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(13) Since the aqueous 70% $HClO_4$ and the diamine **1** used in these reactions were not deuterated, the ratio of D^+ donor:H^+ donor in these reactions was *ca.* 4:1.
(14) Although it is clear from earlier studies[4c,10] that the Cr(II) species is present as a bis en complex, the Cr(III) species may be present as either $Cr(en)_3{}^{3+}$ or $Cr(en)_2(ligand)_2{}^{3+}$, since the bis and tris en complexes of Cr(III) appear to be of comparable stability [see C. L. Rollinson and J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 196, 200 (1946)]. Earlier polarographic studies[10c] of reduction of $Cr(en)_3{}^{3+}$ in aqueous solution have indicated that electrode process observed is $Cr(en)_3{}^{3+} + e \rightleftarrows Cr(en)_3{}^{2+} \rightleftarrows Cr(en)_2(ligand)_2{}^{2+} + en$. This process exhibited "pseudo-reversible" behavior in alkaline solution at relatively high en concentrations. In our studies starting with preformed $Cr(en)_2(ligand)_2$ and low concentrations of en we believe we are observing only the reversible electron transfer process: $Cr(en)_2(ligand)_2{}^{2+} \rightleftarrows Cr(en)_2(ligand)_2{}^{3+} + e$.
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A New Ring Expansion Procedure. VI. The Decomposition of the Magnesium Salts of Some 1-(α-Bromobenzyl)-1-cycloalkanols and Bicycloalkanols

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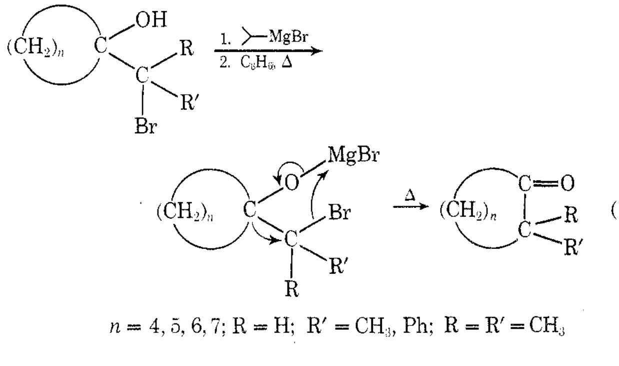
The results of the new ring expansion procedure applied to 2-methylcyclopentanone, 2-methylcyclohexanone, camphor, and bicyclo[2.2.2]octanone-2 are presented and discussed. Particular attention is afforded to the factors affecting product distribution. Each ketone was converted to its corresponding 2-phenyl-substituted ring-enlarged ketone by the decomposition of the magnesium salt from the 1-(α-bromobenzyl)-1-cycloalkanol.

Previously published papers[1] describe a new and relatively simple procedure by which one may achieve a ring enlargement (eq 1). The bromohydrins were prepared from olefins by treatment with aqueous *N*-bromosuccinimide, or ketones by reaction with benzylmagnesium chloride followed by a free-radical bromination.[1] Ring-enlarged ketones of reasonable purity were obtained in overall fair yields.



(1)

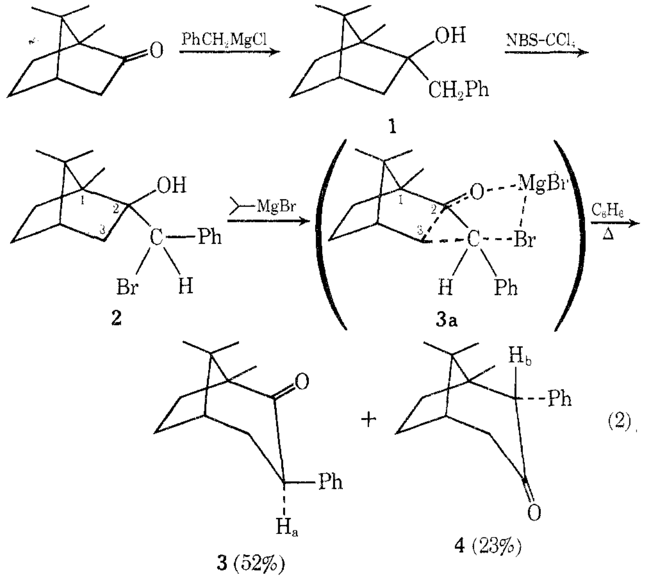
$n = 4, 5, 6, 7$; $R = H$; $R' = CH_3$, Ph; $R = R' = CH_3$

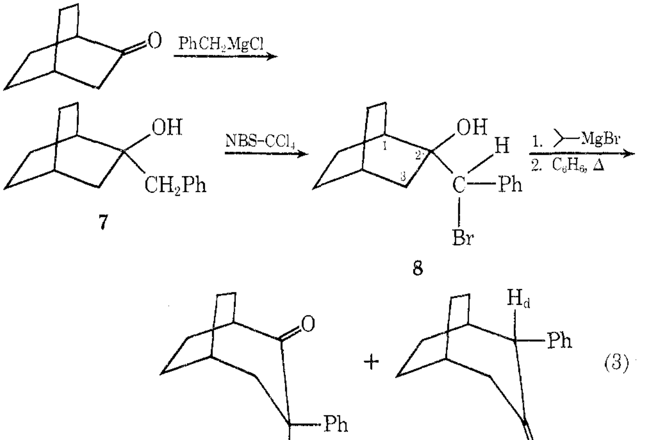
The studies of Geissman and Akawie[2] have mechanistically classed the rearrangement as a pinacol type involving a migration to an incipient electron-deficient carbon atom produced from an electrophilic attack by magnesium on the halogen atom (eq 1). A high degree of carbonium ion character is involved in the transition state, since they observed that secondary and tertiary halides rearrange regardless of the migrating group but primary halides only rearrange when a good migrating group is involved.

