(37), 93 (100), 92 (13), 91 (32), 83 (12), 81 (12), 79 (37), 77 (27), 67 (10), 65 (10), 57 (63), 55 (28), 53 (13), 43 (16), 41 (58), 39 (38). *Anal.* Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.07. Found: C, 88.10; H, 12.03.

exo-4-*tert*-**Butyltricyclo[3.2.0.0^{2,7}]heptane** (**11**).—The compound was collected by glc employing an XF-1150 column: ir (CCl_4) 3055, 3030, 2960, 2900, 2856, 1470, 1395, 1365, 1300, 1245, 1210, 1075, 955, 890 cm^{-1}; nmr (CCl_4) δ 0.80 (s, 9 H), 0.8–1.7 (m, 4 H), 1.7–2.15 (m, 4 H), 2.15–2.6 (m, 1 H); mass spectrum *m/e* (rel intensity) 150 (M^+, 1) 135 (2), 107 (5), 93 (6), 91 (7), 79 (9), 77 (7), 69 (9), 67 (8), 66 (100), 57 (33), 41 (20), 39 (11).

3-*tert*-**Butyltricyclo[4.1.0.0^{2,7}]heptane** (**12**).—The compound was collected by glc employing a Carbowax 20M column: ir (CCl_4) 3083, 2990, 2960, 2860, 1475, 1393, 1365, 1238, 1225, 1130, 975 cm^{-1}; nmr (CCl_4) δ 0.88 (s, 9 H, *tert*-butyl), 1.51 (t, 2 H, C-1,7) superimposed on 0.9–1.6 (broad m, 5 H), 2.36 (m, 2 H, C-2,6); mass spectrum *m/e* (rel intensity) 150 (M^+, 5) 135 (4) 107 (2), 94 (48), 93 (14), 91 (12), 79 (29), 77 (13), 57 (100), 41 (31), 39 (16). *Anal.* Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.07. Found: C, 88.08; H, 12.06.

4-*tert*-**Butyltricyclo[4.1.0.0^{2,7}]heptane** (**13**).—The compound was collected by glc employing a Carbowax 20M column: ir 3090, 2995, 2960, 2860, 1475, 1390, 1365, 1290 (d), 1240, 1175, 1135, 1060, 980 cm^{-1}; nmr (CCl_4) δ 0.78 (s, 9 H, *tert*-butyl), 1.46 (t, 2 H, C-1,7) superimposed in 0.8–1.3 (broad m, 5 H), 2.34 (m, 2 H, C-2,6); mass spectrum *m/e* (rel intensity) 150 (M^+, 12), 135 (4), 107 (9), 94 (25), 93 (18), 91 (14), 79 (28), 77 (12), 57 (100), 41 (20), 39 (15). *Anal.* Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.07. Found: C, 88.09; H, 12.09.

The nmr spectra of **12** and **13** did not change significantly when taken in chloroform, benzene, pyridine, or methanol.

3-Methyl-7,7-dibromobicyclo[4.1.0]heptane.—Commercial 4-methylcyclohexene (Eastman Kodak White Label) was found to contain 11% of isomeric impurities, mainly 3-methylcyclohexene, as shown by glc analysis on an ethylene glycol–silver nitrate column. Hence 4-methylcyclohexyl acetate was prepared and pyrolyzed[34] at 570° to give 4-methylcyclohexene in 80% yield, n^{24}D 1.4389 (lit.[34] n^{20}D 1.4414), which was shown by glc to be free of isomers.

Dropwise addition of 253 g (1 mol) of bromoform to a cold slurry (both at −15°) of 1 mol of potassium *tert*-butoxide, 29 g (0.96 mol) of 4-methylcyclohexene, and 500 ml of pentane followed by the usual work-up gave 144 g (54%) of 3-methyl-7,7-dibromobicyclo[4.1.0]heptane: bp 62–64° (0.25 mm); n^{26}D 1.5419; ir 2970, 2900, 2820, 1445, 1380, 1335, 1460 cm^{-1}. *Anal.* Calcd for $C_8H_{12}Br_2$: C, 35.85; H, 4.51; Br, 59.63. Found: C, 36.02; H, 4.59; Br, 59.68.

All attempts to crystallize this dibromide at low temperatures failed. Glc in all columns listed in footnote 31 except the last three (not tried) showed only one peak.

Reduction of the dibromide with sodium in liquid ammonia employing ether as a cosolvent followed by the usual work-up gave 3-methylbicyclo[4.1.0]heptane, collected by glc (silicone 200, to remove a 6% impurity), mass spectrum *m/e* 110 (M^+). Analysis of this material in a 60-m polyethylene glycol capillary glc column[35] showed two peaks with very close retention times in an area ratio of 43:57.

Addition of the Simmons–Smith reagent[36] to 4-methylcyclohexene gave 3-methylbicyclo[4.1.0]heptane having a mass spectrum identical with that of the sample obtained from reduction of the dibromide. Capillary column glc analysis showed the same two peaks in an area ratio of 44:56.

