(s, 4 H), 7.22 (br s, 10 H); λ_{max} 209 nm (log ϵ 4.38), 233 (4.46), 390 (1.70); mass spectrum m/e (rel intensity) M^+ 312 (44), 91 (100).

B. Borohydride Method. A mixture of tetramethylammonium borohydride (1.78 g), tellurium powder (1.27 g), and water (100 mL) was heated on the steam bath under nitrogen until the initially produced purple color was discharged. After cooling to room temperature, a solution of benzyl chloride (2.53 g) in EtOH (20 mL) was added slowly with stirring, air being rigorously excluded. After stirring for a further 2 h, the reaction mixture was worked up as in the above experiment to give crystalline **2** (2.56 g, 82%), mp 49–57 °C.

Photochemical Decomposition of 1. A solution of dibenzyl ditelluride (**1**, 50 mg) in $CDCl_3$ (0.5 mL) in an NMR tube was irradiated in the presence of nitrogen, using a Hanovia lamp, until no more tellurium deposited. The only detectable reaction product (by both NMR and GC) was monotelluride **2**, which was unchanged after a further 4 h of irradiation (nitrogen), as confirmed in a control reaction using crystalline **2**.

Repetition of the above irradiation of **1** in the presence of oxygen showed (by NMR) that monotelluride **2** was initially formed, but then slowly disappeared with the formation of the following products (by NMR and GC): benzaldehyde (42%), benzyl alcohol (21%), toluene[12] (21%), and 1,2-diphenylethane (7%). The relative amounts of these products were somewhat variable, and seemed dependent upon oxygen concentration.

Thermolysis of 1. Ditelluride **1** was heated at 120 °C without solvent for 10 min under nitrogen and under red lights. The dark melt was dissolved in $CDCl_3$, filtered from tellurium, and analyzed by NMR, which indicated **2** as the only product formed.

Photochemical Oxidation of 2. In a typical photooxidation in $CDCl_3$ under conditions used for **1**, the following were detected (NMR and GC) after 24 h: benzaldehyde (42%), benzyl alcohol (24%), unchanged **2** (8%), toluene[12] (4%), and 1,2-diphenylethane (5%). In another experiment using a low concentration of **2** and excess pure oxygen, only benzaldehyde (66%) and benzyl alcohol (33%) were detected. The photooxidation of **2** was done in CCl_4. The products detected were benzaldehyde (56%), benzyl alcohol (12%), dibenzyl (2%), toluene (2%), and benzyl chloride (8%).

Photochemical Oxidation of 4. A photooxidation of diselenide **4** in $CDCl_3$, using insufficient oxygen, showed the following products (NMR and GC) after 30 h: unchanged **4** (20%), benzaldehyde (25%), benzyl alcohol (14%), toluene[12] (25%), and 1,2-diphenylethane (5%).

Dibenzyltellurium Dibromide (3). From 1. A solution of **1** (0.500 g) in CCl_4 was treated in the dark with a solution of bromine in CCl_4. The reaction was monitored by NMR, and GC showed that benzyl bromide was not present. After 10 min, the black precipitate was removed by filtration and the solution concentrated to give **3** (0.340 g, 63%) as white prisms: mp 136–137 °C; NMR δ 4.60 (s, 4 h), 7.40 (m, 10 H); mass spectrum m/e (rel intensity) 389 (M − Br, 62), 91 (100). Anal. Calcd for $C_{14}H_{14}Br_2Te$: C, 35.80; H, 3.00; Br, 34.02; Te, 27.17. Found: C, 35.66; H, 2.93; Br, 34.26; Te, 27.27.

Treatment of **3** in CCl_4 with bromine gave only benzyl bromide, as shown by NMR and by GC.

From 2. A solution of bromine (0.160 g) in CCl_4 was added carefully to a solution of **2** (0.344 g) in CCl_4. After 10 min, concentration followed by crystallization (CCl_4–Et_2O) gave **3** (0.375 g, 72%), identical (IR, melting point) with material obtained from **1**.

Acknowledgment. This work was supported by the National Science Foundation through a grant (MPS 74-03279).

Registry No.—**1**, 20727-11-1; **2**, 62654-03-9; **3**, 62654-04-0; **4**, 1482-82-2; tellurium, 13494-80-9; benzyl chloride, 100-44-7; benzaldehyde, 100-52-7; benzyl alcohol, 100-51-6; toluene, 108-88-3; 1,2-diphenylethane, 103-29-7.

