the isomeric structures.

SCHEME III



To determine whether polynitro alcohols that deformylate more readily than 2-fluoro-2,2-dinitroethanol can also give direct adducts with activated acetylenes, the reaction of 2,2-dinitropropanol with ethyl propiolate was investigated. Using methylene chloride as solvent and pyridine as catalyst gave ethyl β-(2,2-dinitropropoxy)acrylate in 79% yield with a ratio of *trans* to *cis* isomers of 3.4:1. This is the first example of the Michael addition without prior deformylation of a 2,2-dinitroalkanol, and shows that the alcohol is not deformylated under these conditions. The reaction of 1,1-dinitroethane with ethyl propiolate in aqueous base, on the other hand, gave ethyl 4,4-dinitro-2-pentenoate with a *trans* to *cis* ratio of 1:3.

With the exceptions of the pyridine-catalyzed additions to ethyl propiolate, all of these reactions with activated acetylenes took place predominantly by *trans* additions. Winterfeldt and Preuss[14] also observed predominately *trans* addition in reactions of alcohols with dimethyl acetylenedicarboxylate catalyzed by tertiary amines, and *cis* additions with methyl propiolate.

The formation of fluorodinitroethyl ethers in Michael reactions of 2-fluoro-2,2-dinitroethanol in aqueous solution confirms the presence of an appreciable amount of 2-fluoro-2,2-dinitroethoxide ion in the equilibria. The course of the reaction is influenced by the reactivity of the acceptor. The most reactive acceptor used in this work, dimethyl acetylenedicarboxylate, gave only ethers, whereas ethyl propiolate gave addition with deformylation as well, and the olefinic acceptors gave only deformylation products. Nonaqueous pyridine-catalyzed reactions gave no evidence of deformylation, and yielded ethers with the more reactive acceptors only.

Experimental Section

Caution.—Safety shielding should be used in work with fluorodinitro compounds. 2-Fluoro-2,2-dinitroethanol is a severe skin irritant, and contact should be avoided.

Ethyl 4-Fluoro-4,4-dinitrobutyrate.—Ethyl acrylate (2.0 g, 0.020 mol) was added dropwise with stirring over a 5-min period to a solution of 2.0 g of potassium hydroxide and 3.1 g (0.020 mol) of 2-fluoro-2,2-dinitroethanol[6] in 30 ml of water at 10–15°. After 5 min, the product was extracted with 25 ml of methylene chloride and distilled to give 2.5 g (56% yield) of ethyl 4-fluoro-4,4-dinitrobutyrate, bp 67–68° (0.1 mm), n^{25}D 1.4280.

Anal. Calcd for $C_6H_9FN_2O_6$: C, 32.1; H, 4.0; N, 12.5; F, 8.5. Found: C, 31.8; H, 3.7; N, 12.3; F, 8.3.

The proton nmr spectrum in carbon tetrachloride displayed a multiplet between δ 3.5 and 2.9 for the β-methylene, a triplet at 2.6 for the α-methylene, and a quartet at 4.2 and a triplet at 1.3 for the ethyl group. The fluorine nmr spectrum exhibited a triplet at ϕ^* 104.9, J_{HF} = 17 cps.

Methyl 4-Fluoro-4,4-dinitrobutyrate.—Triethylamine, 4.0 g (0.040 mol), was added dropwise with stirring at 28–32° to a solution of 6.24 g (0.040 mol) of 2-fluoro-2,2-dinitroethanol and 3.44 g (0.040 mol) of methyl acrylate in 50 ml of methylene chloride, and the resulting solution was allowed to stand at 25° for 7 days. The dark reaction mixture was washed with 100 ml of 1% sulfuric acid and was distilled to give 3.2 g (38% yield) of methyl 4-fluoro-4,4-dinitrobutyrate, bp 53° (0.05 mm), n^{25}D 1.4310.

