X-Y recorder. The electrochemical cell was maintained at constant temperature via water circulating from a thermostatic bath, internally maintained at the desired temperature ±0.04 °C.

Standard McIlvaine buffers, 1 M in ionic strength, were used throughout the study for pH values above 4, and some runs were done in 1 M perchloric acid (pH 0.60).

Acknowledgment. We are grateful to the National Institutes of Health for Grant NS 12608 from NINCDS for support of this work.

Registry No. (±)-**1b**·HBr, 13402-56-7; **1c** (free base), 6539-57-7; **1d** (free base), 51-61-6; (±)-**2b**, 84279-60-7; **2d**, 84279-61-8; (±)-**3b**, 84279-57-2; **3c**, 14309-62-7; **3d**, 50673-96-6; (±)-**4b**, 84279-62-9; (±)-**5b**, 84303-14-0; **5c**, 84279-58-3; **5d**, 84279-59-4; **6b**, 4821-01-6; **6d**, 3131-52-0.

Dehydration of 1-Substituted Secondary and Tertiary Bicyclo[3.3.1]nonan-9-ols. A Substituent-Driven Rearrangement to 4-Substituted and/or Angularly Substituted Hexahydroindenes

Fabrizio Balata, Anna R. Dello Jacono, and Augusto Gambacorta*

Istituto di Chimica Organica, Università, 00185 Rome, Italy

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The acid-catalyzed dehydration of substituted bicyclo[3.3.1]nonan-9-ols (**1–9**) has been studied as a route to substituted hexahydroindenes via skeletal rearrangement. The nature of the substituent at C_1 strongly affects the rearrangement. Thus 1-substituted secondary alcohols **1–3** (R = Ph, CH_3, H) afford 4-substituted 2,3,4,5,6,7-hexahydroindenes **1b–3b**, while a mixture of 3a-carbethoxyhexahydroindenes (**4a,b**) is produced from **4** (R = CO_2Et). Tertiary alcohols **5–9** afford *cis*-3a-substituted 2,3,3a,6,7,7a-hexahydroindenes **1a–9a**. These processes are discussed in terms of relative stabilities of the intermediate carbonium ions.

The *cis*- or *trans*-hydrindan system is an important structural moiety in several natural compounds, and much attention has been devoted to the synthesis and chemistry of this system in the past and also in recent times.[1]

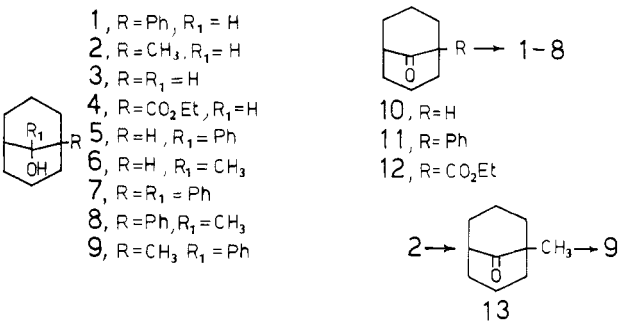
The observation that calculated strain energies of bicyclononanes show a higher value for bicyclo[3.3.1]nonane in comparison with *cis*- or *trans*-hydrindan[2] led us to the hypothesis that this latter system can be produced in carbonium ion skeletal isomerizations of the former. Only a few examples of this rearrangement are reported in the literature,[3,4] but, to our knowledge, no systematic investigation is available. Thus, in view of the quite easy preparation of substituted bicyclo[3.3.1]nonanes,[5] we were prompted to study their conversion into substituted hydrindanes, our initial purpose being the effect of the substituents in driving the rearrangement and determining the stereochemistry of the products.

Earlier observations[3,4] showed bicyclo[3.3.1]nonan-9-ols as the most suitable starting materials for this study. Therefore, four secondary (**1–4**) and five tertiary (**5–9**) bicyclo[3.3.1]nonan-9-ols were prepared and dehydrated in order to obtain hexahydroindenes.

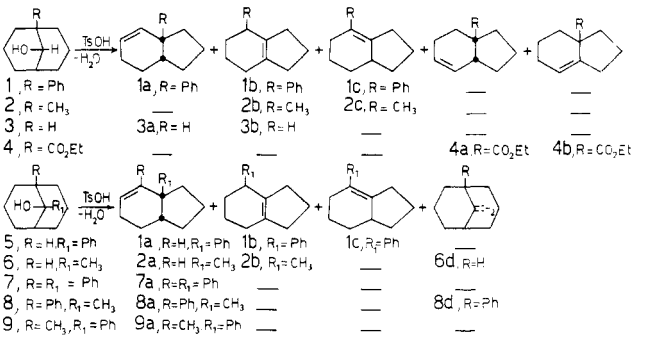
Results

Ketones **10**,[3] **11**,[6] and **12**[7] were used as starting materials for obtaining alcohols **1–9** (see Scheme I). Routine

Scheme I



Scheme II



modifications of **10** gave **3**,[3] **5**,[8] and **6**.[8] In a similar way **1**,[6] **7**, and **8** were obtained from **11**. The hydroxy ester **4** was prepared directly from **12**, while known modifications[9] of this latter compound gave **2**. Chromic oxidation of **2**

