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AZULENES AND RELATED SUBSTANCES—XIII*

CYCLOHEPT[f]INDENE (Part 2):† SYNTHESIS OF INDENOS(5',6'-6,7)TROPONE AND INDENO(5',6')TROPYLIUM FLUOROBORATE‡

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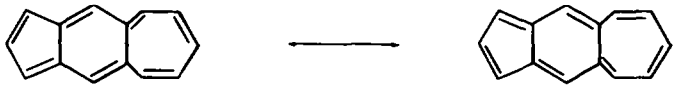
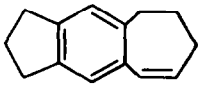
Abstract—Synthesis of indeno(5',6'-6,7)tropone (IX) and indeno(5',6')tropylium (X) fluoroborate are described. The tropone shows no tendency to tautomerize to XXI, a derivative of cyclohept[f]indene. In an attempt to generate cyclohept[f]indene, the action of triethylamine on the tropylium (X) fluoroborate was investigated, but without success.

THE cyclohept[f]indene system (I), first postulated[1-3] in 1953 as a possible non-benzenoid aromatic system, continues to attract attention.[4-8] For the parent system (I), a non-alternant hydrocarbon, both $4n + 2\pi$-electron rule[9] as well as Craig's rule[10] predict aromatic stabilization. Recent Hückel Molecular Orbital[7,8] and Self-consistent Field calculations[7] suggest that I should have aromatic character similar



I



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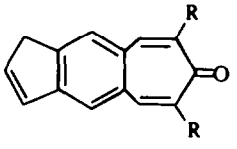
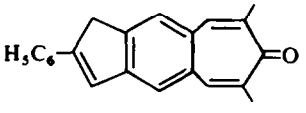


III: R=COOEt

IV: R= Ph



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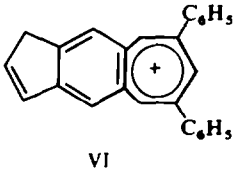
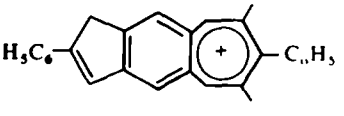
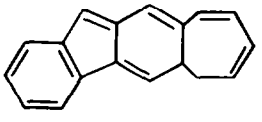


VI



VII



VIII

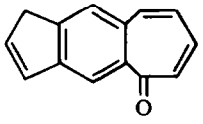
* Part XII: *Tetrahedron* **20**, 2821 (1964)

† Part 1: *J. Indian Chem. Soc.* **30**, 789 (1953)

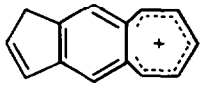
‡ Abstracted from the Ph.D thesis (Bombay University, 1966) of S. A. Patwardhan. Communication No. 1590, N. C. L. Poona.

to that of azulene. However, all attempts to synthesize system I have failed so far. Thus, attempted[1,2] dehydrogenation of II, failed to give any trace of I, while recent studies have shown that the tropones III,[4] IV[5] as well as V[6] show no tendency to enolise. Furthermore, salts derived from the tropylium ions VI[5] or VII[6] failed to generate system I, on interaction with a trialkylamine.[11] A recent attempt[7] to prepare the extended system VIII, also met with failure.

In an extension of our earlier investigations,[1] we were synthesizing ketone IX and salts of tropylium ion X in order to study their behaviour, when the works of Bertelli[4,5] appeared. Though, our conclusions are in accord with the results obtained by this author and later by others,[6,7] our compounds have no extra substituents and thus provide important extension of the earlier findings.



