REACTION OF BENZYNE WITH CYCLIC OLEFINS—II[a]

ENE ADDITION TO SOME CYCLOALKENES

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Abstract—Addition of benzyne to 1-methylcyclohexene, (+)-carvomenthene, (+)-limonene, α- and β-pinenes and δ^3-carene has been investigated. Structures to the ene products formed are assigned on the basis of spectroscopic evidence. Arguments are advanced in favour of a concerted ene mechanism for the addition of benzyne to these olefins.

INTRODUCTION

Interest in the ene cycloaddition[1] as a useful reaction in organic synthesis is of recent origin. *o*-Benzyne (dehydrobenzene) is known[2] to undergo ene reaction in competition with the 2 + 2 and 2 + 4 cycloadditions with a variety of olefins and dienes. This powerful enophilic character of benzyne is reflected by its facile reaction with alkenes,[3] alkynes,[4] allenes[5] and strained σ bonds[6] to furnish phenylated products in many synthetically useful reactions. Mechanistically, the ene reaction of benzyne may proceed either in concerted[3h,i] manner or in a stepwise process involving a diradical[3a,b6] or a dipolar[4,7] species. A concerted process for an ene reaction is generally preferred[1] when optimum geometry for a cyclic six electron process i.e., a near planar carbon framework with suprafacial placement of hydrogen for a 1,5-shift, is readily attainable. In a recent study,[3i] geometrical requirements for such a process involving benzyne has been qualitatively correlated with the angle (ϕ) between the plane of the p-orbitals and the plane containing the C–C–H bond. However, with increase in angle (ϕ) the stepwise and nonstereospecific 2 + 2 cycloaddition becomes a major pathway and precludes a concerted ene reaction. In view of the report[9] that the first excited triplet level of benzyne is very close to the ground state, there also exists a possibility that stabilised allylic radicals might be intervening in benzyne-olefin ene reaction. Such intermediates have been encountered and established[10] in the case of addition of azo esters to cyclic olefins. Since, additions involving a cycloalkenyl radical should result in an incomplete shift of the double bond, it should be possible to intercept this species with positionally or isotopically labelled substrates and complete product analysis. It was, therefore, of interest to investigate the reaction of benzyne with assorted, positionally labelled olefins. The choice of some monoterpenic olefins for benzyne addition was further dictated by the possibility of interesting side reactions and the desire to synthesise phenylated monoterpenes of potential perfumery value.
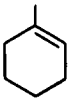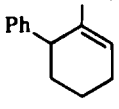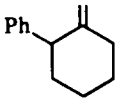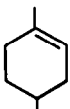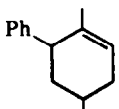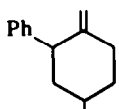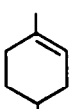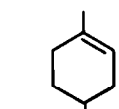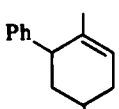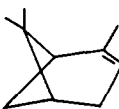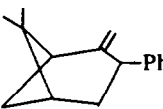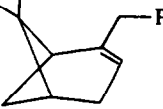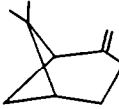
During the present investigation, we have chosen six mono- and bicyclic-olefins namely, 1-methylcyclohexene (**1**), (+)-carvomenthene (**2**), (+)-limonene (**3**), α-pinene (**4**), β-pinene (**5**) and δ^3-carene (**6**) as coreactants for benzyne generated from the thermal decomposition of benzene diazonium-carboxylate (BDC) according to the procedure of Friedman and Logullo.[11] The yield and percentage of the ene products obtained are depicted in Table 1. All the olefins except β-pinene (**5**) gave a mixture of products and these were separated by chromatography on silver nitrate impregnated[12] silica gel. The structure elucidation of the phenylated cycloalkenes (**7** to **16**) is based on elemental analysis and complimentary spectroscopic evidence. The PMR spectral parameters of these compounds are summarised in Table 2. No cycloadducts derived through a 2 + 2 addition were encountered in these reactions.

