This material was identical with authentic X prepared by standard methods.[14]

In a repeat of this experiment using a longer reaction time only a small yield (about 15%) of a colorless oil was recovered which could be distilled at 75° under 80 μ. Spectral data showed the oil to be XI: δ (CCl_4) 2.25 (3 H, singlet), 3.70 (6 H, singlet) and 6.19 (3 H, broad singlet).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 71.13; H, 7.88.

When 1.0 g (~3 mmol) of VII was treated with sodium in liquid ammonia, an ether extract yielded 470 mg of a light yellow oil which was purified over 62 grade Davison silica gel (2% $CH_3COOC_2H_5$ in hexane) to get 380 mg of a colorless oil. This oil could be distilled at 80° (100 μ). Spectral data showed the oil to be XIV: λ_{max} (MeOH) 223 nm (ε 7500) (sh), 273 (1600) and 280 (1660); δ (CCl_4) 1.35 (3 H, triplet J = 7 Hz), 2.23 (3 H, singlet), 3.70 (3 H, singlet), 3.90 (2 H, quartet, J = 7 Hz) and 6.15 (3 H, singlet).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.31; H, 8.47.

Work-up of the reaction mixture on the acid side yielded by ether extraction 370 mg of an oil which was purified by partition chromatography over 120 g of diatomaceous earth using heptane saturated with MeOH. The third and fourth holdback volumes gave 300 mg of an oil which upon distillation at 90° (100 μ) gave crystals, mp 52–53°, which proved to be XIII: λ_{max} (MeOH) 225 nm (ε 8360) (sh), 275 (1670) and 282 (1670); δ (CCl_4) 1.32 (3 H, triplet J = 7–8 Hz), 2.17 (3 H, singlet), 3.83 (2 H, quartet, J = 7–8 Hz), 5.90 (1 H, broad exchangeable singlet) and 6.08 (3 H, singlet).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.72; H, 7.83.

Hence, it may be noted that the ease of ether cleavage in V, VI, and VII is increased significantly as R_2 goes from H to CH_3 to C_2H_5.

Registry No.—V, 24741-92-2; VI, 24741-93-3; VII, 24741-94-4; VIII, 24741-95-5; IX, 24741-96-6; X, 3209-13-0; XI, 4179-19-5; XIII, 24741-99-9; XIV, 24742-00-5.

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(14) H. Walbaum and A. Rosenthal, *Ber.*, **67**, 770 (1924).

Photochemistry of Cycloalkenes. VII. Limonene[1]

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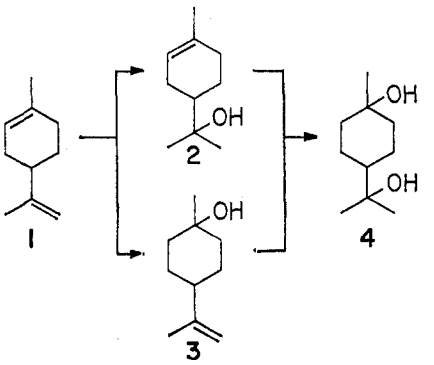
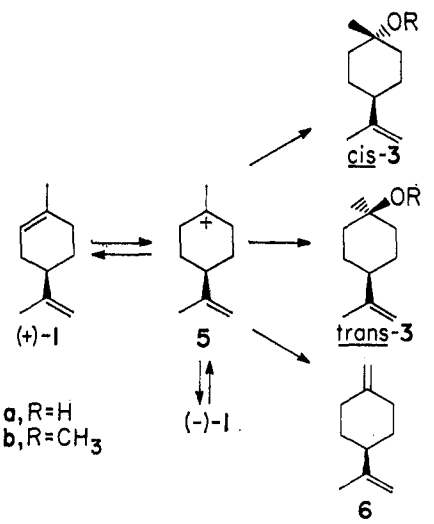
Recent studies have shown that photosensitized irradiation of cyclohexenes and -heptenes in hydroxylic solvents results in a light-initiated protonation of the olefin.[2,3] Since this behavior is specifically limited to six- and seven-membered-ring olefins, photoprotonation should afford the unique synthetic advantage of permitting the selective protonation of a cyclohexene or -heptene moiety of a complex molecule in the presence of other double bonds contained in either a larger ring or an acyclic environment.[2] This synthetic capability has now been demonstrated in the case of the diene limonene (**1**).



Acid-catalyzed hydration of limonene affords a mixture of products, including α- (**2**) and β-terpineol (**3**) and terpin (**4**), resulting from competing protonation of both double bonds.[4] In one case in which selective reaction was observed, attack occurred at the C_8–C_9 double bond to afford α-terpineol (**2**).[5] By contrast it has now been found that xylene-sensitized irradiation of (+)-limonene [(+)-**1**] in aqueous solution affords a 1.2:1 mixture of *cis*- and *trans*-β-terpineol (**3a**), respectively, as well as a small amount of the exocyclic isomer **6** with no detectable formation of the C_8–C_9 addition products α-terpineol (**2**) or terpin (**4**). Likewise, irradiation in methanolic solution affords a 1.6:1 mixture of the corresponding methyl ethers *cis*- and *trans*-**3b** as the only detectable addition products. Thus photoprotonation affords a powerful method of effecting reaction selectively at the C_1–C_2 position of limonene and, by analogy, inducing selective protonation of any cyclohexene or -heptene chromophore in the presence of an acyclic, exocyclic, or larger ring cyclic olefin.