Registry No.—*cis*-**7**, 29339-16-0; *trans*-**7**, 29339-17-1; **8**, 29339-18-2; **9**, 29339-19-3; **10**, 29339-20-6; **11**, 29339-21-7; **12**, 29488-51-5; **13**, 29339-23-9; methyllithium, 917-54-4; 3-methyl-7,7-dibromobicyclo[4.1.0]heptane, 29339-24-0; *cis*-3-*tert*-butylbicyclo[4.1.0]heptane, 29339-25-1; *trans*-3-*tert*-butylbicyclo[4.1.0]heptane, 29339-26-2.

(34) E. Gil-Av, J. Herling, and J. Shabtai, *J. Chromatogr.*, **1**, 508 (1958).

(35) We are indebted to Dr. E. P. Blanchard, Jr., of the E. I. du Pont de Nemours and Co., Inc., for the capillary column analyses.

(36) R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

Derivatives of Bicyclobutane and Bicyclo[2.1.0]pentane. Establishment of the Structures of 3- and 4-*tert*-Butyltricyclo[4.1.0.0^{2,7}]heptane and 5- and *exo*-4-*tert*-Butyltricyclo[3.2.0.0^{2,7}]heptane[1]

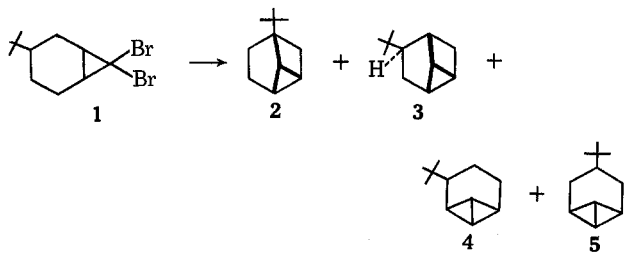
WILLIAM R. MOORE* AND BARBARA JEAN KING[2]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received November 24, 1970

The structures of bicyclo[2.1.0]pentane derivatives **2** and **3** have been established by hydrogenation to **8** and **15**, respectively, compounds which were synthesized independently. Treatment of **2** with aluminum chloride resulted in rearrangment to an isomer assigned structure **11**. Bicyclobutane derivative **4** was isomerized by magnesium bromide in ether to **17**, **18**, and **19**, while **5** gave **20** and **21**. These results distinguish between **4** and **5** and, when product ratios are considered, provide a basis for suggesting how the rearrangements occur.

The treatment of a mixture of 57% *cis*- and 43% *trans*-3-*tert*-butyl-7,7-dibromobicyclo[4.1.0]heptane (**1**) with methyllithium produced four tricyclic hydrocarbons **2**, **3**, **4**, and **5**.[3] While the spectral properties of these products were sufficient to define **2** and **3** as *tert*-butyl derivatives of tricyclo[3.2.0.0^{2,7}]heptane (**6**) and **4** and **5** as *tert*-butyl derivatives of tricyclo[4.1.0.0^{2,7}]heptane (**7**), the position of the *tert*-butyl group



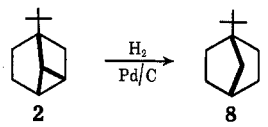
in each case was assigned solely on the basis of mass spectral data. Since our arguments really set, rather than rely on precedent, we undertook to define the structures chemically by unequivocal means and hoped that in the process we would establish some reaction patterns for these and related systems.

(1) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society (1549-A4) and to the National Science Foundation (GP 1306) for support of this research.

(2) National Institutes of Health Predoctoral Fellow, 1962–1965.

(3) W. R. Moore and B. J. King, *J. Org. Chem.*, **36**, 1877 (1971).

Bicyclopentane Derivatives 2 and 3.—It was found previously that **6** could be hydrogenated cleanly to norbornane over palladium on carbon.[4] Under similar conditions, **2** was hydrogenated readily to give a single product which we identified as 1-*tert*-butylnorbornane

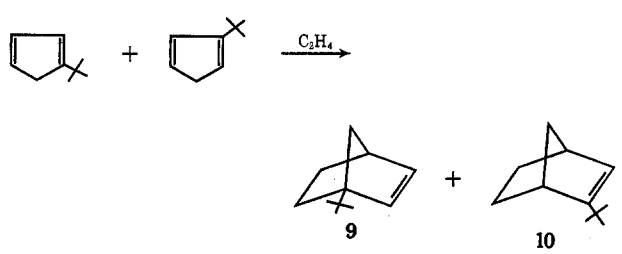


2 **8**

(**8**) on the basis of the nmr spectrum which, in particular, showed only one bridgehead proton as a broad singlet at δ 2.14.

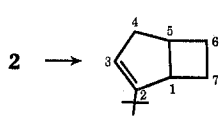
To establish the structure of **8** unequivocally, we sought an alternate synthesis. Since several attempts to couple *tert*-butyl and 1-norbornyl derivatives failed, we turned to the synthesis of 1-*tert*-butylnorbornene (**9**).

Perhaps surprisingly, sodium cyclopentadienide can be alkylated with *tert*-butyl bromide to give a modest yield of a mixture of 1- and 2-*tert*-butylcyclopentadiene.[5] This mixture was condensed with ethylene to give a 4:1 mixture of two adducts. The major product proved to be 2-*tert*-butylnorbornene (**10**). This material was identical with the major product obtained from the acid-catalyzed dehydration of 2-*tert*-butyl-2-hydroxynorbornane,[6] prepared by adding *tert*-butyllithium to norcamphor. The minor product from the Diels–Alder reaction, identified as **9** on the basis of nmr and mass spectra, was hydrogenated to give a sample of **8** identical with that derived from **2**.