(1) Dauben, W. G.; Ponaras, A. A.; Chollet, A. *J. Org. Chem.* **1980**, *45*, 4413. Parker, K. A.; Iqbal, T. *Ibid.* **1982**, *47*, 337. Stork, G.; Shiner, C. S.; Winkler, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 310.
(2) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.
(3) Foote, C. S.; Woodward, R. B. *Tetrahedron* **1964**, *20*, 687.
(4) Lam, Choi-nang; Mellor, J. M. *J. Chem. Soc., Perkin Trans. 2* **1975**, 80.
(5) Peters, J. A. *Synthesis* **1979**, 321.
(6) Baiocchi, L.; Gambacorta, A.; Nicoletti, R.; Petrillo, V. *Ann. Chim. (Rome)* **1971**, *61*, 744; *Chem. Abstr.* **1972**, *76*, 112772.
(7) Colvin, E. W.; Parker, W. *J. Chem. Soc.* **1965**, 5764.
(8) Baiocchi, L.; Giannangeli, M. *Boll. Chim. Farm.* **1971**, *110*, 207; *Chem. Abstr.* **1971**, *75*, 129386.
(9) Graham, S. H.; Jones, D. A. *J. Chem. Soc.* **1969**, 188.

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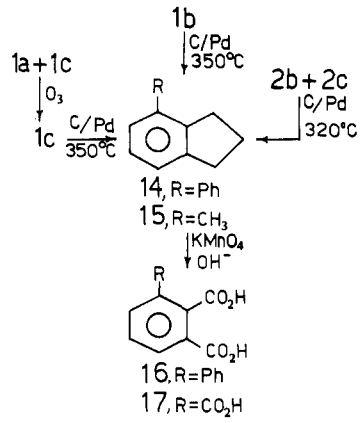
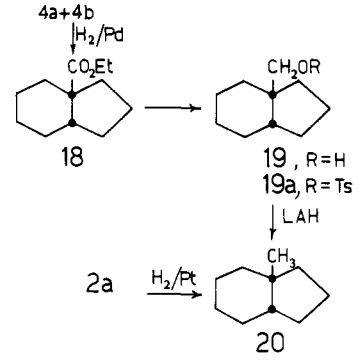
Scheme III



Scheme IV



followed by alkylation afforded **9**.

Dehydrations were carried out in refluxing benzene with *p*-toluenesulfonic acid (TsOH) as a catalyst. The structures of all products obtained from each substrate are reported in Scheme II.

The hexahydroindenes **3a,b** were recognized by comparison with authentic samples obtained by acetolysis of 9-(tosyloxy)bicyclo[3.3.1]nonane.[3] Dehydrogenation of **1b**, obtained from **1**, afforded 4-phenylindan (**14**), which was oxidized to 3-phenylphtalic acid (**16**; see Scheme III). The same products were obtained after dehydrogenation and oxidation of **1c**, which was produced, together with **1a**, by dehydration of **5** and separated, as unaffected material, after ozone treatment of the mixture. Accordingly, dehydrogenation of the mixture **2b,c**, obtained from **2**, gave 4-methylindan (**15**) as the only product. Subsequent oxidation of **15** afforded hemimellitic acid (**17**).

Structures **2a**, **4a**, and **4b** as well as the cis ring fusions for **2a** and **4a** were established by chemical correlations with known compounds (see Scheme IV). The mixture **4a,b** was hydrogenated and gave **18** as the only product, as expected.[11] **18** was converted by lithium aluminium hydride treatment into the already described cis alcohol **19**,[10] from which the *cis*-3a-methylhexahydroindan (**20**) was obtained. This one was shown to be identical with that directly prepared from **2a** by hydrogenation. The structures of **1a**, **7a**, **8a**, and **9a** were established through their spectroscopic properties (see Experimental Section), and cis ring fusions were assumed by analogy with **2a–4a**.

All the reactions were repeated in the presence of the appropriate GC internal standards, and the relative amounts of the reaction products were measured. Results for secondary (**1–4**) and tertiary (**5–9**) bicyclo[3.3.1]nonan-9-ols are reported in Tables I and II, respectively. In Table II the compositions of the reaction mixtures at different reaction times and with different amounts of TsOH are also reported.

(10) Kronenthal, R. L.; Becker, E. I. *J. Am. Chem. Soc.* **1957**, *79*, 1095.
(11) See: Shoppee, C. W. "Chemistry of Steroids"; Butterworths: London, 1964; p 326.

Table I. Dehydration of Secondary Bicyclo[3.3.1]nonan-9-ols in Refluxing Benzene with TsOH (0.08 mol)

substrate	reaction time, h [a]	GC standard	reaction products (GC %) [b]
1	7	C_{18}	**1a** (13), **1b** (80), **1c** (trace), unidentified (2)
2	11	C_{12}	**2b** (90) **2c** (8)
3	3	C_{10}	**3a** (17), **3b** (76), unidentified (4)
4 [c]	21	C_{14}	**4a** (26), **4b** (53), unidentified (6)

[a] Time for total consumption of the substrate. [b] All GC percentages are given with reference to the internal standard. [c] 0.5 mol of TsOH and toluene as solvent were used.