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Nitroacetoxylation of Isoprene

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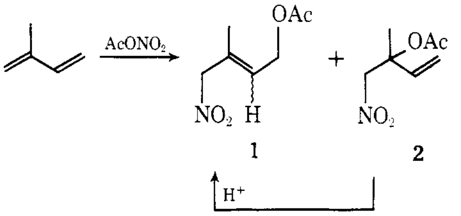
The C_5 carbon skeleton of isoprene is of fundamental importance in organic chemistry, since this basic unit is encountered in many natural products. It is therefore not surprising that numerous attempts have been made to utilize isoprene preparatively as a C_5 building block in the synthesis of naturally occurring substances such as terpenoids in general and vitamin A and carotenoids in particular.[1] In order to effectively use isoprene for these purposes, it has to be appropriately functionalized.[2] The only reaction in this regard which appears to have gained industrial importance[3] is the low-temperature addition of anhydrous hydrogen chloride. Yields of over 90% of isolated product have been reported,[4] indicating very little polymerization of starting material.

The present contribution describes a novel and preparatively efficient *bis* functionalization of isoprene: *nitroacetoxylation.* Treatment of isoprene with acetyl nitrate at room temperature leads, in a fast and highly exothermic reaction, to a virtually quantitative weight yield of an approximately 7:3 mixture of nitro acetates **1** and **2**. It appears that within the temperature range of about −20 to 30 °C the ratio of **1** to **2** is not changed substantially, although the highest content of the 1,4-addition product is observed at 25–30 °C. Complete conversion of tertiary acetate **2** into the 1,4-addition product is achieved by treating **2** in acetic acid with a catalytic amount of sulfuric acid. Moreover, subjecting the initial reaction product to rearrangement conditions results in the isolation of **1** as a 85:15 trans/cis mixture in over 80% yield.



A close formal analogy is evident between the low-temperature hydrogen chloride addition and the nitroacetoxylation reaction. Both processes appear to proceed virtually exclusively via a heterolytic pathway.[5] This is borne out by (a) the equally high regiospecificity for both the proton and nitro group introductions at C_1 of the isoprene skeleton, (b) the negligible degree of polymerization of starting material observed, and (c) the mixtures of 1,4- and 1,2-addition products obtained.[6] The predominant E configuration for nitro acetate **1** may be primarily the result of the spatial requirements of the O-acetyl and nitromethyl groups.

The novel structures thus produced appear potentially useful as C_5 synthons, especially in the area of polyolefin terpenoids. Pertinent studies are currently being carried out in this laboratory.

Experimental Section

Infrared (IR) spectra were determined as films. The superscripts s, m, and w designate strong, medium, and weak absorption bands. NMR spectra were recorded in deuteriochloroform solutions on a Varian T-60 spectrometer with tetramethylsilane as internal standard. A Hewlett-Packard Model 5720 gas chromatograph equipped with 6-ft UC-W 98 10% columns was used for GC analysis. The temperature program was set from 100 to 200 °C at 10 °C/min. *Caution: Thermal instability of acetyl nitrate has been reported.*[5b] *It is also recommended that nitro acetates* 1 *or* 2 *not be heated above 100 °C either neat or in solution.*

3-Methyl-4-nitro-2-buten-1-yl Acetate (1) and 3-Methyl-4-nitro-1-buten-3-yl Acetate (2). Nitric acid (90%, 100 g, 1.43 mol) was dropped into stirred and ice bath cooled acetic anhydride (735 g, 7.2 mol) at such a rate that the internal temperature was maintained at 20–25 °C.[7] This was followed by the dropwise addition of isoprene (68 g, 1 mol), which required 1 h and continuous cooling with an ice bath in order to maintain the internal temperature at a constant 25 °C. The reaction mixture was stirred for an additional 1 h at room temperature and worked up by quenching in ice and water and extracting with methylene chloride. Solvent and excess acetic anhydride were removed in vacuo (aspirator, then high vacuum) at ≤40 °C water bath temperature[8] to give 194.2 g of dark yellow oily residue. GC analysis indicated that besides a small amount of acetic anhydride, the crude mixture consisted essentially only of 1 and 2 in the ratio of 7:3. The *Z* isomer of 1 was estimated to be 5% of the total weight. The pure compounds *E*-1, *Z*-1, and 2 were isolated from a similar experiment via silica gel column chromatography using benzene–ethyl acetate mixtures for elution.

Nitro Ester *E*-1:[9] IR 1740^s, 1635^m, 1560^s cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.85 (broadened s, 3 H, CH$_3$), 2.05 (s, 3 H, OAc), 4.65 (d, J = 7 Hz, 2 H, OCH$_2$), 4.85 (s, 2 H, -CH$_2$NO$_2$), 5.78 (t, J = 7 Hz, 1 H, vinyl); λ_{max} (EtOH) 280 nm (ε 370); λ_{max} (0.1 N KOH) 221 nm (ε 8840), 284 (7255); MS *m/e* M$^+$ not observed, 127 (8%, M$^+$ − NO$_2$), 85 (9%, M$^+$ − NO$_2$ − CH$_3$CO), 43 (100%, CH$_3$CO).