9 **10**

In the course of establishing the structure of **2**, we examined its behavior with aluminum chloride, since it seemed possible that it might rearrange to **9**. However, rather than **9**, the major product was an isomer assigned structure **11**. The nmr spectrum of **11** shows a triplet



11

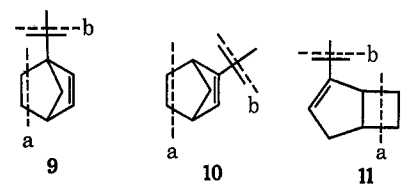
at δ 5.41 for the olefinic proton and a nine-proton singlet at δ 1.07, a downfield shift which indicates that the *tert*-butyl group is attached to a double bond. The signals from the remaining eight "saturated" protons give rise to a series of multiplets centered at *ca.* δ 1.8–3.65, the downfield shifts being consonant with a structure in which the protons concerned are allylic, on a four-membered ring, or both, and, in some cases, tertiary as well.

The mass spectrum of **11** also is highly informative. We have prepared a number of $C_{11}H_{18}$ hydrocarbons in this work and have found that, in general, the compounds give fragment peaks at about the same mass numbers, but the relative intensities of the peaks are usually quite different. However, the mass spectra of **9**, **10**, and **11** are *almost identical*. Furthermore, as can be seen in Table I, the spectra of all three compounds bear a striking similarity to that of the mixture of 1- and 2-*tert*-butylcyclopentadiene. These facts imply that loss of ethylene, as shown in structures **9**–**11**, must be the major primary fragmentation path for the three C_{11} compounds.[7]

TABLE I
MASS SPECTRA OF RELATED HYDROCARBONS

	Relative intensities			
m/e	**9**	**10**	**11**	*tert*-Butylcyclopentadiene[a]
150	2.5	6	1.5	
135	2	3	3	
122	33	25	25	24
107	100	100	100	100
91	12	17	12	52
79	9	9	9	16
77	7	8	7	10
65	6	5	6	11
57	33	29	32	38

[a] A mixture of 2- and 3-*tert*-butylcyclopentadiene was used.



a ⟶ *m/e* 122
a,b ⟶ *m/e* 107

While the mass spectral data clearly establish the bicyclo[3.2.0]hept-2-ene system, they do not distinguish between the 2 and 3 positions for the location of the *tert*-butyl group. However, the nmr signal from the olefinic proton assigned to C-3 of **11** is a triplet due to modest coupling ($J \sim 2$ Hz) with the C-4 methylene group and, as shown by double resonance techniques, coupling to the C-1 proton is very small. These facts provide a rational basis for assigning the *tert*-butyl group to C-2.[8]

The rearrangement of **2** to **11** can be viewed as opening[9a] of the highly strained 1,7 bond to give cation **12**, followed by rearrangement to **13** and loss of a proton. Since **9** is not formed (*via* a 4-*tert*-butylnorborn-

(4) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

(5) R. Alder and H. J. Ache, *Chem. Ber.*, **95**, 503 (1962).

(6) We had hoped that **9** might be a product from this dehydration as a consequence of a Wagner–Meerwein rearrangement, but at most minor amounts of it were formed.

(7) Mass spectra were determined with a 360° cycloidal instrument which precluded measurement of metastable peaks; *cf.* K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, N. Y., 1962, p 157.

(8) We wish to thank Paul D. Mogolesko and Stephen D. Clark for 100-MHz spectra and carrying out the double resonance experiments.

(9) (a) Although aluminum chloride was the catalyst and one could formulate the rearrangement in terms of an intramolecular hydride shift from C-6 to C-7, it is more likely that a trace of hydrogen chloride served as a proton transfer agent. (b) This pathway is similar to the rearrangment of certain bicyclo[2.2.1]heptane derivatives to [3.2.0] systems: S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.*, **79**, 505 (1957); E. E. van Tamelen and C. I. Judd, *ibid.*, **80**, 6305 (1958).

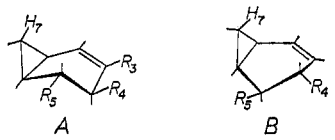
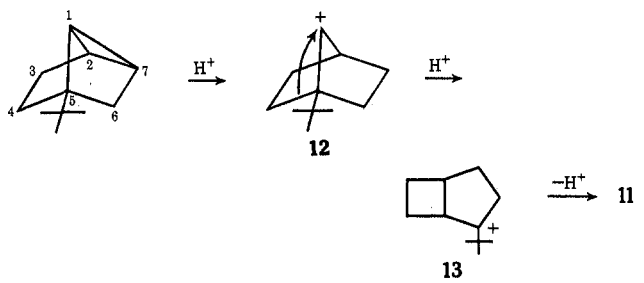
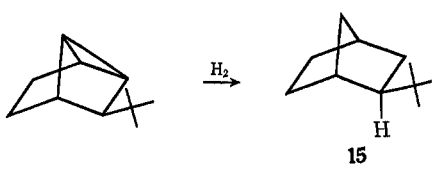


Figure 1.—Conformations of bicyclo[4.1.0]hept-2-enes. A (class A): **16**, $R_3 = R_4 = R_5 = H$; **18**, R_3 = *tert*-Bu, $R_4 = R_5 = H$; **19**, $R_3 = R_4 = H$, R_5 = *tert*-Bu; **21**, $R_3 = R_5 = H$, R_4 = *tert*-Bu. B (class B): **17**, $R_4 = H$, R_5 = *tert*-Bu; **20**, R_4 = *tert*-Bu, $R_5 = H$.