Table II. Dehydration of Tertiary Bicyclo[3.3.1]nonan-9-ols in Refluxing Benzene

substrate	amt TsOH, mol	reaction time, h [a]	GC standard	products (GC %) [b]
5	0.08	24 [c]	C_{18}	**1a** (15), **1b** (trace), **1c** (38)
	0.16	0.5		**1a** (89), **1b** (8), **1c** (trace)
	0.16	24		**1a** (68), **1b** (25)
6	0.08	0.3	C_{12}	**2a** (5), **6d** (94)
	0.08	1.5		**2a** (76), **2b** (13), **2c** (trace)
	0.08	24		**2a** (55), **2b** (43)
	0.16	0.3		**2a** (96), **2b** (1)
7	0.08	0.5	C_{24}	**7a** (97)
8	0.08	4	C_{20}	**8a** (65), **8d** (31)
	0.08	24		**8a** (93)
9	0.08	0.5	C_{20}	**9a** (96)

[a] At the time reported the substrate was completely consumed. [b] All GC percentages are given with reference to the internal standard. [c] Substrate was still present in 47%.

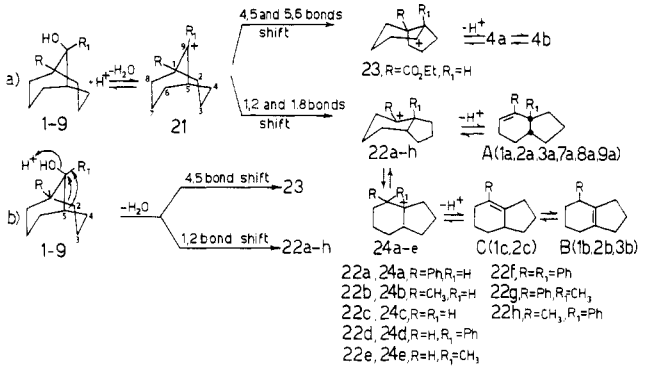
Discussion

The data presented show that dehydration of substituted bicyclo[3.3.1]nonan-9-ols occurs with skeletal rearrangement and affords substituted hexahydroindenes in high yields. The process is sharply affected by the nature of the substituent at the C_1 position in the substrate.

Dehydration of secondary alcohols (Table I) carrying electron-releasing groups (**1–3**) is easy, and 4-substituted 2,3,4,5,6,7-hexahydroindenes are produced in high yields (**1b–3b**). On the contrary, more severe conditions for temperature, catalyst, and reaction time are required when the substituent is a carboethoxy group. In this case (compound **4**) the resulting hexahydroindenes (**4a,b**) carry the substituent at the angular position.

Tertiary alcohols (Table II) behave in a similar way. Thus 1,9-disubstituted substrates (**7–9**) afford *cis*-3a,4-disubstituted 2,3,3a,6,7,7a-hexahydroindenes (**7a–9a**) as the only products. The same kind of compounds (**1a** and **2a**) also predominate in the dehydration mixtures of the unsubstituted tertiary alcohols **5** and **6**, but, in these cases, competitive rearrangements occur, leading to 4-substituted 2,3,4,5,6,7-hexahydroindenes (**1b** and **2b**). Their relative

Scheme V



amounts increase when the reaction time is prolonged; accordingly, short reaction times, obtained with larger amounts of TsOH, result in higher amounts of **1a** and **2a**.

In the case of 9-methyl-substituted alcohols **6** and **8**, the formation of the 9-methylenebicyclo[3.3.1]nonanes **6d** and **8d** is a kinetically favored process with respect to the skeletal rearrangement. This latter compound, however, is thermodynamically favored, as shown by the easy conversion of **6d** and **8d** into the more stable **2a** and **8a**. Compounds of the same type as **6d** and **8d** have already been found in similar reactions.

The processes leading to the products can be rationalized in terms of the relative stabilities of both intermediate carbonium ions and produced alkenes (see Scheme V).

The ions **22a–h** and **23** are likely the key intermediates and can be alternatively formed through the shift to the C_9 of the bonds C_1–C_2 (and C_1–C_8) or C_4–C_5 (and C_5–C_6), respectively. The route to these intermediates can follow either a stepwise or a concerted mechanism. In the former (a) the unstable species **21**[12] is first formed and subsequently rearranged, while in the latter (b) the expulsion of the protonated hydroxyl group is anchimerically assisted by the antiperiplanar bonds. Evidence for the latter route has been reported,[3] but the long reaction time required in the dehydration of **5** and the formation of **6d** and **8d** as byproducts to **2a** and **2a** seem to be in agreement with a stepwise process.

Whatever is the route to **22a–h** and **23**, their alternative formation is sharply driven by the nature of the substituent at C_1 in the substrate. Thus, ions **22a–h** are favored when the substituent is an electron-releasing group, while **23** alone is produced when the substituent is an electron-withdrawing group.

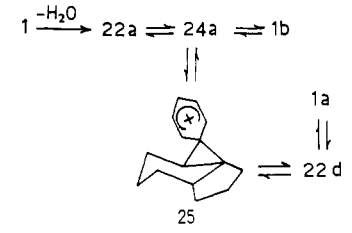
The evolution of **23** gives rise to the mixture **4a,b**, and, in the same way, the species **22a–h** afford the cis-fused A-type hexahydroindenes. However, if R and/or R_1 are hydrogens, subsequent competitive rearrangements of **22a–e** take place, leading to the tertiary ions **24a–e**, from which C- and B-type hexahydroindenes are produced.

