appeared. Nmr analysis of the reaction mixture and integration of the spectrum indicated a composition consisting of 32.7 mol % of methanesulfonyl chloride, 2.0 mol % of unchanged methanesulfinyl chloride, 61.3 mol % of acetyl chloride, 1.4 mol % of acetic anhydride, and 2.0 mol % of acetic acid. The results suggested some loss of chlorine and some diffusion of moisture into the mixture during the period of standing.

Although the reaction was slow in going to completion an attempt to separate, as quickly as possible, excess chlorine from a mixture of sulfinyl chloride and acetic anhydride resulted in forming an appreciable amount of sulfonyl chloride. Chlorine (9.0 g, 0.127 mol) was dissolved in a mixture of methanesulfinyl chloride (9.9 g 0.1 mol) and acetic anhydride (10.2 g, 0.1 mol) held at a temperature below −20°. The mixture was quickly transferred to a distilling apparatus and subjected to the reduced pressure (15 mm) of a water pump. At first the pot temperature dropped from −20 to −30° as the chlorine vaporized. Gentle heat was applied and when the pot temperature reached 10° the colorless residue was removed and a sample was taken for nmr analysis. Although the nmr spectrum of the original mixture had shown only two peaks, characteristic of methanesulfinyl chloride and acetic anhydride, the final mixture showed four peaks: δ 3.64 (CH$_3$SO$_2$Cl), 3.33 (CH$_3$SOCl), 2.64 (CH$_3$COCl), and 2.17 ppm ((CH$_3$CO)$_2$O.[7] Integration indicated that 8% of the methanesulfinyl chloride had been converted into the sulfonyl chloride.

The Preparation of Ethanesulfinyl Chloride.—Employing a procedure similar to that described for methanesulfinyl chloride, a mixture of ethyl disulfide (12.2 g, 0.1 mol) and acetic anhydride (20.4 g, 0.2 mol) was chlorinated to the greenish yellow of excess chlorine and then distilled at reduced pressure. When the excess chlorine had been removed the remaining liquid was completely colorless. Removal of acetyl chloride and distillation gave 19.5 g (86% yield) of faintly colored ethanesulfinyl chloride boiling 66–67.5° (27 mm) and having n^{30}D 1.4903 (lit.[3] n^{25}D 1.4954). The acetyl chloride collected weighed 31.5 g (Calcd 31.4 g) and was yellow from excess chlorine. Addition of cyclohexene readily discharged the color.

The Preparation of Butanesulfinyl Chloride.—A mixture of n-butyl disulfide (17.7 g, 0.1 mol) and acetic anhydride (20.4 g, 0.2 mol) was chlorinated at −10° to a faint color of excess chlorine. Heating under reduced pressure until the pot temperature reached 50° gave a faintly colored product which had n^{31}D 1.477 (lit.[2] n^{25}D 1.4849). The nmr spectrum showed a small peak indicating the presence of acetyl chloride. Reheating to a pot temperature of 95° (25 mm) caused further darkening of the product but the nmr spectrum showed no peak for acetyl chloride. The yield after the second heating was 26.2 g (93%).

The Preparation of Benzenesulfinyl Chloride.—A mixture of freshly recrystallized phenyl disulfide (21.8 g, 0.1 mol) and acetic anhydride (20.4 g, 0.2 mol) was cooled to −10° and chlorinated. Although the disulfide did not dissolve in the anhydride, chlorination converted it rapidly into the sulfenyl chloride and caused the mixture to liquefy. The reaction mixture never became completely colorless as more chlorine was added but addition was terminated when a greenish yellow color indicated an excess of chlorine. After removing the acetyl chloride and excess chlorine at reduced pressure the residue in the pot was heated to 50° (15 mm) and held at this temperature until boiling ceased. The pale amber product (32.0 g, theoretical yield 32.4 g) had n^{30}D 1.600 (lit.[3] n^{25}D 1.6062) and readily solidified when stored in Dry Ice. A portion, frozen in a capillary, melted at ca. 2°.

In an early experiment, after removing the acetyl chloride at reduced pressure, the residue was heated to 135° (15 mm) but no benzenesulfinyl chloride would distil. The contents of the pot began to darken and further heating was discontinued because a previous attempt to distil p-toluenesulfinyl chloride in our laboratory had led to an explosion.