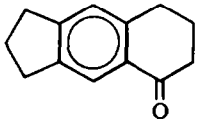
IX



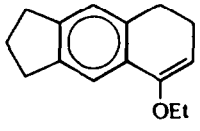
X

Indeno(5',6'-6,7)*tropone*

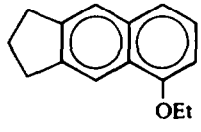
For the synthesis of the tropone IX, the vinyl ether-dihalocarbene method[12,13] could be successfully adopted. However, the preparation of the required enol-ether (XII) entailed considerable difficulty. The reaction of the tetralone XI with ethyl orthoformate in presence of usual acid catalysts (H_2SO_4,[14] ethanolic HCl,[15] *p*-TsOH[16]) followed by usual work-up always resulted in only partial (<70%) conversion attended by much polymerization. It was later discovered that



XI



XII



XIII

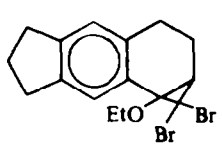
Amberlyst-15,[17] a macroreticular sulphonic acid resin (based on styrene-divinylbenzene) especially suited for non-aqueous media, is an excellent catalyst for the preparation of the enol ether (XII),* which could now be obtained in over 90% purity (GLC). The impurity present in the crude enol-ether was not the starting ketone, but another ethyl ether (NMR), which was suspected to be the naphthyl ether (XIII). This was confirmed by preparation of an authentic sample of XIII‡ and comparison

* We find that Amberlyst 15 is an excellent catalyst for the preparation of enol-ethers and diethyl ketals from a variety of ketones and aldehydes.

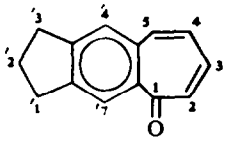
‡ This was prepared by Pd-C dehydrogenation of the tetralone (XI), followed by ethylation (K_2CO_3, diethyl sulphate) of the resulting naphthol.

of its NMR spectrum with the extra (though minor) signals in the NMR spectrum of the crude enol ether; the naphthyl ether (XIII) could later be isolated from the carbene addition reaction, being the impurity initially present in the starting enol-ether.

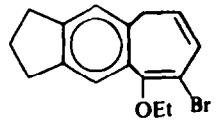
Action of dibromocarbene ($CHBr_3$ and t-BuOK) on enol ether XII furnished as major product (~60%) a crystalline solid having analytical and spectral data fully consistent with the desired XIV. Dehydrobromination-rearrangement of this carbene adduct (XIV) could be effected by refluxing with $AgNO_3$ in MeOH aq[12] or better by simply heating with active alumina. Both methods yielded the same product composed of the required tropone (XV) and a minor compound. The expected tropone structure



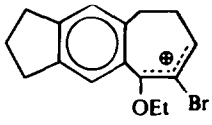
XIV



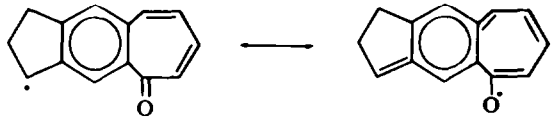
XV



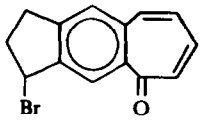
XVI



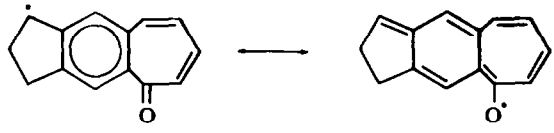
XVII



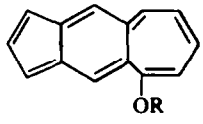
XIX



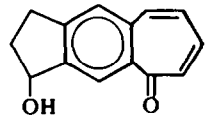
XVIII



XX



XXI: R=H
XXII: R=Me



XXIII

is supported by its method of isolation (extraction with conc. aq HCl), UV[18] (λ_{max}^{EtOH} 236, 313 nm, $\lambda_{infl.}$ 262, 327, 347 nm), IR[18] (ν_{KBr}^{max} 1645, 1575–1585 and 1542 cm^{-1}) and NMR spectra[19] (in CCl_4: tropone ring protons, 4H multiplet located between δ 6·25–7·18; in $F_3C.COOD$, these protons shift downfield to the region δ 7·83–9·1, because of conversion to the tropylium structure). The minor product analysed for $C_{16}H_7OBr$ and from its UV[20] (λ_{max} 276 nm, ε 28,720), IR (KBr; =C—O—C 1190,

1130 cm^{-1}) and NMR spectral data (=C—O—$\underline{CH_2}CH_3$, 2H quartet centred at δ 3·8, J = 7 Hz; two benzene ring protons, 1H singlets at δ 6·9 and 7·35; two olefinic protons, 1H doublet centred at δ 6·13, with J = 11 Hz and, 1H multiplet centred at δ 7·1) is assigned structure XVI. This structure is also expected on mechanistic considerations,[12,13] as arising from XVII (or its equivalent).