The presence of **1a** in the dehydration mixture deserves a further comment. In this case the phenonium ion **25** can be likely accounted as intermediate between **24a** and **22d**, from which **1a** is produced (see Scheme VI). This is in agreement with the known better migratory aptitude of the phenyl group as compared with the methyl group. Accordingly no traces of **2a** are present in the dehydration mixture of **2**.

Experimental Section

The melting points are uncorrected. ^{1}H NMR spectra were recorded on a Perkin-Elmer R 32 instrument and are reported

Scheme VI



in δ units relative to Me_4Si as an internal standard. IR spectra were obtained on a Perkin-Elmer 257 instrument. Mass spectra were recorded on an AEI-MS12 spectrometer. E. Merck silica gel (70–230 mesh) was used for column chromatography. TLC was performed on precoated EM silica gel 60 F-254 plates. GC analyses were carried out on a HP-5880 instrument (FID) by using either a 3-m-long column (2% OV-17 on Chromosorb G, 80–100 mesh) or a 2-m-long column (2% Carbowax 20M on Chromosorb G, 80–100 mesh). The term capillary column refers to a 16-m-long column coated with FFAP. Preparative GC was carried out on a C. Erba GC instrument with a 2-m-long column (5% Carbowax 20M on Chromosorb G, 60–80 mesh).

Ketones **10–12** were prepared according to the published methods.[3,6,7] Dehydrations were carried out, unless otherwise stated, by refluxing 0.3 M solutions of the appropriate substrate in dry benzene with *p*-toluensulfonic acid (TsOH) as a catalyst in an 0.08 molar ratio with respect to the substrate and removing the produced water with a Dean–Stark trap. All dehydration mixtures were washed with $NaHCO_3$ (saturated solution) and dried over Na_2SO_4, and the solvent was removed under reduced pressure.

Dehydration of 1-Phenylbicyclo[3.3.1]nonan-9-ol (1): 4-Phenyl-2,3,4,5,6,7-hexahydroindene (1b). Alcohol **1** (3 g), obtained from **11** as determined in the literature,[6] was dehydrated overnight. GC analysis of the crude residue (2.6 g) in comparison with the dehydration mixture of **5** (see below) showed traces of **1a** and **1c** besides a third major component. Repeated short-path distillations (75 °C, 0.15 mm) gave **1b**: 0.9 g; ^{1}H NMR (CCl_4) 7.10 (m, 5 H), 3.28 (br t, 1 H), 2.50–1.15 (m, 12 H); mass spectrum, *m/e* (relative intensity) 198 (M^+, 100), 170 (61), 155 (16), 142 (27), 117 (16), 115 (14), 91 (27). Anal. Calcd for $C_{15}H_{18}$: C, 90.91; H, 9.09. Found: C, 90.73; H, 9.05. **1b** (0.3 g) was adsorbed on C/Pd (10%, 0.3 g) and dehydrogenated by heating at 350 °C for 5 h. Elution with Et_2O followed by short-path distillation (160 °C, 10 mm) gave 210 mg of 4-phenylindan (**14**): ^{1}H NMR (CCl_4) 7.30–6.60 (m, 8 H), 2.85 (t, J = 7 Hz, 2 H), 2.75 (t, J = 7 Hz, 2 H), 2.10 (m, 2 H). **14** (0.1 g) was suspended in 15 mL of 2% NaOH, 0.9 g of $KMnO_4$ was added, and the mixture was refluxed overnight. Sodium metabisulfite was added and the solution washed with Et_2O. After acidification and extraction with ethyl acetate, solvent removal gave 3-phenylphtalic acid (**16**): 0.04 g; mp 180–181 °C (from $EtOH/H_2O$) (lit.[13] mp 181 °C).

Dehydration of 1-Methylbicyclo[3.3.1]nonan-9-ol (2): 4-Methyl-2,3,4,5,6,7-hexahydroindene (2b) and 4-Methyl-2,3,5,6,7,7a-hexahydroindene (2c). Alcohol **2** (3 g), obtained from **12** as described in the literature,[9] was dehydrated for 12 h under the usual conditions. GC analysis of the crude residue (2.5 g) showed two compounds in a 11:1 ratio. Pure samples were collected by preparative gas chromatography, and the more abundant compound was identified as **2b**: ^{1}H NMR (CCl_4) 2.70–1.10 (m, 13 H), 0.97 (d, J = 7 Hz, 3 H); mass spectrum, *m/e* (relative intensity) 136 (M^+, 33), 121 (100), 108 (23), 93 (73), 79 (49), 67 (16). Anal. Calcd for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 88.15; H, 11.80. The less abundant compound was recognized as **2c**: ^{1}H NMR (CCl_4) 2.70–1.10 (m, 13 H), 2.10 (s, 3 H); mass spectrum, *m/e* (relative intensity) 136 (M^+, 42), 121 (74), 107 (26), 93 (91), 80 (95), 79 (100). The crude mixture **2b,c** (0.3 g) was adsorbed on Pd/C (10%, 0.3 g) and dehydrogenated at 320 °C for 4 h. Elution with Et_2O gave 0.25 g of an oil [one peak via GC (capillary column)]. Short-path distillation (82 °C, 20 mm) afforded 4-methylindan (**15**): ^{1}H NMR (CCl_4) 7.15–6.75 (m, 3 H),

(12) Kirchen, R. P.; Sorensen, T. S. *J. Am. Chem. Soc.* **1978**, *100*, 1487.