Registry No.—Methanesulfinyl chloride, 676-85-7; ethanesulfinyl chloride, 1718-44-1; butanesulfinyl chloride, 13455-88-4; benzenesulfinyl chloride, 4972-29-6.

(7) The nmr spectra were recorded on a Varian A60 nmr spectrometer.

Michael-Type Additions with 2,2-Dimethyl-1,3-dinitropropane

HENRY FEUER, ADEL F. HALASA, AND MELVIN AUERBACH
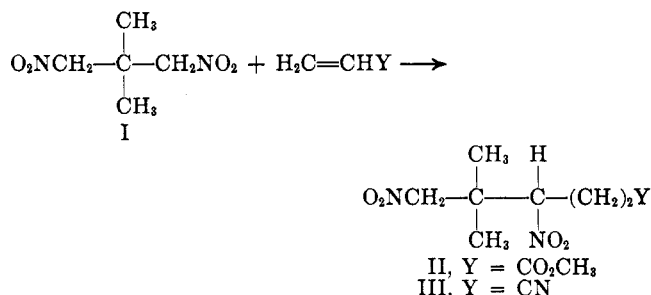
Department of Chemistry, Purdue University, Lafayette, Indiana 47907

The Michael-type reaction of α,ω-dinitroalkanes with compounds containing activated double bonds has been found to afford exclusively di- or tetra-adducts.[1–4] On the other hand, Michael additions with 2,2-dimethyl-1,3-dinitropropane (I) led to mono- and diadducts depending on the acceptors and reaction conditions.

The reaction of compound I with such acceptors as methyl acrylate and acrylonitrile afforded only the monoadducts methyl 4,6-dinitro-5,5-dimethylhexanoate (II) and 4,6-dinitro-5,5-dimethylhexanenitrile (III), respectively. The identity of compounds II and III was established by infrared and nmr spectra and by correct elemental analyses.
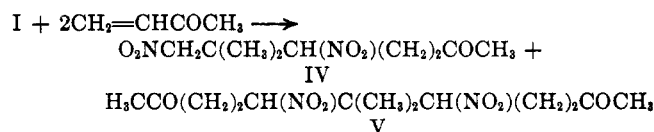
Compounds II and III were the only products obtained when I and a large excess of the acceptors were employed in such solvents as ethanol or THF at 40–45° in the presence of catalytic amounts of base and when reaction times were extended up to 72 hr.

$$O_2NCH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2NO_2 + H_2C=CHY \longrightarrow$$
$$I$$

$$O_2NCH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}}-(CH_2)_2Y$$

II, Y = CO$_2$CH$_3$
III, Y = CN

The reaction of I with 2 equiv of methyl vinyl ketone in 95% ethanol in the presence of catalytic amounts of sodium hydroxide at 40–45° for 36–48 hr gave a mixture consisting of about 40% monoadduct, 5,7-dinitro-6,6-dimethyl-2-heptanone (IV), and 10% diadduct, 5,7-dinitro-6,6-dimethyl-2,10-undecanedione (V).

Only compound IV was obtained in 48% yield when THF was employed as the solvent under otherwise similar reaction conditions.

The addition of I to 4 equiv of methyl vinyl ketone (95% ethanol, sodium hydroxide) produced, after 24 hr, only monoadduct IV and, after 48 hr, only diadduct V. The latter was also obtained when compound IV was treated with methyl vinyl ketone.

I + 2CH$_2$=CHCOCH$_3$ ⟶
   O$_2$NCH$_2$C(CH$_3$)$_2$CH(NO$_2$)(CH$_2$)$_2$COCH$_3$ +
                      IV
   H$_3$CCO(CH$_2$)$_2$CH(NO$_2$)C(CH$_3$)$_2$CH(NO$_2$)(CH$_2$)$_2$COCH$_3$
                      V

(1) H. Feuer and C. N. Aquilar, *J. Org. Chem.*, **16**, 161 (1951).

(2) H. Feuer and R. Harmetz, *ibid.*, **26**, 1061 (1961).

(3) For a general discussion of Michael reactions reference is made to E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

(4) For a thorough survey of Michael reactions concerning polynitro compounds, see P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **64**, 19 (1964).