The results of the ring-enlargement procedure applied to 2-methylcyclopentanone, 2-methylcyclohexanone, camphor, and bicyclo[2.2.2]octanone-2 are presented and discussed. Each ketone was converted to the 2-phenyl-substituted ring-enlarged ketone by the decomposition of the magnesium salt from the 1-(α-bromobenzyl)-1-cycloalkanol.

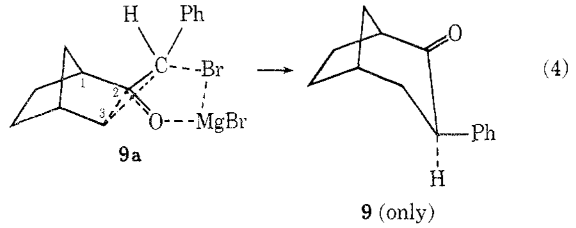
Results and Discussion

1,8,8-Trimethyl-3-phenyl[3.2.1]bicyclooctanone-2 (3) and 1,8,8-Trimethyl-2-phenyl[3.2.1]bicyclooctanone-3 (4) from Camphor and 3-Phenyl[3.2.2]bicyclononanone-2 (5) and 2-Phenyl[3.2.2]bicyclononanone-3 (6) from Bicyclo[2.2.2]octanone-2. The bromohydrins[3] 2 and 8 were prepared as shown (eq 2 and 3) and the indicated structures were based upon ir and nmr spectra. The conversion of 2 and 8 to their magnesium salts, followed by decomposition, afforded the ketones 3 and 4 in overall 52 and 23% yields, and 5 and 6 in overall yields of 43 and 20%, respectively (based on 1 and 7). The products 3 and 4 were separated by column chromatography, and the structures assigned were based upon elemental analysis, deuterium exchange and the ir and nmr spectra. The nmr signal at τ 6.45, a broad triplet, was ascribed to H$_a$ in 3. The treatment of 3 with trifluoroacetic acid-*d* revealed that only H$_a$ was exchanged.[4] The benzyl hydrogen singlet signal at τ 6.53 was ascribed to H$_b$ in 4. The ketone 4 readily formed the 2,4-dinitrophenylhydrazone derivative, whereas 3 did not even under coercing conditions. These results, explained from steric considerations, were also consistent with the structures assigned for 3 and 4. The products 5 and 6 were separated by fractional crystallization and column chromatography and the structures assigned were based upon elemental analysis and ir and nmr spectra. The benzyl proton in 5 (H$_c$) appeared as two doublets at τ 6.0 and 6.2, and the benzyl proton in 6 (H$_d$) appeared as a broad singlet at τ 6.35.





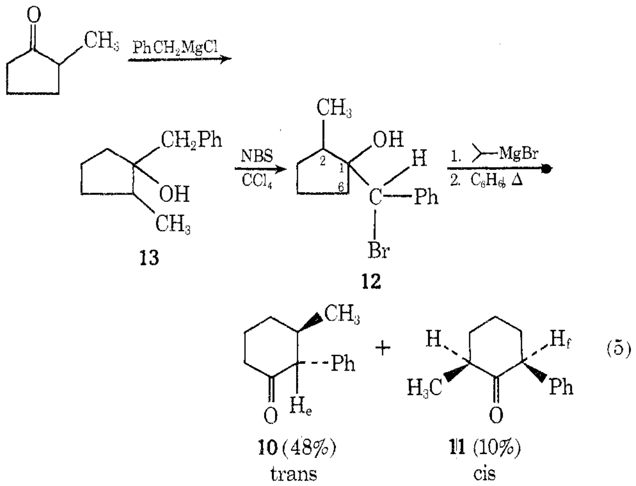
Previous studies have observed that many reaction types involving alkyl migrations to incipient electron-deficient centers (carbon[5] and nitrogen[6]) in the norbornyl system preferred methylene over methine migration and at the same time involved generation of a relatively unstable boat transition state. Our results with camphor (eq 2) and that previously reported with 2-norbornanone[1b] (eq 4) are no exceptions. A new factor to account for the preference for methylene migration was offered by Sauers,[7,8] namely, that because of the eclipsing of the groups on C-2 and C-3 a greater relief of torsional strain accompanies C-2–C-3 bond migration as opposed to C-1–C-2 bond migration, which would entail much less relief of torsional strain, since the groups on C-2 and the bridgehead group at C-1 are disposed at dihedral angles of about 44 and 79°. The justification for the predominance of 3 over 4 may lie then in two favorable features in the transition state for 3 as opposed to 4, namely, a more stable pseudo-chair conformation (while that for 4 would be a boat) and a greater relief of torsional strain accompanying C-2–C-3 bond migration (3a, eq 2). The production of the minor product 4 may be ascribed to a somewhat offsetting favorable electronic effect accompanying C-1–C-2 bond migration (tertiary carbon). Similarly, the production of only 9 (eq 4) may be explained by invoking Sauers'[7] new factor.



