Competition between Wagner–Meerwein Rearrangement and Intramolecular Electrophilic Substitution in the 3-Diphenylmethylene Isobornyl System

JEAN PIERRE MORIZUR, BERNARD FURTH, and JEAN KOSSANYI*

Laboratoire de Chimie Organique Structurale, Bât. F, Université de Paris VI,
4 Place Jussieu, 75230 Paris Cedex 05, France

Received September 27, 1972

Epimerization of 3-diphenylmethyleneisobornyl acetate (4), between 25 and 60° and in acid medium (HOAc–H_2SO_4), yields preferentially the endo isomer **4**. Prolonged treatment, under the same reaction conditions, makes the reaction proceed through an irreversible electrophilic substitution toward the indene-type hydrocarbon **8**. Structure of the latter is documented with spectroscopic data as well as with chemical proof by transformation into diketone 9, the stereochemistry of which is discussed. The acid-catalyzed dehydration of diphenylmethyleneisoborneol (2) depends upon the acid strength of the dehydrating agent and of the temperature. In the presence of PTSA and at 60°, only Wagner–Meerwein rearrangement, leading to hydrocarbons **12** and **13** in the 1:9 ratio, is observed. Around 130° and using potassium bisulfate as dehydrating agent, 2,6-hydrogen shift and Nametkin rearrangement occur together with the Wagner–Meerwein rearrangement; a 30:1:15:5 mixture of hydrocarbons **12**, **13**, **14**, and **15** is then obtained. Above 130°, the dehydration leads to the indene-type structure **8**.

The influence of an unsaturated substituent upon the solvolysis of bridged bicyclic compounds has received but little attention. Interaction between carbonium ions and olefinic double bonds, which stabilizes the charge by allylic isomerization, reduces considerably the usual rearrangements of the bridged system and induces selectively the attack of the ion from the less hindered side of the molecule. Thus, acetolysis of 3-*exo*-bromo-2-methylenenorbornane leads exclusively to a mixture of 3-*exo*-acetoxy-2-methylenenorbornane and 2-acetoxymethylnorbornene.[1] On the other hand, a 3-benzylidene substituent stabilizes the carbonium ion and limits, at room temperature, the acetolysis to only *cis,trans*-benzylidene and exo–endo isomerizations.[2] In these two examples, the nucleophilic attack at the level of carbon 3 takes place in the same way as in the absence of the conjugated double bond.

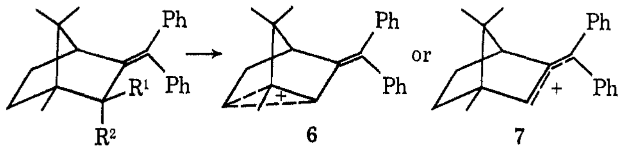
In order to extend the results obtained for *trans*-3-benzylideneisobornyl acetate,[2] the acetolysis of 3-diphenylmethyleneisoborneol (2) and derivatives has been investigated.

Results

3-Diphenylmethyleneisobornyl acetate (4) is prepared from the corresponding alcohol 2, obtained by $LiAlH_4$ reduction of 3-diphenylmethylenecamphor (1).[3] Acetolysis of compound 4, at room temperature and in the presence of traces of sulfuric acid, leads to an equilibrated mixture of 20% of 4 and 80% of its endo isomer 5, together with a hydrocarbon, the proportion of which increases with time and the structure of which will be discussed later. The same ratio (1:4) is reached when starting from pure compound 5. The high relative amount of the endo isomer is quite unusual. Thus, acetolysis of apoisobornyl, *exo*-camphenilyl, or β-fenchoisocamphoryl brosylates gives exclusively exo acetates.[4] Similarly, acetolysis of bornyl or isobornyl chloride yields only isobornyl acetate.[5]

Bicyclo[2.2.1]heptane derivatives are known to give, in acid medium, nonclassical ions by anchimeric assistance of the C_1–C_6 σ bond; as a result, molecules with exo leaving groups react faster than their endo epimers, and the attack of the ion by the nucleophile occurs from the exo side. On the other hand, a localized ion should give a mixture of endo and exo isomers, in which the former, being thermodynamically the more stable, should predominate.[6] These considerations exclude ion 6 (Scheme I) as the principal intermediate in the acetolysis of compound 4 and rather favor a "localized" ion as in the isomerization of isobornyl chloride into bornyl chloride induced by Lewis acids.[7] For compound 4 (or 5), stabilization of the charge by the conjugated diphenylmethylene group probably accounts for the absence, even at 60°, of the expected rearrangements of the bridged bicyclic system. Thus, the intermediate ion can be depicted as 7 (Scheme I). This result parallels the one obtained for *trans*-3-benzylideneisobornyl acetate,[2] although Wagner–Meerwein rearrangement was then observed when the reaction was carried out at 60°. As the difference in stability between endo and exo epimers is small,[8] the stereochemistry of the major reaction product reflects the steric effect of the 7-syn methyl and cis phenyl groups on the approach of the ion by the nucleophile, under a thermodynamic control of the reaction.