2-yl cation), the rearrangement of **12** to **13** may be concerted with opening of the three-membered ring.[9b]



Hydrogenation of **3** gave a single product which has been identified as *exo*-2-*tert*-butylnorbornane (**15**).



The Cu(I)-catalyzed coupling of the Grignard reagent prepared from *exo*-2-chloronorbornane[10] with *tert*-butyl chloride gave as the major C_{11} product a compound identical with that obtained from hydrogenation of **3**. On steric grounds, one would expect that the exo isomer would form preferentially in the coupling reaction. In addition, these samples of 2-*tert*-butylnorbornane have nmr spectra identical with that reported for the product of the addition of *tert*-butyllithium to norbornene, which, also on steric grounds, has been assigned the exo configuration.[11] These exo assignments were confirmed by our observation that reduction of **10** with diimide gave an isomer of **15**. Since diimide gives cis addition from the less-hindered side of a double bond,[12] this product clearly is the endo isomer. The same product was obtained upon hydrogenation of **10** over palladium on carbon.

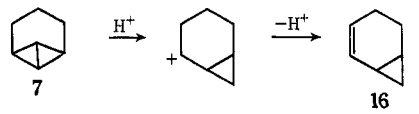
Bicyclobutane Derivatives 4 and 5.—Bicyclobutanes in general are very sensitive to acids and compounds **4** and **5** are not exceptions. As we noted previously,[3] some care is required to prevent acid-catalyzed rearrangement in the isolation and analysis of these compounds. However, it appeared that this propensity to rearrange could be used to advantage in elucidating the structures of **4** and **5**.

(10) This Grignard reagent presumably was a 55:45 mixture of the exo and endo isomers: (a) E. A. Hill, *J. Org. Chem.*, **31**, 20 (1966); (b) N. G. Krieghoff and D. O. Cowan, *J. Amer. Chem. Soc.*, **88**, 1322 (1966); (c) F. R. Jensen and K. L. Nakamaye, *ibid.*, **88**, 3437 (1966).

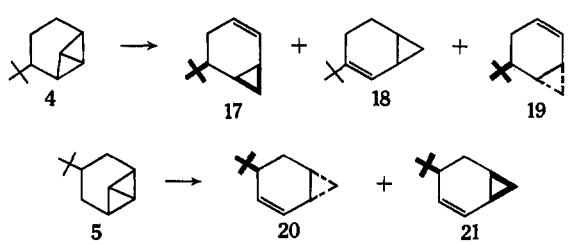
(11) J. E. Mulvaney and Z. G. Gardlund, *J. Org. Chem.*, **30**, 917 (1965).

(12) E. E. van Tamelen and R. J. Timmons, *J. Amer. Chem. Soc.*, **84**, 1067 (1962).

Compound **7** undergoes acid-catalyzed rearrangement to the vinylcyclopropane **16**.[4] In applying this reaction to the case at hand, we investigated a number of reagents to find conditions which would achieve reproducible results and found that magnesium bromide in ether led to the desired rearrangement but avoided the subsequent rearrangement of the primary products observed with more potent catalysts. Rearrangement of **4** and **5** proceeded cleanly; **4** gave three products, **17** (58%), **18** (38%), and **19** (4%), while **5** gave only two products, **20** (92%) and **21** (8%). The structures assigned to these products on the basis of arguments which follow are shown in Scheme I.



SCHEME I



The mass, nmr, ir, and uv data taken together establish that all of these products are *tert*-butyl derivatives of **16**. The fact that, as expected, one of the bicyclobutanes gives two products while the other gives three, one of which is the only trisubstituted olefin, is sufficient to distinguish between **4** and **5** and to establish that the trisubstituted olefin which must come from **4** must have structure **18**. Once the distinction between **4** and **5** has been made, the position, but not the stereochemistry, of the *tert*-butyl group in the other four products has also been made. Furthermore, the mass spectra of **20** and **21** clearly support the presence of an allylic *tert*-butyl group; both compounds give base peaks at *m/e* 93 (loss of *tert*-butyl), while in **17** and **19** the *m/e* 93 peaks are much weaker.

The stereochemical assignments can be deduced if one examines the conformational possibilities for the rearrangement products. It becomes apparent that the requirement of keeping the nonbonded interactions involving the *tert*-butyl group at a minimum causes the compounds to fall into the two conformational classes shown in Figure 1. Compounds in class A, which includes the parent compound **16** as well, have a pseudo chair conformation while compounds in class B have a pseudo boat conformation. In going from conformation A to conformation B, the plane of the three-membered ring is tilted toward the double bond causing the cyclopropyl proton designated as H_7 of the class B compounds to fall in the shielding region of the double bond. This effect is reflected in the nmr spectra. Each of the two compounds which fall in class B shows the signal from one proton shifted 0.3–0.4 ppm upfield from the highest field signals found in the spectra of the class A compounds.

