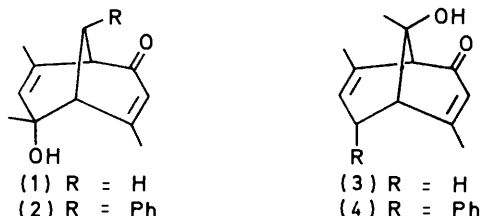


Dehydration of Some 9-Methyl-9-hydroxybicyclo[3.3.1]nona-3,7-dien-2-ones

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Dehydration of 9-hydroxy-4,8,9-trimethylbicyclo[3.3.1]nona-3,7-dien-2-one (3) by toluene-*p*-sulphonic acid in benzene gives a trimethylbicyclo[4.3.0]nonatrienone (7) by rearrangement. Dehydration of 9-hydroxy-4,8,9-trimethyl-6-phenylbicyclo[3.3.1]nona-3,7-dien-2-one (4) similarly gives a bicyclo[4.3.0]nonatrienone (6) and also the nonrearranged 9-methylenebicyclo[3.3.1]nonadienone (5). The mechanism of rearrangement is discussed and contrasted with the behaviour in acid of other hydroxybicyclo[3.3.1]nonadienones.

IN the course of studying the photochemistry of the bicyclic alcohols (1) and (2), we have observed¹ their ready photorearrangement to give (3) and (4) respectively. As photodehydration competed with photorearrangement we decided to study the thermal dehydration of alcohols (1)–(4). We now describe the



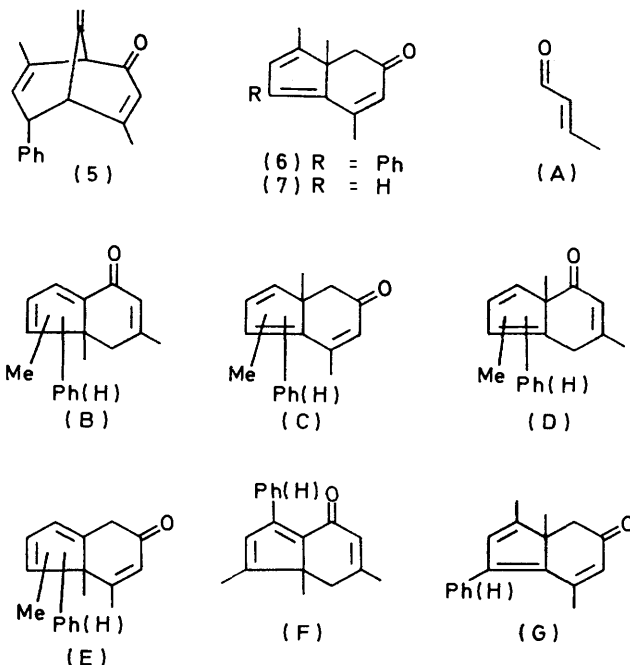
products of these reactions and contrast the behaviour of (1)–(4) in acid solution with that of related hydroxybicyclo[3.3.1]nonadienones.

Dehydration of alcohol (3) with toluene-*p*-sulphonic acid in benzene gave a single oily product characterized as its crystalline 2,4-dinitrophenylhydrazone, but on dehydration of alcohol (4) under similar conditions, two products, an oil and a yellow solid, could be isolated. Further reaction of the oil in benzene in the presence of acid gave the yellow solid.

Spectra of the oil from (4) were consistent with the retention of the chromophore of the $\alpha\beta$ -unsaturated ketone [ν_{\max} 1670 cm^{-1} ; λ_{\max} 244 (ϵ 7860) and 340 nm (ϵ 387)] and indicated four vinylic resonances at τ 4.23, 4.48, 5.22, and 5.31. The presence of only two methyl resonances at τ 8.16 and 8.98 and other spectroscopic data, including results of decoupling experiments given in the Experimental section defined the structure as (5), a product of simple dehydration.