SCHEME I



6

7

2, $R^1 = OH; R^2 = H$
3, $R^1 = H; R^2 = OH$
4, $R^1 = OAc; R^2 = H$
5, $R^1 = H; R^2 = OAc$

Structure of Hydrocarbon 8.—Isolated from the acid-catalyzed acetolysis of compound 4, this hydro-

---

(1) C. W. Jefford and W. Wojnarowski, *Helv. Chim. Acta*, **53**, 137 (1970).

(2) J. Kossanyi, B. Furth, and J.-P. Morizur, *Tetrahedron*, **26**, 395 (1970).

(3) A. Haller, *C. R. Acad. Sci.*, **113**, 22 (1891).

(4) A. Couter, E. C. Friedrich, N. J. Holmes, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 378 (1965).

(5) J. Simonsen and L. N. Owen, "The Terpenoids," Vol. II, Cambridge University Press, New York, N. Y., 1949, p 315.

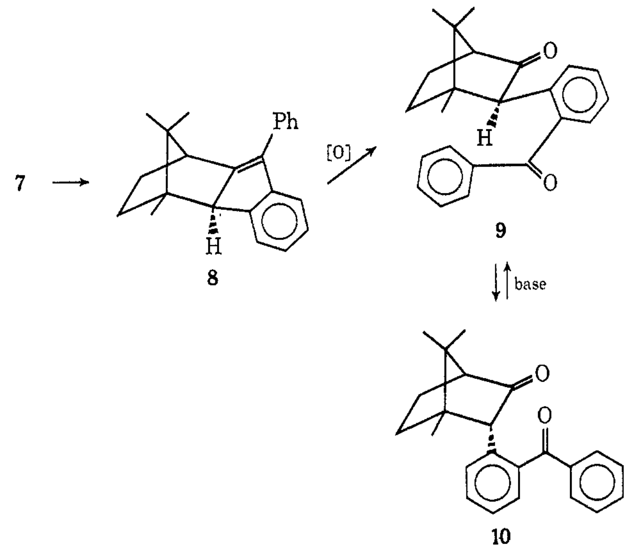
(6) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, **87**, 375 (1965).

(7) H. Meerwein and K. van Emster, *Ber.*, **53**, 1815 (1920).

(8) "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 115.

carbon accounts for 25% of the reaction mixture after 20 min at 60°, and is the only reaction product after 1.25 hr at 70°. The absence of Wagner–Meerwein rearrangement, or 2,6-hydrogen shift, at this temperature makes one presume that this hydrocarbon is formed directly from the allylic ion **7**. The phenylindene structure **8** (Scheme II) has been attributed to it from spectral evidences and chemical proofs.

SCHEME II

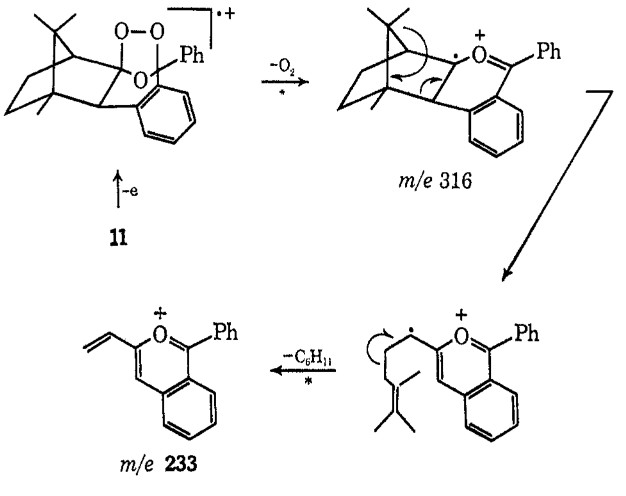


Its nmr spectra shows three methyl groups (at 0.26, 0.80, and 1.23 ppm) and no olefinic protons; the strongly shielded methyl group results from the anisotropy effect of one phenyl group[9] on the 7-syn methyl substituent; the presence of only nine aromatic protons also favors structure **8**. Other evidence arises from the uv absorption of the compound [238 nm (ε 20,000)] which can be compared to that[10] of 3-phenylindene itself [230 nm (ε 18,000)]. Mass spectrometric measurements give a molecular ion at *m/e* 300 which corresponds to $C_{23}H_{24}$. Chemical proofs of structure **8** comes from its oxidation to diketone **9** either using Jones reagent[11] or by ozonolysis according to the Pappas procedure[12] (Scheme II).

In the latter case, the intermediate ozonide **11**, which can be isolated, shows a mass spectrometric fragmentation (depicted in Scheme III) which favors the postulated structure: the molecular ion (*m/e* 348, $C_{23}H_{24}O_3$ from high-resolution mass measurement) expels successively one oxygen molecule (to yield ion *m/e* 316) and 83 mass units (C_6H_{11}) to form the stable pyrylium ion (*m/e* 233) which constitutes the base peak of the spectra (Scheme III). Ozonide **11** gives almost quantitatively diketone **9** when submitted to Jones reagent.

For compound **9**, the spectroscopic data [ir 1748 and 1668 cm^{-1}, uv 235 nm (ε 13,000)] as well as mass spectrometric results (molecular ion at *m/e* 332 corresponding to $C_{23}H_{24}O_2$ from high-resolution mass measurement) support the presence of two carbonyl groups, one of them being part of a benzophenone moiety.