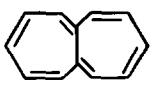
NBS bromination of the tropone (XV) yielded essentially a single bromo derivative, which from its NMR spectrum (1H triplet centred at δ 5·67, J = 4·5 Hz) has clearly bromine at the benzylic position in the 5-membered ring. Of the two possible structures (bromine at 1′ or 3′), structure XVIII is preferred on energy considerations of the intermediates involved.

Dehydrobromination of the above bromo tropone proved to be a rather complex reaction and either $AgNO_3$ in DMSO[21] or methylsulphinyl carbanion[22]* furnished in only low yields two crystalline products. The less polar product (brownish yellow plates, m.p. 100–101°) while showing no OH absorption, displayed a strong tropone carbonyl absorption at 1575 cm^{-1} in its IR spectrum (Nujol). In its NMR spectrum (CCl_4), it displayed signals assignable to indene ring methylene (2H, broad singlet at δ 3·47, $W_{\frac{1}{2}}$ = 5 Hz), two benzene ring protons (1H singlets at δ 7·6 and 8·4) and four tropone ring protons (complex multiplet located between δ 6·33–7·5). It is clear from these data that this is the required product IX, and that it has no tendency to exist in its enolic tautomer XXI. Its UV absorption (λ_{max}^{EtOH} 352, 328 nm) is fully consistent with IX (bathochromic shift with respect to the UV absorption of the parent tropone, due to extended conjugation) and quite different from that expected for XXI (which has a different π-electron system). The second product, from its elemental analysis and spectral data is formulated as 1′ or 3′-hydroxy-indano(5′,6′-6,7)tropone.

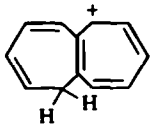
In another set of experiments bromotropone (XVIII) was treated with excess of methylsulphinyl carbanion, followed after a time with excess MeI in an effort to prepare the methyl ether XXII. However, no trace of this compound could be detected (NMR).

Indeno(5′,6′)tropylium fluoroborate and its reactions

Heptalene (XXIV) has been successfully synthesized[11] by a simple deprotonation of 1-heptalenium ion (XXV). It was of obvious interest to see if this approach could be



XXIV



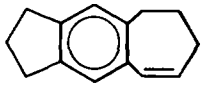
XXV

extended to the synthesis of cyclohept[f]indene (I). For this purpose indeno(5′,6′)-tropylium fluoroborate (X fluoroborate) has been synthesized and its reaction with Et_3N investigated.

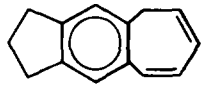
Indano(5′,6′-3,4)cycloheptene (XXVI)[1] on interaction with two more equivalents of NBS, followed by dehydrobromination of the crude product with 1,5-diaza-

* Other reagents tried with unsatisfactory results include: NaI-DMF,[4] LiCl-Li_2CO_3-DMF[23] and 1,5-diazabicyclo[5,4,0]undec-5-ene.[24]

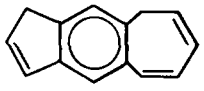
bicyclo[5.4.0]undec-5-ene[24] (DBU) yielded a product from which two pure hydrocarbons (m.p. 48–50° and, m.p. 82–85°) could be isolated. On the basis of spectral characteristics, especially the UV absorption, the lower melting compound (λ_{max} 272 nm, ε 6490) has been assigned structure XXVII, while the other hydrocarbon (m.p. 82–85°; λ_{max} 240, 290 nm, ε 13,140, 8550 respectively) has been found to be required indeno(5',6'-1,2)cycloheptatriene (XXVIII or XXIX).