The oil from (3) and the yellow solid from (4) clearly were related products. Their spectra suggested products of dehydration having a highly conjugated ketone [ν_{\max} 1675 cm^{-1} ; λ_{\max} 360 nm (ϵ >3000)] and the retention of three methyl groups. The product from (3) showed three vinylic resonances and the product from (4) two vinylic resonances. Decoupling experiments established that in the product from (3) two of the vinyl protons are attached to adjacent carbons and one of these protons has an allylic coupling to a methyl group, also attached to an sp^2 carbon. The presence of

a diene chromophore was confirmed by preparation of a Diels–Alder adduct with maleic anhydride. The adduct obtained with the product from (4) has λ_{\max} 240 nm (ϵ 15,210) indicating the presence of a styrene chromophore in this adduct. Further decoupling experiments established the retention of partial structure (A) in the product from (3) and in both the product from (4) and its adduct. The only partial structures that accommodate the above spectral data and the observation of singlet methyl resonances at τ 9.03 in the product from (3) and at τ 8.83 in the product from (4) associated with methyl groups attached to sp^3 carbon are (B)–(E). Structures (D) and (E) may be rejected by the observ-

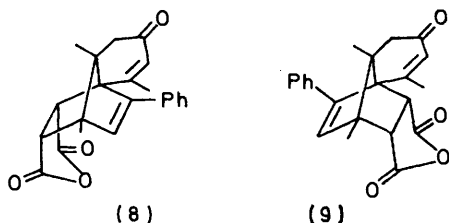


ation of extensive conjugation (λ_{\max} 360 nm). The positions of the unplaced methyl group and phenyl (hydrogen) group are defined by observation of an allylic coupling to the methyl group and the requirement that the maleic anhydride adduct has a styrene chromophore. Only two structures (F) and (G) are possible.

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Distinction between these structures may be made by observation of the considerable shielding of the methyl resonance at τ 8.31 in (6) [the product from (4)] by the phenyl group, relative to the equivalent resonance at τ 7.88 in (7) [the product from (3)]. This establishes the proximity of the phenyl and methyl groups and has adequate precedent in the similar shielding observed in (4) and (5). Further distinction between possible structures (F) and (G) may be made by consideration of the observed u.v. spectrum. The position of the long wavelength band at λ_{\max} 360 nm agrees well with a calculated value for (6) and (7) based on application of Woodward's Rules. Structures of type (F) should not have a band so far into the red.

Assignment of a structure to the maleic anhydride adduct of (6) cannot be made unambiguously. *endo*-Addition can lead to either (8) or (9). Although on steric grounds addition to give (8) might have been expected, there is adequate precedent² for other polar factors to control the mode of such additions. The possibility of 1,5-sigmatropic rearrangement of the diene leading to a new diene capable of adduct formation must be considered, but is unlikely in view of the abnormally high activation energy for rearrangement in (6) owing to partial loss of conjugation consequent upon

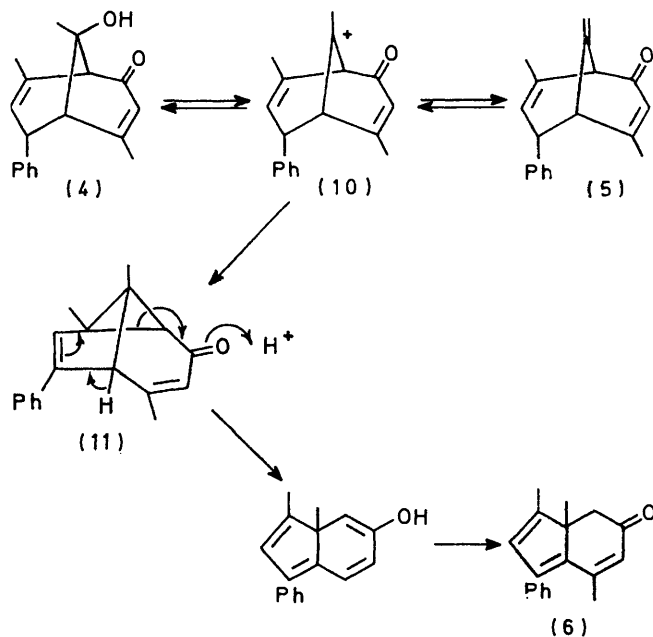


rearrangement. The spectroscopic features of the adduct are consistent with either structure (8) or (9).

