vs. O-alkylated product ratio of 1:1 (35%). Reaction in toluene gave **5** in 8% yield. Reaction of **5** with aqueous NaOH gave 2,4,6-trimethyl-7-carbethoxy-7-(4′-hydroxybutyl)cycloheptanone (**13**) identical (by vpc, ir, and nmr) with a genuine sample [from the base hydrolysis of 2,4,6-trimethyl-7-carbethoxy-7-(4′-acetoxybutyl)] cycloheptanone].[2]

Intramolecular Alkylation of 5.—To a suspension of 52% NaH (washed with hexane, 1.31 g, 0.028 mol) in hexamethylphosphoramide (75 ml), **5** (10 g, 0.028 mol) was added with stirring at room temperature. The resultant mixture was stirred for 24 hr at 140° to give a neutral solution which was filtered and distilled to give a mixture containing **8** and **9** in 40:60 ratio (2.94 g, 0.011 mol, 39% if only **8**, **9**): bp 130–150° (0.15 mm); ir (CCl_4) 1680 (vinyl ether), 1725 (ketone), and 1740 cm^{-1} (ester); nmr (CCl_4) τ 5.88 (2, m, $CO_2CH_2CH_3$), 6.40 (m, CH_2O), 8.33 (s, vinyl CH_3), 8.8 (t, 3, CH_2CH_3), 8.2–8.8 (m), 8.95–9.2 (m, 6, CH_3); vpc–mass spectrum (5% SE-30, 75 eV) *m/e* peak 1 (minor isomer of **8**) 280, peak 2 (major isomer of **8**) 280, peak 3 (minor isomer of **9**) 280, peak 4 (major isomer of **9**) 280, peak 5 (minor amount, **1**) 298. Preparative tlc (on silica, extracted with $CHCl_3$) gave a mixture of fractions 1–4 (**1** was left behind) which was analyzed. *Anal.* Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06. Found: C, 72.62; H, 10.03.

Decarboxylation of 8 and 9.—A mixture of lithium iodide dihydrate (4.4 g, 0.026 mol) and the above mixture of **8** and **9** (5.20 g, 0.019 mol) in dry collidine (25 ml) was heated at reflux for 30 hr. The cooled mixture was then poured into ice water (40 ml)–diethyl ether (40 ml) and carefully acidified with cold 1 *N* HCl. The resultant organic layer was then washed with 2 *N* Na_2CO_3 (30 ml) and saturated NaCl (2 × 30 ml), dried (Na_2SO_4), and distilled to give **2** and **10** in 60:40 ratio (0.7 g, 0.0034 mol, 18%): bp 75° (0.15 mm); ir (neat) 1700 cm^{-1}, no OH; nmr (CCl_4) τ 6.45 (m, CH_2O), 8.0–8.8 (m, CH_2, CH), 8.4 (s, vinyl CH_3), 8.95–9.2 (m, 6, CH_3CH); vpc–mass spectrum (5% SE-30, 70 eV) *m/e* (rel intensity) peak 1 (**10**) 208 ($M\cdot^+$, 27), 193 (25), 166 (28), 155 (38), 154 (98), 139 (98), 126 (34), 125 (48), 112 (98), 111 (100), 109 (35), 97 (40), 95 (60), 84 (42), 83 (98), 69 (98), 55 (98), $M + 1 = 16.1$ (calcd for $C_{14}H_{24}O$, $M + 1 = 15.6$),[11] peak 3 (isomer of **2**) 208 ($M\cdot^+$, 60), 193 (62), 179 (10), 165 (68), 151 (37), 139 (34), 137 (35), 126 (98), 112 (67), 111 (73), 109 (52), 95 (78), 81 (65), 69 (93), 55 (100), and similar fragmentation for peak 4 (isomer of **2**). Also obtained was a fraction consisting mainly of **1** (identical vpc, ir, and nmr with those of a genuine sample)[2] and small amounts of **2** and **10** (0.6 g, 0.0027 mol, 14% if all 1), bp 125° (0.15 mm). Peak 2 (*m/e* 208) is probably **11** (see below).

Treatment of the mixture of **2**, **10**, and **11** (0.4 g, *ca.* 0.002 mol) with 1 *N* HCl (2 ml) in methanol (5 ml) gave a mixture of **1**, **10**, and **11** (minor amount). Distillation gave 1,3,5-trimethylbicyclo[4.4.1]undecan-11-one (**10**, *ca.* 0.15 g, 0.0007 mol, 35%): bp 70° (0.15 mm); ir (film) 1700 cm^{-1}; nmr (CCl_4) τ 7.0–8.8 (m, 15), 9.02 [s, 3, bridgehead CH_3, shifted downfield by $Eu(DPM)_3$], 9.01 (d, 6, CH_3CH, $J = 7$ Hz); vpc retention time for **10** as in above sample. About 10% (by vpc area of a separate peak) of **11** was present: ir 1640 cm^{-1}; nmr τ 4–4.5, 5.05 (br d), 5.3 ($CH{=}CH_2$).[2]

Registry No—**2** (10-ene), 33015-94-0; **2** (5a-ene), 37931-56-9; **3**, 37931-57-0; **4**, 110-52-1; **5**, 37931-58-1; **8** (major isomer), 37931-59-2; **8** (minor isomer), 37931-60-5; **9** (major isomer), 37931-61-6; **9** (minor isomer), 37931-62-7; **10**, 37931-63-8.