In the bicyclooctyl system the results also dictate that electronic control is not a primary factor in determining the product distribution (eq 3). However, since, in the bicyclooctyl system the groups on C-2 and C-3 are eclipsed,[9] a greater relief of torsional strain accompanies C-2–C-3 bond migration as opposed to C-1–C-2 bond migration, which would entail much less relief of torsional strain because the groups on C-2 and the hydrogen at C-1 are staggered. Therefore the product distribution (5 and 6) may also be governed by the extent of relief of torsional strain[8] in the respective transition states. The production of 6 may be due to the fact that a twisting in the flexible bicyclooctyl system reduces the magnitude of torsional strain relative to the norbornyl system where no product resulting from C-1–C-2 bond migration was isolated[10,11] (eq 4).

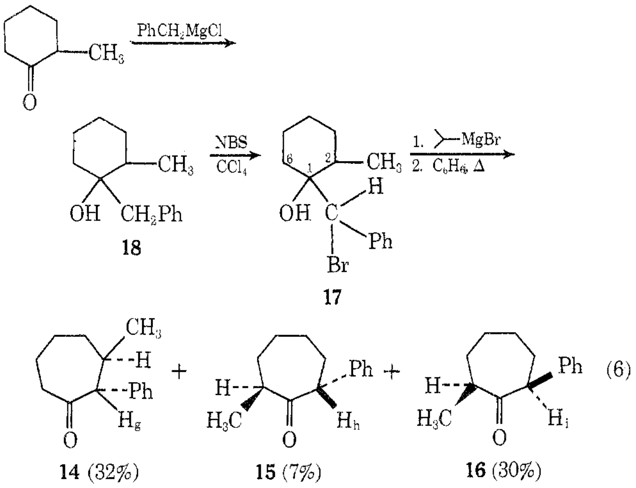
In summary, the product distribution in the bicyclic systems studied here and previously[1b,d,12] appears to be governed primarily by relief of torsional strain[8] with electrical and boat-chair considerations playing a minor role.[1b,d,12]

3-Methyl-2-phenylcyclohexanone (10) and 2-Methyl-6-phenylcyclohexanone (11) from 2-Methylcyclopentanone. The bromohydrin[3] 12 was converted to the magnesium salt and decomposed to produce the ketones 10 and 11 in overall 48 and 10% yields, respectively (based upon 13) (eq 5). The ketones[13] 10 and 11 were separated by column chromatography and the structures assigned for 10 and 11 were based upon elemental analysis and ir and nmr spectra. The benzyl hydrogen in 10 (H$_e$) appeared as a doublet at τ 6.95 and the benzyl hydrogen in 11 (H$_f$) appeared as a broad quartet at τ 6.50.



The major product **10** arises from the migration of the more highly substituted bond, which is what one would expect from electronic control of the product distribution in this type of rearrangement.[2] A similar result was obtained from the Tiffeneau–Demjanov ring enlargement of 2-methyl-1-aminomethylcyclopentanol, which yielded 3-methylcyclohexanone.[14] To attribute the product distribution as being solely governed by electronic control seems somewhat naive; undoubtedly conformational and steric considerations play a role.[11]

***trans*-3-Methyl-2-phenylcycloheptanone (14) and *cis*- and *trans*-2-methyl-7-phenylcycloheptanone (16 and 15) from 2-Methylcyclohexanone.** The bromohydrin[3] **17** was prepared as previously described and was converted to the ring-enlarged ketones **14**, **15**, and **16** in overall 32, 7, and 30% yields, respectively (based upon **18**) (eq 6). The mixture of products **14**, **15**, and **16** obtained could be only partially separated by column chromatography. That the original mixture contained only **14**, **15** and **16** was established from the following: ir spectrum; elemental analysis; the nmr spectrum showed a doublet at τ 6.78 (H_g, **14**) and the methyl group signal as a doublet at τ 9.19; the benzyl hydrogens in **15** and **16** appeared at τ 6.10 (H_h) as a weak, broad multiplet and at τ 6.36 (H_i) as a broad quartet, the methyl groups both appeared as doublets at τ 9.02 and 9.06, respectively; when the mixture was treated with trifluoroacetic acid-*d* at 75° for 24 hr the nmr spectrum showed that only all the signals attributed to the benzyl hydrogens were absent. The relative composition (eq 6) for each ketone was obtained from the nmr spectrum from the value of the ratio of the area for each benzyl hydrogen to one-fifth of the total area for the phenyl hydrogens. The yields so obtained were identical with those obtained from the value of the ratio of the area for each benzyl hydrogen to one-third of the total area for the methyl hydrogens. The yields, when calculated from the nmr integrations with partially separated samples (pure **14** separated) obtained from column chromatography, were in good agreement with the previously obtained values. The ketone **14**, because of its more accessible carbonyl group, could also be separated by the selective conversion to the semicarbazone. The presence of a doublet at τ 6.74 (H_g, **14**) confirmed it to be the semicarbazone of **14**. The cis–trans relationship between **15** and **16** was established from an acid-catalyzed equilibration of the mixture, the nmr spectrum of which revealed that the only change compared to the nmr spectrum of the untreated mixture was an almost complete conversion of **15** to **16**. Both signals for the benzyl proton and methyl protons for **15** vanished while those for **16** became more intense.[15]