Formation of (6) and (7) from (4) and (3) respectively requires an unusual rearrangement, for which, however, some precedent exists. The generation from (4) and the subsequent probable fate of the carbonium ion (10) are shown in the Scheme. Precedent for this mode of rearrangement of 9-substituted bicyclo[3.3.1]nonanes exists. Solvolytic rearrangement of (12) leads³ to products derived from the carbonium ion (13) with the likely intermediacy of the bridged ion (14). Lewis acid catalysed rearrangement of (15) is reported⁴ to give (16) and (17), and (18) with Lewis acids⁵ gives rearrangement products. Similar rearrangements of bicyclo[3.3.1]nonan-9-ones⁶ are known. In rearrangement of (4) the intermediacy of (11) is probable, offering an alternative mode of deprotonation to formation of

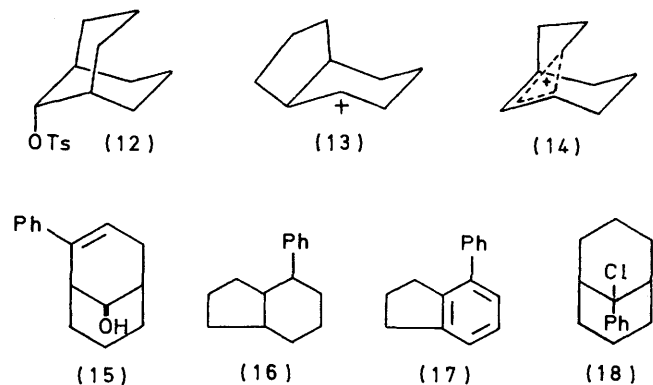
(5). Acid catalysed opening of (11) to give (6) is unexceptional.

The facility for rearrangement of (3) and (4) to the novel bicyclo[4.3.0]nonatrienones is of interest when



SCHEME

compared to the behaviour of other hydroxybicyclo[3.3.1]nonadienones. Dehydration of alcohols (1) and (2) has been described elsewhere,⁷ and gives only olefins (19) and (20) respectively. Formation of rearrangement



products *via* an intermediate of type (11) is not favoured. Similarly, acid catalysed dehydration of (21) gives only (20) showing the greater stability of this diene relative to the alternative (22), which is only accessible by

² K. L. Williamson and Y. F. Hsu, *J. Amer. Chem. Soc.*, 1970, **92**, 7385.

³ C. S. Foote and R. B. Woodward, *Tetrahedron*, 1964, **20**, 687.

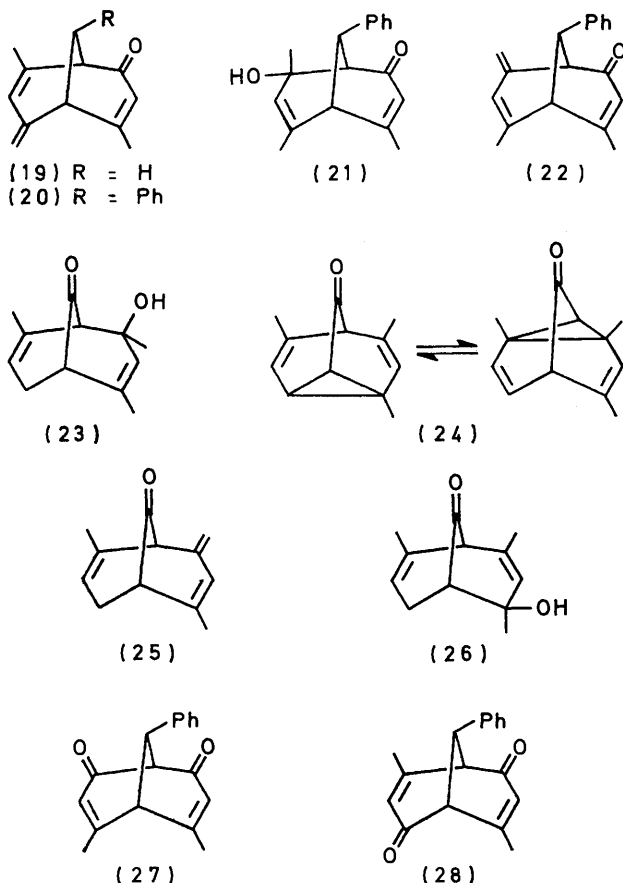
⁴ N. Barbulescu and M. Govea, *Analele Univ. C.I. Parhon, Ser. Stiint, Nat.*, 1961, **10**, 151 (*Chem. Abs.*, 1963, **59**, 1506b); G. L. Buchanan, *Topics Carbocyclic Chem.*, 1969, **1**, 199.

⁵ L. Baiocchi, M. Giannangeli, and G. Palazzo, *Gazzetta*, 1973, **103**, 71.

⁶ R. D. M. Murray, W. Parker, R. A. Raphael, and D. B. Jhaveri, *Tetrahedron*, 1962, **18**, 55.