SCHEME III



The nmr spectrum of diketone **9** exhibits three methyl groups (two overlapped at 0.92 ppm and one at 1.05 ppm), two methylene groups (m centered at 1.74 ppm), one tertiary hydrogen (broad signal at 2.20 ppm assigned to the bridgehead proton), one other tertiary proton (s at 4.43 ppm), and nine aromatic protons (m between 7.3 and 8.0 ppm). The exo configuration of the benzophenone moiety is deduced from the narrow signal (half-width *ca.* 2 Hz) of the singlet at 4.43 ppm, as can be expected for an uncoupled proton. In order to verify the given stereochemistry of the benzophenone moiety in diketone **9**, exo–endo epimerization has been carried out in basic medium. This leads to a 3:7 mixture (Scheme II) of compounds **9** and **10**, respectively, the latter showing in its nmr spectrum a small long-range coupling (half-width of 4 Hz) for the exo hydrogen atom linked to C-3. This result is consistent with a W-type coupling with the exo H-5 proton. Compared to the usual chemical shifts found for the exo–endo protons in bicyclo[2.2.1]-heptane systems, an unexpected shielding of the exo H-3 proton is observed: 4.30 ppm (in compound **10**) compared to 4.43 for the endo proton (in compound **9**). In spite of these reversed chemical shifts, which certainly are the result of different shielding caused by the benzophenone substituent, the observed long-range coupling is a more valuable argument for the postulated stereochemistry.

Ion **7** should be involved, also, in the acid-catalyzed dehydration of 3-diphenylmethyleneisoborneol (**2**). An earlier report[13] indicates that alcohol **2** yields a 1:3 mixture of 5-diphenylmethylene-2,3,3-trimethyltricyclo[2.2.1.$0^{2,6}$]heptane (**12**) and 7-diphenylmethylenecamphene (**13**) when heated for 0.5 hr at 160° in the presence of $KHSO_4$. The apparent discrepancy between this result and what one would have expected from the above-described acetolysis of **4** prompted us to reinvestigate the acid-catalyzed reaction of alcohol **2**.

Dehydration of 3-Diphenylmethyleneisoborneol (2).—Treatment of a benzene solution of alcohol **2** by *p*-toluenesulfonic acid at 60° yields a 1:9 mixture of hydrocarbons **12** and **13**, respectively (Scheme IV). These two compounds have been identified from their nmr spectra, which have already been discussed

---

[9] See, for instance, B. L. Shapiro, M. J. Gattuso, and G. R. Sullivan, *Tetrahedron Lett.*, 223 (1971), and references cited therein.

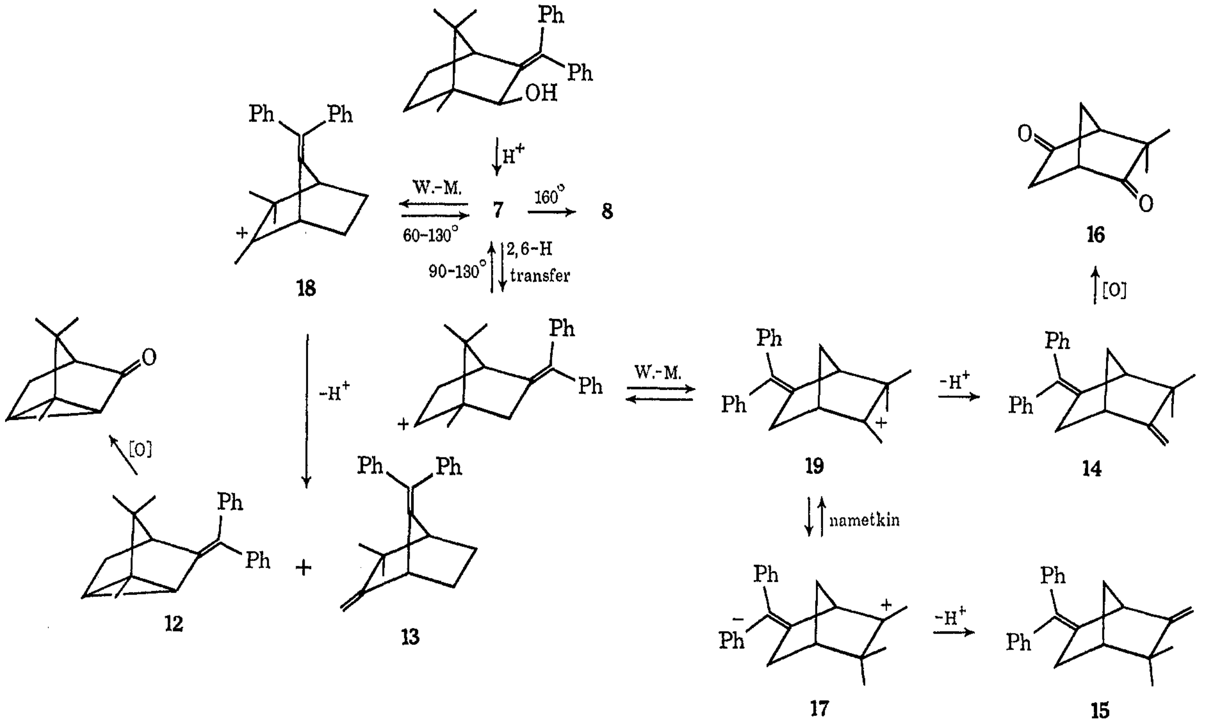
[10] L. Skattebøl and B. Boulette, *J. Org. Chem.*, **31**, 81 (1966).