The products which result from the migration of the more highly substituted C-1–C-2 bond and the less substituted C-1–C-6 bond are produced in almost equal amounts. This appears to be a characteristic feature of the 2-methylcyclohexyl system: Tchoubar[14] reported obtaining a mixture of 2-methyl- and 3-methylcycloheptanones from the Tiffeneau–Demjanov ring expansion with 2-methyl-1-aminomethylcyclohexanol; Gutsche and Chang[16] reported a mixture of 2-methyl- and 3-methylcycloheptanones in equal amounts from the diazomethane ring expansion of 2-methylcyclohexanone. Our results (eq 6) and those reported[14,16] indicate that the product distribution cannot be solely governed by electrical effects; undoubtedly conformational and steric considerations play a salient role.

In the simple cyclic systems electrical, conformational, and steric considerations play a role with the latter two varying in importance with the particular ring system involved.

Experimental Section[17]

1-(α-Bromobenzyl)-1-cyclo- and -bicycloalkanols were prepared by the dropwise addition of an ether solution of the ketone to benzylmagnesium chloride, after which the mixture was refluxed for 24 hr, except for alcohol **18** which was refluxed for 3 hr. The reaction mixture was decomposed with a saturated NH_4Cl solution and the organic layer was separated, washed with water, and dried ($MgSO_4$). The solvent was removed under vacuum (rotary evaporator) and the residue was distilled.

The alcohol **1** was prepared with 76 g (0.50 mol) of camphor in 100 ml of ether and 75.6 g (0.60 mol) of benzyl chloride, 16 g (0.66 mol) of magnesium, and 300 ml of ether. Distillation[18] yielded 88.4 g (0.36 mol, 73%) of **1**: bp 112–114° (0.3 mm) [lit.[19] bp 162–163° (6 mm)]; ir 3560 cm^{-1}; nmr τ 7.32 (s, $-CH_2Ph$).

The alcohol 13 was prepared with 49.0 g (0.50 mol) of 2-methylcyclopentanone in 100 ml of ether and 75.6 g (0.60 mol) of benzyl chloride, 16 g (0.66 mol) of magnesium, and 300 ml of ether. Distillation yielded 80.0 g (0.43 mol, 84%) of **13**: bp 88–89° (0.75 mm); ir 3525 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}O$: C, 82.05; H, 9.53. Found: C, 81.95; H, 9.66.

The alcohol 18 was prepared with 33.6 g (0.30 mol) of 2-methylcyclohexanone in 80 ml of ether and 50.4 g (0.40 mol) of benzyl chloride, 11 g (0.45 mol) of magnesium, and 250 ml of ether. Distillation produced 49.4 g (0.24 mol, 81%) of **18**: bp 125–126° (2 mm) [lit.[20] bp 115° (0.8 mm)]; ir 3560 cm^{-1}.

The alcohol 7 was synthesized with 9.5 g (0.077 mol) of bicyclo[2.2.2]octanone-2[21] in 25 ml of ether and 12.6 g (0.10 mol) of benzyl chloride, 2.7 g (0.11 mol) of magnesium, and 90 ml of ether. Distillation afforded 15.2 g (0.074 mol, 90%) of **7**: bp 100–104° (0.05 mm); ir 3590 cm^{-1}; nmr τ 7.22 (s, $-CH_2Ph$).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83. 29; H, 9.23.

1,7,7-Trimethyl-2-(α-bromobenzyl)-2-norbornanol (2). Into a flask was placed 24.4 g (0.10 mol) of **1**, 17.8 g (0.100 mol) of *N*-bromosuccinimide, 1 g of benzoyl peroxide, and 200 ml of CCl_4. The mixture was brought to reflux, at which time a vigorous reaction occurred. When the reaction subsided the mixture was refluxed for an additional 45 min. The mixture was cooled and the succinimide was removed by suction filtration, after which the solvent was removed under vacuum (rotary evaporator). The residual oil isolated was used directly without purification:[3] ir 3550 cm^{-1}; nmr τ 4.83 [s, -C(**H**)(Br)(Ph)].