Anal. Calcd for $C_5H_7N_2FO_6$: C, 28.6; H, 3.3; N, 13.3; F, 9.0. Found: C, 28.3; H, 3.6; N, 12.7; F, 9.1.

5-Fluoro-5,5-dinitro-2-pentanone.—A solution of 1.0 g of potassium hydroxide in 30 ml of water was added at 20° with stirring to a solution of 4.6 g (0.030 mol) of 2-fluoro-2,2-dinitroethanol and 2.1 g (0.030 mol) of methyl vinyl ketone in 70 ml of water. After 30 min, the product was extracted with 40 ml of methylene chloride and distilled to give 3.5 g (72% yield) of a pale yellow liquid, bp 71–72° (0.1 mm), n^{25}D 1.4355.

Anal. Calcd for $C_5H_7N_2FO_5$: C, 30.6; H, 4.6; N, 14.3; F, 9.7. Found: C, 30.3; H, 4.4; N, 14.0; F, 9.6.

The proton nmr spectrum in carbon tetrachloride consisted of a superposition of a doublet of triplets and an AB pattern at δ 2.7–3.5 for the methylenes and a singlet at 2.2 for the methyl. The fluorine spectrum exhibited a triplet (J = 15 cps) at ϕ^* 104.2.

4-Fluoro-4,4-dinitrobutyronitrile.—A solution of 1.8 g (0.045 mol) of sodium hydroxide in 20 ml of water was added at 25° with stirring to a solution of 2.1 g (0.040 mol) of acrylonitrile and 6.2 g (0.040 mol) of 2-fluoro-2,2-dinitroethanol in 40 ml of water. After 20 min, the product was extracted with 25 ml of methylene chloride and distilled to give 2.0 g (28% yield) of 4-fluoro-4,4-dinitrobutyronitrile, bp 88–89° (0.1 mm), n^{25}D 1.4440.

Anal. Calcd for $C_4H_4N_2FO_4$: C, 27.1; H, 2.3; N, 23.7; F, 10.7. Found: C, 26.7; H, 2.5; N, 23.2; F, 11.2.

The proton nmr spectrum (CCl_4 solution) showed a triplet (J = 6.3 cps) at δ 2.74 for the α-methylene and a doublet of triplets (J_{HF} = 18 cps, J_{HH} = 6.3 cps) at 3.18 for the β-methylene.

Ethyl β-(2-Fluoro-2,2-dinitroethoxy)acrylate.—To a solution of 15.8 g (0.20 mol) of pyridine in 150 ml of methylene chloride was added dropwise with stirring at 5–7° a mixture of 15.4 g (0.10 mol) of 2-fluoro-2,2-dinitroethanol and 9.8 g (0.10 mol) of ethyl propiolate. The reaction mixture was allowed to stand at room temperature for 18 hr and the resulting black solution was washed with a cold solution of 22 g of sulfuric acid in 120 ml of water. Removal of the solvent and molecular distillation of the residue at 98–101° (0.025 mm) gave 19.2 g (76% yield) of colorless liquid, $n^{25}D$ 1.4575.

Anal. Calcd for $C_7H_9N_2FO_7$: C, 33.3; H, 3.6; N, 11.1; F, 7.5. Found: C, 33.3; H, 3.8; N, 10.9; F, 7.5.

The nmr spectra ($CDCl_3$ solution) were consistent with a 5.3:1 ratio of *trans*- to *cis*-ethyl β-(2-fluoro-2,2-dinitroethoxy)acrylate. The proton spectrum showed a triplet at δ 1.2 and quartets at 4.30 (*trans*) and 4.25 (*cis*) for the ethoxy groups, overlapping doublets (J_{HF} = 16.4 cps) at 5.3 for the fluorodinitroethoxy groups, *trans* olefinic doublets (J_{HH} = 12.6 cps) at 7.7 and 5.6, and *cis* olefinic doublets (J_{HH} = 7.5 cps) at 6.8 and 5.07. The fluorine spectrum showed a triplet (J = 16 cps) at ϕ^* 109.4.