[11] K. Bowden, I. M. Heilbron, E. R. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

[12] J. J. Pappas and W. P. Keaveney, *Tetrahedron Lett.*, 4273 (1966).

[13] D. C. Kleinfelter, R. W. Aaron, T. J. Gerteisen, J. M. Miller, and T. B. Bennett, *J. Org. Chem.*, **32**, 3521 (1967).

SCHEME IV



elsewhere.[13] Furthermore, ozonolysis of tricyclene **12** leads to the already known[14] 2,3,3-trimethyltricyclo-[2.2.1.0^{2,6}]heptanone (Scheme IV) and to benzophenone. On the other hand, hydrocarbon **13**, which contains two olefinic protons, partly isomerizes into tricyclene **12** when heated to around 300°; this verifies its camphenic structure.

Under more drastic conditions ($KHSO_4$, 160°), 3-diphenylmethyleneisoborneol (**2**) forms a single product, with yields as high as 80%, in all points identical with hydrocarbon **8**. The difference between this result and that of the literature[13] led us to determine the temperature above which hydrocarbon **8** is formed to the detriment of **12** and **13**. The critical value of 130° has been found. In the 90–130° temperature range, a mixture of four hydrocarbons, **12**, **13**, 5-diphenylmethylenecamphene (**14**), and 6-diphenylmethylenecamphene (**15**) is obtained (Scheme IV). At 130°, the relative proportions of the hydrocarbons are 30:1:15:5, respectively. Each of them leads to the same mixture of the four hydrocarbons when heated to around 130° in the presence of $KHSO_4$. Furthermore, pure samples of hydrocarbons **12**, **13**, **14**, or **15** lead to compound **8** when kept for 1 hr at 160° in the presence of $KHSO_4$. Thus, the equilibrium mixture in acid medium, obtained from these hydrocarbons, undergoes an irreversible displacement to hydrocarbon **8** under conditions of thermodynamic control.

Proof of structure of hydrocarbon **14** comes from its nmr spectra (two olefinic protons, one at 4.77 and the other at 4.55 ppm as indication of a camphenic skeleton) and, mainly, from the diketone formed by ozonolysis; this diketone is shown to be identical with 5-oxocamphenylone (**16**), obtained by oxidation of camphenylone following ref 15.

Hydrocarbon **15**, obtained in low yields, has been identified only from its spectroscopic data. High-resolution mass spectrometry gives the expected $C_{23}H_{24}$ formula for the molecular ion. The nmr spectrum displays two olefinic protons and one strongly deshielded aliphatic proton at 3.33 ppm. By comparison with the spectra of *cis*- and *trans*-6-benzylidenecamphene (obtained[2] from *trans*-benzylideneisoborneol), for which the H-1 bridgehead proton gives a signal at 3.28 and 3.67 ppm, respectively, the 6-diphenylmethylenecamphene structure **15** has been attributed to this compound.

Discussion

The absence of Wagner–Meerwein rearrangement during the acetolysis of compound **4** (or **5**) reflects the stability of the allylic ion **7** which, in the presence of a large excess of the nucleophile, proceeds either reversibly toward a mixture of acetates **4** and **5** or irreversibly toward hydrocarbon **8**. The preferred endo attack by the nucleophile, combined with the electrophilic substitution of the cis benzene ring by the carbonium ion from the exo side of the bicyclic system, emphasizes the stereoselectivity of the reaction.

In the absence of nucleophile, therefore, under dehydrating conditions, alcohol **2** gives three reactions depending upon the thermal conditions and the strength of the acid. In the presence of PTSA and at 60°, only Wagner–Meerwein rearrangement, leading to hydrocarbons **12** and **13**, is observed to the exclusion of 2,6-hydrogen transfer or Nametkin rearrangement (migration of the exo[16] methyl group); absence of the latter at the level of ion **18**, which forms hydrocarbon **13**, is verified from the high optical activity (+218°) of this compound. Nametkin rearrangement would have induced, then, racemization of product **13**.

---

[14] S. S. Nametkin and S. S. Zabrodina, *C. R. Acad. Sci. USSR*, **36**, 142 (1942); *Chem. Abstr.*, **37**, 5712^6 (1943).

[15] J. Meinwald, J. Shelton, G. Buchanan, and A. Courtin, *J. Org. Chem.*, **33**, 99 (1968).

[16] P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 699 (1967), and references cited therein.

By use of $KHSO_4$ instead of PTSA and, mainly, of a higher temperature (100–130°), the energy, given to the system, becomes sufficient to induce a 2,6-hydrogen shift (ion **17**) to form hydrocarbon **14** by subsequent Wagner–Meerwein rearrangement. Nametkin rearrangement of ion **19** forms compound **15**.