(13) Butterworths, E. C.; Heilbron, I. M.; Hey, D. H.; Wilkinson, R. *J. Chem. Soc.* **1938**, 1386.

2.90 (t, J = 7 Hz, 2 H), 2.83 (t, J = 7 Hz, 2 H), 2.20 (s, 3 H), 2.15 (m, 2 H). **15** (0.1 g) was refluxed overnight in 15 mL of 2% NaOH containing $KMnO_4$ (0.9 g). After the usual workup, concentration of the acidified aqueous solution gave needles of hemimellic acid (**17**): 80 mg; mp 194–197 °C (lit.[14] mp 194–197 °C).

Dehydration of Bicyclo[3.3.1]nonan-9-ol (3): 2,3,4,5,6,7-Hexahydroindene (3b) and *cis*-2,3,3a,6,7,7a-Hexahydroindene (3a). Alcohol **3** (3 g), obtained from **10** as described in the literature,[3] was dehydrated as usual for 5 h. GC analysis of the crude residue (2.3 g) showed three compounds in a 19:4:1 ratio. GC comparison (capillary column) with the known reaction mixture obtained by acetolysis of 9-(tosyloxy)bicyclo[3.3.1]nonane[3] allowed assignment of structures **3b** and **3a** to the two more abundant compounds, respectively.

1-Carbethoxybicyclo[3.3.1]nonan-9-ol (4). Ketone **12**[7] (6 g) was dissolved into 100 mL of dry dioxane, 0.54 g of $NaBH_4$ was added, and the mixture was stirred overnight. After solvent removal under reduced pressure, the residue was dissolved in ethyl acetate and washed with 0.5 N HCl and H_2O. Drying of the organic layer over Na_2SO_4, solvent removal, and distillation (116 °C, 0.1 mm) gave **4**: 5.5 g; ^1H NMR (CCl_4) 4.10 (q, J = 7 Hz, 2 H), 3.82 (d, J = 3 Hz, 1 H), 2.93 (br s, 1 H, exchanged with D_2O), 1.23 (t, J = 7 Hz, 3 H), 2.20–1.00 (m, 13 H); IR (CCl_4) 3550, 2980, 2920, 1710 cm^{-1}, mass spectrum, m/e (relative intensity) 212 (M^+, 6), 194 (70), 184 (25), 153 (31), 121 (100), 110 (50).

Dehydration of 1-Carbethoxybicyclo[3.3.1]nonan-9-ol (4): 3a-Carbethoxy-2,3,3a,4,5,6-hexahydroindene (4b) and *cis*-3a-Carbethoxy-2,3,3a,4,5,7a-hexahydroindene (4a). Alcohol **4** (3.5 g) and TsOH (1.4 g) were dissolved into toluene (60 mL) and refluxed for 24 h. The usual workup gave a residue (2.8 g) which, after distillation (110 °C, 1.5 mm), afforded a mixture of three compounds in a GC ratio of 9:4:1. Pure samples of the two more abundant compounds were collected by preparative GC. The first more abundant product was identified as **4b**: ^1H NMR (CCl_4) 5.38 (br s, 1 H), 4.07 (q, J = 7 Hz, 2 H), 3.00–1.00 (m, 12 H), 1.22 (t, J = 7 Hz, 3 H); mass spectrum, m/e (relative intensity) 194 (M^+, 8), 121 (100), 93 (20), 91 (12), 79 (24). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.23; H, 9.28. Found: C, 74.25; H, 9.31. The second compound was recognized as **4a**: ^1H NMR (CCl_4) 5.61 (br d, J = 1.7 Hz, 2 H), 4.07 (q, J = 7 Hz, 2 H), 2.87 (m, 1 H), 2.50–1.00 (m, 10 H), 1.22 (t, J = 7 Hz, 3 H); mass spectrum, m/e (relative intensity) 194 (M^+, 5), 121 (100), 93 (26), 91 (26), 79 (31). The mixture **4a,b** (1 g), dissolved in EtOH (100 mL), was hydrogenated by using 0.4 g of Pd/C (10%) and afforded 0.97 g of *cis*-3a-carbethoxyhexahydroindan (**18**) as the only product (GC on capillary column): ^1H NMR (CCl_4) 4.08 (q, J = 7 Hz, 2 H), 2.38 (br s, 1 H), 2.20–1.00 (m, 14 H), 1.25 (t, J = 7 Hz, 3 H); mass spectrum, m/e (relative intensity) 196 (M^+, 16), 141 (29), 123 (100), 122 (58), 93 (21), 81 (98). **18** (0.7 g) was dissolved in dry Et_2O (10 mL), and 2.5 mL of an 0.8 M etheral solution of $LiAlH_4$ was added under stirring. After 2 h the excess of $LiAlH_4$ was destroyed by addition of NH_4Cl (saturated solution), and the organic phase was separated. Solvent removal gave 0.6 g of *cis*-3a-(hydroxymethyl)hexahydroindane (**19**): bp 84 °C (2 mm); ^1H NMR (CCl_4) 3.37 (d, J = 10.5, 1 H), 3.18 (d, J = 10.5, 1 H), 1.90–0.90 (m, 16 H); IR (CCl_4) 3625, 2910 cm^{-1}. The 3,5-dinitrobenzoate, crystallized from EtOH, melted at 88–89 °C (lit.[10] mp 88–88.5 °C). The tosyloxy derivative **19a** (0.5 g) was also prepared according to the literature.[10]