1,8,8-Trimethyl-3-phenylbicyclo[3.2.1]octanone-2 (3) and 1,8,8-Trimethyl-2-phenylbicyclo[3.2.1]octanone-3 (4). To an ice-cooled, stirred solution of 2 in 300 ml of anhydrous benzene, a solution of isopropylmagnesium bromide [from 14 g (0.11 mol) of isopropyl bromide, 2.9 g (0.12 mol) of magnesium, and 50 ml of ether] was added dropwise. After the addition the ice bath was removed and the solution was stirred at room temperature for 24 hr and then refluxed for 1 hr. The mixture was cooled and decomposed with a saturated solution of NH_4Cl. The organic layer was separated, washed with a 10% sodium carbonate solution and water, and finally dried ($MgSO_4$). The solvent was removed under reduced pressure (rotary evaporator). The residue was distilled twice, affording 18.0 g (0.075 mol, 75%) of a colorless oil: bp 115-116° (0.10 mm); ir 1710 cm^{-1} (C=O); nmr τ 6.53 [br s, O=CC(**H**)(Ph)], 6.45 [t, O=CC(**H**)(Ph)].

The mixture (3 and 4) (1.0 g) was chromatographed (25 g of Woelm acid-washed Alumina, Grade I) using pentane (100 ml), pentane-benzene (75% v/v, 100 ml), benzene (100 ml), and chloroform as eluents. The major product, 3, was isolated in 70% yield as a waxy solid, mp 64.5-66°, and was equivalent to 12.6 g (0.052 mol, 52%) based upon 1: ir (CCl_4) 1710 cm^{-1} (C=O); nmr τ 6.45 [t, O=CC(**H**)(Ph)], 2.75-3.20 (br m, phenyl hydrogens), and 9.04 (s, -CH_3 all). Two recrystallizations from pentane gave a solid, mp 66-67°.

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.40; H, 9.19.

Several attempts to prepare the 2,4-DNP were fruitless.

The minor product, 4, from the chloroform elution was isolated in 30% yield as a waxy solid, mp 70.5-73°, and was equivalent to 5.4 g (0.023 mol, 23%) based upon 1: ir (CCl_4) 1710 cm^{-1} (C=O); nmr τ 6.53 [s, O=CC(**H**)(Ph)]. Two recrystallizations (pentane) yielded a solid, mp 78-79.5°.

Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.34; H, 9.12.

The 2,4-DNP of 1,8,8-trimethyl-2-phenylbicyclo[3.2.1]octanone-3, yellow needles (EtOH), had a melting point of 211-212°.

Anal. Calcd for $C_{23}H_{26}N_4O_4$: C, 65.38; H, 6.20; N, 13.26. Found: C, 65.28; H, 6.27; N, 13.30.

In another experiment 10 g (0.041 mol) of 3 (41% based upon 1) was isolated directly from the initial distillate by successive recrystallizations from hexane.

Two 1-g samples of 3 were dissolved in a tenfold excess of trifluoroacetic acid and trifluoroacetic acid-*d*, respectively. The solutions were heated at 50° for 2 hr, neutralized with a 20% solution of sodium carbonate, and extracted with ether, and the ether was dried ($MgSO_4$). The solvent was removed and the products were crystallized from hexane: the nmr spectrum of the sample treated with CF_3CO_2H was identical with the nmr spectrum of untreated 3; the nmr spectrum of the sample treated with CF_3CO_2D was also identical with that of untreated 3 except that the signals attributed to the benzyl hydrogen were absent.

2-(α-Bromobenzyl)bicyclo[2.2.2]octanol-2 (8) was prepared as described for 2 starting with 6.5 g (0.030 mol) of 7, 5.7 g (0.030 mol) of *N*-bromosuccinimide, 0.1 g of benzoyl peroxide, and 75 ml of CCl_4. The reaction occurred after a 5-min induction period, after which the mixture was refluxed for 30 min. After removal of the solvent 9.6 g of solid remained: ir 3550 cm^{-1}; nmr τ 4.87 [s, -C(**H**)(Br)(Ph)].

3-Phenylbicyclo[3.2.2]nonanone-2 (5) and 2-Phenylbicyclo-[3.2.2]nonanone-3 (6). To the crude product 8, dissolved in 100 ml of benzene and cooled with an ice bath, 19.8 ml of a 1.52 *M* ethereal solution of isopropylmagnesium bromide[22] was added dropwise. The mixture was stirred for 20 min while in the ice bath, 40 min at room temperature, and 2 hr at reflux, after which it was worked up as before. After the solvent was removed there remained 6.85 g of a waxy, yellow solid. Trituration with pentane gave 1.50 g (0.0073 mol, 24% based upon 7) of 5: mp 101-104°; ir (CCl_4) 1710 cm^{-1} (C=O); nmr τ 6.10 [q, O=CC(**H**)(Ph)]. An analytical sample was prepared by subliming it twice at 90-95° (0.05 mm), mp 108-109.5°.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.18; H, 8.52.

Upon cooling the above pentane solution an additional 2.50 g of crystalline product was obtained, which nmr spectral analysis revealed to be a mixture of 5 and 6. The mixture (2.50 g) was chromatographed (50 g of Woelm acid-washed Alumina, Grade I) using pentane (300 ml), pentane-benzene (75% v/v, 250 ml), pentane-benzene (50% v/v, 200 ml), benzene (200 ml), and chloroform (200 ml) as eluents. In this manner an additional 1.25 g of 5 was obtained resulting in an overall yield of 2.75 g (0.013 mol, 43% based upon 7). In addition 1.25 g (0.0060 mol) of 6 was obtained (20% based on 7): mp 48-51°; ir (CCl_4) 1708 cm^{-1} (C=O); nmr τ 6.35 [br s, O=CC(**H**)(Ph)]. An analytical sample of 6 was prepared by two sublimations at 65-70° (0.05 mm), mp 49.5-52°.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.46. Found: C, 83.93; H, 8.40.

