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SYNTHESIS OF NEW TRUXENE DERIVATIVES: POSSIBLE PRECURSORS OF FULLERENE PARTIAL STRUCTURES ?

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Abstract: Preparations of compound 4 and of truxene derivatives 5, 6a,b, 7, 8, 10a,b, 11, 12a,b, and 13a,b are described. These substances are potential starting materials for the synthesis of bowl shaped polyaromatic compounds containing structural elements of fullerenes.

Syntheses of bowl-shaped partial structures of buckminsterfullerene and its congeners present a major challenge today, and the last few years have witnessed very intensive research in this field¹⁻²³. These activities induce us to record our preparation of relevant compounds and tentative follow-up experiments here. The trindenes (**1a**, **1b**) and truxene (1H-tribenzo[a,f,k]trindene, **2**) are flat elements of the curved fullerene surface and are therefore possible starting points for further work 1.2, 22.

In preliminary experiments, attempts were made at threefold annelation of sixmembered rings to 1. This would yield a sumanene (C_{21}) derivative. Trindane was available by cyclocondensation of cyclopentanone in the presence of aqueous hydrochloric acid (22%). It was transformed into 1a/1b in two steps (21 % overall yield) following Katz et. al. ²⁴ and could be oxidized by chromate / acetic acid to give monoketone 3 (61 %) following ref. ¹. Although 1 was easy to deprotonate by butyl lithium, it was too sensitive for further conversions. No useful acylation or alkylation products incorporating C₂ units and no epoxidation products could be obtained from it in acceptable yields. 3 could be dimerized reductively to 4 in a



McMurry reaction (92%). Twofold ring closure (as indicated) would give a C_{30} compound with six five-membered and four six-membered rings. Unfortunately, all attempts were in vain to effect such conversions by flash vacuum pyrolysis, dehydrogenation, oxydation, or bromination / elimination.

Therefore work was concentrated on truxene, 2, and its derivatives. The most convenient preparation of this starting material was the condensation of 1-indanone in HOAc / conc. aqueous HCl (98 % yield). When 2 was metalated with excess butyl lithium, a deep red solution of the tris-anion was formed. It could be quenched with D_2O (to give 2- D_3) or reacted with gaseous formaldehyde to give 5,10,15-tri(hydroxymethyl)truxene, 5, in 65 % yield. The unsymmetric (*anti*) arrangement of the substituents follows from the NMR spectrum. Alternatively, the tris-anion could be trapped with carbon dioxide. The resulting tris-acid, **6a** (m.p. ~225°C, decomp.), was converted into the acid chloride **6b**. Both **6a** and **6b** could not be obtained in analytically pure form, but reduction of **6b** with lithium aluminiumhydride resulted in the formation of **5** again (52 % over three steps).

We aimed at a simple trifold ring closure to a bowl shaped C_{30} compound comprising half of C_{60} with additional functional groups around the rim. Initial attempts at Friedel-Crafts type ring closures of **5**, **6a** and **6b**, however, lead only to tarring. Dehydration of **5** should give 5,10,15-trimethylenetribenzo[*a*,*f*,*k*]triindene which was obtained by the De Lucchi group² from the trihydroxy-trimethyl compounds (isomeric to **5**) in a very low yield in 1994. As a matter of fact, the trimethylene compound is not stable at room temperature ². In our hands, polymerization prevailed under various standard dehydration conditions for 5. All work with truxene and its derivatives was handicapped by the very poor solubility of these compounds in most solvents.



Alternatively, the 2 anion was reacted with benzoyl chloride. Depending on the ratio of the reactants, compounds 7 or 8 were formed. 7 could be characterized fully: Only one isomer (*anti*) was present. Due to the extreme insolubility of 8 this was not obtained in an analytically pure form. Attempted reactions of both compounds with phosphorus pentachloride under various conditions gave tarry mixtures in which neither ring-closed hydrocarbons nor intermediate chloro compounds could be detected by mass spectroscopy and chromatography.