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[11] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1963, p 37.

Communications

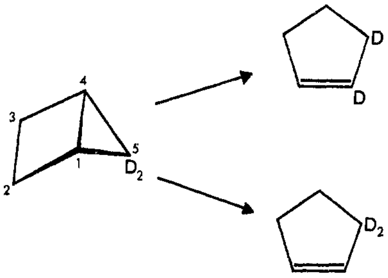
See Editorial, *J. Org. Chem.*, **38**, No. 19, 4A (1972)

Thermal Rearrangement of 5,5-Dideuteriobicyclo[2.1.0]pentane[1]

Summary: Through a deuterium-labeling study the thermal rearrangement of bicyclo[2.1.0]pentane to cyclopentene has been shown to involve a hydrogen rather than a carbon migration.

Sir: 5,5-Dideuteriobicyclo[2.1.0]pentane has been prepared and employed by Gassman, Atkins, and Lumb[2] in their investigations of the rhodium dicarbonyl chloride dimer catalyzed isomerization of that bicyclic system to cyclopentene. The rearrangement product indicated extensive scrambling of deuterium label at some stage of the reaction.

We have used this dideuterio compound to study the gas phase thermal isomerization of bicyclopentane to cyclopentene.[3-5] The results obtained provide the first experimental distinction between mechanistic options requiring C(1)–C(4) bond cleavage and C(5)–H hydrogen migration (eq 1), and others postulating C(1)–C(5) bond cleavage with C(3) carbon migration (eq 2).



(1)

(2)

Isomerizations analogous to each of these alternatives, and others consistent with either, have been observed in some acetyl- and ethoxycarbonyl-substituted bicyclopentanes.[6-9]

The deuterated substrate was prepared through reaction of cyclobutene[10] with 60% deuterated benzylmercuriiodomethane,[11] secured in turn from partially

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[1] Supported by the National Science Foundation through Grant GP-31415.

[2] P. G. Gassman, T. J. Atkins, and J. T. Lumb, *Tetrahedron Lett.*, 1643 (1971); *J. Amer. Chem. Soc.*, **94**, 7757 (1972).

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deuterated diazomethane[12] and benzylmercuric iodide in tetrahydrofuran.[11]

The 5,5-dideuteriobicyclo[2.1.0]pentane was purified through preparative glpc on a 5 m × 6 mm 20% tris(cyanoethoxy)propane on Chromosorb P column at 30°. The purified sample, shown by analytical glpc to be free (<0.2%) of cyclopentene, was pyrolyzed at 300° for 63 min to give labeled cyclopentene, which was purified by glpc and analyzed by proton nmr. The data gathered from analyses of labeled and unlabeled samples on 2 days are given in the Table I; the standard deviations given stem from averages over nine integrations.

TABLE I

INTEGRATED ABSORPTION INTENSITIES FOR CYCLOPENTENE-d_x

Run	Compd	Vinyl H	Allylic H	Methylene H
1	d_0	1.79 ± 0.06	3.73 ± 0.09	2.00 ± 0.03
1	d_2[a]	1.28 ± 0.05	3.22 ± 0.08	2.00 ± 0.02
2	d_0	1.88 ± 0.04	3.94 ± 0.07	2.00 ± 0.02
2	d_2[a]	1.34 ± 0.05	3.27 ± 1.02	2.00 ± 0.02

[a] By nmr, 14.2 atom % deuterium content.

These data indicate 1.43 ± 0.05 vinyl protons and 3.44 ± 0.06 allylic protons in the labeled product. The predicted pairs of values for cyclopentene having 14.2 atom % deuterium content would be, according to eq 1 and 2, 1.43, 3.43, and 2.00, 2.86. The rearrangement thus clearly involves a hydrogen shift from C(5), and bicyclopentane and cyclopropane may share a common mechanism for isomerization to the corresponding olefins.

Assuming a statistical distribution among d_0, d_1, and d_2 bicyclopentane molecules, calculations suggest that a k_H/k_D ratio larger than 1.5 would have given detectably different integrated absorption intensities for the cyclopentene product.

Whether the isomerization to cyclopentene is a reaction best ascribed to the stabler folded bicyclopentane molecule[13] or to the easily accessible planar closed-shell 1,3-ethano-π-cyclopropane molecule[14] is a question demanding additional work on less symmetrical analogs. Such an effort now seems justified.

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