It is noteworthy that, in the absence of nucleophile, no evolution toward the indene structure **8** is observed for a temperature lower than 130°, although this occurs even at room temperature in the presence of acetic acid. The energy of the transition state for electrophilic substitution on the benzene ring being high, in the absence of electron-withdrawing groups, the formation of the reaction intermediate must lower sufficiently the activation energy of the reaction and make it possible even at room temperature.

Over 130°, the single product **8** formed in the reaction under thermodynamic control, starting from any hydrocarbon **12** to **15** or from alcohol **2** (in the presence of only $KHSO_4$), reflects the irreversible displacement of the reaction toward intramolecular electrophilic substitution.

Such a reaction should occur, also, with 3-benzylideneisoborneol; for this reason, this compound has been submitted to acid-catalyzed ($KHSO_4$) dehydration at 160°. No product related to **8** has been found in this case but only the previously described[2] hydrocarbons. Introduction of an electron-donor group for stabilizing the allylic ion, using 3-*p*-methoxybenzylideneisoborneol, does not lead either to any indene-type compound when treated by $KHSO_4$ at 160°. Thus, the intramolecular electrophilic substitution is apparently limited to the diphenylmethylene substituent.

The nmr spectra of compounds **12** and **13** have already been described[13] and the ones obtained here are compatible with them. However, slight differences have been found for the position of their uv maximum absorption. A 1:3 mixture of **12** and **13** is reported[13] to have $\lambda_{\max}^{\mathrm{EtOH}}$ 239 nm (log ϵ 4.14), while our results on pure samples give $\lambda_{\max}^{\mathrm{MeOH}}$ 259 nm (log ϵ 4.20) for **12**, $\lambda_{\max}^{\mathrm{MeOH}}$ 249 nm (log ϵ 4.26) for **13**, and $\lambda_{\max}^{\mathrm{MeOH}}$ 239 nm (log ϵ 4.30) for the substituted indene **8**.

It should be noted, to conclude, that small variations in acid strength of the dehydrating agent or in temperature may induce the reaction to proceed toward different hydrocarbons.

Experimental Section

Physical Measurements.—Melting points, taken on a Leitz-Weltzlar apparatus, are uncorrected. Optical rotations were measured with a Perkin-Elmer Model 141 instrument. Elemental analyses were performed at the University of Paris VI. Gas chromatographic analyses were carried out on a Varian Aerograph HiFi Model 1400 equipped with a 0.25 in. × 10 ft column containing 15% silicone GE XE-60 (nitrile gum) on 80–100 mesh Chromosorb W. Ir spectra (CCl_4 solution) were obtained using a Perkin-Elmer Model 257 apparatus. Uv spectra were determined in methanol solution on a SP 800 Unicam instrument. Nmr spectra were run on a Varian 60-Mc instrument with tetramethylsilane as internal standard. Mass spectra have been obtained at 70 eV, through the direct inlet system of a Hitachi RMU-6E device (ion source at 150°).

3-Diphenylmethylenecamphor (1), $[\alpha]^{25}\mathrm{D}$ +230°, was prepared according to Haller.[3]

3-Diphenylmethyleneisoborneol (2), $[\alpha]^{25}\mathrm{D}$ −173°.—A solution of **1** (3.16 g, 0.01 mol) in 100 ml of anhydrous ether was added to a cooled slurry of lithium aluminum hydride (120 mg) in 30 ml of anhydrous ether. The reaction mixture was stirred overnight at room temperature. The excess of $LiAlH_4$ was destroyed with 10% HCl (30 ml), and the ethereal layer was washed successively with saturated Na_2CO_3 solution and water, then dried (Na_2SO_4) and concentrated. The solid residue, when recrystallized twice from petroleum ether (bp 40–50°), gave 2.5 g (80%) of 3-diphenylmethyleneisoborneol (**2**): mp 87–88°; uv max 247 nm (ϵ 11,800); ir 3590, 3480, 1608, 1500, and 1067 cm^{-1}; nmr (CCl_4) δ 7.20 (m, 10, aromatic H), 4.19 (s, 1, CHOH), 2.53 (d, 1, J = 3.6 Hz, bridgehead H), 2.00–1.20 [complex m, 5, $(CH_2)_2$ and OH], 1.14 (s, 3), 0.87 (s, 3), and 0.82 (s, 3).

Anal. Calcd for $C_{23}H_{26}O$: C, 86.74; H, 8.23. Found: C, 86.33; H, 8.14.

The mother liquors contain a mixture of the endo and exo isomers.

3-Diphenylmethyleneborneol (3), $[\alpha]^{25}\mathrm{D}$ +524°.—The endo epimer **3** was purified by thin layer chromatography (silica gel, benzene) of the above mixture after distillation of the solvent: mp 93–96°; uv max 251 nm (ϵ 13,000); ir 3630, 1606, 1503, and 1056 cm^{-1}; nmr (CCl_4) δ 7.21 (m, 10), 4.45 (s, 1), 2.38 (d, 1, J = 4.2 Hz), 2.30–1.10 (complex m, 5), 0.92 (s, 3), 0.88 (s, 6).