The results described in Table 1, along with other circumstantial evidence, can be interpreted in terms of a concerted ene addition. Reaction of benzyne with (+)-carvomethene (**2**) g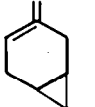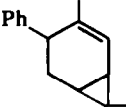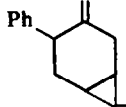ives optically active (Experimental) adducts (**9** and **10**). Although the extent of retention of chirality in **9** and **10** is not known, yet the formation of optically active products from (**2**) rule out the intermediacy of a symmetrical allylic radical (**17**). Several examples are recorded[13] in the literature where additions to (+)-carvomenthene (**2**) involving a species like (**17**) or its polar equivalent have led only to racemic products. In the reaction of benzyne with 1-methylcyclohexene (**1**) only ene products (**7** and **8**) are formed, whereas the analogous free radical reaction[14] of (**1**) with diethyl azodicarboxylate furnished adducts (**18**), (**19**) and (**20**) in which the later predominated. The above evidence together with the consistent absence of products with unshifted double bond rules out the possibility of

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Table 1. Summary of ene products from the Benzyne cyc-loalkene reaction

Starting cycloalkene	Yield[a] (%)	Structure and composition[b] of products
1	22	7 57% + 8 43%
2	10	9 65% + 10 35%
3	26	11 88% + 12 12%
4	12	13 70% 14 30%
5	32	14
6	23	15 60% + 16 40%

[a] Yields based on anthranilic acid used.
[b] Compositions are based on the PMR integrations of total reaction product.

*While this work was in progress, similar conclusions were reached by Ahlgren and Akermark[3f] through the study of reaction between benzyne and 1,2-dideuteriocyclohexene.

Table 2. PMR parameters for the ene products listed in Table 1.

Compound	Multiplicity,[a] chemical shift[b] and coupling constants if any
(7)	δ7·31 (5H, s, aromatic), 5·57 (1H, t with st olefinic), 3·28 (1H, m, benzylic), 1·52 (3H, broad s, allylic methyl).
(8)	δ7·32 (5H, s, aromatic), 4·8 & 4·23 (2H, s with st, terminal methylene), 3·2 (1H, m, benzylic).
(9)	δ7·31 (5H, s, aromatic), 5·81 (1H, m, olefinic), 3·35 (1H, m, benzylic), 1·58 (3H, broad, s, allylic methyl), 0·85 (6H, q, J = 6·5 H$_x$, isopropyl methyls).
(10)	δ7·36 (5H, s, aromatic), 4·95 & 4·85 (2H, s and with st, terminal methylene), 3·75 (1H, t, J = 4 Hz, benzylic), 0·91 (6H, d, J = 6 Hz, isopropyl methyls).
(11)	δ7·3 (5H, s, aromatic), 5·46 (1H, m, olefinic), 4·98 & 4·82 (2H, s, terminal methylene, 3·45 (2H, s, benzylic), 1·65 (3H, broad s, allylic methyl).
(12)	δ7·4 (5H, s, aromatic), 5·83 (1H, b, olefinic), 4·81 & 4·75 (2H, s with st, terminal methylene), 3·76 (1H, t, J = 4·5 hz, benzylic), 1·62 (3H, s, allylic methyl).
(13)	δ7·35 (5H, s, aromatic), 4·93 & 4·66 (2H, m, terminal methylene), 3·41 (1H, m, benzylic), 1·13 & 0·95 (6H, s, tertiary methyls).
(14)	δ7·28 (5H, s, aromatic), 5·3 (1H, bs, olefinic), 3·33 (2H, s, benzylic), 1·2 & 0·73 (6H, s, tertiary methyls).
(15)	δ7·31 (5H, s, aromatic), 5·78 (1H, bs, olefinic), 3·31 (1H, m, benzylic), 1·63 (3H, q, J = 1·3 Hz, allylic methyl), 1·03 & 0·93 (6H, s, tertiary methyls).
(16)	δ7·26 (5H, s, aromatic), 4·88 (2H, m, terminal methylene), 3·29 (1H, m, benzylic), 1·12 − 1·08 (6H, s, tertiary methyls).