⁷ C. N. Lam and J. M. Mellor, *J.C.S. Perkin II*, in the press.

Wittig reaction. Attempted dehydration of (23) could lead to either a barbaralone (24) or a triene [e.g. (25)]. No evidence of dehydration to a tricyclic product was



obtained, and under mild conditions only an equilibrium mixture of (23) and (26) was obtained.

EXPERIMENTAL

The preparation of alcohols (1)–(4) and (23),¹ and of ketones (5), (19), (20), and (22)⁷ has been reported elsewhere.

Dehydration of 9-Hydroxy-4,8,9-trimethyl-6-phenylbicyclo[3.3.1]nona-3,7-dien-2-one (4).—The ketone (4) (52 mg) was heated under reflux with toluene-*p*-sulphonic acid (12 mg) in benzene (15 ml) for 18 h. Work-up and preparative t.l.c. over silica gel afforded unchanged starting material (22 mg); 4,8-dimethyl-9-methylene-6-phenylbicyclo[3.3.1]nona-3,7-dien-2-one (5) (15 mg) as a yellow oil, ν_{\max} 1670 and 1630 cm^{-1} ; λ_{\max} 244 (ϵ 7860) and 340 nm (387); τ 2.7–3.0 (5H, m, 6-C₆H₅), 4.23 (1H, m, 3-H), 4.48 (1H, m, $J_{6,7}$ 2 Hz, 7-H), 5.22 and 5.31 (each 1H, s, 9-CH₂), 6.04 (1H, m, $J_{5,6}$ 7 Hz, 6-H), 6.69 (1H, s, 1-H), 6.73 (1H, d, $J_{5,6}$ 7 Hz, 5-H), 8.16 (3H, q, J 1.5 and 2.4 Hz, 4-Me), and 8.98 (3H, d, J 1.5 Hz, 8-Me). Decoupling experiments established the relationship between resonances at τ 4.23 and 8.98, 4.48 and 8.16, and 6.04 and 8.16; M^+ 250; and 1,5,9-trimethyl-7-phenylbicyclo[4.3.0]nona-4,6,8-trien-3-one (6) (11 mg) as a yellow solid, m.p. 118–119° [from chloro-

form-light petroleum (b.p. 60–80°)] (Found: C, 86.9; H, 7.2. C₁₈H₁₈O requires C, 86.4; H, 7.2%); ν_{\max} 1675 cm^{-1} ; λ_{\max} 245 (ϵ 25,200) and 360 nm (16,940); τ 2.7–2.9 (5H, m, 7-C₆H₅), 4.04 (1H, m, 4-H), 4.11 (1H, m, 8-H), 7.81 (2H, s, 2-H), 8.03 (3H, q, J 1.6 and 0.5 Hz, 9-Me), 8.31 (3H, d, J 1.2 Hz, 5-Me), and 8.83 (3H, s, 1-Me). Decoupling experiments established the relationship between resonances at τ 4.04 and 8.31 and at 4.11 and 8.83; M^+ 250.

Ketone (6) was further characterised by reaction with maleic anhydride in toluene to give one of the isomeric 2,6,7-trimethyl-4-oxo-10-phenyltricyclo[5.2.2.0^{1,6}]undeca-2,10-diene-8,9-dicarboxylic anhydride adducts (8) or (9), m.p. 195° (from chloroform-*n*-pentane) (Found: C, 75.6; H, 5.7. Calc. for C₂₂H₂₀O₄: C, 75.9; H, 5.8%); ν_{\max} 1770 and 1700 cm^{-1} ; λ_{\max} 239 (ϵ 15,210) and 315 nm (66); τ 2.7–3.0 (5H, m), 4.05 (1H, m), 4.16 (1H, s), 7.01 (1H, d, J 8.6 Hz), 7.16 (1H, d, J 8.6 Hz), 8.08 (1H, m), 8.13 (3H, d, J 1.6 Hz), 8.21 (1H, m), 8.39 (3H, s), and 8.81 (3H, s). Decoupling experiments established the relationship between resonances at τ 4.05 and 8.13; M^+ 348.

