R. H. WIGHTMAN, (Miss) R. J. WAIN, AND D. H. LAKE¹ Department of Chemistry, Carleton University, Ottawa, Canada

Chemistry, Curreton Oniversity, Ottawa, C

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Some new unsaturated tricyclic hydrocarbons have been synthesized using a sequence of some general usefulness.

De nouveaux hydrocarbures tricycliques insaturés ont été synthétisés utilisant une série de réactions qui pourraient s'avérer d'utilisation générale.

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Introduction

Polycyclic unsaturated systems containing chiefly non-six-membered rings represent an area of organic chemistry currently full of theoretical interest (1) and synthetic challenges (2). From the synthetic point of view we wish to report a generally useful sequence which has provided us with several new tricyclic compounds containing a bicycloalkeno-benzenoid system. The compounds should serve as excellent precursors to test chemically the theoretical predictions (1) concerning stability and/or aromaticity of similar carbon skeletons containing more unsaturations. The general scheme is outlined in Scheme 1. Additionally, slight variations in the synthetic sequence (3a) or modification (3b) of the final products (i.e. 4a-d, 5b-d) would give other ring systems of potential interest in this expanding field.

Results and Discussion

The Synthetic Sequence

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The pinacol reaction leading to the diols 1a-dis well-documented (4), even in the mixed series, *i.e.* preparation of 1c (5). Since we were primarily interested in the product from this "mixedpinacol" reaction much of our effort was devoted to separation and characterization of the products 1c-4c in this series.²

The mixed pinacol reaction gave a somewhat variable yield of products 1a (~10%), 1b

 $(\sim 40\%)$, 1c $(\sim 50\%)$; however, it was possible to obtain analytical samples of the mixed diol (1c), either by preparative t.l.c. or careful sublimation of the diol mixture. No useful methods were found for separation of preparative quantities of the diols, hence the mixture was carried through the next step.

Dehydration of the diols was accomplished with phosphorus oxychloride in pyridine (4, 6)to minimize possible rearrangements. Due to the varying instability of the dienes,³ no rigorous attempt was made to purify them. However, separation of the diene mixture 2a-c could readily be accomplished by g.l.c. and preparative-scale g.l.c. techniques were employed at this stage. The individual dienes were then immediately allowed to react with maleic anhydride (4) to yield Diels-Alder adducts, 3a-c. Product distribution at the diene stage did not correspond exactly to that of the diol mixture, presumably due to the differences in stabilities of the various dienes.

Transformation of the anhydrides 3a-d into the corresponding aromatic products was accomplished by heating with a slight excess of phosphorus pentoxide, P_2O_5 , or excess 10% palladium-on-charcoal. The synthesis of 4a, originally prepared via an alternate route (8), has already been reported using the P_2O_5 method (7*a*), while a similar "aromatization" was accomplished using Pd/C (7*b*). Treatment of 4a with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) produced the dihydro-*as*-indacene (6) as indicated by comparison with the reported n.m.r. data (9). This final reaction was not further investigated,

¹Taken in part from the thesis submitted by D.H.L. in partial fulfillment of the requirements of the M.Sc. degree at Carleton University, Ottawa, Canada, 1969. Present address: Cambrian College of Applied Arts and Technology, Sudbury, Ontario.

²No attempt had been made to characterize 1c and 2c by the original author (5).

³Stability of the dienes increases with ring size. We have an indication that the decomposition involves cycloaddition of oxygen and subsequent cleavage to ketoalcohols.

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since the chemistry of the system has already been elegantly investigated by Katz and coworkers (9). However, this method is a significantly simpler approach to 4a (21% overall yield in four steps from cyclopentanone after our modification of the P₂O₅ treatment). Also, it serves to illustrate how benzenoid products can be used in quest of the more interesting compounds containing additional unsaturations.