When this reaction was carried out in aqueous solution, a mixture of ethyl 4-fluoro-4,4-dinitrocrotonate and ethyl β-(2-fluoro-2,2-dinitroethoxy)acrylate was obtained. A mixture of 7.7 g (0.050 mol) of 2-fluoro-2,2-dinitroethanol and 4.9 g (0.050 mol) of ethyl propiolate was added dropwise with stirring over a period of 10 min at 0–5° to a solution of 2.4 g (0.060 mol) of sodium hydroxide in 100 ml of water. The reaction mixture was kept at 0–3° for 1.5 hr, and at 18–20° for 45 min. Extraction with 50 ml of methylene chloride and distillation gave 1.2 g of ethyl 4-fluoro-4,4-dinitrocrotonate, bp 66–69° (0.05 mm), $n^{25}D$ 1.4480, and 1.5 g of ethyl β-(2-fluoro-2,2-dinitroethoxy)acrylate, bp 95–100° (0.025 mm) (in a molecular still), $n^{25}D$ 1.4570.

Ethyl 4-Fluoro-4,4-dinitrocrotonate.—Fluorodinitromethane[5] (5.0 g 0.04 mol) was added, with stirring, to a solution of 1.0 g of sodium hydroxide and 3.33 g (0.035 mol) of ethyl propiolate in 50 ml of water at 0–5°. After 45 min a cold solution of 2.0 g of sodium hydroxide in 20 ml of water was added and the mixture was stirred for an additional 45 min. The product was extracted with 35 ml of methylene chloride and distilled to give 2.0 g (26% yield) of colorless liquid, bp 65–66° (0.1 mm), $n^{25}D$ 1.4481.

Anal. Calcd for $C_6H_7N_2FO_6$: C, 32.9; H, 3.2; N, 12.6; F, 8.6. Found: C, 32.5; H, 2.9; N, 12.3; F, 8.9.

The infrared spectrum showed absorption peaks at 3.20 (vw), 3.31 (w), 3.40 (w), 5.77 (s), 6.20 (s), 6.80 (w), 6.90 (w), 7.09 (m), 7.20 (m), 7.60 (s), 8.05 (s), 8.36 (s), 9.40 (m), 9.77 (m), 10.25 (w), 11.27 (w), 12.10 (w), 12.40 (w), and 12.60 (m).

Nmr spectra (no solvent) indicated a 1:2.5 ratio of *trans* to *cis* isomers. The fluorine spectrum showed a doublet (J = 18 cps) at ϕ^* 109 for the *trans* isomer and a broadened peak at ϕ^* 93 for the *cis* isomer. The proton spectrum showed for the *trans* isomer, a quartet (J = 7.3 cps) at δ 4.34 for the methylene, a triplet at 1.35 for the methyl, and a doublet of doublets (J_{HH} = 15.6 cps, J_{HF} = 18 cps) at 7.3 for the β-olefinic hydrogen. The α-olefinic hydrogens and both olefinic hydrogens of the *cis* isomer overlapped at δ 6.5–7.05. The *cis* isomer methylene appeared as a triplet (J = 7.3 cps) at 4.33, and the methyl appeared at 1.35.

Dimethyl 2-Fluoro-2,2-dinitroethoxyfumarate.—A mixture of 7.7 g (0.050 mol) of 2-fluoro-2,2-dinitroethanol and 7.1 g (0.050 mol) of dimethyl acetylenedicarboxylate was added dropwise at 3–5° over a 15 min period with stirring to a solution of 7.9 g (0.10 mol) of pyridine in 75 ml of methylene chloride. The mixture was kept at 0–5° for an additional 60 min and then was washed with a cold solution of 11 g of sulfuric acid in 50 ml of water. The methylene chloride solution was dried and stripped of solvent. Molecular distillation at 100–105° (0.05 mm) gave 13.0 g (88% yield) of an oil which solidified at room temperature, mp 42–44°.