TABLE I

NMR SPECTRA OF *dl*-5,7-DINITRO-6,6-DIMETHYL-2,10-UNDECANEDIONE (Va), *meso*-5,7-DINITRO-6,6-DIMETHYL-2,10-UNDECANEDIONE (Vb), AND THEIR DISEMICARBAZONES (VIa AND VIb)[a]

Compd	CH₃	CH₂-CH₂	CHNO₂	(CH₃)₂	NH	NH₂
Va[b]	2.10 s (6)[d]	2.40 m (8)	4.50 t (2)	1.20 s (6)		
Vb[b]	2.10 s (6)	2.40 m (8)	4.50 t (2)	1.20 d (6)		
VIa[c]	1.80 s (6)	2.20 s (8)[e]	4.60 t (2)	1.10 s (6)	3.30 s (2)	6.20 s (4)
VIb[c]	1.80 s (6)	2.20 s (8)	4.65 t (2)	1.10 d (6)	3.30 s (2)	6.20 s (4)

[a] In parts per million (ppm); multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet. [b] In deuterated chloroform. [c] In deuterated dimethyl sulfoxide. [d] Proton area. [e] The singlet was rather broad, probably due to the effect of exchange on spin–spin multiplets: J. N. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution in NMR Spectroscopy," Vol. 1, Pergamon Press Ltd., Oxford, England, 1965, p 488.

The structure of compounds IV and V was ascertained by elemental analysis, infrared and nmr spectra, and by conversion into the corresponding semicarbazone derivatives which in their turn analyzed correctly. The symmetrical structure of the diadduct was established by the fact that it was separated by fractional recrystallization with absolute ethanol into its *dl* form Va (mp 81–82°) and *meso* form Vb (mp 94–95°), the infrared spectra of which were practically superimposable. Their respective semicarbazones VIa and VIb were prepared and found to differ in melting points; however, the infrared spectra of VIa and VIb were superimposable.

Additional evidence of the diastereomeric relationship of Va and Vb was derived from their nmr spectra which were very similar (see Table I) except for the signal of the *gem*-dimethyl group. This appeared as a singlet in Va and as a doublet in Vb. The difference in this signal was also apparent in the nmr spectra of the semicarbazones VIa and VIb. The unexpected nonequivalence of the two methyl groups in Va and Vb is a consequence of the restricted rotation of these groups adjacent to an asymmetric center.[5] In the *meso* compound each of the methyl groups has a different environment, while in the racemic mixture they are equivalent. Therefore, it can be stated that Vb has the *meso* configuration and that Va constitutes the racemic mixture.

The *meso* compound Vb was partially isomerized to Va on treatment with base and subsequent acidification. The nmr spectrum showed three signals of the methyl group in the 1.1–1.3-ppm range as one would expect from a mixture of Va and Vb. Also the infrared spectrum of the mixture was essentially superimposable with that of Va and Vb.

Experimental Section

Methyl 4,6-Dinitro-5,5-dimethylhexanoate (II).—A solution consisting of 2,2-dimethyl-1,3-dinitropropane[6] (I) (16.20 g, 0.1 mol) in 200 ml of anhydrous THF and 8 ml of "Triton B" was cooled to 5° and methyl acrylate (26.0 g, 0.30 mol) was added over a period of 15 min. The reaction mixture was stirred for 48 hr at 40–45° and then acidified with glacial acetic acid. Evaporating the solvent *in vacuo*, dissolving the oily residue in isopropyl ether and cooling to −70° gave 14.5 g (63% conversion; 91% yield) of crude II. Four recrystallizations from isopropyl ether gave analytically pure II: mp 70–71°; λ$_{max}^{Nujol}$ 5.80 (carbonyl), 6.45 and 7.30 μ (nitro); nmr 3.73 (OCH₃, singlet), 2.35 ((CH₂)₂, multiplet), 4.71 (CHNO₂, triplet), 4.50 (CH₂NO₂, singlet), and 1.30 ppm ((CH₃)₂, singlet).

Anal. Calcd for C₉H₁₆O₆N₂: C, 43.54; H, 6.50; N, 11.29. Found: C, 43.81; H, 6.60; N, 11.18.