The reaction of 3d with phosphorus pentoxide usually yieded two hydrocarbons, easily separable by g.l.c. and partially separable by column chromatography. The minor constituent (ca. 10– 20%), m.p. 133–135°, was identified as bicycloocteno-[a,d]-benzene (5d) by comparison with an authentic sample⁴ obtained via an unambiguous synthesis (10). The major product, m.p. 83–85°, has been characterized as the hitherto unknown bicyclo-octeno-[a,c]-benzene (4d). Combustion analysis and mass spectral data established the empirical formula; n.m.r. data (two aromatic, eight benzylic, and 16 methylenic protons) indicated the functionality and i.r. and u.v. comparisons (vide infra) corroborated the correct isomeric designation.

The identification of 4c and 5c has been noted (11), albeit in milligram quantities and via a rather lengthy synthesis (12) which favors the linear⁵ isomer 5c. Our sequence now makes available synthetically useful amounts of the potentially more interesting⁶ angular isomer 4c. In our sequence the hydrocarbon mixture obtained by "aromatization" of 3c with P_2O_5 appears to contain approximately 90% of 4c

and 10% of 5c as judged by i.r. and u.v. comparisons of reported values.

Treatment of the anhydride 3b with P_2O_5 at elevated temperatures produced a mixture of two hydrocarbons from which a crystalline solid, m.p. 140°, could easily be isolated. This product was identified as bicyclohepteno-[a,d]-benzene (5c), primarily on the basis of strong i.r. bands in the region 860–900 $\rm cm^{-1}$ and comparative u.v. data. Once again the empirical formula was ascertained by mass spectrum and combustion analysis, while the three gross structural features (two aromatic, eight benzylic, and 12 methylenic protons) were clearly distinguishable in the n.m.r. The ratio of the two components varied greatly, depending on the duration and temperature of the P_2O_5 treatment. Removal of 5c was almost complete after several crystallizations and g.l.c. investigation showed that the mother liquors contained essentially the second compound which could be obtained as a solid, m.p. 54°. This product was identified as bicyclohepteno-[a,c]-benzene (4c).⁷ Structure proof was again dependent on combustion analysis plus mass spectral and n.m.r. data for the gross structure, while i.r. and u.v. data (vide infra) were necessary to identify the substitution pattern.

The Isomers: Formation and Characterization

The formation of the linear isomer, often in appreciable quantities from 3b with P_2O_5 , was somewhat puzzling and frustrating at first. However, this isomerization, which had not previously been noted (7a), appears to be yet another example of the acid-catalyzed rearrangement of polyalkylated benzenes (16). Much work has been reported over the years on the s-octahydroanthracene : s-octahydrophenanthrene equilibrium under a variety of acidic conditions (e.g., H_2SO_4 , AlCl₃, HF/BF₃). A recent paper (17) suggests that the most plausible mechanism involves protonation of the ring system followed by rearrangement via a spiro-carbonium ion intermediate (similar to the dienone-phenol rearrangement). It seems quite probable, there-

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⁴We thank Professor F. Sondheimer for kindly providing a sample and other relevant data.

⁵Angular and linear designate 1,2:3,4- and 1,2:4,5substitution patterns respectively.

⁶Several unsuccessful attempts to prepare the fully unsaturated hydrocarbon derived from the linear isomer 5c have been reported (13a, b). Recently, however, it has been calculated that the non-benzenoid hydrocarbon containing the angular system 4c is more favorable (14a, b).

⁷Although very incomplete data were reported and only the melting points agree, it seems possible that our sample is the same as that reported by Rosenfelder and Ginsburg (15) via a completely different route. Unfortunately, Professor Ginsburg has no sample of his product (personal communication).

fore, that some rearrangement would be occurring under the conditions of the P_2O_5 experiments. Although not useful as a large-scale preparative method, it is interesting to note that isomerically pure angular hydrocarbons could be obtained if the corresponding anhydrides were treated under non-acidic conditions, *e.g.*, heating with excess Pd/C. Thermal reaction of 3c with catalytic amounts of Pd/C merely produced the aromatic anhydride 7.⁸