Dehydration of 9-Phenylbicyclo[3.3.1]nonan-9-ol (5). (a) Under the Usual Conditions. 4-Phenyl-2,3,4,5,6,7,7a-hexahydroindene (1c). The alcohol **5** (1.1 g), prepared from **10** as described in the literature,[8] was dehydrated as usual for 24 h, and the crude mixture (0.95 g) was adsorbed on SiO_2 (27 g). Elution with hexane gave a hydrocarbon fraction (0.52 g), and subsequent elution with hexane–ethyl acetate (8:2) afforded 0.4 g of unreacted substrate. GC analysis of the hydrocarbon fraction in comparison with the dehydration mixture of **1** showed the presence of **1b** in traces along with two main products in a GC ratio of 2.5:1. Attempts to collect pure samples via preparative GC were unsuccessful, but a sample of the more abundant compound was isolated after ozonolysis of the mixture in the following way. The hydrocarbon mixture (0.2 g) in pentane (14 mL) was treated with ozone at −78 °C. After the ozonide was precipitated, the solvent was removed under reduced pressure, and KI (1 g) in AcOH/MeOH (1:3, 4 mL) was added to the residue at 0 °C. After 1 h stirring at room temperature, aqueous $Na_2S_2O_5$ was added and the mixture extracted with Et_2O. Solvent removal gave a residue (0.3 g) which was adsorbed on SiO_2 (15 g). Elution with n-hexane afforded 0.12 g of **1c**: bp 75 °C (0.15 mm; short path); ^1H NMR (CCl_4) 7.10 (s, 5 H), 2.75 (br t, 1 H), 2.60–1.00 (m, 12 H); mass spectrum, m/e (relative intensity) 198 (M^+, 59) 170 (24), 155 (100), 142 (32), 117 (48), 115 (44), 91 (80). Anal. Calcd for $C_{15}H_{18}$: C, 90.91; H, 9.09. Found: C, 90.80; H, 9.10. Dehydrogenation of **1c** (60 mg), carried out as described for **1b**, afforded 4-phenylindan (**14**). The less abundant compound was identified as **1a** via GC (see below).

(b) With TsOH/Substrate Ratio 0.16. *cis*-3a-Phenyl-2,3,3a,6,7,7a-hexahydroindene (1a). Alcohol **5** (2 g) and TsOH (0.24 g) were refluxed in dry benzene (60 mL). After 0.5 h the reaction was terminated, and the usual workup afforded 1.7 g of a mixture of **1b** (5% via GC) and a second more abundant compound (95% via GC). Repeated distillations (160 °C, 10 mm) gave pure **1a**: ^1H NMR (CCl_4) 7.70–7.00 (m, 5 H), 5.86 (tt, J_{ab} = 10 Hz, J_{bc} = 3 Hz, 1 H), 5.58 (br d, J = 10 Hz, 1 H), 2.75 (br s, 2 H), 2.50–1.00 (m, 9 H); mass spectrum, m/e (relative intensity) 198 (M^+, 70), 170 (29), 155 (100), 142 (30), 117 (59), 115 (47), 91 (64). Anal. Calcd for $C_{15}H_{18}$: C, 90.91; H, 9.09. Found: C, 90.90; H, 9.10.

Dehydration of 9-Methylbicyclo[3.3.1]nonan-9-ol (6). (a) Under the Usual Conditions. 9-Methylenebicyclo[3.3.1]nonane (6d). Alcohol **6** (1 g), prepared from **10**,[8] was dehydrated as usual. After 0.5 h the reaction was stopped and afforded 0.8 g of an oil which was distilled (short path, 177 °C, 760 mm) and identified as **6d**: ^1H NMR (CCl_4) 4.59 (s, 2 H), 2.40 (br s, 2 H), 2.20–1.00 (m, 12 H); IR (CCl_4) 3070, 2980, 1665 cm^{-1}; mass spectrum, m/e (relative intensity) 136 (M^+, 54), 121 (66), 93 (88), 79 (100). Anal. Calcd for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 88.18; H, 11.73. In a second run, 0.2 g of **6** were used, and the reaction time was prolonged for 1.5 h. A GC analysis of the crude product (0.16 g), in comparison with the dehydration mixture of **2**, showed the presence of **2c** (traces) along with **2b** (10%) and a third abundant compound (90%) successively identified as **2a** (see below).