2-Methyl-1-(α-bromobenzyl)-1-cyclopentanol (12) was prepared as described for 2 (0.100 mol of 13 employed). After removal of the solvent a light yellow oil remained: ir 3500 cm^{-1}; nmr τ 4.80 [s, -C(**H**)(Br)(Ph)].

3-Methyl-2-phenylcyclohexanone (10) and 2-Methyl-6-phenylcyclohexanone (11). The ring expansion of 12 was accomplished as for 2 except that the mixture was stirred at room temperature for 1 hr and refluxed for 15 min. The product was distilled twice, yielding 11.0 g (0.058 mol, 58% based upon 13) of a mixture of 10 and 11: bp 79-80° (0.05 mm); ir 1715 cm^{-1} (C=O); nmr τ 6.95 [d, O=C-C(**H**)(Ph)], 6.35-6.70 [br q, O=CC(**H**)(Ph)].

The mixture (1.0 g) was chromatographed (25 g of Woelm acid-washed Alumina, Grade I) using pentane (200 ml) and chloroform (200 ml) as eluents. The major product (from $CHCl_3$ eluent) 10 was isolated in 82% yield as a white, waxy solid, equivalent to 9.0 g (0.048 mol, 48% based upon 13). Recrystallization from pentane gave 10: mp 49.5-51.5°; ir ($CHCl_3$) 1700 cm^{-1} (C=O); nmr τ 6.95 [d, O=CC(**H**)(Ph)].

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.73; H, 8.69.

The 2,4-DNP of 2-phenyl-3-methylcyclohexanone had a melting point of 150-151°, orange needles (EtOH).

Anal. Calcd for $C_{19}H_{20}N_4O_4$: C, 61.95; H, 5.47; N, 15.21. Found: C, 62.34; H, 5.47; N, 15.42.

The minor product (from pentane eluent) 11 was isolated in 18% yield as a waxy solid, equivalent to 2.0 g (0.010 mol, 10% based upon 13). Recrystallization from pentane afforded pure 11: mp 61-62°; ir ($CHCl_3$) 1690 cm^{-1} (C=O); nmr τ 6.35-6.70 [br q, O=CC(**H**)(Ph)]. The analytical sample melted at 62-62.5° (lit.[23] mp 51-52°).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.76; H, 8.77.

2-Methyl-1-(α-bromobenzyl)-1-cyclohexanol (17) was prepared as described for 2 on a 0.100-mol scale except that a vigorous reaction was not observed and the mixture was refluxed for 1 hr. The residual light yellow oil was used directly:[3] ir 3550 cm^{-1}; nmr τ 4.73 [d, -C(**H**)(Br)(Ph)].

***trans*-3-Methyl-2-phenylcycloheptanone (14) and *cis*- and *trans*-2-methyl-7-phenylcycloheptanone (16 and 15).** The ring enlargement was achieved following the procedure described for 2 except that the mixture was refluxed for 45 min and stirred at room temperature for 90 min. Vacuum distillation afforded 13.8 g of a light yellow oil: bp 128-133° (1.5 mm); ir 1720 cm^{-1} (C=O); nmr τ 6.10 (weak, br, benzyl hydrogen), 6.36 (br q, benzyl hydrogen), 6.78 (d, benzyl hydrogen), 9.02 (d, -CH_3), 9.06 (d, -CH_3), 9.19 (d, -CH_3), indicating a mixture of three isomers. An analytical sample of this mixture was prepared by distillation, bp 104-106° (0.15 mm).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.90; H, 8.83.

The mixture (2.0 g) was chromatographed (100 g of Merck grade alumina) using hexane (250 ml), hexane-benzene (75, 50, and 25% v/v, respectively, 250 ml each), and benzene (500 ml) as eluents. In this manner 0.43 g of 14 was isolated as a colorless oil in the final 500 ml of benzene; the latter was equivalent to 3.0 g (0.015 mol, 15% based upon 17), nmr τ 6.78 [d, O=CC(**H**)(Ph)]. A mixture (0.61 g) of 16 [nmr τ 6.36, br q, O=CC(**H**)(Ph)] and 15 [nmr τ 6.10, weak, br m, O=CC(**H**)(Ph)], which resisted further separation, was obtained as a colorless oil in the first 600 ml of eluent. The nmr spectrum of this mixture (15 and 16) indicated a composition of 0.48 g of 16 and 0.13 g of 15 which was equivalent to 3.3 g (0.016 mol, 16%) of 16 and 0.9 g (0.004 mol, 4%) of 15, both yields based upon 17. The yields were based on the ratio of the integration of the benzyl hydrogens to the total integration of the phenyl hydrogens.