Nitro Ester *Z*-1:[9] ^{1}H NMR (CDCl$_3$) δ 1.94 (broadened s, 3 H, CH$_3$), 2.05 (s, 3 H, OAc), 4.66 (d, J = 7 Hz, 2 H, OCH$_2$), 5.08 (s, 2 H, -CH$_2$NO$_2$), 5.83 (t, J = 7 Hz, 1 H, vinyl).

Nitro Ester 2: IR 1720^s, 1630^w, 1535^s cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.63 (s, 3 H, CH$_3$), 2.05 (s, 3 H, OAc), 4.85 (s, 2 H, CH$_2$NO$_2$), 5.25–6.0 (m, 3 H, vinyl group); λ_{max} (EtOH) 280 nm (ε 250); λ_{max} (0.1 N KOH) 231 nm (ε 10 320), 285 (6720); MS *m/e* M$^+$ not observed, 127 (23%, M$^+$ − NO$_2$), 85 (95%, M$^+$ − NO$_2$ − CH$_3$CO), 67 (100%, M$^+$ − NO$_2$ − AcOH).

Allylic Rearrangement 2 → 1. Nitro ester 2 (100 mg) was dissolved in 1 mL of a solution of 230 mg of concentrated sulfuric acid in 33.7 mL of acetic acid. After 16 h at 75 °C the reaction was quenched with ice. There was obtained 91 mg of a 7:3 *E/Z* mixture of 1 as determined by GC.

Allylic Rearrangement of a Crude Mixture of 1 and 2. The crude product (194.2 g) obtained in the experiment described above was dissolved in 450 mL of acetic acid to which had been added 7.3 g of concentrated sulfuric acid. Stirring at 75 °C overnight, quenching with ice, and extractive workup yielded 162.8 g (94%) of brown oil. For the purpose of yield determination, an aliquot (1.401 g) was evaporatively distilled[10] in a Kugelrohr apparatus [oven temperature 120–140 °C (0.5–0.8 mm)]. The light yellow distillate [1.158 g, 82% (based on isoprene)] was shown by GC analysis to be an 85:15 mixture of *E*1 and *Z*-1.

Acknowledgments. We thank the staff of our Physical Chemistry Department for the determination of the spectral data.

Registry No.—*E*-1, 62842-04-0; *Z*-1, 62842-05-1; 2, 61447-07-2; isoprene, 78-79-5; acetyl nitrate, 591-09-3.

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Carbon-13 Spectral Parameters of Some Polycyclic Hydrocarbons

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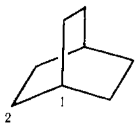
In connection with work on polycyclic hydrocarbons substituted at the bridgehead position, in particular those derived from the molecules 1–5 below, we felt it desirable to report the ^{13}C NMR spectra of the parent hydrocarbons. While chemical shifts of the carbon atoms in bicyclo[2.2.2]octane (1) and norbornane (2) have been well documented,[1,2] and the ^{13}C–H one-bond coupling constants have been reported for 2[3] and tricyclo[4.1.0.0^{2,7}]heptane (5),[4] there is a surprising lack of information on the remainder. In addition to chemical shift data, we were particularly interested in the one-bond bridgehead carbon–proton couplings. There has been considerable activity in recent years in the measurement of $'J(^{13}C–H)$, and in attempts to correlate this parameter with the s character of the carbon bonding orbital, according to the empirical relationship described by Muller and Pritchard.[5]

$$\% \text{ s} = \frac{J(^{13}C–H)}{5}$$

Although this suggested correlation has been criticized, there is good evidence that the empirical relationship holds for hydrocarbons, but is rather less tenuous when applied to molecules containing heteroatoms. ^{13}C–H coupling constants have been suggested to correlate similarly with other phenomena that are sensitive to hybridization, and hence the electronegativity of the carbon orbital, such as the pK_as of the corresponding amines and carboxylic acids,[6] as well as the acidity of the proton.[7]

The substrates 1, 2, and 4 were obtained as previously reported,[8] and 5 was obtained by known procedures.[9] Bicyclo[2.1.1]hexane (3) was synthesized from bicyclo[2.1.1]hexan-2-one by sodium cyanoborohydride reduction of the derived *p*-toluenesulfonylhydrazone.



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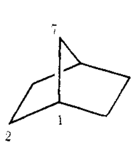

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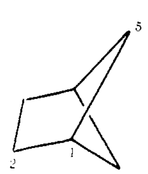

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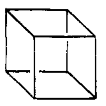

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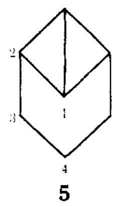

5

Table I contains the carbon-13 chemical shifts, of which the values for 1 and 2 are in excellent agreement with those recorded. For shifts previously unknown, viz., in 3, 4, and 5, assignments were made with the aid of off-resonance de-