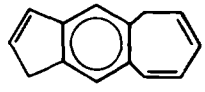
XXVI



XXVII



XXVIII



XXIX

The indenocycloheptatriene (XXVIII/XXIX) was converted to the corresponding tropylium ion (X) by the general method of Dauben *et al.*[25,26] Thus, when the indenocycloheptatriene in ether was exposed at low temp to triphenylcarbonium fluoroborate, rapid hydride abstraction occurred to give indeno(5',6')tropylium (X) fluoroborate, as orange powder (m.p. >300°), quite sensitive to air and light; UV (H_2SO_4): λ_{max} 266 (ε 3262), 324 nm (ε 5013), $\lambda_{infl.}$ 299 (ε 3024), 403 (ε 7565), 427 nm (ε 7638); NMR (F_3C COOD): indene ring methylene (2H singlet at δ 4·07), olefinic and aromatic protons (complex overlapping multiplets located between δ 7·17–9·83). When this fluroborate was treated with Et_3N, essentially under the conditions successfully employed by Dauben and Bertelli[11] for heptalene synthesis, we failed to isolate any material, as judged from spectral data (UV, IR, PMR), corresponding to I.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Pet. ether refers to the fraction b.p. 40–60°. All solvent extracts were finally washed with brine, before drying (Na_2SO_4). Alumina used for chromatography was washed with HNO_3[27] and activated at 450° for 6 hr; the various grades were prepared and standardized according to Brockmann procedure.[28] The following instruments were used for spectral data: Perkin-Elmer Spectrophotometer, model 350 (UV-visible); Perkin-Elmer Infracord, model 137E (IR); Varian Associates A-60 spectrometer (NMR, TMS as internal standard).

6,7-*Cyclopentano*-1-*tetralone* (XI). γ-(5-Hydrindyl)-butyric acid[1] (20 g) was added to polyphosphoric acid (from 120 g P_2O_5 and 60 ml, 85% orthophosphoric acid)[29] at ~100° and the mixture stirred and heated at this temp for 2 hr and left at room temp for ~15 hr, after which it was worked up in the usual manner. The product (16·2 g) consisted[30] of the required XI plus some 20% of the isomeric angular isomer 5,6-cyclopentano-1-tetralone and these were separated by fractionation, as described[30] to furnish pure XI (12·0 g), m.p. 35–36° (pet. ether): IR (liq. film): 1680, 1620, 1422, 1350, 1260, 1170, 908, 848 cm^{-1}. (Lit.[31], m.p. 38–39°).

6,7-*Cyclopentano*-1-*ethoxy-dialin* (XII). The above ketone (5·0 g), triethyl orthoformate (25·5 ml) and Amberlyst 15‡ (1·2 g) were shaken (N_2) at 0–5° for 3 hr. The blue coloured soln was decanted from the catalyst, which was washed with dry C_6H_6. The washings were combined with the original soln and the mixture freed of solvent and excess triethyl orthoformate from a waterbath under reduced pressure. The residue was distilled to give a colourless liquid (4·2 g), b.p. 150–155°/1·5 mm; GLC (temp 200°) showed over 90% purity. IR (liq.): C=C—OR[3,2] 1650, 1260 and 1240 cm^{-1}. NMR (CCl_4): $-OCH_2C\underline{H}_3$ (3H, δ = 1·4, t, J = 7·0 Hz), $-OC\underline{H}_2CH_3$ (2H, δ = 3·85, q, J = 7·0 Hz), $-C\underline{H}=C-$ (1H, δ = 4·82, t, J = 4·0 Hz), aromatic protons (1H singlets at δ = 6·90 and 7·33).