Anal. Calcd for $C_8H_9N_2FO_9$: C, 32.4; H, 3.0; N, 9.4; F, 6.4. Found: C, 32.1; H, 3.1; N, 9.2; F, 6.4.

The infrared spectrum showed the following peaks: 3.24 (w), 3.34 (w), 3.39 (w), 3.45 (w), 4.01 (w), 5.80 (s), 6.1 (m), 6.22 (s), 6.98 (s), 7.5 (m), 7.6 (m), 7.88 (m), 8.9 (s), 9.08 (s), 10.0 (w), 10.4 (m), 11.82 (m), and 12.6 (s). The proton nmr spectrum ($CDCl_3$ solution) exhibited methoxy singlets at δ 3.75 and 3.85, a doublet at 5.3 (J_{HF} = 17 cps) for the methylene, and a singlet at 6.41 for the methine. The fluorine spectrum showed a triplet (J = 17 cps) at ϕ^* 111.5.

Dimethyl 2-Fluoro-2,2-dinitroethoxyfumarate and Dimethyl 2-Fluoro-2,2-dinitroethoxymaleate.—To a solution of 5.0 g (0.125 mol) of sodium hydroxide in 150 ml of water were added, at 0–5°, 15.4 g (0.10 mol) of 2-fluoro-2,2-dinitroethanol and 14.2 g (0.10 mol) of dimethyl acetylenedicarboxylate. The reaction mixture was stirred at ambient temperature for 4 hr, while 10% sodium hydroxide was added periodically to maintain pH 9–11. The product was extracted with 70 ml of methylene chloride, dried over sodium sulfate, and distilled to give 3.2 g (11% yield) of a colorless liquid, bp 128–130° (0.2 mm), $n^{25}D$ 1.4595.

Anal. Calcd for $C_8H_9N_2FO_9$: C, 32.4; H, 3.0; N, 9.4; F, 6.4. Found: C, 31.8; H, 2.8; N, 9.6; F, 5.8.

The proton nmr spectrum ($CDCl_3$ solution) was consistent with a 3:1 ratio of dimethyl 2-fluoro-2,2-dinitroethoxyfumarate to maleate. The latter showed a $FC(NO_2)CH_2$ doublet at δ 5.2, a broadened singlet at 5.6 for the olefinic proton, and a singlet at 3.8 for the methoxy group. The fluorine spectrum showed a triplet (J_{HF} = 16 cps) at ϕ^* 109.8. The distillation residue consisted of 10 g of viscous oil, with the elemental analysis identical with that of the distilled material. The fluorine nmr spectrum showed a multiplet at ϕ^* 110.5 and the proton spectrum showed superimposed doublets at δ 4.8 and multiplets at 3.7–3.9.

Ethyl 4,4-Dinitro-2-pentenoate.—A solution of 4.4 g (0.11 mol) of sodium hydroxide in 30 ml of water was added dropwise with stirring at 10° to a suspension of 12.0 g (0.10 mol) of 1,1-dinitroethane and 4.9 g (0.050 mol) of ethyl propiolate in 90 ml of water. After 18 hr at ambient temperature, the product was extracted with 20 ml of methylene chloride and was distilled to give 1.8 g (16.5% yield) of a pale yellow viscous oil, bp 88–89° (0.1 mm), $n^{25}D$ 1.4670.

Anal. Calcd for $C_7H_{10}N_2O_6$: C, 38.5; H, 4.6; N, 12.8. Found: C, 38.2; H, 4.4; N, 12.3.

The nmr spectrum (CCl_4 solution) was consistent with a 3:1 ratio of *cis*- to *trans*- ethyl 4,4-dinitro-2-pentenoate. The olefinic protons appeared as pairs of doublets at δ 7.28 and 6.37 (J = 15.8 cps) for the *trans* isomer and at 6.92 and 6.27 (J = 12.3 cps) for the *cis*- isomer. The ethoxy groups showed quartets at 4.17, J = 7.1 cps (*cis*), and 4.24, J = 7.1 cps (*trans*), and triplets at 1.25 (*cis*) and 1.29 (*trans*). Singlets at 2.42 (*cis*) and 2.37 (*trans*) were assigned to $CH_3C(NO_2)_2$.