Truxentrione (9) could be made in over 90 % yield by an improved procedure. It was transformed into the 2:3 syn / anti mixture 10a,b with benzyl

Grignard reagent. The compounds could be separated by column chromatography. Acid catalyzed dehydration presented no problems in this case, and both isomers gave 5,10,15-tribenzaltruxene, 11. Although 11 had a relatively sharp m.p., its ¹³C NMR spectrum showed clearly that it was a mixture of stereoisomers. Bromination, epoxidation and mild oxidation of 11 resulted in complex mixtures from which no pure compounds could be isolated up to now. Pyrolysis gave mostly tars. Only small amounts of decomposition products were obtained which had considerably smaller molecular masses. Similarly, melting with AlCl₃ / NaCl, heating with Pd/C, and attempted photochemical cyclization / dehydrogenation were to no

avail.



Lithiated ethyne and phenylethyne transformed 9 into chromatographically separable stereoisomer mixtures of substituted propargyl alcohols 12a, 12b and

13a, 13b with 1: 10 and 1: 2.5 syn : anti ratios, respectively. Interestingly, anti-12b forms a 1: 1 clathrate with diethyl ether on crystallization.- Direct pyrolysis of 12a,b at 1000°C again lead to soot formation only, and experiments towards acid catalyzed Meyer-Schuster or Rupe rearrangements were also unsuccessful.

Fundamental difficulties encountered in the present study resulted partly from solubility problems. These might be overcome by introducing alkyl groups around the rim of the compounds. Failures of here descibed attempts at ring closures are indicative of the strain introduced by forcing the structures into a bowl shape. Cationic processes involved in some of the attempted syntheses turned out to be not well suited. Positive results from the literature ¹⁻²³ encourage us to concentrate now carbene intermediates and more forcing pyrolysis conditions with our carbon skeletons. These experiments are pursued actively and will be recorded in the near future.

Experimental

1,1'-Bis(trindanylidene) (**4**) - TiCl₄ (1.91 g, 10.1 mmol) was dissolved in 30 ml of THF and cooled to 0°C. Zinc dust (1.35 g, 20.5 mmol) and pyridine (0.7 ml) were added, and the mixture was stirred under nitrogen until a deep-black coloration was present. A solution of trindanone (**3**¹, 2 g, 9.41 mmol) in 30 ml of THF was dropped in within 0.5 h. The mixture was heated for 3 h at 60°C, cooled, and poured onto ice. Extraction by ether was followed by drying (Na₂SO₄) and concentration. The residue was recrystallized from methanol to give a yellow solid. M.p. 191°C (dec.), yield 1.7 g (92%).- IR (KBr) v_{max} (cm⁻¹) 2900 s, 2850 s, 1440 m, 1420 m, 1390 w, 1300 m, 1270 m, 1230 m, 1120 m, 980 m, 910 m, 820 m, 760 m.- ¹H-NMR (CDCl₃, 300 MHz): δ 2.7-3.0 (m, 24 H), 1.8-2.2 (m, 8 H).- MS: 392 (M+).- Anal. calc. for C₃₀H₃₂ (392.6) C 91.78, H 8.22; found C 91.69, H 8.05.

lH-Tribenzo[a,f.k]trindene (*truxene*, **2**) - 1-Indanone (13.6 g, 104 mmol) was added to a mixture of 60 ml of acetic acid and 30 ml of concentrated hydrochloric acid. The solution was stirred for 16 h at 100°C, then poured onto ice. The solid

precipitate was washed with water, acetone and dichloromethane to give a white powder (11.8 g, 35 mmol, 98 %) which had no m.p. up to 350° C.- IR (KBr) v_{max} (cm⁻¹) 3068 w, 2877 m, 1602 w, 1463 s, 1385 s, 1156 m, 1019 m, 729 s.- MS (70eV), m/z (%): 342 (M+, 100), 341 (70), 340 (30), 339 (40), 169 (22).