It is also significant that compounds in class A have ultraviolet absorption maxima at somewhat longer

wavelengths than the maxima found for class B compounds. While the differences are small (4–5 nm), they support the idea of two conformational classes which differ in terms of the orientation of the three-membered ring with respect to the double bond.[13]

The distribution of rearranged products from **4** and **5** deserves some comment. If random bond breaking occurred, the product ratios would be **17**:**18**:**19** = 25:50:25 from **4** and **20**:**21** = 50:50 from **5**. The observed ratios of 58:38:4 and 92:8 are obviously far from random. Moreover, the trisubstituted olefin **18** is not the major product from **4** as one might expect if free cyclopropyl cations were intermediates. Inasmuch as both **4** and **5** must be locked in a conformation having the *tert*-butyl group equatorial, it is worth noting that the major products would be formed if a peripheral bond of the bicyclobutane ring were broken and a trans axial proton were lost.

Thus, it is possible that with the catalyst system we have employed, the main pathway for rearrangement involves transfer of a proton to a bond of the bicyclobutane, probably *via* a prior complex, followed by loss of a proton to an external base, as shown in Figure 2.[14] The reaction of the catalyst with **4** on the side away from the *tert*-butyl group would explain the preference for formation of **17**.

Experimental Section[15]

Hydrogenation of 2.—A solution of 20 mg of compound **2** in 10 ml of ethanol with 100 mg of 30% Pd/C absorbed 1 equiv of hydrogen within 2 hr at 25° (1 atm). After filtering, adding water, and extracting with pentane, glc (Carbowax 20M) showed a single peak which was collected to give 1-*tert*-butylnorbornane (**8**): ir 2960, 1395, 1370, 1330, 1310, 920 cm^{-1}; nmr (CCl_4) δ 0.92 (s, 9 H, *tert*-butyl), 1.0–1.8 (overlapping m, 10 H), 2.14 (broad s, 1 H, C-4); mass spectrum *m/e* (rel intensity) 152 (M^+, 10), 137 (56), 123 (61), 109 (27), 96 (41), 95 (58), 83 (19), 82 (13), 81 (100), 69 (17), 68 (21), 67 (38), 57 (74), 55 (42), 53 (15), 43 (19), 41 (67), 39 (22). *Anal.* Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.62; H, 13.19.

***tert*-Butylcyclopentadiene.**—Sodium cyclopentadienide was prepared in liquid ammonia and alkylated with *tert*-butyl bromide following the method of Alder and Ache[5] to give a mixture of 1- and 2-*tert*-butylcyclopentadiene (10% yield): bp 53° (42 mm); [lit.[5] bp 33° (12 mm)]; ir (CCl_4) 3060, 2960, 1625, 1610, 1600 cm^{-1}; nmr (CCl_4) δ 1.17 and 1.19 (overlapping s, 9 H), 2.88 (m, 2 H), 5.8–6.65 (m, 3 H); mass spectrum, see Table I. Glc (2% SAIB at 80°) showed two partially resolved peaks in a ratio of 62:38.

1- and 2-*tert*-Butylnorbornene (9 and 10).—The mixture of 1- and 2-*tert*-butylcyclopentadiene (6 g) was heated with ethylene for 2.5 hr at 250° (175 atm). Glc analysis (XE-60, 120°) of the product (5.5 g) showed two peaks, t_r 1.00 and 1.30, in a ratio of 4:1 which were collected (XF-1150). The minor product was identified as 1-*tert*-butylnorbornene (**9**): ir (CCl_4) 3050, 2960, 1610, 1395, 1365, 1345 cm^{-1}; nmr (CCl_4) δ 0.97 (s, 9 H, *tert*-butyl) superimposed on 0.8–1.8 (m, 6 H), 2.80 (m, 1 H, C-4), 5.98 (apparent d, 2 H, C-2,3, probably center lines of AB q); mass spectrum, see Table I. *Anal.* Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.07. Found: C, 88.10; H, 12.04.

Hydrogenation of **9** over 30% palladium on carbon in ethanol at 25° (1 atm) gave a single product having a retention time (XF-1150) and ir spectrum identical with those of the sample of **8** derived from **2**.

(13) It appears that interaction of the 1,7 bond with the p orbital at C-2 may be greater in the class A compounds.

(14) Although anhydrous conditions were employed, it is probable that a trace of water is necessary to effect rearrangement: W. R. Moore and N. L. Boardway, unpublished results.

(15) The general procedures given in footnote 31 of ref 3 were followed. Ultraviolet spectra were recorded with a Cary Model 14 spectrophotometer which was flushed with nitrogen employing oxygen-free isooctane as a solvent. Glc retention times are relative to the indicated peak (t_r = 1.00).

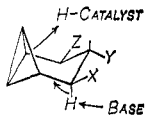


Figure 2.—Rearrangement of tricyclo[4.1.0.$0^{2,7}$]heptanes. **4** (X = Y = H, Z = *tert*-butyl) → **17**; **4** (X = *tert*-butyl, Y = Z = H) → **18**; **5** (X = Z = H, Y = *tert*-butyl) → **20**.