Anal. Found: C, 86.70; H, 8.21.

3-Diphenylmethyleneisobornyl Acetate (4), $[\alpha]^{25}\mathrm{D}$ −265°.—A 15-g (0.0471 mol) portion of the exo alcohol **2** in anhydrous pyridine (50 ml) solution was added to a pyridine solution (100 ml) of 10.2 g (0.1 mol) of acetic anhydride. The mixture was maintained for 24 hr at 70°, then cooled and evaporated to dryness. The obtained crystals were recrystallized twice from ligroin to give 15.2 g (90%) of the exo acetate **4**: mp 168–169.5°; ir 1733, 1601, 1495, and 1405 cm^{-1}; nmr (CCl_4) δ 7.23 (m, 10), 5.56 (s, 1), 2.61 (d, 1, J = 3.0 Hz), 1.90–1.30 (m, 7, out of which a sharp signal appeared at 1.47 attributed to the acetate methyl group), 1.15 (s, 3), 1.00 (s, 3), and 0.95 (s, 3).

Anal. Calcd for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83. Found: C, 83.44; H, 8.04.

3-Diphenylmethylenebornyl Acetate (5), $[\alpha]^{25}\mathrm{D}$ +380°.—A 159-mg (5×10^{-4} mol) portion of the endo alcohol **3**, dissolved in 2 ml of anhydrous pyridine, was added to 0.1 g (10^{-3} mol) of acetic anhydride in 1 ml of pyridine. After it was heated for 24 hr at 70°, the reaction mixture was cooled and evaporated to dryness and the crude residue was recrystallized twice from ligroin to yield 150 mg (83%) of the endo acetate **5**: mp 152–154°; ir 1731, 1604, 1498, and 1041 cm^{-1}; nmr (CCl_4) δ 7.21 (s, 10), 5.86 (s, 1), 2.48 (d, 1, J = 3.8 Hz), 2.25–1.25 (m, 7, one intense signal at 1.51 ppm integrated for 3 H and was attributed to the acetate methyl group), 1.01 (s, 3), 0.88 (s, 3), and 0.85 (s, 3).

Anal. Calcd for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83. Found: C, 83.37; H, 7.85.

Isomerization of 4. A.—A 500-mg portion of acetate **4**, dissolved in 20 ml of glacial acetic acid containing 20 mg of concentrated sulfuric acid, was stirred for 24 hr at room temperature. The solution was then poured into 30 ml of water and neutralized with a dilute solution of $NaHCO_3$. After extraction with CCl_4, the organic layer was dried over anhydrous Na_2SO_4. The mixture of endo and exo epimers (4:1) was analyzed by nmr. The two isomers did not separate from each other by tlc nor by glc. Four recrystallizations in ligroin gave pure endo acetate **5** identical with the above-described compound.

B.—In another run, $LiAlH_4$ reduction of the crude reaction mixture gave pure alcohols **2** and **3** after preparative tlc (silica gel, benzene).

C.—Acetate **4** (100 mg) in 4 ml of acetic acid containing 12 mg of concentrated sulfuric acid, was heated for 20 min at 60°. After treatment, the crude reaction products were analyzed by nmr: 60% endo acetate **5**, 15% exo acetate **4**, and 25% hydrocarbon **8** (the determination of the relative proportion of compound **8** was based on the signal of the methyl group shielded to 0.26 ppm). Absence of hydrocarbons **12–15** was verified by glc (XE 60 on Chromosorb W, 195°) and by tlc (silica gel impregnated with 10% $AgNO_3$, ligroin). Composition of the reaction mixture as a function of time and temperature is shown in Table I.

Characterization of Hydrocarbon 8, $[\alpha]^{25}\mathrm{D}$ −17°6.—The crude oily mixture, obtained after treatment of the acetolysis product (1.25 hr, 70°) of 2.0 g of acetate **4**, was filtered over neutral alumina using petroleum ether (bp 40–45°) as eluent. Distillation of the solvent under vacuum gave 1.58 g (95%) of

TABLE I

Reaction time	1 hr[a]	4 hr[a]	8 hr[a]	16 hr[a]	24 hr[a]	20 min[b]	75 min[c]
4, %	64	26	19	18	17.5	15	
5, %	36	74	76	72	70.5	60	
8, %		1	5	10	12	25	100

[a] 25°. [b] 60°. [c] 70°.

hydrocarbon **8** exhibiting one single glc peak: bp 135–140° (0.05 mm); uv max 238 nm (ε 20,000); nmr (CCl_4) δ 7.30 (complex m, 9, aromatic H), 3.18 (s, $W_{1/2}$ = 2 Hz, 1, CH, tertiary endo), 2.55 (broad signal, $W_{1/2}$ = 7 Hz, 1, bridgehead H), 2.10–1.60 (complex m, 4, $-CH_2CH_2-$), 1.23 (s, 3), 0.80 (s, 3), and, 0.26 (s, 3); mass spectrum (70 eV) *m/e* (rel intensity) 300 (67), 285 (17), 257 (29), 231 (40), 217 (69), 202 (39), 83 (100), and 55 (50).

Anal. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.73; H, 8.00.