Proof of structure of the new aromatic hydrocarbons required a complete spectral investigation. The mass spectra of each pair of isomers exhibited fairly intense molecular ions and all other significant m/e's were the same. The n.m.r. spectra could not be used to distinguish isomers; the only potentially useful value (the chemical shift of the singlet representing two aromatic protons) varied slightly but no significant trends were observed. The most useful values were the strong i.r. bands ascribed to out-of-plane C-H deformation vibrations of the hydrogens on the benzene ring (18). Good agreement with the values quoted was found: for the angular isomers a range of 830-800 cm⁻¹ (two adjacent hydrogens), and for the linear isomers a range of $890-850 \text{ cm}^{-1}$ (one isolated hydrogen). Another useful trend was noticed when comparing the u.v. spectra of various pairs of isomers. Although the λ_{max} were not always identical, the linear isomer invariably exhibited a larger extinction coefficient (ε) than the angular isomer. Finally, it was noted that the linear isomer always had the higher melting point.

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In addition to making available several pre-

⁸The aromatization of anhydrides such as 3c can be readily accomplished (4, 7b) while similar decarboxylations involving prolonged heating with metals (Zn, Cu, Pd/C) have been previously noted (7b and refs. therein). Excess Pd/C appears to accelerate the latter process but no kinetic studies were attempted at this time. cursors for potential non-benzenoid aromatic hydrocarbons, this study has provided the missing compounds in an interesting series of tetraalkylated benzenes. Much spectroscopic information was unavailable in this series and we have repeated the syntheses of the 5–5 linear (5a) (16) and 5–6 linear (21) compounds for a more complete comparison. Table 1 summarizes the pertinent information.

Experimental

Melting points were determined on a Kofler hot stage and are uncorrected. The n.m.r. spectra were obtained on a Jeolco C-60 spectrometer and are expressed in p.p.m. (τ) from internal tetramethylsilane in deuterochloroform. The i.r. spectra (v_{max} in cm⁻¹) were measured on a Perkin–Elmer 237B or 257 spectrophotometer either as solutions or liquid film, and u.v. spectra $[\lambda_{max} \text{ in } nm (\epsilon)]$ were recorded with a Cary 14 or Perkin-Elmer 202 instrument. Mass spectra were obtained from an MS12 spectrometer (AEI). The g.l.c. was performed on Hewlett-Packard (F and M) instruments. Analytical investigations were performed on a Model 402 equipped with flameionization detector, helium carrier gas (50 ml/min), and a glass column (6' $\times \frac{1}{4}$ ") packed with six-ring polyphenyl ether (PPE-5% on Chromosorb W 80/100 mesh). For preparative separations a Model 776 was used with a stainless steel column ($80'' \times 3/4''$) packed with UCW98 (2% on Chromosorb W 60/80 mesh) and nitrogen carrier gas (400 ml/min). Temperatures and retention times are noted as required. The t.l.c. was accomplished using Silica gel G (0.25 mm layers) on glass plates. Microanalyses were performed by Organic Microanalyses (Dr. C. Daesslé), Montreal, Quebec.

The preparation of some of the starting materials (1a, b, d and 3a, b, d) has been adequately described elsewhere (4). Therefore the "mixed" series (1c-3c) will be used as the experimental example (5).

Preparation of "Mixed" Diols (1a-c)

To a well-stirred mixture of coarse aluminum powder (100 g, 3.7 mol) in dry benzene (600 ml), was added a solution of cycloheptanone (276 g, 2.46 mol), cyclopentanone (206 g, 2.46 mol), and mercuric chloride (46 g, 0.17 mol) in dry benzene (600 ml). The mixture was stirred and heated at reflux for 6 h, then cooled. Extra benzene (600 ml) then water (250 ml) was added dropwise and the stirred mixture was again heated for 3 h before being cooled and filtered. The solid was thoroughly washed with hot benzene and the combined organic filtrates were dried (anhydrous sodium sulfate). After removal of the solvent, the thick, residual oil was dissolved in a minimal amount of petroleum ether (b.p. 30-60°) and upon cooling, white crystals (m.p. 64-68°) slowly formed. Further concentration of the mother liquors eventually produced a total yield of 189 g (35%). The t.l.c. (30% ethyl acetate : 70% benzene) showed three spots with R₁ values of 0.19, 0.31, and 0.42. Preparative t.l.c. or slow sublimation (90°/0.1 mm Hg) produced three crystalline solids (approximate ratio 1:5:4). The