The major product from the Diels–Alder reaction was identified as 2-*tert*-butylnorbornene (**10**): ir (CCl_4) 3050, 2960, 1615, 1395, 1365, 1325 cm^{-1}; nmr (CCl_4) δ 1.03 (s, 9 H, *tert*-butyl) superimposed on 0.9–1.8 (m, 6 H), 2.76 and 2.87 (overlapping multiplets, 2 H, C-1,4), 5.53 (broad d, 1 H, C-3); mass spectrum, see Table I. *Anal.* Calcd for $C_{11}H_{18}$: C, 87.92; H, 12.07. Found: C, 87.82; H, 12.15.

2-*tert*-Butyl-2-hydroxynorbornane.—A solution of 5.1 g (0.047 mol) of norcamphor (Columbia Organic Chemicals Co.) in 5 ml of petroleum ether (bp 30–60°) was added dropwise to 0.047 mol of *tert*-butyllithium in 25 ml of pentane (Lithium Corp. of America) while cooling with an ice bath. The mixture was allowed to warm to room temperature (1 hr) and then was hydrolyzed. Extraction with pentane followed by distillation gave a forerun of norcamphor and 0.8 g of 2-*tert*-butyl-2-hydroxynorbornane (based on the method of synthesis, the *tert*-butyl group should be *exo*): bp 80° (1 mm); mp 63.5–64.5°; ir (CCl_4) 3610, 3500, 1395, 1365, 1310, 1160, 995 cm^{-1}; nmr (CCl_4) δ 0.92 (s, ~9 H, *tert*-butyl) superimposed on 0.8–2.4 (m); mass spectrum *m/e* (rel intensity) 168 (M^+, <0.1), 150 (0.1), 135 (3), 111 (100), 93 (29), 83 (84), 67 (62), 66 (20), 57 (60), 55 (47), 43 (54), 41 (56), 39 (22). *Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.34; H, 11.82.

Treatment of this alcohol with hydrogen chloride under a variety of conditions including concentrated hydrochloric acid, hydrogen chloride in methanol–ether, and anhydrous hydrogen chloride in ether produced olefin **10** as the major product (identified on the basis of its glc retention times and infrared spectrum) along with complex mixtures of other materials which were not investigated. Under anhydrous conditions, a small amount of **9** may be formed.

Rearrangement of 2.—Compound **2** (100 mg) was stirred with 50 mg of aluminum chloride in 6 ml of ether at 25°. The isomerization of **2** was followed by glc analysis of aliquots. After 8 hr, the mixture was hydrolyzed and the products were extracted with pentane. Glc analysis (XF-1150, 50°) showed three peaks, t_r 0.90, 1.00, and 1.17, in ratios of 90:5:5 and a small amount of less volatile material (t_r 7.5, 9.0). The second peak was due to **2** and the first peak was identified as 2-*tert*-butylbicyclo[3.2.0]-hept-2-ene (**11**): ir (CCl_4) 3040, 2960, 1628, 1390, 1365 cm^{-1}; nmr[8] (CCl_4) δ 1.07 (s, 9 H, *tert*-butyl), 1.55–2.70 (5 H, endo C-4, C-6, C-7, complex multiplets centered at ~1.8, ~2 H, and 2.3, ~3 H), 2.89 (m ~ quintet, 1 H, C-5), 3.33 (m ~ t, 1 H, *exo*-C-4), 3.65 (m ~ t, 1 H, C-1), 5.41 (broadened t, J ~ 2 Hz, 1 H, C-3); mass spectrum, see Table I. *Anal.* Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 88.05; H, 12.09.

Hydrogenation of 3.—Inasmuch as **3** was very difficult to obtain free of **2**, a 1:1 mixture of **2** and **3** was hydrogenated over 30% Pd/C in ethanol at 25° (1 atm). Glc (XE-60, 98°) showed a 1:1 mixture of two peaks, t_r 0.88 and 1.00. The second peak was due to **8**. The more volatile compound was identified as *exo*-2-*tert*-butylnorbornane (**15**) by comparison of glc retention times (seven columns) and ir and mass spectra with those of the sample prepared from 2-chloronorbornane.

The following procedure is based on a method used for the preparation of hexamethylethane.[16] The Grignard reagent was prepared from 10.7 g (81 mmol) of *exo*-2-chloronorbornane[17] in ether. Then a solution of 1.36 g (7.4 mmol) of *tert*-butyl iodide and 6.77 g (73 mmol) of *tert*-butyl chloride was added followed by portionwise addition of 0.27 g of anhydrous cuprous chloride. Following hydrolytic work-up, fractional distillation gave 0.5 g of material, bp 59° (9.0 mm), that glc (XE-60, XF-1150) showed was mainly one compound which was collected and identified as **15**: ir (CCl_4) 2960, 1398, 1368 cm^{-1}; nmr, identical with that in the literature;[11] mass spectrum *m/e* (rel intensity) 152 (M^+, 0.2), 137 (2), 109 (3), 95 (100), 81 (12), 67 (26), 66 (14), 57 (35), 56 (58), 55 (12).

(16) R. C. Marker and T. S. Oakwood, *J. Amer. Chem. Soc.*, **60**, 2598 (1938).