Evaporating the combined mother liquors *in vacuo* and distilling the remaining oil at 35–40° (0.3–0.4 mm) gave 6 g (37% recovery) of I. (The distillation was carried out in a sublimator and I was collected as a solid on the cold finger.)

4,6-Dinitro-5,5-dimethylhexanenitrile (III).—A solution containing compound I (16.20 g, 0.1 mol), 150 ml of anhydrous THF, and 2 ml of "Triton B" was cooled to −10° and freshly distilled acrylonitrile (15.9 g, 0.3 mol) was added in 20 min. Then the reaction mixture was warmed to 40–45° and stirred for 48 hr. Evaporating the solvent *in vacuo*, washing the remaining oil with water, taking up the organic layer in ether and drying over anhydrous magnesium sulfate gave, after removing the ether *in vacuo*, an oil Distilling the oil at 35–40° (0.2–0.3 mm) gave 14.0 g (86% yield) of unreacted I which had collected on the cold finger used as a trap.

Dissolving the residue in ether, decolorizing with "Darco," adding enough acetone to the filtrate to obtain a homogeneous solution, and cooling gave, after recrystallization with diisopropyl ether, pure III (2.0 g, 14% conversion, 71% yield): mp 59–61°; λ$_{max}^{Nujol}$ 4.60 (nitrile), 6.45 and 7.30 μ (nitro); nmr 2.50 ((CH₂)₂, multiplet), 4.50 (CH₂NO₂, singlet), 4.85 (CHNO₂, triplet), and 1.30 ppm ((CH₃)₂, singlet).

Anal. Calcd for C₈H₁₃O₄N₃: C, 44.64; H, 6.09; N, 19.53. Found: C, 44.87; H, 6.06; N, 19.48.

5,7-Dinitro-6,6-dimethyl-2-heptanone (IV).—To compound I (8.10 g, 0.05 mol) dissolved in 100 ml of anhydrous THF were added at 0.5° with stirring ten drops of 20% sodium hydroxide and then methyl vinyl ketone (14.0 g, 0.2 mol). The reaction mixture was allowed to stir for 2 hr at this temperature and then at 40–45° for 48 hr. Evaporating the solvent *in vacuo*, dissolving the residue in isopropyl ether and subsequent cooling to about −50° afforded 5.9 g (48% yield) of compound IV, mp 55–58°. Three recrystallizations from isopropyl ether gave the analytical sample: mp 59–60°; λ$_{max}^{Nujol}$ 5.80 (carbonyl), 6.45 and 7.30 μ (nitro); nmr, 2.25 (CH₃, singlet), 2.55 ((CH₂)₂, multiplet), 4.70 (CHNO₂, triplet), 4.60 (CH₂NO₂, singlet), and 1.35 ppm ((CH₃)₂, singlet).

Anal. Calcd for C₉H₁₆O₅N₂: C, 46.54; H, 6.94; N, 12.06. Found: C, 46.44; H, 7.07; N, 12.06.

The semicarbazone of compound IV was prepared in the usual manner.[7] A 90% yield of product was obtained which after recrystallization from absolute ethanol had mp 161–162°.

Anal. Calcd for C₁₀H₁₉O₅N₅: C, 41.52; H, 6.62; N, 24.21. Found: C, 41.53; H, 6.64; N, 24.38.

5,7-Dinitro-6,6-dimethyl-2,10-undecanedione (V). A. Employing 2,2-Dimethyl-1,3-dinitropropane (I).—Into a 500-ml erlenmeyer flask were placed 95% ethanol (160 ml), compound I (16.20 g, 0.10 mol), freshly distilled methyl vinyl ketone (28.0 g, 0.4 mol), and ten drops of 20% sodium hydroxide. Keeping the reaction mixture at −30 to −40° for 96 hr and then cooling to −70° afforded 14.0 g (46% yield) of crude *meso*-5,7-dinitro-6,6-dimethyl-2,10-undecanedione (Vb). Three recrystallizations from absolute ethanol gave analytically pure Vb: mp 95–96°; λ$_{max}^{Nujol}$ 5.78 (carbonyl), 6.45 and 7.30 μ (nitro).

Anal. Calcd for C₁₃H₂₂O₆N₂: C, 51.64; H, 7.34; N, 9.27. Found: C, 51.52; H, 7.11; N, 9.40.