Ethyl β-(2,2-Dinitropropoxy)acrylate.—Pyridine (5.0 g) was added at 22–25° dropwise with stirring to a solution of 7.5 g (0.050 mol) of 2,2-dinitropropanol and 4.9 g (0.050 mol) of ethyl propiolate in 60 ml of methylene chloride, and the reaction mixture was allowed to stand at ambient temperature for 18 hr. The solution was washed with 150 ml of 8% aqueous sulfuric acid, and the solvent was removed. Molecular distillation at 115–120° (0.025–0.05 mm) gave 9.8 g (79% yield) of light yellow liquid, $n^{25}D$ 1.4750.

Anal. Calcd for $C_8H_{12}N_2O_7$: C, 38.7; H, 4.8; N, 11.3. Found: C, 38.6; H, 4.9; N, 11.2.

The nmr spectrum (CCl_4 solution) indicated a 3.4:1 ratio of *trans* to *cis* isomers. The ethoxy methyl groups appeared as overlapping triplets at δ 1.23, and the ethoxy methylenes showed quartets at 4.11 (J = 7.0 cps) for *trans* and 4.06 (J = 7.2 cps) for *cis*. The $CH_3C(NO_2)_2$ signals overlapped at δ 2.28 and singlets at 4.81 (*trans*) and 4.90 (*cis*) were assigned to $-CH_2-C(NO_2)_2-$. Doublets at δ 6.62 (J = 6.9 cps), 4.92 (J = 6.9 cps), 5.41 (J = 12.4 cps), and 7.53 (J = 12.4 cps) were assigned to the *cis*-α-, *cis*-β-, *trans*-α-, and *trans*-β-olefinic protons, respectively.

Registry No.—2-Fluoro-2,2-dinitroethanol, 17003-75-7; 2,2-dinitropropanol, 918-52-5; ethyl 4-fluoro-4,4-dinitrobutyrate, 21823-62-1; methyl 4-fluoro-4,4-dinitrobutyrate, 15895-14-4; 5-fluoro-5,5-dinitro-2-pentanone, 21850-68-0; 4-fluoro-4,4-dinitrobutyronitrile, 21823-64-3; *trans*-ethyl β-(2-fluoro-2,2-dinitroethoxy)acrylate, 21823-96-1; *cis*-ethyl β-(2-fluoro-2,2-dinitroethoxy)acrylate, 21823-97-2; *trans*-ethyl 4-fluoro-4,4-dinitrocrotonate, 21823-98-3; *cis*-ethyl 4-fluoro-4,4-dinitrocrotonate, 21823-99-4; dimethyl 2-fluoro-2,2-dinitroethoxyfumarate, 21824-00-0; dimethyl 2-fluoro-2,2-dinitroethoxymaleate, 21824-01-1; *cis*-ethyl 4,4-dinitro-2-pentenoate, 21824-02-2; *trans*-ethyl

4,4-dinitro-2-pentenoate, 21824-03-3; *trans*-ethyl β-(2,2-dinitropropoxy)acrylate, 21824-04-4; *cis*-ethyl β-(2,2-dinitropropoxy)acrylate, 21824-05-5.