(17) H. Kwart and R. K. Miller, *ibid.*, **78**, 5008 (1956).

p-Toluenesulfonylhydrazide (124 mg, 0.67 mmol) and 30 mg (0.20 mmol) of **10** in 1.5 ml of diglyme were heated in a bath at 160° for 18 hr. After cooling, adding water, and extracting with pentane, glc (XF-1150), showed a 1:2 mixture of **10** and its reduction product, *endo*-2-*tert*-butylnorbornane: ir (CCl_4) 2960, 1395, 1365 cm^{-1} (the fingerprint region is clearly different from that of **15**); nmr (CCl_4) δ 0.92 (s, 9 H, *tert*-butyl), 1.1–2.9 (m, 9 H), 2.22 (broad s, 2 H, C-1,4); mass spectrum *m/e* (rel intensity) 152 (M^+, 0.6), 137 (2.5), 109 (8), 95 (100), 81 (16), 67 (37), 66 (13), 57 (57), 56 (66), 55 (16). Hydrogenation of **10** in ethanol over 30% Pd/C gave the same compound. Less than 1% of **15** was found. Glc (XE-60, 96°) (t_r): **10** (1.00), **15** (1.36), *endo*-2-*tert*-butylnorbornane (1.55).

Rearrangement of 4.—A solution of magnesium bromide in ether was prepared by adding 1.80 g (9.6 mmol) of 1,2-dibromoethane in 25 ml of ether dropwise to 0.25 g (10 mmol) of magnesium in 75 ml of ether at reflux. The solution was filtered, sealed under nitrogen with a "No-Air" stopper, and stored at 5°. Compound **4** (200 μl) was added to 12 ml of the magnesium bromide solution. After 80 min at 25° glc showed that the starting material was absent. Water and pentane were added and the organic layer was separated, washed with water, dried (Na_2SO_4), and concentrated by distillation of the solvent through a 26 × 1 cm Vigreux column. Glc analysis (XF-1150, 65°) showed three new peaks (t_r, **4** = 1.00): **17** (58%, 1.09), **18** (38%, 1.18), and **19** (4%, 1.44). The products were collected by glc (Carbowax 20M); spectral data are given below. Preliminary reactions established that the product ratios did not change with time. Aluminum chloride, stannic chloride, and mercuric chloride, all in ether, quickly led to complex mixtures as a consequence of subsequent rearrangement of the initial products.

endo-**5**-*tert*-**Butylbicyclo[4.1.0]hept-2-ene** (**17**).—Spectral data: ir (CCl_4) 3060, 3030, 2960, 1635, 1390, 1365, 1025 cm^{-1}; uv λ_{max} (ethanol) 198 ± 1 nm (ϵ 5200); nmr (CCl_4) δ 0.05–0.27 (m, 1 H, endo C-7), 0.98 (s, 9 H, *tert*-butyl) superimposed on 0.75–1.50 (m, 4 H), 1.75–2.03 (m, 2 H, C-4), 5.55 (d of t, 1 H, C-3), 5.85 (br d, 1 H, C-2); mass spectrum *m/e* (rel intensity) 150 (M^+, 2), 135 (5), 107 (7), 94 (22), 93 (20), 91 (19), 83 (18), 80 (19), 79 (49), 78 (15), 77 (20), 57 (100), 55 (15). *Anal.* Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 88.07; H, 12.11.

3-*tert*-**Butylbicyclo[4.1.0]hept-2-ene** (**18**).—Spectral data: ir (CCl_4) 3065, 3050, 3000, 2960, 1640, 1390, 1365 (d), 1020 cm^{-1}; uv λ_{max} (ethanol) 204 ± 1 nm (ϵ 4300); nmr (CCl_4) δ 0.35 to ~0.8 (m, ~2 H, C-7), 0.98 (s, 9 H, *tert*-butyl) superimposed on ~1.0–1.4 (m, ~2 H), 1.4–2.15 (m, 4 H), 5.72 (m, 1 H, C-2); mass spectrum *m/e* (rel intensity) 150 (M^+, 21), 135 (50), 107 (54), 94 (35), 93 (48), 91 (31), 79 (48), 77 (26), 57 (100), 55 (22). *Anal.* Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.95; H, 12.13.

exo-**5**-*tert*-**Butylbicyclo[4.1.0]hept-2-ene** (**19**).—Spectral data: ir (CCl_4) 3065, 3035, 3000, 2960, 1645, 1395, 1365, 1025 cm^{-1}; uv λ_{max} (ethanol) 202 ± 1 nm (ϵ 4800); nmr (CCl_4) δ 0.30 to ~0.9 (m, 2 H, C-7), 0.97 (s, 9 H, *tert*-butyl) superimposed on ~1.0–2.1 (m, 5 H), 5.30 (m, 1 H), 5.90 (m, 1 H); mass spectrum *m/e* (rel intensity) 150 (M^+, 6), 135 (6), 107 (8), 94 (16), 93 (22), 91 (15), 79 (26), 77 (15), 57 (100).