Addition of dibromocarbene to 6,7-*cyclopentano*-1-*ethoxy-dialin*. A mixture of the above enol-ether (4·2 g), t-BuOK (4·5 g), and olefin-free pet. ether (60 ml) was stirred (N_2) at 5° and $CHBr_3$ (3 ml) introduced over 30 min. The resulting dark brown mixture was stirred for another 6–7 hr at the same temp and finally left overnight (15 hr) at room temp (~25°). The mixture was filtered to remove dark polymeric material, which was well-washed with ether and the washings combined with the original filtrate. Removal of solvent yielded a product (7·5 g; gum), chromatographed over Al_2O_3/I (38 cm × 3 cm). Pet. ether (250 ml × 8) eluted the required adduct XIV (4·51 g, m.p. 92–96°), which was recrystallized from EtOH aq, colourless needles, m.p. 95–96°. IR (KBr): 1450, 1232, 1125, 1060, 863, 790 cm^{-1}. NMR (CCl_4): $-OCH_2C\underline{H}_3$ (3H, δ = 1·16, t, J = 7 Hz), $-OC\underline{H}_2CH_3$ (2H, δ = 3·40, q, J = 7 Hz), aromatic protons (1H singlets at δ = 6·83 and 7·36). (Found: C, 49·44; H, 4·90; Br, 41·20. $C_{16}H_{18}OBr_2$ requires: C, 49·76; H, 4·66; Br, 41·42%).

Further elution with 25% C_6H_6 in pet. ether (200 ml × 4) yielded a yellow viscous liquid (570 mg). This was rechromatographed over SiO_2-gel to furnish a white solid, m.p. 40–42° (pet. ether), identified as the cyclopentano-naphthyl ether XIII (*vide infra*). This material is the impurity (< 10%) present in the starting enol-ether.

6,7-*Cyclopentano*-1-*ethoxy-naphthalene* (XIII). 6,7-Cyclopentano-1-tetralone (XI; 0·4 g) was heated with 10% Pd-C (0·2 g) at 300–320° for 1 hr and the resulting black mass extracted with ether. The product was ethylated (0·4 g K_2CO_3, 0·4 ml diethyl sulphate and 6 ml acetone; 2 hr reflux) and the resulting material chromatographed on Al_2O_3/I (26 cm × 0·8 cm). Pet. ether (10 ml × 6) eluted the desired XIII, which was recrystallized from pet. ether, m.p. 40–42°, yield 0·16 g. NMR (CCl_4): $-OCH_2C\underline{H}_3$ (3H, δ = 1·52, t, J = 7 Hz), non-benzylic $C\underline{H}_2$ (2H, δ = 2·16, q, J = 7 Hz), two benzylic $C\underline{H}_2$ (4H, δ = 3·0, bt, J = 7 Hz), $-OC\underline{H}_2CH_3$ (2H, δ = 4·14, J = 7 Hz), C_2, C_3, C_4-protons (3H, 1H quartet at δ = 6·6 and, 2H unsymmetrical triplet at δ = 7·1), C_5-proton (1H, δ = 7·48, s), C_8-proton (1H, δ = 8·01, s). (Found: C, 85·17; H, 7·48. $C_{15}H_{16}O$ requires: C, 84·87; H, 7·6%).

Dehydrobromination-rearrangement of XIV: *formation of indano*(5',6'-6,7)*tropone* (XV). (i) *With* $AgNO_3$. The dibromo carbene adduct XIV (0·5 g), $AgNO_3$ (0·9 g), MeOH (20 ml) and water (2 ml) were refluxed (4 hr), the mixture cooled, diluted with H_2O and the yellow soln (with pale green fluorescence) extracted with C_6H_6 (25 ml × 4). The extract was washed with water, dried and freed of solvent (reduced pressure) to give a residue (300 mg), which was chromatographed on Al_2O_3/I (12 cm × 0·7 cm):

Fract. 1: 25% C_6H_6 in pet. ether 60 ml 14 mg, pale yellow solid. Fract. 2: C_6H_6 25 ml 27 mg, yellow gum.

Fract. 3: 1% MeOH in C_6H_6 80 ml 85 mg, yellow solid. Fract. 4: MeOH 20 ml 30 mg, orange gum.

Fraction 1 was recrystallized from EtOH aq to furnish pale yellow needles of the bromo derivative XVI, m.p. 68–69°. (Found: C, 63·39; H, 5·87; Br, 25·90. $C_{16}H_{17}OBr$ requires: C, 62·96; H, 5·57; Br, 26·20%).