The 2,4-DNP of *cis*-2-methyl-7-phenylcycloheptanone (16)[14] was prepared directly from the mixture (15 and 16), mp 152-153°, orange needles (EtOH).

Anal. Calcd for $C_{20}H_{22}N_4O_4$: C, 62.82; H, 5.80; N, 14.65. Found: C, 62.35; H, 5.88; N, 14.62.

The center portion of the chromatogram contained a mixture of all three components (0.96 g). The ratio of the areas for the benzyl protons in the integration of the nmr spectrum indicated a composition of 0.49 g of **14**, 0.38 g of **16**, and 0.09 g of **15**. The overall yields therefore are 6.4 g (0.032 mol, 32%) of **14**, 6.0 g (0.030 mol, 30%) of **16**, and 1.4 g (0.0070 mol, 7%) of **15**, all based on **17**.

In a separate experiment, 0.30 g (0.0015 mol) of the initial distillate, 0.60 g of sodium acetate, 0.40 g (0.0036 mol) of semicarbazide HCl, 4 ml of water, and 7 ml of ethanol were combined. After standing for 7 days, 0.11 g (0.00043 mol, 28%) of 3-methyl-2-phenylcycloheptanone (**14**) was isolated from the mixture as its semicarbazone: mp 210.5–213°; nmr ($CDCl_3$) τ 6.74 (d, benzyl hydrogen). This represents a 20% yield based on **17**. Two recrystallizations from 42% aqueous ethanol yielded a solid, mp 218.5–219.5°.

Anal. Calcd for $C_{15}H_{21}N_3O$: C, 69.47; H, 8.16; N, 16.20. Found: C, 69.46; H, 7.96; N, 16.08.

Lastly, two 0.1-g aliquots of the initial mixture were combined with a fivefold excess of CF_3CO_2H and CF_3CO_2D, respectively. The samples were heated at 75° for 24 hr and cooled, and their nmr spectra were obtained: nmr (CF_3CO_2H) revealed that the only change in the spectrum[24] of this sample and the spectrum of the untreated initial mixture was a marked decrease in the intensity of the benzyl proton in **15**, τ 6.33, and a marked increase in the intensity of the benzyl proton in **16**, τ 6.55; nmr (CF_3CO_2D) revealed that the only change in the nmr spectrum of this sample and the spectrum of the untreated initial mixture was that signals attributed to the benzyl protons were almost absent. In a second and related experiment 1 g of the initial mixture was treated with 10 g of CF_3CO_2H for 24 hr at 75° and the product was isolated as described for **3**. The results were the same as above:[24] nmr τ 6.10 (br m, benzyl hydrogen of **15**, barely detectable), 6.36 (br q, benzyl hydrogen of **16**), and 6.78 (d, benzyl hydrogen of **14**).

Registry No.—**1**, 50986-74-8; **2**, 51016-54-7; **3**, 50986-99-7; **4**, 50987-00-3; **4** 2,4-DNP, 50987-01-4; **5**, 50986-75-9; **6**, 50986-76-0; **7**, 50986-77-1; **8**, 50986-78-2; **10**, 50987-02-5; **10** 2,4-DNP, 50987-03-6; **11**, 50987-04-7; **12**, 50986-79-3; **13**, 50986-80-6; **14**, 50987-05-8; **14** semicarbazone, 50987-06-9; **15**, 50987-07-0; **16**, 50987-08-1; **16** 2,4-DNP, 50987-09-2; **17**, 50986-81-7; **18**, 50986-82-8; camphor, 76-22-2; benzyl chloride, 100-44-7; 2-methylcyclopentanone, 1120-72-5; 2-methylcyclohexanone, 583-60-8; bicyclo[2.2.2]octanone-2, 2716-23-6; isopropyl bromide, 75-26-3.

References and Notes

(1) (a) A. J. Sisti, *J. Org. Chem.*, **33**, 453 (1968); (b) *Tetrahedron Lett.*, 5327 (1967); (c) *J. Org. Chem.*, **33**, 3953 (1968); (d) *ibid.*, **35**, 2670 (1970); (e) A. J. Sisti and M. Meyers, *ibid.*, **38**, 4431 (1973).

(2) T. A. Geissman and R. I. Akawie, *J. Amer. Chem. Soc.*, **73**, 1993 (1951).

(3) All bromohydrins herein were used directly without purification, since they were relatively unstable.

(4) The product **3** was treated in two experiments with trifluoroacetic acid and trifluoroacetic acid-*d* and the isolated product in each case was identical with **3** from the ring-expansion reaction (eq 2) (except for deuterium exchange which resulted with CF_3CO_2D). Thus the thermodynamically more stable isomer for **3**, and presumably **4**, was isolated directly from the expansion reaction. The structural assignments depicted (eq 2) would appear to be the more stable ones for **3** and **4**.

(5) R. R. Sauers and R. J. Tucker, *J. Org. Chem.*, **28**, 876 (1963).

(6) J. Berson and P. Reynolds-Warnhoff, *J. Amer. Chem. Soc.*, **86**, 595 (1964); J. Berson and D. Willner, *ibid.*, **86**, 609 (1964).