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Homogeneous Hydrogenation of Diolefins Catalyzed by Tricarbonyl Chromium Complexes. I. Stereoselective 1,4 Addition of Hydrogen[1]

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Arene–$Cr(CO)_3$ complexes catalyze selectively the homogeneous hydrogenation of conjugated dienes by 1,4 addition to give predominantly *cis* monoenes. With 1,4-dienes, conjugation to the 1,3-dienes precedes addition. With *cis*-1,3-dienes, isomerization by a 1,5-hydrogen shift during hydrogenation is indicated. Reduction rates are decreased by methyl substituents on C-1 and C-4 of the 1,3-diene system. Although 1,5-hexadiene is not reduced or isomerized, 1,5-cyclooctadiene is readily isomerized to 1,4- and 1,3-dienes and reduced to cyclooctene. Kinetic studies with computer simulation techniques show that, in a mixture, 1,3-cyclohexadiene is reduced twice as fast as 1,4-cyclohexadiene with methyl benzoate–$Cr(CO)_3$. A mixture of conjugated methyl linoleate (9,11- and 10,12-octadecadiene) is reduced 22 times faster than methyl linoleate (9,12-diene). The arene–$Cr(CO)_3$ catalysts are highly stereoselective for *trans,trans*-conjugated dienes (relative rates: *cis,cis*, 1.0; *cis,trans*, 8.0; and *trans,trans*, 25). The mechanism advanced for conjugate addition involves $H_2Cr(CO)_3$ and its 1,3-diene adduct, which undergoes 1,4-hydrogen insertion across a cisoid 1,3-diene system.

Several organometallic and metal coordination compounds are now recognized for their catalytic activity in addition and transfer reactions of hydrogen with mono- and polyolefins in solution.[3] Iron pentacarbonyl is an effective homogeneous catalyst for the hydrogenation[4] and isomerization[5] of olefinic compounds. It forms stable and isolable π complexes with diene and triene fatty esters.[6,7] These complexes are useful reaction intermediates in studies of homogeneous catalysis.[8]

Our previous work has shown that olefin–$Fe(CO)_3$ complexes catalyze the hydrogenation of methyl sorbate (*trans*-2,*trans*-4-hexadienoate) to a mixture of methyl 2,3,4-hexenoate, as well as to methyl hexanoate.[9] By contrast, arene–$Cr(CO)_3$ complexes catalyze selectively the hydrogenation of methyl sorbate to methyl 3-hexenoate in yields of 90–99%.[10] Changing substituents in both substituted complexes, butadiene–$Fe(CO)_3$ and arene–$Cr(CO)_3$, modifies the order of catalytic activity, but the selectivity remains essentially the same. The order of catalytic activity of various carbonyl complexes of Cr, Mo, and W was related to thermal stability of the complexes during hydrogenation.[11] With mesitylene–$M(CO)_3$ complexes, for example, activity varied in the order Mo > W > Cr, and selectivity in the order Cr > Mo > W.

In a preliminary communication,[12] we have shown by deuterium tracer studies that the reduction of methyl sorbate catalyzed by methyl benzoate–$Cr(CO)_3$ proceeds by 1,4 addition. A catalytic mechanism was postulated (Scheme I) in which the active complex intermediates included chromium tricarbonyl (**1**), its dideuteride (**2**) as well as its dihydride (**2a**), and the dideuteride chromium tricarbonyl diene adduct (**3**) as well as its corresponding dihydride (**3a**). This paper reports details of this catalytic reaction with various diolefins. The kinetics of competitive hydrogenation and catalytic isomerization were also examined to elucidate the mechanism further.

Results and Discussion

Diene Hydrocarbons.—Generally, methyl benzoate–$Cr(CO)_3$ was used in this work because its activity and thermal stability were high under the conditions of hydrogenation (160–175°). Although benzene–$Cr(CO)_3$ is less active than methyl benzoate–$Cr(CO)_3$, cycloheptatriene–$Cr(CO)_3$ is more active, but its thermal lability limits its use to lower temperatures (100–125°). Data in Table I are from hydrogenation with methyl benzoate–$Cr(CO)_3$ and hexadiene isomers. Conjugated hexadienes were most rapidly and completely reduced at 160° to the 1,4-addition monoenes as main products. On the other hand, under the same conditions, 1,4-hexadiene was very slowly reduced. Raising the temperature from 160 to 175° resulted in 77% reduction to a mixture of 2- and 3-hexenes as main products. Since

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