[a] s = singlet, t = triple, q = quartet & st = fine structure.
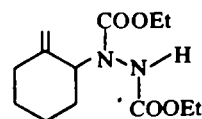[b] The chemical shift position given is that of the centre of the signal.
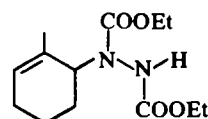
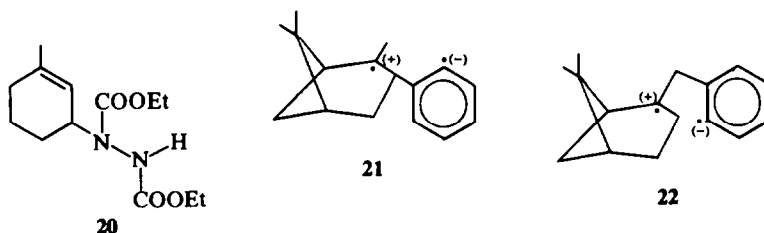17   18   19

formation of allylic radicals in the ene reaction of benzyne.* Alternately, the formation of ene products from α- and β-pinene in a stepwise process would require the formation of intermediates (21 and 22) respectively and would be expected to leak partly into the rearranged products. The total absence of

any rearrangement products from (4 and 5) and δ^3-carene (6), well known for their marked propensity to undergo rearrangements under polar[15] and radical[16] conditions, points to the non-intervention of a dipolar or diradical species with any significant life time in the benzyne reaction. It is therefore, safe to conclude that the ene reaction with benzyne in these cases proceeds in a concerted fashion.

EXPERIMENTAL

All b.ps are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 137 Infracord Spectrometer as neat liquids. PMR spectra were determined in CCl₄ or CDCl₃ solutions on a Varian A-60 spectrometer using TMS as the internal standard. VPC analysis were carried out using F & M Model-700 VPC instrument on a silicone rubber column (6 ft) employing H₂ as the career gas. Column chromatographic separations were carried out on AgNO₃ impregnated silica gel prepared according to the procedure of Gupta and Dev.[12] Optical rotations were measured in CHCl₃ at room temp (25–30°).

Starting materials. 1-Methylcyclohexene (1) and β-pinene (5) were purchased from the Aldrich Chemical Co. (USA), α-pinene (4) and δ^3-carene (6) were obtained from the Camphor and Allied Chemical Co. (India). (+)-Limonene (3) was kindly donated by Dr. E. Klein of Dragoco and (+)-carvomenthene (2) was prepared by the catalytic hydrogenation of (2) as described in literature.[13a]

General procedure for benzyne reaction. Anthranilic acid (5 g; 33 moles) and a few drops of trifluoroacetic acid were dissolved in dry THF (50 ml) and isoamylnitrite (10 ml) was added dropwise at 5°. The mixture was stirred for 1 h, quickly filtered and washed with THF (15 ml). The wet solid was immediately transferred into a RB flask with dry THF (50 ml) and cyclic olefin (10–50 mmoles) was added. The mixture was stirred at a gentle reflux (bath temp 80°) for 3 h and then poured into water (150 ml). The organic components were extracted with light petroleum (50 ml × 3) and washed with brine before drying over Na₂SO₄. Removal of light petroleum and fractional distillation of the residue under vacuum gave a fore run of the starting olefin followed by the ene adduct.

Reaction of benzyne with 1. 1-Methylcyclohexene (4·0 g, 42 mmoles) was reacted with BDC as described above. Distillation gave (1·2 g, 22%) mixture of 7 and 8, b.p. 85–90°/mm. The mixture was adsorbed on a AgNO₃-silica gel column (30 g) and eluted with light petroleum to furnish 7, IR specturm: 705, 1601 cm⁻¹ (aromatic). (Found: C, 90·43: H, 9·41. C₁₃H₁₆ requires: C, 90·64; H, 9·36). Further elution of the column gave 8, IR spectrum: 890, 1640, 3080 (terminal methylene), 701, 760, 1605 cm⁻¹ (aromatic). (Found: C, 90·34; H, 9·42. C₁₃H₁₆ requires: C, 90·64; H, 9·36%).