(b) With a TsOH/Substrate Ratio of 0.16. *cis*-3a-Methyl-2,3,3a,6,7,7a-hexahydroindene (2a). Alcohol **6** (2 g) and TsOH (0.36 g) were refluxed in benzene for 0.5 h, and the reaction mixture was worked up as usual. Short-path distillation of the residue (175 °C, 760 mm) afforded 1.5 g of **2a**: ^1H NMR (CCl_4) 5.55 (tt, J_{ab} = 9 Hz, J_{bc} = 3 Hz, 1 H), 5.38 (br d, J_{ab} = 9 Hz, 1 H), 2.30 (m, 2 H), 2.10–0.90 (m, 9 H), 1.03 (s, 3 H); mass spectrum, m/e (relative intensity) 136 (M^+, 37), 121 (100), 107 (30), 93 (85), 79 (78). Anal. Calcd for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 88.25; H, 11.72. **2a** (10 mg) was hydrogenated in ethanol (2 mL) over PtO_2 (3 mg) and gave *cis*-3a-methylhexahydroindan (**20**) identical (GC analysis, capillary column) with that obtained from *cis*-3a-[(toxyloxy)methyl]hexahydroindan (**19a**) after treatment with $LiAlH_4$.

1,9-Diphenylbicyclo[3.3.1]nonan-9-ol (7). Compound **11** (3 g) dissolved in dry Et_2O (30 mL) was added dropwise to an etheral stirred solution of phenylmagnesium bromide prepared from Mg (0.75 g) and bromobenzene (3 g). After 1 h under reflux, HCl (0.5 N) was added and the organic layer separated. Solvent removal gave a residue (3.7 g) which was adsorbed on SiO_2 (180 g). Petroleum ether elution afforded 3.4 g of liquid **7** which was not further purified as decomposition occurred during distillation: ^1H NMR (CCl_4) 7.80–6.90 (m, 10 H), 3.00–1.20 (m, 13 H), 0.98 (s, 1 H, exchanged with D_2O); IR (neat) 3580, 3020, 1600 cm^{-1}; mass spectrum, m/e (relative intensity) 292 (M^+, 100), 274 (10), 186 (46), 185 (34), 144 (26), 130 (42), 105 (92), 107 (96).

Dehydration of 1,9-Diphenylbicyclo[3.3.1]nonan-9-ol (7): *cis*-3a,4-Diphenyl-2,3,3a,6,7,7a-hexahydroindene (7a). The alcohol **7** was dehydrated under the usual conditions for 0.5 h, and the usual workup of the reaction mixture afforded 1.8 g of crystalline **7a**: mp 95–96 °C (hexane–ethyl acetate); ^1H NMR ($CDCl_3$) 7.60–6.65 (m, 10 H), 6.21 (t, J = 4 Hz, 1 H), 2.50–1.20 (m, 11 H); mass spectrum, m/e (relative intensity) 274 (M^+, 100), 231 (49), 144 (45), 130 (46), 129 (41), 91 (58). Anal. Calcd for

(14) Graebe, C.; Leonhardt, M. *Justus Liebigs Ann. Chem.* **1896**, *290*, 226.

$C_{21}H_{22}$: C, 91.97; H, 8.03. Found: C, 91.93; H, 8.04.

1-Phenyl-9-methylbicyclo[3.3.1]nonan-9-ol (8). Ketone 11 (3 g) in Et_2O was added to a stirred ethereal solution of methylmagnesium iodide prepared from Mg (0.35 g) and CH_3I (1.2 mL). After 0.5 h under stirring, the usual workup afforded a residue (2.9 g) which was adsorbed on SiO_2 (150 g). Elution with hexane–ethyl acetate (8:2) gave 8: 2.5 g; bp 160 °C (3 mm; short path); ^1H NMR (CCl_4) 7.15 (s, 5 H), 2.55 (br s, 1 H, exchanged with D_2O), 2.25 (s, 3 H), 2.40–1.00 (m, 13 H); IR (CCl_4) 3600 cm^{-1}; mass spectrum, m/e (relative intensity) 230 (M^+, 0.6), 214 (100), 196 (34), 186 (36), 157 (42), 143 (44). Anal. Calcd for $C_{16}H_{22}O$: C, 83.48; H, 9.56. Found: C, 83.40; H, 9.45.

Dehydration of 1-Phenyl-9-methylbicyclo[3.3.1]nonan-9-ol (8): *cis*-3a-Methyl-4-phenyl-2,3,3a,6,7,7a-hexahydroindene (8a) and 1-Phenyl-9-methylenebicyclo[3.3.1]nonane (8d). Alcohol 8 (1 g) was dehydrated us usual. After 4 h the substrate was consumed, and the GC analysis showed two peaks in 2:1 ratio. The amount of the more abundant compound increased as the reaction time was prolonged. After 24 h, **8a** was isolated as the only product: bp 108 °C (0.1 mm; short path); ^1H NMR (CCl_4) 7.10 (s, 5 H), 5.75 (t, J = 5 Hz, 1 H), 2.75 (br s, 2 H), 1.06 (s, 3 H, 2.40–1.00 (m, 9 H); mass spectrum, m/e (relative intensity) 212 (M^+, 74), 197 (28), 169 (52), 155 (22), 141 (18), 130 (100), 91 (26). Anal. Calcd for $C_{16}H_{20}$: C, 90.57; H, 9.43. Found: C, 90.50; H, 9.40.

In a second run 0.5 g of 8 was used, the reaction was stopped after 4 h, and the less abundant compound was identified as **8d**: ^1H NMR (CCl_4; in 1:2 mixture with **8a**; the integration values are referred to the methyl signal at δ 1.06) 7.10 (m, 7.5 H), 5.75 (t, J = 5 Hz, 1 H), 4.67 (d, J = 2 Hz, 0.5 H), 4.00 (d, J = 2 Hz, 0.5 H), 2.70–1.00 (m, 17.5 H), 1.06 (s, 3 H); mass spectrum (via GC/MS coupling), m/e (relative intensity) 212 (M^+, 100), 183 (29), 169 (43), 155 (21), 141 (31), 131 (61).