(7) R. R. Sauers and J. A. Beisler, *J. Org. Chem.*, **29**, 210 (1964).

(8) The principle of least motion may be another factor promoting C-2–C-3 bond migration over C-1–C-2 bond migration; more of the carbon atoms in the molecule are in motion and with a greater degree when the C-1–C-2 bond migrates than when the C-2–C-3 bond migrates.

(9) E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 125.

(10) The nitrous acid deamination of 2-aminomethyl[2.2.2]bicyclooctane has been reported to yield primarily 2-hydroxy[3.2.2]bicyclononane (70%), resulting from C-2–C-3 bond migration, compatible with the observations herein; see K. Alder, H. Krieger, and H. Weiss, *Ber.*, **88**, 144 (1955).

(11) Arguments for the predominance of one of the diastereoisomeric bromohydrins (**2, 12**) can be presented. From that isomer, conformational and steric considerations for the preferred migration of one bond over the other can be offered (assuming the migrations to be trans and coplanar). Such a detailed mechanistic argument would be too ambitious for the data presented. One, however, cannot overlook these considerations as possible additional factors affecting the product distribution.

(12) A. J. Sisti, G. M. Rusch, and H. K. Sukhon, *J. Org. Chem.*, **36**, 2030 (1971).

(13) It has been demonstrated experimentally with a representative number of ring-enlarged ketones[1b,d,4] that under the reaction conditions the more stable isomers are isolated. The structures assigned for **10** and **11** would appear to be the more stable.

(14) B. Tchoubar, *Bull. Soc. Chim. Fr.*, 160 (1949).

(15) It is assumed that the cis isomer **16** is more stable than the trans isomer **15.** Recent evidence (M. Hanack, "Conformational Theory," Academic Press, New York, N. Y., 1965, pp 151 and 163) indicates that cycloheptanone probably exists in a twist chair conformation and it would seem reasonable that the methyl group in the equatorial position might be more stable, as in 2-methylcyclohexanone; thus the cis isomer **16** (phenyl equatorial) should be the more stable.

(16) C. Gutsche and C. Chang, *J. Amer. Chem. Soc.*, **84**, 2263 (1962).

(17) All melting points are uncorrected. Infrared spectra, all of pure liquid films unless otherwise stated, were determined with a Perkin-Elmer Model 257 Grating Infrared. The nmr spectra, in CCl_4 solutions unless otherwise specified, were determined with a Varian A-60 instrument.

(18) Initially heat was applied to the condenser to prevent the unreacted camphor, which sublimed, from obstructing the condenser. During the distillation of **1** the condenser was cooled in the usual manner.

(19) A. I. Shavrygin, *Zh. Obshch. Khim.*, **21**, 749 (1951).

(20) J. Cook and C. Hewett, *J. Chem. Soc.*, 62 (1936).

(21) Prepared by the oxidation of bicyclo[2.2.2]octanol-2 according to the procedure of Walborsky [A. Youssef, M. Baum, and H. Walborsky, *J. Amer. Chem. Soc.*, **81**, 4709 (1959)]. The alcohol was prepared from bicyclo[2.2.2]oct-5-en-2-yl acetate [J. Hine, J. Brown, L. Zalkow, W. Garden, and M. Hine, *J. Amer. Chem. Soc.*, **77**, 594 (1955)] by conversion to the unsaturated alcohol [H. Goering, R. Greiner, and M. Sloan, *ibid.*, **83**, 1391 (1961)] followed by reduction [K. Mislow and J. Berger, *ibid.*, **84**, 1956 (1962)].

(22) The Grignard was standardized by the procedure of Gilman [H. Gilman, E. Zollner, and J. Dickey, *J. Amer. Chem. Soc.*, **51**, 1576 (1929)].

(23) R. Ireland and J. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

(24) The shift in τ values undoubtedly is due to a solvent effect (CCl_4 to CF_3CO_2H), and the values obtained for treated and untreated samples whose spectra were measured in CCl_4 were almost identical.

A New Synthesis of β,γ-Unsaturated Carbonyl Compounds[1]

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Treatment of 1-alkylidene-2-alkoxycyclopropanes with mercuric acetate in aqueous alcohol, followed by treatment of the vinylmercuric derivative thus produced with hydrogen sulfide, affords γ,γ-disubstituted β,γ-unsaturated carbonyl compounds, free from the corresponding α,β-unsaturated isomers, in high yields.

The ready availability of 1-alkylidene-2-alkoxycyclopropanes, **1**, from addition of alkylidene carbenes to vinyl ethers[3] made a study of the further reactions of this hitherto unavailable class of compounds of interest. In preliminary exploratory work, 1-cyclohexylidene-2-*tert*-butoxycyclopropane, **2**, was shown to yield the dimethyl acetal of 3-cyclohexylidenepropanal, **3**, on treatment with a cation-exchange resin in methanol, and 3-cyclohexylidenepropanal 2,4-dinitrophenylhydrazone, **4**, on treatment with 2,4-dinitrophenylhydrazine reagent.[4] All attempts to isolate 3-cyclohexylidenepropanal after acidic treatment of **2** failed. Because routes to β,γ-unsaturated carbonyl-con-