Dehydration of 9-Hydroxy-4,8,9-trimethylbicyclo[3.3.1]nona-3,7-dien-2-one (3).—The ketone (3) (120 mg) was heated under reflux in benzene with toluene-*p*-sulphonic acid (40 mg) for 18 h. Work-up and preparative t.l.c. over silica gel afforded starting material (60 mg), and as a less polar yellow oil, 1,5,9-trimethylbicyclo[4.3.0]nona-4,6,8-trien-3-one (7) (50 mg), ν_{\max} 1685 and 1580 cm^{-1} ; λ_{\max} 233 (ϵ 15,240), 278 (12,320), and 350 nm (3040); τ 3.95 (1H, d, $J_{7,8}$ 9.3 Hz, 7-H), 4.09 (1H, m, 4-H), 4.14 (1H, m, 8-H), 7.88 (3H, d, J 1.1 Hz, 5-Me), 7.94 (2H, m, 2-H), 8.12 (3H, m, 9-Me), and 9.03 (3H, s, 1-Me). Decoupling experiments established the relationship between resonances at τ 3.95 and 4.14, at 4.09 and 7.88, and at 4.14 and 8.12; M^+ 174; 2,4-dinitrophenylhydrazone, m.p. 172–174° (from chloroform-ethanol) (Found: C, 61.2; H, 5.2. C₁₈H₁₈N₄O₄ requires C, 61.0; H, 5.1%); M^+ 354.

8-Hydroxy-4,6,8-trimethyl-9-phenylbicyclo[3.3.1]nona-3,6-dien-2-one (21).—The dienone (27)⁸ (5 g) dissolved in tetrahydrofuran (50 ml) was added to a stirred solution of methylmagnesium iodide [from magnesium (5 g)] in tetrahydrofuran (75 ml) and heated under reflux for 4 h. Work-up afforded crystalline the dienone (21) (5 g), m.p. 128–129° (from ethyl acetate) (Found: C, 80.6; H, 7.45. C₁₈H₂₀O₂ requires C, 80.6; H, 7.5%); ν_{\max} 3430, 1655, and 1605 cm^{-1} ; λ_{\max} 240 (ϵ 6410) and 327 nm (103); τ 2.8–3.0 (5H, m, 9-C₆H₅), 4.30 (1H, m, 3-H), 4.67 (1H, m, 7-H), 6.43 (1H, t, $J_{1,9} = J_{5,9}$ 2 Hz, 9-H), 7.06 (1H, m, 1- or 5-H), 7.18 (1H, m, 1- or 5-H), 8.12 (6H, m, 4- and 6-Me), and 8.53 (3H, s, 8-Me); M^+ 268.

Dehydration of 8-Hydroxy-4,6,8-trimethyl-9-phenylbicyclo[3.3.1]nona-3,6-dien-2-one.—The ketone (21) (1.5 g) was heated under reflux with toluene-*p*-sulphonic acid (0.4 g) in benzene (100 ml) for 2 h. Acid was removed by partitioning with water and the organic phase was worked up to give directly a pale yellow solid (1.1 g). Recrystallisation afforded 4,8-dimethyl-6-methylene-9-phenylbicyclo[3.3.1]nona-3,7-dien-2-one (20), m.p. 81–82° [from ethyl acetate-light petroleum (b.p. 60–80°)], identical with an authentic sample prepared by either similar dehydration of (2) or by Wittig reaction with (28).⁸

Dehydration of 4-Hydroxy-2,4,6-trimethylbicyclo[3.3.1]nona-2,6-dien-9-one (23).—The alcohol (23) (60 mg) was heated under reflux with toluene-*p*-sulphonic acid (30 mg)

⁸ P. A. Knott and J. M. Mellor, *J. Chem. Soc. (C)*, 1971, 670.

in benzene (10 ml) for 4 h. Work-up afforded unchanged starting material (30 mg), and as an oil, 2-hydroxy-2,4,6-trimethylbicyclo[3.3.1]nona-2,6-dien-9-one (26) (30 mg), ν_{\max} 3500, 1695, and 980 cm^{-1} ; λ_{\max} 344 nm (ϵ 26); τ 4.28 (1H, q, J 1.5 Hz, 3-H), 4.60 (1H, m, 7-H), 7.8—8.6 (4H, m, 1-, 5-, and 8-H), 8.06 (3H, d, J 1.5 Hz, 4-Me), 8.31 (3H, m, 6-Me), and 8.64 (3H, s, 2-Me); m/e 192 (M^+ :

$\text{C}_{12}\text{H}_{16}\text{O}_2$ requires m/e 192), 177 ($M - \text{Me}$), 174 ($M - \text{H}_2\text{O}$), and 164 ($M - \text{CO}$).

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