Concentrating the combined mother liquors, cooling to −70°, filtering, and recrystallizing four times from absolute ethanol

(5) R. H. Bible, Jr., ["Interpretation of NMR Spectra," Plenum Press, New York, N. Y., 1965, pp 74–75] discusses possible causes of nonequivalency.

(6) H. B. Hass and J. F. Bourland, *Ind. Eng. Chem.*, **35**, 1150 (1943).

(7) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 253.

gave 6.0 g (20% yield) of analytically pure *dl*-5,7-dinitro-6,6-dimethyl-2,10-undecanedione (Va), mp 81–82°.

Anal. Found for $C_{13}H_{22}O_6N_2$: C, 51.98; H, 7.49; N, 8.86.

The disemicarbazones VIa and VIb of compounds Va and Vb were prepared in the usual manner.[7]

Compound VIa was insoluble in common organic solvents. The analytical sample, mp 209–210° dec, was obtained after washing with water, 95% ethanol, and anhydrous ether.

Anal. Calcd for $C_{15}H_{28}O_6N_8$: C, 43.26; H, 6.78; N, 26.91. Found: C, 43.53; H, 6.86; N, 26.40.

Compound VIb after recrystallization from absolute ethanol had mp 204–205° dec.

Anal. Found for $C_{15}H_{28}O_6N_8$: C, 43.72; H, 6.71; N, 26.41.

B. Employing 5,7-Dinitro-6,6-dimethyl-2-heptanone (IV).—To a solution of compound IV (2.32 g, 0.01 mol) in 50 ml of 95% ethanol was added eight drops of 20% sodium hydroxide. After cooling to 5°, freshly distilled methyl vinyl ketone (3.5 g, 0.05 mol) was added slowly with stirring. Adjusting the reaction temperature to 40–45°, stirring the reaction mixture for 24 hr, cooling to −78°, and filtering afforded 2.5 g (83% yield) of compound V, mp 92–94°.

Partial Conversion of *meso*-5,7-Dinitro-6,6-dimethyl-2,10-undecanedione (Vb) into the *dl* isomer Va.—To a solution of 1.32 g (0.02 mol) of potassium hydroxide in 50 ml of anhydrous methanol was added pure Vb (3.02 g, 0.01 mol) with stirring at 0–5°. The clear solution was stirred 1 hr at 0–10° and concentrated *in vacuo*. Dissolving the solid residue in 50 ml of water adding acetic acid (1.20 g, 0.02 mol) with stirring at 0–5°, filtering, washing the residue with water, and drying *in vacuo* gave a mixture of Va and Vb, mp 71–91°.

Chlorocarbonylation of Adamantane

I. TABUSHI, J. HAMURO, AND R. ODA

Department of Synthetic Chemistry, Kyoto University, Kyoto, Japan

In a current study of free-radical substitution of adamantane, the authors observed that in various radical halogenating conditions, the ratio of formation of 1- and 2-adamantyl radicals from the parent hydrocarbon was rather normal (3–5, with statistical correction) and was not sensitive to the hydrogen abstracting reagents employed. However, when adamantane was treated with halogen compounds of relatively large bond dissociation energies (such as CCl_4 or $CHCl_3$) in the presence of initiators, a remarkably increased selectivity was observed.[1] We now wish to report the free-radical chlorocarbonylation of adamantane to give an additional example of competitive substitution on the 1 and 2 position of adamantane. Especially, the reaction affords a very convenient preparative route to 2-adamantanecarboxylic acid (and its derivatives) which can only be obtained *via* a multistep synthesis.[2] Radical chlorocarbonylation of alkyl,[3] cycloalkyl,[3] or aralkyl[4,5] was performed photochemically or thermally

(peroxide induced) in the literature. In thermal chlorocarbonylation of adamantane, methyl 1- and 2-adamantanecarboxylates were obtained in good yield.