Oxidation of Hydrocarbon 8. Diketone 9, $[\alpha]^{25}D$ +45°3. **A.**—Jones reagent[11] was added in excess to a solution of hydrocarbon **8** (400 mg, 1.33 mmol) in acetone (20 ml). The mixture was concentrated *in vacuo* and water (25 ml) was added. After three extractions with ether, the mixed organic extract was washed successively with saturated Na_2CO_3 solution and water, then dried (Na_2SO_4) and concentrated to give 420 mg (95%) of an oil which crystallized on standing. Recrystallization from ether–petroleum ether gave pure diketone **9**: mp 138–139°; uv max 253 nm (ε 13,000); ir 1748, 1668, 1600, 1576, 1485, and 1450 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 332 (40), 317 (14), 304 (44), 286 (11), 271 (6), 194 (42), 165 (20), 105 (100), and 77 (35).

B.—The procedure of Pappas[12] was used with the following modification. A solution of hydrocarbon **8** (400 mg, 1.33 mmol) in 25 ml of a $MeOH-CHCl_3-Me_2S$ mixture (6:3:1) cooled at −78° was treated with 1 equiv of ozone and concentrated. The tlc (SiO_2, benzene) examination of the crude product showed two spots. The ir, nmr, melting point, and tlc behavior of the more polar material (120 mg, 27%) was identical with that of the previously described diketone **9**. The less polar compound (200 mg, 43%) proved to be due to the corresponding ozonide **11**: $[\alpha]^{25}D$ +44°1; ir 1606, 1580, 1208, 1135, 1055, and 1020 cm^{-1}; nmr δ 7.6–6.6 (m, 9), 2.95 (s, 1), 2.15 (s, 1), 1.70 (s, 4), 1.35 (s, 3), and 0.95 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 348 (7), 320 (3), 316 (17), 233 (100), 211 (12), 194 (25).

Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94. Found: C, 79.44; H, 7.06.

Oxidation of **11** (200 mg) by Jones reagent yielded 175 mg (89%) of diketone **9**.

Epimerization of Diketone 9.—A solution of 33 mg (0.1 mmol) of diketone **9** in a mixture of pyridine (0.5 ml) and water (0.1 ml) was heated for 2 hr at 95°. After removal of the solvents, 5 ml of ether was added. The ethereal solution, washed first with dilute HCl and then with water, was dried (Na_2SO_4) and concentrated. The crude oily residue was found to be a 3:7 mixture of the two epimers **9** and **10** by direct nmr measurement.

Dehydration of Alcohol 2 by PTSA.—A 3.18-g (10^{-2} mol) portion of exo alcohol **2** in 35 ml of benzene containing 50 mg of PTSA was heated for 40 min at 60°. After cooling, the solution was washed successively with a saturated solution of $NaHCO_3$ and water. Direct glc (195°) analysis of the organic layer indicated a 1:9 mixture of hydrocarbons **12** and **13**, respectively. Distillation of the solvent, followed by filtration over neutral alumina (eluent ligroin), gave 2.51 g (83%) of the two hydrocarbons as a mixture. Column chromatography (10% $AgNO_3$ impregnated Florisil) gave first compound **12** (175 mg, elution with petroleum ether), then product **13** (1.46 g, elution with a 95:5 petroleum ether–benzene solution).

5-Diphenylmethylene-2,3,3-trimethyltricyclo[2.2.1.0^{2,6}]heptane (12), $[\alpha]^{25}D$ +24°, had mp 65–66°; uv max 259 nm (ε 16,000); ir 1660, 1603, 1495, 1447, 1283, 1132, 1074, 1038, and 863 cm^{-1}; nmr (CCl_4) δ 7.15 (s, 5), 7.11 (s, 5), 2.06 (broad s, 1), 1.95–1.28 (m, 4), 1.10 (s, 3), 0.97 (s, 3), 0.85 (s, 3).

Anal. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.73; H, 8.00.

2,3,3-Trimethyltricyclo [2.2.1.0^{2,6}]heptan-5-one, $[\alpha]^{25}D$ −67°5. —A 300-mg (1 mmol) portion of hydrocarbon **12** in a mixture of methanol (30 ml) and chloroform (10 ml) was treated with 1 equiv of ozone at −50°. Decomposition of the reaction mixture with 1.5 ml of methanol containing 0.5 g of INa and 0.4 ml of AcOH was followed by concentration *in vacuo*. The residue, dissolved in 50 ml of ether, was washed out successively with sodium thiosulfate and sodium bicarbonate aqueous solutions, then with water. Separation of trimethyltricyclanone and benzophenone, carried out by preparative glc (30% SE-30 on Chromosorb W, 10 ft, 180°) after concentration, gave 90 mg (50%) of benzophenone and 33 mg (21%) of the expected trimethyltricyclanone: mp 108–109° (sublimation at around 72°); ir 1755 cm^{-1}; uv max (MeOH) 208.5 nm (ε 5400), 271.5 (72), and 276 (67); mol wt, 150 (mass spectrum) (lit.[14] mp 111–112°).