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TABLE 1.	Physical and	spectral	data of	various	tetra-alkyl	benzenes
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	1,2:3,4-Substitution (angular)				1,2:4,5-Substitution (linear)					
Substituents	The u.v * The ir.†		The n.m.r.‡	The m.p. (b.p./mm Hg)	m.p. im Hg) Reference	The u.v.	The i.r.	The n.m.r.	The m.p. (b.p./mm Hg)	Reference
Tetramethyl-§	268 (265) 273 (220) 277 (208)	804	3.09	205°/760		269 (700) 278 (750)	869	3.09	79–81°	
Bicyclopenteno- 4a and 5a	269 (774) 273 (643) 279 (904)	765 810	3.05	39–40	8,9	277 (3860) 281 (4040) 287 (4180)	870	2.97	52–54	16, 19
Cyclohexeno-, cyclopenteno-	269 (556) 273 (468) 278 (556)	800 830	3.12 3.30	65/0.6	20	276 (2290) 280 (2350) 286 (2590)	851 908	3.08	125/6	21
Bicyclohexeno-§	270 (310) 273 (360) 278 (215)	800	3.19	295/760	22	275 (1550) 280 (1300) 285 (1950)	850	3.29	72–74	22
Cyclohepteno-, cyclopenteno- 4c and 5c	268 (575)¶ 274 (490)	812 (820)¶	3.05 (3.20)¶	275/760	11	272 (1650)¶ 276 (1580)	830¶ 880	3.14¶	170–172/16	11, 13b
Bicyclohepteno- 4b and 5b	269 (341) 278 (299)	806	3.22	5354	76	269 (919) 278 (1191)	830 895 965	3.15	139–140	
Bicycloocteno- 4d and 5d	270 (368) 276 (316) 280 (347)	825	3.10	83-85		271 (981) 275 (790) 280 (1235)	872	3.27	132–133	10

*A_{max}(ɛ): measured in saturated hydrocarbon solvents.
*In cm⁻¹ (carbon disulfide solution or neat liquid film) of benzene substitution pattern.
tr-Values (p.p.m.) in deuterochloroform of aromatic protons only.
Sobtained from commercial sources: tetramethyls- (J. T. Baker Chemical Co., U.S.A.); 1,2:3,4-bicyclohexeno- (Fluka AG, Switzerland); 1,2:4,5-bicyclohexeno- (Aldrich Chemical Co., U.S.A.).
Yalues obtained from literature sources (see indicated refs.).
Personal communication from Professor Sondheimer (data from thesis of J. Mayer).

slowest moving product, m.p. $108-109^{\circ}$, was identified as 1a (4) while the fastest moving component, m.p. $77-78^{\circ}$, was 1b (4). The product with intermediate mobility was 1c,⁹ m.p. $63-64^{\circ}$ (5). Spectra: i.r. 3400 (strong —OH); n.m.r. 7.90 (2H singlet, exchangeable in D₂O, —OH), 8.15-8.70 (2OH multiplet, —CH₂'s).

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.73; H, 11.11. Found: C, 72.82; H, 11.17.