Adamantane was chlorocarbonylated with an equivalent molar amount of oxalyl chloride in the presence of benzoyl peroxide (Scheme I). On methanolysis of the products, methyl adamantanecarboxylates were obtained (consisted of 55% 1 and 45% 2 isomers; preparative yield 82%) which were easily separated by fractional distillation. The high yield of chlorocarbonylation and lack of cleavage product indicate that both 1- and 2-adamantyl radical are stable although the former is in nonplanar configuration. The reactivity ratio of the 1 to 2 position was calculated as 3.67 (with statistical correction) in good agreement with that of radical halogenation.[6]

Chlorocarbonylation of adamantane with fivefold excess of oxalyl chloride (as employed for paracyclophane)[5] gave on methanolysis only a small amount of the mixed (1- and 2-) monocarboxylates but also gave a mixture of the dicarboxylates in 53% yield (bp 160–170° (0.5 mm)), the major part of which was identified as dimethyl adamantane-1,3-dicarboxylate. Of interest was the chlorocarbonylation of 1-bromoadamantane (eq 1) which gave 1-chloroadamantane (*ca.* 41%) as the major product, methyl 3-chloroadamantane-1-carboxylate (*ca.* 24%) and 1,3-dichloroadamantane (*ca.* 8%) together with unidentified isomers of methyl chloro- and/or bromo adamantanecarboxylates.

Detailed description and mechanistic interpretation will be presented in a later paper.

Experimental Section

Chlorocarbonylation of Adamantane.—To a solution of 15 g of adamantane and 7.5 g of oxalyl chloride in 20 ml of chlorobenzene kept at 80–90° was added a mixture of 2.9 g of benzoyl peroxide, 7.5 g of oxalyl chloride, and 10 ml of chlorobenzene over a 3-hr period. The solution was further stirred at that temperature range for 20 hr. After cooling and addition of 50 ml of methanol, the combined solution was stirred for an additional 5 hr. Distillation gave 6.1 g of recovered adamantane (it sublimed) and 10.4 g (82% yield) of methyl adamantanecarboxylate (bp 92–97° (9 mm)) which comprised 55% of the 1 and 45% of the 2 isomer. Separation of these was accomplished by fractional distillation with a rotatory band (No. 25 plate) at 135–139.5° (25 mm); pure methyl adamantane-1-carboxylate distilled first and the pure 2 isomer distilled last. Identification of the esters was made by vpc of the esters and the corresponding carboxylic acids and by a mixture melting point determination of the 1-carboxylic acid with an authentic sample (by nmr) of the 2-carboxylate (CCl_4, TMS; τ 6.36 singlet (3 H), 7.47 broad (1 H), 7.70 broad (2 H on β position[7] and 8.17 broad (12 H)). The index of refraction for the 2-ester was $n^{28}D$ 1.4970.

Anal. Calcd for the 2-ester: H, 9.28; C, 74.23. Found: H, 9.13; C, 74.01.

The melting point of the corresponding 2-carboxylic acid was 143° (lit.[2] 143.5–144.5°).

Chlorocarbonylation of 1-Bromoadamantane.—To a solution of 1 g of 1-bromoadamantane and 0.6 g of oxalyl chloride in 5 ml of chlorobenzene kept at 80–90° was added a mixture of 0.25 g of benzoylperoxide, 0.6 g of oxalyl chloride, and 3 ml of chlorobenzene over a 1-hr period. The solution was then stirred at 80–95° for 12 hr. After cooling and addition of 30 ml of meth-

(1) I. Tabushi, J. Hamuro, and R. Oda, *J. Amer. Chem. Soc.*, **89**, 7127 (1967).

(2) H. Stetter, H. Held, and J. Mayer, *Ann. Chem.*, **658**, 151 (1962).

(3) M. S. Kharasch and H. C. Brown, *J. Amer. Chem. Soc.*, **64**, 329 (1942).

(4) M. S. Kharasch, S. S. Kane, and H. C. Brown, *ibid.*, **64**, 1621 (1942).

(5) E. Hedaya and L. M. Kyle, *J. Org. Chem.*, **32**, 197 (1967).

(6) See ref 1 and also G. W. Smith and H. D. Williams, *J. Org. Chem.*, **26**, 2207 (1961), for autoxidation and photochlorination.

(7) Nmr spectra of some 2-substituted adamantanes were reported where α and β hydrogens shifted considerably, supporting our assignment. See C. R. Fort, Jr., and P. von R. Schleyer, *ibid.*, **30**, 789 (1965).