It is of further interest to note that the recovered unreacted limonene was found to have undergone extensive racemization (84%) as would be expected for

(1) Part VI: P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **91**, 7466 (1969).

(2) P. J. Kropp and H. J. Krauss, *ibid.*, **89**, 5199 (1967).

(3) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969), and references cited therein.

(4) For a recent review of the chemistry of limonene, see J. Verghese, *Perfum. Essent. Oil Rec.*, **59**, 439 (1968).

(5) L. Kuczynski and H. Kuczynski, *Rocz. Chem.*, **25**, 432 (1951).

the reversible formation of the symmetrical carbonium ion intermediate **5**. This is further support for the previously proposed intermediacy of a free carbonium ion in the photoaddition of hydroxylic media to cyclohexenes and -heptenes.[2,3]

Experimental Section[6]

Irradiation of (+)-Limonene. A. Under Aqueous Conditions.—A solution containing 3.0 g of limonene, $[\alpha]^{22}D$ +112°, and 3.0 g of *m*-xylene in 150 ml of 50% aqueous *t*-butyl alcohol containing 1% sulfuric acid was irradiated for 2 hr. Gas chromatographic analysis revealed the continued presence of limonene (17%) and the formation of the diene 6 (2%), a 1.2:1 mixture of *cis*- and *trans*-β-terpineol (**3**, 74%), and several unidentified minor products.

The reaction mixture was neutralized with sodium hydroxide solution and the organic materials were isolated by extraction with ether in the usual fashion. Isolation by preparative gas chromatography of the first component afforded a colorless liquid, *m/e* 138, which was not further characterized but is assumed to be *p*-menth-8-ene.[7]

Isolation of the second component afforded a colorless liquid [*m/e* 136 (34), 93 (100), and 79 (57)] which exhibited an infrared spectrum identical with that of *p*-mentha-1(7),8-diene (**6**).[8] Isolation of the third component afforded recovered limonene, $[\alpha]^{30}D$ +18° (*c* 0.20, ethanol).

Isolation of the fourth component afforded ***trans*-β-terpineol** as colorless needles: mp 28–28.5° (sealed capillary); nmr spectrum τ 5.37 (s, 2, CH_2-9), 8.30 (s, CH_3-10), and 8.81 (s, CH_3-7); *m/e* 136 (52), 121 (32), 107 (32), 99 (32), 93 (60), 71 (100), 69 (41), 68 (34), and 43 (64). The infrared spectrum was identical with that reported by Mitzner, *et al.*, for "*cis*-β-terpineol"[9] and with that reported by Henbest and McElhinney for the "*trans*" isomer.[10]

Isolation of the final component afforded ***cis*-β-terpineol** as colorless needles: mp 33–34° (sealed capillary); nmr spectrum τ 5.36 (s, 2, CH_2-9), 8.31 (s, CH_3-10), and 8.79 (s, CH_3-7); *m/e* 154 (tr), 136 (84), 121 (42), 108 (28), 107 (48), 94 (19), 52 (93), 84 (20), 79 (24), 71 (100), 69 (42), 68 (29), 67 (20), 58 (20), 55 (23), and 43 (64). The infrared spectrum was identical with that reported for "*trans*-β-terpineol" by Mitzner, *et al.*,[9] and for the "*cis*" isomer by Henbest and McElhinney,[10] lit.[10] mp 36°.

B. In Methanol.—A 150-ml methanolic solution containing 3.0 g of (+)-limonene and 3.0 g of *m*-xylene was irradiated for 10 hr. Gas chromatographic analysis revealed the continued presence of limonene (6%) and the formation of *p*-mentha-1(7),8-diene (6) and the ethers *cis*- and *trans*-**3b** in yields of 39, 28, and 18%, respectively.

Isolation of the principal ether product afforded ***cis*-*p*-menth-8-en-1-yl methyl ether** as a colorless liquid: λ_{max} 6.02 and 11.22 μ; nmr spectrum τ 5.31 (s, 2, CH_2-9), 6.78 (s, 3, CH_3O–), 8.29 (s, CH_3-10), and 8.83 (s, 3, CH_3-7); *m/e* 168.1531 (calcd for $C_{11}H_{20}O$: 168.1514), 85 (100), 72 (36), 55 (64), 43 (34), and 39 (50).