Preparation of Bicyclic Dienes (2a-c)

Essentially the method of Greidinger and Ginsburg (4) was followed. Thus the mixture of diols (189 g), excess phosphorus oxychloride (150 g), and dry pyridine (1500 ml) was stirred at room temperature for 0.5 h, then heated under reflux for 6 h. The pyridine was removed under reduced pressure, the residue dissolved in ice-water (41) and stirred for 2 h. This mixture was extracted with hexane $(3 \times 300 \text{ ml})$ and the combined organic extracts were washed successively with 5% aqueous hydrochloric acid $(2 \times 300 \text{ ml})$, 5% aqueous sodium bicarbonate $(2 \times 300 \text{ ml})$, water $(1 \times 300 \text{ ml})$, and saturated aqueous sodium chloride (1 \times 200 ml) before drying (anhydrous sodium sulfate) and removing solvent. The vield of crude oily dienes was 153 g. Separation was achieved by repeated 8 ml injections on a preparative scale g.l.c. instrument at 165°. Yields of components were as follows: 2a (8.5 g), 2b (62.7 g), 2c (34.2 g), mixture of 2b and 2c(6.9 g).

Preparation of Anhydrides (3a-c)

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The dienes were immediately dissolved in hexane, treated with excess maleic anhydride, and heated under reflux for several hours, as outlined by Greidinger and Ginsburg (4). The reaction mixture was dissolved in benzene and excess maleic anhydride removed by water extraction. After drying (anhydrous sodium sulfate) and removing the solvent, the residue was recrystallized from hexane. Thus, (i) 2a (8.5 g, 0.063 mol) and maleic anhydride (17.6 g, 0.180 mol) gave 3a (13.5 g, 92%), m.p. 103°; reported m.p. 104° (4). (ii) Compound 2b (62.7 g, 0.33 mol) and maleic anhydride (128 g, 1.3 mol) gave 3b (75 g, 80%), m.p. 157°; reported m.p. 158° (4); (iii) Compound 2c (34.2 g, 0.21 mol) and maleic anhydride (72 g, 0.74 mol) gave 3c (43.3 g, 62%), m.p. 135–137°. Spectrel i.r. 1850 and 1775 (anhydride); n.m.r. 6.65 (2H, d), 7.0–9.2 (18H, m).

Anal. Calcd. for C₁₆H₂₀O₃: C, 73.85; H, 7.70. Found: C, 73.91; H, 7.62.

Preparation of Aromatic Hydrocarbons.

The aromatic hydrocarbons were prepared by heating the corresponding anhydrides with a slight excess of phosphorus pentoxide at elevated temperatures (7a) for short periods of time (ca. 2-5 min). Our method involved mixing the two components in an elongated flask connected to a Hickman-type still and air condenser. The flask was briefly inserted into a preheated furnace (350°) and following a somewhat vigorous reaction, the distillate was collected. Filtration through a short column

⁹Oxidation with lead tetraacetate and treatment with 2,4-dinitrophenylhydrazine showed two spots on t.l.c. corresponding to the 2,4-dinitrophenylhydrazones of cyclopentanone and cycloheptanone.

of silica gel (using petroleum ether as eluant) was usually sufficient to rid the product of any colored impurities. The following reactions were carried out:

(i) 3a (3.5 g, 0.017 mol) and phosphorus pentoxide (3.0 g, 0.021 mol) gave a colorless oil (1.67 g, 65%) which formed white needles, m.p. 40°; reported for 4a, m.p. 40° (8, 9).

(ii) Compound 3b (5.0 g, 0.0192 mol) and phosphorus pentoxide (3.5 g, 0.021 mol) gave a colorless oil (2.50 g, 70%). Crystallization from methanol/ether produced 5b, white crystals, m.p. 139–140°. Spectra: n.m.r. 3.15 (2H, s, aromatic H), 7.0–7.5 (8H, m, benzylic H's) and 8.0–8.6 (12H, m --CH₂'s); i.r. and u.v. (see Table 1) indicated a 1,2:4,5 tetra-substitution pattern; mass spectrum, molecular ion m/e 214.

Anal. Calcd. for C₁₆H₂₂: C, 89.72; H, 10.28. Found: C, 89.72; H, 10.28.

From the mother liquors could be isolated a second compound 4b, m.p. 53-54°. Spectra: n.m.r. 3.22 (2H, s, aromatic H's), 7.0-7.5 (8H, m, benzylic H's), and 8.0-8.6 (12H, m $-CH_2$'s); i.r. and u.v. (see Table 1) consistent with a 1,2:3,4-substitution pattern; mass spectrum, molecular ion m/e 214.