Rearrangement of 5.—Compound **5** (120 μl) was added to 15 ml of 0.1 *M* magnesium bromide in ether. After 4 days at 25°, the mixture was worked up as above. Glc (XF-1150, 65°) showed the absence of **5** and two new peaks (t_r, **5** = 1.00), **20** (92%, 1.06) and **21** (8%, 1.26), which were collected; spectral data are given below. The same ratios were observed at shorter times when the rearrangment was incomplete.

exo-**4**-*tert*-**Butylbicyclo[4.1.0]hept-2-ene** (**20**).—Spectral data: ir (CCl_4) 3060, 3030, 2995, 2960, 1630, 1395, 1365, 1020 cm^{-1}; uv λ_{max} (ethanol) 198 ± 1 nm (ϵ 4800); nmr (CCl_4) δ −0.15 to +0.05 (m, 1 H, endo C-7) 0.83 (s, 9 H, *tert*-butyl) superimposed on ~0.8–1.3 (m, 4 H), 1.6–2.4 (m, 2 H), 5.60 and 5.90 (two d, part of AB q centered at 5.75, 2 H, C-2,3); mass spectrum *m/e* (rel intensity) 152 (M^+, 2) 135 (1), 107 (4), 94 (20), 93 (100), 92 (16), 91 (25), 79 (19), 77 (27), 57 (68). *Anal.* Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 88.12; H, 12.21.

endo-**4**-*tert*-**Butylbicyclo[4.1.0]hept-2-ene** (**21**).—Spectral data: ir 3065, 3030, 3000, 2960, 1635, 1395, 1365, 1020, cm^{-1}; uv λ_{max} (ethanol) 203 ± 1 nm (ϵ 5600); nmr (CCl_4) δ 0.4–0.8 (m, 2 H, C-7), 0.85 (s, 9 H, *tert*-butyl) superimposed on 0.9–2.2 (m, 5 H), ~5.3 (m, 1 H), ~5.9 (m, 1 H); mass spectrum *m/e* (rel intensity) 150 (M^+, 1), 135 (2), 107 (2), 94 (16), 93 (100), 92 (11), 91 (26), 79 (22), 77 (29), 57 (93).

Registry No.—**2**, 29339-27-3; **3**, 29339-28-4; **4**, 29339-29-5; **5**, 29339-30-8; **8**, 29339-31-9; **9**, 29339-32-0; **10**, 29339-33-1; **11**, 29339-34-2; **15**, 1125-54-8; **17**, 29339-36-4; **18**, 29339-37-5; **19**, 29339-38-6; **20**, 29339-39-7; **21**, 29339-40-0; 2-*tert*-butyl-2-hydroxynorbornane, 29339-41-1.

Palladium(II)-Catalyzed Aromatic Substitution[1]

P. M. HENRY

Research Center, Hercules Incorporated, Wilmington, Delaware 19899

Received November 5, 1970

Pd(II) salts in the presence of nucleophiles (X^-) oxidize aromatics or mercurated aromatics to coupled aromatics. With phenylmercury salts the reaction is $2PhHg^+ + Pd^{II} + X^- \rightarrow Ph_2 + Pd^0 + 2Hg^{2+} + X^-$. However, if certain oxidants are added to the reaction mixture, the course of the reaction changes to give substituted aromatics: $PhHg^+ + Pd^{II} + X^-$ (+ Ox.) → $PhX + Hg^{2+} + Pd^{II}$. Examples of the reaction were obtained for OAc^-, N_3^-, Cl^-, NO_2^-, Br^-, CN^-, and SCN^- as nucleophiles; Cr(VI), $Pb(OAc)_4$, $NaClO_3$, $KMnO_4$, $NaNO_3$, and $NaNO_2$ as oxidants; and benzene, toluene, phenyl acetate, and mercurated benzene and toluene as aromatic substates. Acetic acid was generally used as solvent, but in some cases acetonitrile and nitrobenzene were used. The reaction gives a substitution pattern characteristic of an electrophilic substitution reaction. The reaction most likely proceeds either *via* a Pd(II) aryl or by generation of a Pd(IV) species by the oxidant, followed by attack of the Pd(IV) species on the aromatic substrate.

Although direct hydroxylations or acetoxylations of benzenoid compounds do not occur readily,[2] several metal ion catalyzed direct substitution reactions involving Fe(II)[3] and Pb(IV)[4-6] have recently been reported. This paper will describe a Pd(II)-catalyzed direct aromatic substitution not only of acetate but of other groups as well.

The possibility that Pd(II) will catalyze the oxidation of aromatic compounds by inorganic oxidants is suggested by our previous work on the Pd(II)-catalyzed oxidation of olefins in the presence of such oxidants. It has been previously reported[7] that Cu(II) changes the nature of olefin oxidations by Pd(II). Thus, in

(1) Hercules Research Center Contribution No. 1538.

(2) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam, 1965.

(3) G. A. Hamilton, R. J. Workman, and L. Woo, *J. Amer. Chem. Soc.*, **86**, 3390 (1964).

(4) D. R. Harvey and R. O. C. Norman, *J. Chem. Soc.*, 4860 (1964).

(5) R. E. Partch, *J. Amer. Chem. Soc.*, **89**, 3662 (1967).

(6) E. C. Taylor, H. W. Altland, R. H. Danforth, G. McGillivray, and A. McKillop, *ibid.*, **92**, 3520 (1970).

(7) P. M. Henry, *J. Org. Chem.*, **32**, 2575 (1967).