1-Methyl-9-phenylbicyclo[3.3.1]nonan-9-ol (9). Pyridinium dichromate (25 g) was added to a solution of **2** (3 g) in dry CH_2Cl_2 (250 mL), and the mixture was stirred overnight. After filtration through Celite, solvent removal gave **13** (2.95 g).[9] This latter compound (2.5 g), dissolved in Et_2O (10 mL), was treated with an ethereal solution of phenylmagnesium bromide prepared from Mg (0.45 g) and bromobenzene (2.9 g). After 0.5 h under reflux, the usual workup afforded 2.65 g of **9**: bp (short path) 135 °C (0.1 mm); ^1H NMR (CCl_4) 7.67 (m, 2 H), 7.15 (m, 3 H), 1.68 (s, 1 H, exchanged with D_2O), 2.50–1.20 (m, 13 H), 0.92 (s, 3 H); IR (CCl_4) 3620 cm^{-1}; mass spectrum, m/e (relative intensity) 230 (M^+, 100) 212 (27), 159 (31), 120 (36), 105 (68), 91 (27). Anal. Calcd for $C_{16}H_{22}O$: C, 83.48; H, 9.56. Found: C, 83.42; H, 9.52.

Dehydration of 1-Methyl-9-phenylbicyclo[3.3.1]nonan-9-ol (9): *cis*-3a-Phenyl-4-methyl-2,3,3a,6,7,7a-hexahydroindene (9a). Alcohol **9** (2 g) was dehydrated in the usual conditions. After 0.5 h, the work-up gave 1.8 g of liquid **9a**: bp 150 °C (3 mm; short path); ^1H NMR (CCl_4) 7.16 (m, 5 H), 5.73 (br t, 1 H), 1.43 (q, J = 1.5 Hz, 3 H), 2.50–1.20 (m, 11 H); mass spectrum, m/e (relative intensity) 212 (M^+, 98) 197 (37), 183 (23), 169 (100), 129 (45), 91 (73). Anal. Calcd for $C_{16}H_{20}$: C, 90.57; H, 9.43. Found: C, 90.52; H, 9.45.

Quantitative GC Analyses. All described dehydrations were repeated with 50 mg of substrate and addition of an equimolecular amount of the appropriate GC standard. Standards, reaction conditions, and product yields are reported in Tables I and II.

Registry No. 1, 36399-43-6; **1a**, 83846-13-3; **1b**, 83846-14-4; **1c**, 83846-15-5; **2**, 21328-58-5; **2a**, 83846-16-6; **2b**, 60223-07-6; **2c**, 83846-17-7; **3**, 15598-80-8; **3a**, 6731-22-2; **3b**, 695-90-9; **4**, 83846-18-8; **4a**, 83846-19-9; **4b**, 29494-35-7; **5**, 33832-17-6; **6**, 33832-25-6; **6d**, 61097-71-0; **7**, 83846-20-2; **7a**, 83846-21-3; **8**, 83846-22-4; **8a**, 83846-23-5; **8d**, 51953-76-5; **9**, 83846-24-6; **9a**, 83846-25-7; **13**, 22516-97-8; **14**, 83846-26-8; **15**, 824-22-6; **18**, 83846-27-9; **19**, 83846-28-0.

Condensation–Cyclization of Acetoacetanilides with 1,3,5-Trinitrobenzene. Formation and Structure of Some Stable Delocalized Anions Containing the Bicyclo[3.3.1]nonane Skeleton

Lalitha Mary Gnanadoss* and N. Radha

Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli, India

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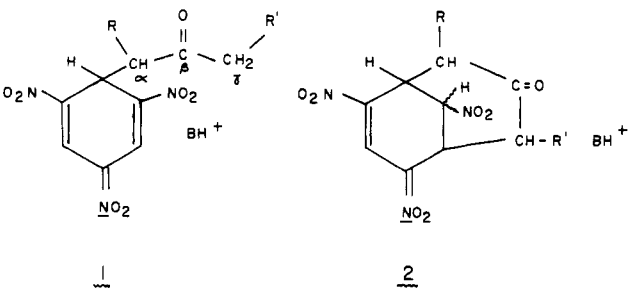
A series of new bicyclic anions containing the bicyclo[3.3.1]nonane skeleton have been prepared from 1,3,5-trinitrobenzene and carbanions derived from substituted acetoacetanilides. The condensation–cyclizations are initiated by triethylamine. A mechanistic picture for the cyclization is shown as proceeding through a delocalized carbanion intermediate.

The study of σ complexes arising from the interaction of electron-deficient aromatics with bases has developed widely in the last 2 decades.[1-6] It has been known that Meisenheimer complexes like 1 are formed from 1,3,5-trinitrobenzene, ketones, and aliphatic amines.[2-6] The σ complexes such as 1 can be readily converted to 2 provided the following conditions are fulfilled. (1) There should be a potential nucleophilic site γ to the tetrahedral ring carbon in 1. (2) No bulky substituents should be present at the C-γ position. (3) The ketone used should be acidic



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