anti-5,10,15-Tri(hydroxymethyl)1H-tribenzo[a,f,k]trindene (5,10,15-tri(hydroxymethyl)truxen, **5**) - A suspension of **2** (4 g, 11.7 mmol) in 50 ml of THF was cooled to -78°C and 22.5 ml of a 1.6 M solution of n-BuLi in n-hexane (36 mmol) was added under stirring in 1 h. The solid dissolved and the color changed to deepred. The solution was warmed to room temperature within 2 h, and formaldehyde (gas) was bubbled in. The color changed after 0.5 h to yellow and a precipitate formed. The mixture was hydrolyzed with water after 3 h and extracted with ether. Drying (Na₂SO₄) was followed by removal of the solvents, and the residue was chromatographed on silicagel with ether to give 3.28 g (7.6 mmol, 65 %) of **5**. M.p. 274°C. IR (KBr) v_{max} (cm⁻¹) 3430 b, 3038 w, 2925 m, 2878 m, 1601 w, 1467 m, 1386 m, 1032 s, 743 s. MS (70 eV) m/z (%): 432 (M+,6), 401 (52), 371 (58), 353 (65), 339 (100). ¹H-NMR (d₆-DMSO, 250 MHz): δ 8.05-8.15 (m, 3 H), 7.8-7.95 (m, 3 H), 7.3-7.6 (m, 6 H), 5.18-5.28 (m, 1 H), 5.05-5.14 (m, 2 H), 4.58-4.75 (m, 3 H), 4.4-4.55 (m, 3 H), 2.9-3.3 (broad m, 3 H; OH). Anal. calcd for C₃₀H₂₄O₃ (432.5): C 83.31 , H 5.59; found: C 83.18, H 6.02.

1H-Tribenzo[*a,f,k*]*trindene-5,10,15-tricarboxylic acid* (**6a**) was obtained similarly in impure form by carboxylation of the trisanion. -M.p. ~ 225°C (dec.). Transformation into the *acid chloride* (**6b**) was effected by warming with SOCl₂. **6** had no definite m.p., slow dec. occurred above 210°C.

anti-5,10,15-Tribenzoyl-1H-tribenzo[a,f,k]trindene (tribenzoyltruxene, 7) - A THF solution of the trianion of truxene was prepared from 2 g = 5.85 mmol of truxene and 18 mmol of butyl lithium in n-hexane. The initial suspension of 2 dissolved slowly as the red anion was formed. This solution was added slowly to benzoyl chloride (4.11 g, 29.3 mmol) in 25 ml of THF at 0°C. After stirring for 16 h at room temperature, the mixture was hydrolyzed, extracted with dichloromethane and dried over Na₂SO₄. The solvents were removed and the residue was recrystallized from ethanol / ethyl acetate to give 7 (570 mg, 15 %) as colorless powder, m.p. 278-280°C.- IR (KBr) v_{max} (cm⁻¹) 3050 w, 1681 s, 1592 m, 1444 m, 1263 s, 1189 s, 958 m, 742 s.- ¹H-NMR (CDCl₃, 250 MHz): δ 7.2-7.9 (m, 27 H), 6.19 (s, 1 H), 6.10 (s, 1 H), 5.90 (s, 1 H).- MS (70eV) m/z (%): 654 (M+, 10), 550 (95), 445 (59), 340 (74), 339 (100), 105 (98).- Anal. calcd. for C₄₈H₃₀O₃ (654.8): C 88.05, H 4.62; found: C 88.00, H 4.89.

5-Benzoyl-1H-tribenzo[a,f,k]indene (benzoyltruxene, **8**) was prepared similarly to **7** with the exception that only a 1.1 molar amount of BuLi relative to **2** was applied.- Raw yield 76 %, crystallization from nitrobenzene is possible only with difficulty. M.p. 298°C; 44 % of purified, but not analytically pure product. - IR (KBr) v_{max} (cm⁻¹) 3046 m, 2873 m, 1685 s, 1592 m, 1469 s, 1388 s, 1319 m, 1261 s, 1195 s, 1025 m, 960 s, 852 m, 740 s, 690 s.- MS (70eV) m/z (%): 446 (M+, 23), 342 (57), 341 (100), 105 (28), 77 (17).- NMR spectra could not be obtained because **8** was insoluble.