Fraction 3 was redissolved in C_6H_6 and extracted with conc. HCl aq (2 ml × 5). The acid extract was diluted with ice-water and extracted with ether (20 ml × 4). The extract, after washing with water was dried and freed of solvent to give a solid, which was crystallized from C_6H_6 to yield yellow, shining plates (80 mg), m.p. 92–93° of the required tropone XV. (Found: C, 85·94; H, 6·49. $C_{14}H_{12}O$ requires: C, 85·68; H, 6·16%). (ii) *With alumina*. The adduct XIV (2·4 g) was finely powdered and thoroughly mixed with Al_2O_3/I (60 g) and the whole heated on a steam bath with occasional swirling for 22 hr (silica gel guard tube). The mixture was cooled and the alumina filled in a column and then washed with MeOH (200 ml). The washings were freed of solvent to give a dark brown residue (1·1 g), which was taken up in C_6H_6 and the benzene soln extracted with conc. HCl aq (6 ml × 5). The acid extract was worked up to furnish crystalline indanotropone (350 mg, m.p. 91–93°).

1 (*or* 3)-*Bromoindano*(5',6'-6,7)*tropone*. Indanotropone (XV; 150 mg), NBS (150 mg), benzoyl peroxide (6 mg) in CCl_4 (10 ml) were refluxed (N_2) till succinimide floated (2 hr). The mixture was cooled, filtered to remove succinimide and, the filtrate freed of solvent to give a residue (200 mg) which after recrystallization from C_6H_6-pet. ether yielded yellow crystals (85 mg), m.p. 120–123°. IR (KBr): 1598, 1195, 1178, 890, 850,

‡ Manufactured by Rohn and Haas Co., Philadelphia, U.S.A.

808 cm^{-1}. NMR ($CDCl_3$): 2-C$\underline{H}_2$ (2H, δ = 2·66, m), 3 (or 1)-C$\underline{H}_2$ (2H, δ = 3·25, m), 1 (or 3)-C$\underline{H}$Br (1H, δ = 5·67, t, J = 4·5 Hz), olefinic-aromatic protons (6H overlapping signal located between δ = 6·41 – 7·83). (Found: C, 60·89; H, 4·40; Br, 30·45. $C_{14}H_{11}OBr$ requires: C, 61·1; H, 4·0; Br, 29·07%).

Indeno(5',6'-6,7)tropone and 1 *(or* 3*) hydroxyindano(5',6'-6,7)tropone.* (i) *With* $AgNO_3$ *in* DMSO. To the above bromotropone (75 mg) in DMSO (2 ml), a soln of $AgNO_3$ (55 mg) in DMSO (4 ml) was added, when a yellow precipitate of AgBr separated immediately. The mixture was put in the dark, at room temp for 1 hr, after which it was filtered and the filtrate diluted with water and extracted with C_6H_6. The extract was washed with water, dried and freed of solvent to give a deep red residue (79 mg), which was chromatographed over Al_2O_3/III (18 cm × 0·3 cm):

Fract. 1: 50% C_6H_6 in pet. 25 ml 25 mg, yellow gum ether. Fract. 2: 5% MeOH in C_6H_6 40 ml 14 mg, yellow solid.

Fraction 1 was rechromatographed (Al_2O_3/III, 15 cm × 0·3 cm) to yield with 25% C_6H_6 in pet. ether (15 ml), a pale yellow solid (10 mg), which was recrystallized from MeCN to furnish brownish yellow plates (5 mg), m.p. 100–101°, of the required indeno(5',6'-6,7)tropone. (Found: C, 86·44; H, 5·65. $C_{14}H_{10}O$ requires: C, 86·57; H, 5·19%).