Reaction of benzyne with 2. (+)-Carvomenthene (1·4 g; 10 mmoles) was reacted with BDC as described. Distillation

gave (0·7 g, 10%) of a mixture of 9 and 10, b.p. 130–40°/2 mm. This material was absorbed on a AgNO₃-silica gel column (15 g) and eluted with 10% light petroleum-benzene. The first fraction consisted of 9, b.p. 110–15°/0·1 mm; n_D^{25} 1·5205, $[\alpha]_D^{25} -1\cdot5$ c, 2·5); IR spectrum: 690, 1595 cm⁻¹ (aromatic). (Found: C, 89·54; H, 10·21. C₁₆H₂₂ requires: C, 89·65; H, 10·35). Further elution gave 10, b.p. 110–15°/1 mm, n_D^{25} 1·5231, $[\alpha]_D^{25} +1\cdot75$ (c, 1·7); IR spectrum: 895, 1655, 3130 (terminal methylene), 695, 1595 cm⁻¹ (aromatic). (Found: C, 89·34; H, 10·41. C₁₆H₂₂ requires: C, 89·65; H, 10·35%).

Reaction of benzyne with 3. (+)-Limonene (5·0 g, 36 mmoles) was reacted with BDC as already described. Distillation gave (1·8 g, 26%) of a pleasant smelling oil, b.p. 130–40°/1 mm. This material was adsorbed on a AgNO₃-silica gel column (30 g) and successively eluted with light petroleum and 5% light petroleum-benzene. The first fraction consisted of 11, b.p. 120–25/2 mm, n_D^{25} 1·5325, $[\alpha]_D^{25} +1$ (c, 1·4), IR spectrum: 895, 1640, 3100 cm⁻¹ (terminal methylene). Found: C, 90·21; H, 9·71. C₁₆H₂₀ requires: C, 90·50; H, 9·50). Compound 12 was eluted next and had b.p. 120–25°/2 mm, n_D^{25} 1·5321, IR spectrum: 888, 1645, 3190 cm⁻¹ (terminal methylene). (Found: C, 90·32; H, 971, C₁₆H₂₀ requires; C, 90·50; H, 9·50%).

Reaction of benzyne with 4. α-Pinene (5·0 g, 36 mmoles) was reacted with BDC as described. Distillation gave (0·8 g, 12%) mixture of 13 and 14, b.p. 120–25°/0·5 mm. This mixture was adsorbed on a AgNO₃-silica gel column (20 g) and eluted with pentane. The first fraction consisted of pure 13, IR specturm: 890, 1635, 3135 cm⁻¹ (terminal methylene), 695, 1590 cm⁻¹ (aromatic). (Found: C, 90·41; H, 9·37. C₁₆H₂₀ requires: C, 90·50; H, 9·50). Further elution of the column gave 14, IR spectrum: 695, 1604 cm⁻¹ (aromatic). Found: C, 90·61; H, 9·71. C₁₆H₂₀ requires: C, 90·50; H, 9·50%).

Reaction of benzyne with 5. β-Pinene (5 g; 36 mmoles) was reacted with BDC as described above to give (2·2 g; 32%) of a single adduct 14. This adduct was found identical (IR, PMR) with one of the adducts obtained from α-pinene.

Reaction of benzyne with 6. δ^3-Carene (5 g; 36 mmoles) was reacted with BDC to give after distillation (1·6 g; 23%) of a mixture of adducts. The mixture was adsorbed on a AgNO₃-silica gel column (40 g) and eluted with light petroleum. The adduct 15 was eluted first (80% pure), b.p. 130–40°/3·5 mm, IR spectrum: 700, 1601 (aromatic) and 853 cm⁻¹. (Found: C, 90·32; H, 9·46; C₁₆H₂₀ requires: C, 90·50; H, 9·50). Further elution yielded the adduct 16, b.p. 130–40°/3·5 mm, IR spectrum: 980, 1640, 3120 cm⁻¹ (terminal methylene). (Found: C, 90·38; H, 9·26. C₁₆H₂₀ requires: C, 90·50; H, 9·50%).

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