Truxene-5,10,15-trione (9, *cf.* ^{22b}) - Indane-1,3-dione (10 g, 68.5 mmol) was added in small portions to 100 ml of conc. H₂SO₄, and the mixture was heated for 3 h at 100°C. The mixture was poured onto ice, and the green precipitate was filtered off. It was washed repeatedly with water, acetone, and finally with dichloromethane. The remaining solid was recrystallized from toluene giving yellow platelets. Yield: 7.9 g (90.1 %), m.p. > 350°C. IR ν_{max} (cm⁻¹) 1712 s, 1608 s, 1571 s, 1459 m. - MS (70eV) m/z (%): 384 (M+, 100), 356 (55), 327 (20), 298 (25).

syn-5,10,15-Tribenzyl-5,10,15-trihydroxy-1H-tribenzo[a,f,k]trindene (10a) and anti-5,10,15-tribenzyl-5,10,15-trihydroxy-1H-tribenzo[a,f,k]trindene (10b) - 9 (3.10 g, 8.07 mmol) was given in several portions to a freshly prepared refluxing suspension of benzyl magnesium bromide in ether (3.93 g =162 mmol Mg, 19 ml = 160 mmol benzyl bromide). After 3 h, the solution was cooled to room temperature and poured into a saturated NH₄Cl-solution. The mixture was extracted with ether, dried over Na₂SO₄. Removal of the ether left a residue which was separated by chromatography (silicagel, ether / light petroleum 1:1). After some dibenzyl, first **10b** and later **10a** were eluted.- *syn*-**10a** (1.25g, 24%): m.p. 180°C.- IR (KBr) v_{max} (cm⁻¹) 3544 s, 3061 m, 3026 m, 2924 m, 2857 w, 1600 m, 1579 m, 1493 m, 1453 m, 1380 m, 1325 m, 1084 s, 1030 s, 756 s, 745 s, 698 s.- ¹H-NMR (d₆-DMSO, 250 MHz): δ 8.32 (d, J=7.7 Hz, 3 H), 6.8-7.3 (m, 18 H) 6.45 (d, J=7.0, 6 H), 3.30 (d, J=13.2, 3 H), 2.85 (d, J=13.2, 3 H), 2.22 (s, 3 H).- Anal. cald. for C₄₈H₃₆O₃ (660.8) C 87.25, H 5.49; found C 87.22, H 5.77.- *anti*-Isomer **10b** : (0.85 g, 16%): M.p. 178°C.- IR (KBr) v_{max} (cm⁻¹) 3530 m, 3383 b, 3061 m, 3027 m, 2922 s, 2853 s, 1601 m, 1578 m, 1493 m, 1468 m, 1450 m, 1378 m, 1084 m, 1015 m, 754 s, 744 s.- ¹H-NMR (CDCl₃, 250 MHz): δ 8.75 (m, 3 H), 7.2-7.5 (m, 9 H), 6.89-7.05 (m, 9 H), 6.62-6.75 (m, 6 H), 3.71 (m, 3 H), 3.28-3.55 (m, 3 H), 2.38 (broad s, 2 H), 2.18 (s, 1 H).

5,10,15-Tribenzal-1H-tribenzo[a,f,k]trindene (11) - A mixture of the isomers of 10 (2.30 g, 3.48 mmol) was dissolved in 100 ml of acetic acid and stirred at 100°C. A few drops of conc. sulfuric acid were added. After 3 h at 100°C, the solution was cooled and 100 ml of water were added. A precipitate formed. It was filtered off and washed with water, then purified by chromatography (silicagel, toluene : light petroleum 1:1). 11 crystallized as a yellow powder (1.05 g, 80 %); m.p. 190°C.- IR (KBr) v_{max} (cm⁻¹) 2922 w, 1596 m, 1443 m, 1375 m, 1154 m, 1026 w, 764 s, 737 s.- MS (70eV) m/z (%): 606 (M+, 100), 529 (20), 517 (17), 450 (10).- ¹H-NMR (CDCl₃, 250MHz): δ 8.53 (m, 3 H), 6.5-7.7 (m, 27 H).-Anal. calcd. for C₄₈H₃₀ (606.8): C 95.02, H 4.98; found: C 94.83, H 5.49. The NMR-data indicated the presence of several E/Z isomers of 11.