Fraction 2 was recrystallized from MeCN to give red plates, m.p. 163–167°. λ_{max}^{EtOH} 232, 307, 318 and 344 nm (ε 23860, 5314, 5199 and 4616 respectively). IR (KBr): 3448, 1565, 1322, 1065, 862, 810 cm^{-1}. NMR ($CDCl_3$): benzylic C$\underline{H}_2$ (2H, δ = 3·0, t, J = 7 Hz), C$\underline{H}$OH (1H, δ = 5·36, t, J = 7 Hz), tropone ring protons (4H, ~δ = 7·2, m), benzene ring protons (two 1H singlets at δ = 7·5 and 8·66). (Found: C, 78·91; H, 5·84. $C_{14}H_{12}O_2$ requires: C, 79·23; H, 5·70%). (ii) *With methyl sulphinyl carbanion.* Bromoindanotropone (316 mg) in DMSO (8 ml) was treated with methyl sulphinyl carbanion solution (1·7N, 0·3 ml),[22] while stirring under N_2 at 15–20° (2 hr). The mixture was next diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with H_2O, dried and freed of solvent to give a red residue (258 mg). This was separated, as described above, to yield indenotropone (22 mg) and hydroxyindanotropone (140 mg).

Indano(5',6'-1,2)cycloheptatriene (XXVII) *and indeno(5',6'-1,2)cycloheptatriene* (XXVIII/XXIX). A mixture of indano(5',6'-3,4)cycloheptene (XXVI; 2·0 g), NBS (4·0 g) and benzoyl peroxide (10 mg) in CCl_4 (20 ml) was refluxed till succinimide started floating (30 min). The mixture was cooled, filtered to remove succinimide and the filtrate freed of solvent under reduced pressure (room temp) to furnish a gum (4·2 g). To this gum (1·8 g) in dry C_6H_6 (10 ml), a soln of DBU[24] (1·6 g) in C_6H_6 (10 ml) was added (10 min), while stirring under N_2 at reflux. The dark mixture was stirred and refluxed for another 30 min then cooled and poured onto ice and 1N H_2SO_4 (30 ml). The resulting material was filtered to remove a black suspended solid, which was washed with C_6H_6. The C_6H_6 phase was washed with H_2O, dried and solvent removed under reduced pressure (at ~50°) to furnish a product (364 mg) which was distilled to give a pale yellow distillate (240 mg), b.p. 185–190° (bath)/2 min, which slowly solidified. This product was separated by PLC (silica gel; pet. ether) to furnish two crystalline compounds.

The product with higher R_f (39 mg) was crystallized from pet. ether to give colourless needles of XXVII, m.p. 48–50°. IR (Nujol): 1500, 1440, 895, 848, 800, 792, 698, 694 cm^{-1}. NMR (CCl_4): non-benzylic C$\underline{H}_2$ (2H, δ = 2·07, q, J = 7 Hz), three benzylic CH_2 (6H, δ = 2·9, t, J = 7 Hz), four olefinic protons (4H, δ = 6·2, m), two aromatic protons (1H singlet at δ = 6·9 and 7·05). (Found: C, 91·66; H, 8·24. $C_{14}H_{14}$ requires: C, 92·26; H, 7·74%).

The second product (lower R_f; 170 mg) was recrystallized from pet. ether to give the required XXVIII/XXIX as colourless needles, m.p. 82–85°. IR (KBr): 1625, 1600, 1575, 1480, 1440, 1400, 1220, 950, 895, 888, 850, 800, 746, 728, 700 cm^{-1}. NMR (CCl_4): two benzylic C$\underline{H}_2$ (2H, δ = 2·98, d, J = 7 Hz; 2H, δ = 3·31, bs), olefinic and aromatic protons (8H, overlapping signals located between δ = 5·6 – 7·3. A good elemental analysis could not be obtained because of its sensitivity to atmospheric oxygen.

Indenotropylium fluoroborate. To triphenyl carbinol (70 mg) in Ac_2CO (1·5 ml), fluoroboric acid (d^{20} 1·36; 0·03 ml) was added with cooling. To the resulting clear yellow soln indenocycloheptatriene (XVIII/XXIX; 50 mg) in ether (1·5 ml) was added, when an orange precipitate separated immediately. This product was repeatedly washed with cold dry ether by centrifuging and decanting to give an orange powder (~15 mg). IR (Nujol): 1650, 1608, 1480, 1455, 1060 (BF_4^-), 902, 728 cm^{-1}.

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