Isolation of the minor ether component afforded ***trans*-*p*-menth-8-en-1-yl methyl ether** as a colorless liquid: λ_{max} 5.98 and 11.16 μ; nmr spectrum τ 5.33 (s, 2, CH_2-9), 6.85 (s, 3, CH_3O–), 8.29 (s, CH_3-10), and 8.91 (s, 3, CH_3-7); *m/e* 168.1524 (calcd for $C_{11}H_{20}O$: 168.1514), 136 (41), 93 (44), 72 (49), 69 (45), 55 (60), 43 (100), 42 (79), 41 (66), 40 (44), and 39 (52).

(6) Infrared spectra were obtained on neat samples with a Perkin-Elmer Infracord spectrophotometer. Nuclear magnetic resonance spectra were determined in chloroform-*d*$_1$ solution with a Varian HA-100 spectrometer, using tetramethylsilane as an internal standard. Gas chromatographic analyses were performed on an Aerograph 90-P instrument using 10 ft × 0.25 in. columns packed with 20% SE-30 or Carbowax 20M on 60–80 mesh Chromosorb W. Mass spectra were obtained using an Atlas Model CH-4 or SM-1 spectrometer. Irradiations were conducted using a Hanovia 450-W, medium-pressure mercury arc and a water-cooled Vycor immersion well. Vigorous stirring of the reaction mixture was effected by the introduction of a stream of nitrogen through a jet opening in the bottom of the outer jacket.

(7) Some reduction normally accompanies the photoprotonation of cyclohexenes; see J. A. Marshall and A. R. Hochstetler, *Chem. Commun.*, 296 (1968).

(8) B. M. Mitzner, E. T. Theimer, and S. K. Freeman, *Appl. Spectrosc.*, **19**, 169 (1965).

(9) B. M. Mitzner and S. Lemberg, *Amer. Perfum. Cosmet.*, **81** (3), 25 (1966); B. M. Mitzner, V. J. Mancini, S. Lemberg, and E. T. Theimer, *Appl. Spectrosc.*, **22**, 34 (1968).

(10) H. B. Henbest and R. S. McElhinney, *J. Chem. Soc.*, 1834 (1959).

Registry No.—(+)-**1**, 5989-27-5; *cis*-**3a**, 20288-25-9; *trans*-**3a**, 20288-26-0; *cis*-**3b**, 24655-71-8; *trans*-**3b**, 24655-72-9.

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Studies in the Ganglioside Series. V. Synthesis of 2-Acetamido-2-deoxy-*O*-β-D-glucopyranosyl-(1→3)-*O*-β-D-galactopyranosyl-(1→4)-D-glucose[1]

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In recent communications[2-4] we described a new, highly stable and reactive hexosaminyl bromide of type III which facilitates the synthesis of aminosaccharides. We now report the synthesis of the title compound (VI, Chart I). This trisaccharide has been isolated from hydrolysates of the polysaccharides found in human milk.[5,6] It is structurally related to the so-called "ganglio-*N*-triose-II"[7] which is inherent in the molecule of the abnormal ganglioside accumulating in brain tissue with Tay–Sachs disease.[8,9]

In an earlier report[10] we have shown that selective substitution of lactose can be achieved *via* its isopropylidene derivative I and that bromo sugars react preferentially with the equatorial C-3 hydroxyl group of the benzyl lactoside II under Koenigs–Knorr conditions.

The benzyl lactoside II, previously isolated as a viscous mass, could now be obtained in pure crystalline form. It was observed that hydrolysis of I with hot aqueous acetic acid, a method commonly employed for the removal of an isopropylidene group, was invariably accompanied by partial deacetylation. Trifluoroacetic acid was found to be more suitable. The hydrolysis is carried out in chloroform containing 10% of the reagent and is complete after 20–30 min, whereby only traces of by-products are formed. While this method was being practiced in our laboratory, Goodman[11] reported the use of 90% aqueous trifluoroacetic acid for the hydrolysis of ketals in various sugar derivatives which were, however, devoid of acetoxyl groups.

The Koenigs–Knorr reaction of II with the bromide III afforded, after column chromatography, the pure substituted trisaccharide IV. Catalytic de-*O*-acylation

(1) This work was supported by U. S. National Institutes of Health, PL 480, Agreement No. 425115.

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(4) D. Shapiro and A. J. Acher, *ibid.*, in press.

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(6) R. Kuhn, A. Gauhe, and H. H. Baer, *ibid.*, **89**, 1027 (1956).

(7) R. Kuhn and H. Wiegandt, *ibid.*, **96**, 866 (1963).

(8) L. Svennerholm, *Biochem. Biophys. Res. Commun.*, **9**, 436 (1962).

(9) L. Svennerholm, *J. Neurochem.*, **10**, 613 (1963).

(10) D. Beith-Halahmi, H. M. Flowers, and D. Shapiro, *Carbohyd. Res.*, **5**, 25 (1967).

(11) L. Goodman, *ibid.*, **7**, 510 (1968).