Anal. Calcd. for C₁₆H₂₂: C, 89.72; H, 10.28. Found: C, 89.75; H, 10.21.

Analytical g.l.c. at 175° showed the two components to have retention times of 10.0 (4b) and 11.5 min (5b). The linear:angular ratio of approximately 1:3 in the reaction mixture could be changed dramatically in favor of the linear isomer by prolonging the contact time with phosphorus pentoxide.

(iii) The usual reaction between 3c (5.0 g, 0.019 mol) and phosphorus pentoxide (3.5 g, 0.025 mol) produced after column chromatography a colorless oil (2.98 g, 86%). The n.m.r., i.r., and u.v. comparisons with reported values (see Table 1) indicated that this material was composed of 4c and 5c (approximately 9:1 in favor of the angular isomer). The g.l.c. analysis at 175° showed only one (slightly unsymmetrical) peak with a retention time of 4.5 min.

(iv) The preparation of 3d was precisely as outlined by Greidinger and Ginsburg (4). The reaction of 3d (5.0 g, 0.016 mol) and phosphorus pentoxide (2.5 g, 0.018 mol) produced, after the usual work-up, a white crystalline residue (3.2 g, 80%). The g.l.c. analysis indicated two components with retention times at 175° of 21.3 and 25.7 min. The two compounds could be separated by column chromatography (silica gel) and crystallization (methanol/ether) and were identified as 5d and 4d respectively (ratio of approximately 1:5). Our linear isomer 5d had m.p. 135° and mixture m.p. 135° with an authentic sample⁶ while all spectral data were in complete agreement with literature values. Compound 4d (white needles) had m.p. 83-85° and the following spectra: n.m.r. 3.10 (2H, s, aromatic H's), 7.0-7.5 (8H, m, benzylic H's) and 8.0-8.6 (16H, m, -CH2's); i.r. and u.v. (see Table 1) indicated a 1,2:3,4-substituted benzene ring; mass spectrum, molecular ion m/e 242.

Anal. Calcd. for C₁₈H₂₆: C, 89.27; H, 10.73. Found: C, 89.20; H, 10.59.

Alternate Preparation of 4c

A mixture of 3c (500 mg, 0.0019 mol) and 10% palladium-on-charcoal (700 mg) was heated at 350° for a few minutes. After evolution of gas (ca. 5 min) the mixture was cooled, filtered, and rinsed with ether. The filtrate was evaporated to dryness to yield an oily residue (300 mg, 85%) which was rendered colorless by filtration through a short column of silica gel. Spectroscopic examination (especially i.r. and u.v.) indicated isomerically pure 4c and g.l.c. comparison was identical with a sample prepared via the phosphorus pentoxide method.

Preparation of 7

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When a mixture of 3c (500 mg, 0.0019 mol) and 10% palladium-on-charcoal (100 mg) was treated in a manner similar to that outlined above, there was obtained a solid residue (400 mg, 80%). Crystallization from ethanol yielded white crystals of 7, m.p. 199-201°. Spectra: i.r. (Nujol mull) 1835 and 1775 (aromatic anhydride).

Anal. Calcd. for C16H16O3: C, 74.98; H, 6.24. Found: C, 74.67; H, 6.45.

Preparation of 6

 \hat{A} solution of 4a (300 mg, 0.002 mol) and DDQ (1.0 g, 0.004 mol) in benzene (50 ml) was heated under reflux for 24 h. Hexane (100 ml) was added to precipitate phenolic by-products and the residue, after filtration and evaporation, was subjected to column chromatography on alumina (Woelm, neutral, activity I). Elution with hexane yielded a slightly colored viscous oil. The n.m.r. comparisons with a published spectra (9) indicated the presence of 6 (extra bands in the 3.0-4.0 τ region). The g.l.c. studies showed the sample to contain some starting material.

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