5,10,15-Triethinyl-5,10,15-trihydroxy-1H-tribenzo[a,f,k]trindene (12a, 12b; syn- and anti- mixture) - Lithium acetylide was prepared by condensation of ca. 200 mmol acetylene in 100 ml of THF at -78°C and by treating this solution at the same temperature with 19.5 mmol of 1.6 M butyl lithium. After 1 h, truxentrione (2.46 g, 6.4 mmol) in 50 ml of THF were dropped in, the solution was warmed to room temperature, and stirred for 16 h. The brownish-red mixture was treated with conc. aqueous NH₄Cl, extracted with ether, dried (Na₂SO₄) and evaporated. 2.74 g (93 %) of a crude product were obtained. Separation by column chromatography (silicagel, ether / light petroleum 1 : 1) furnished three fractions:(1) 1.6 g of anti-12b, (2) 1.1 g of an anti/syn mixture, and (3) 0.14 g pure syn-12a.- anti--12b, m.p. 215°C (from ether), crystallized as a 1 : 1 clathrate with diethyl ether as shown by NMR and C,H analysis.- 1H-NMR (CDCl₃, 250 MHz): δ 8.55-8.75 (m, 3 H), 7.65-7.8 (m, 3 H), 7.3-7.5 (m, 6 H), 2.37 (s, 1 H), 2.35 (s, 1 H), 2.19 (s, 1 H), [O-H not discernible], furthermore signals 3.42 (q, 4 H), 1.15 (t, 6 H) for ether. Anal. calcd. for C₃₇H₂₈O₄ (536.6) [ether complex]: C 82.81, H 5.26; found: C 82.93, H 5.51. -

syn- **12a:** M.p. 215°C (dec.). ¹H-NMR (d₆-DMSO, 300 MHz): δ 8.74-8.77 (m, 3 H), 7.8-7.85 (m, 3 H), 7.4-7.48 (m, 6 H), 6.34 (s, 3H) [O-H not discernible].

5,10,15-Trihydroxy-5,10,15-tri(phenylethinyl)-1H-tribenzo[a,f,k]trindene (13a, 13b; syn- and anti- mixture) - 4.75 ml (4.0 g, 39.0 mmol) of phenylacetylene were dissolved in 100 ml of THF under argon and cooled to 0° C. 24.0 ml (38.4 mmol) of a 1.6 M solution of n-BuLi in hexane were dropped in within 30 min. After 30 min of stirring, 2.0 g (5.21 mmol) of 9 were added, and the mixture was slowly warmed to r.t. within 2 h. The mixture was hydrolyzed with water, and the aqueous phase was extracted repeatedly with ethyl acetate. The extract was dried (Na₂SO₄) and concentrated. The raw product was chromatographed on silica gel with ethyl acetate/light petroleum 1:3. Three fractions were obtained: (1) an unidentified impurity, (2) 13b, 1.76 g; 49 %, and (3) 13a, 0.69 g; 19 %.

syn-13a, m.p. 297°C (dec.) from chloroform. - IR (KBr) v_{max} (cm⁻¹) 3529 m, 3600 - 3200 m, 3054 m, 2225 m, 1600 s, 1488 s, 1473 s, 1342 s, 1251 s, 1025 s, 755 s, 690 s. - ¹H-NMR (CDCl₃, 250 MHz): δ 8.71 - 8.75 (m, 3 H), 7.79 - 7.83 (m, 3 H), 7.41 - 7.53 (m, 6 H), 7.29 - 7.33 (m, 6 H), 7.12 - 7.20 (m, 9 H), 7.67 (bs, 3 H, OH).- ¹³C-NMR (DMSO-d₆, TMS_{int}): δ 149.2, 140.6, 137.3, 136.0 (all quart) 131.3, 128.8, 128.7, 128.5, 128.1, 126.6, 124.0 (all tert), 121.6, 90.0, 82.0, 73.7 (all quart).

anti-13b, m.p. 192° C (dec.), from toluene. - IR (KBr) v_{max} (cm⁻¹) 3530 - 3180 b, 3046 m, 2977 m, 2225 m, 1600 m, 1488 s, 1442 m, 1373 s, 1253 s, 1037 s, 840 s, 752 s, 690 s. - ¹H-NMR (CDCl₃, 250MHz): δ 8.82 - 8.91 (m, 3 H), 7.85 - 7.92 (m, 3 H), 7.41 - 7.59 (m, 6 H), 7.29 - 7.35 (m, 6 H), 7.14 - 7.24 (m, 9 H); 2.74, 2.70, 2.66 (3 s, 3 H [3 OH; disappearing on treatment with D_2O] - Anal. calcd. for $C_{51}H_{30}O_3$ (690.8): C 88.67, H 4.38; found: C 88.53, H 4.60.

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