7-Diphenylmethylenecamphene (13), $[\alpha]^{25}D$ +218°, had mp 60–62°; uv max 248 nm (ε 18,300); ir 1657, 1596, 1488, 1458, 1443, 1200, 1106, 1074, 1030, and 883 cm^{-1}; nmr (CCl_4) δ 7.16 (s, 10), 4.81 (s, 1), 4.60 (s, 1), 3.20 (broad s, 1), 2.33 (broad s, 1), 2.16–1.24 (m, 4), 1.11 (s, 3), and 1.02 (s, 3).

Anal. Calcd for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 91.67; H, 8.27.

Dehydration ($KHSO_4$) of Alcohol 2 at 160°.—A mixture of 3-diphenylmethyleneisoborneol (**2**) (4 g, 12.6 mmol) and $KHSO_4$ (5 g) was heated at 160° for 15 min; water was added to the cooled mixture and the contents of the reaction vessel were washed out with ether. The ethereal solution was washed successively with saturated sodium carbonate solution and water, then dried (Na_2SO_4) and concentrated. The crude yellow oil, on column chromatography with alumina using petroleum ether (bp 40–50°) as eluent, gave 3.09 g (82%) of hydrocarbon **8**, exhibiting one single glc peak and identical with the above-described compound.

Dehydration ($KHSO_4$) of Alcohol 2 at 130°.—A 3.18-g (10 mmol) portion of alcohol **2** mixed with 4 g of $KHSO_4$ was heated for 20 min at 130°. After cooling, the reaction mixture was extracted with ether; the ethereal fraction was washed with a saturated aqueous solution of $NaHCO_3$, then with water. Glc analysis of the crude reaction mixture exhibited four peaks corresponding to hydrocarbons **12**, **13**, **14**, and **15** (relative ratios 30:1:15:5, respectively). Evaporation of the solvent followed with filtration over 20 g of neutral alumina (benzene as eluent) yielded 2 g (66%) of the mixture of the four compounds. Column chromatography (10% $AgNO_3$ impregnated Florisil) gave successively hydrocarbons **12** (elution with petroleum ether, bp 45–55°), **13** (elution with 95:5 petroleum ether–benzene solution), and a mixture of **14** and **15** (elution with 85:15 petroleum ether–benzene solution). The latter compounds were separated from each other by preparative glc (30% QF 1 over Chromosorb W, 10 ft, 210°).

5-Diphenylmethylenecamphene (14), $[\alpha]^{25}D$ +166°, had mp 54–58°; uv max 249.5 nm (ε 14,500); ir 1668, 1600, 1496, 1460, 1443, 1192, 1134, 1104, 1090, 1073, 1034, 1012, and 882 cm^{-1}; nmr (CCl_4) δ 7.13 (m, 10), 4.77 (s, 1), 4.55 (s, 1), 2.78 (broad s, 1), 2.21 (d, 1, J = 3, 6 Hz), 1.95–1.23 (m, 4), 1.05 (s, 3), and 0.95 (s, 3); mol wt, 300 (mass spectrum).

5-Oxocamphenylone (16), $[\alpha]^{25}D$ −60°.—A 300-mg (1 mmol) portion of hydrocarbon **14** was treated, as described for the ozonolysis of compound **12**, to give 97 mg (54%) of benzophenone and 41 mg (26%) of 5-oxocamphenylone (**16**): mp 68–70°; ir 1760, 1718, 1150, 960, and 950 cm^{-1}; uv max 292 nm (ε 63); nmr (CCl_4) δ 2.90 (m, 1), 2.53 (unresolved q, 1), 2.30–1.95 (m, 4), 1.12 (s, 3), and 1.00 (s, 3); mol wt, 152 (mass spectrum). (lit. racemic[17] mp 56°; optically active[18] mp 74°, $[\alpha]^{40}D$ −90°).

6-Diphenylmethylenecamphene (15), $[\alpha]^{25}D$ +9°4, had mp 78–81°; uv max 252.5 nm (ε 11,600); ir (CCl_4) 1655, 1603, 1495, 1447, 1200, 1168, 1112, 1102, 1075, 1033, 1017, 1003, and 883 cm^{-1}; nmr (CCl_4) δ 7.16 (m, 10), 4.76 (s, 1), 4.62 (s, 1), 3.33 (broad s, 1), 2.36 (m, 1), 2.13–1.26 (m, 4), 1.07 (s, 6); mol wt, 300 ($C_{23}H_{24}$) (mass spectrum).

Registry No.—**1**, 40428-02-2; **2**, 40428-03-3; **3**, 40488-47-9; **4**, 40488-48-0; **5**, 40488-49-1; **8**, 40488-50-4; **9**, 40488-51-5; **11**, 40488-52-6; **12**, 40488-53-7; **13**, 40488-54-8; **14**, 40488-55-9; **15**, 40488-56-0; **16**, 40488-57-1; 2,3,3-trimethyltricylo[2.2.1.0^{2,6}]heptan-5-one, 28070-35-1.

---

(17) A. Gebhardt-Schmitz, H. Menniken, F. Schmitz, P. Lipp, and M. Lipp, *Tetrahedron Lett.*, 227 (1962).

(18) J. Bredt and P. Pinten, *J. Prakt. Chem.*, **119**, 90 (1928).