Table I. Adsorption of Methane on Silica

Gilmer and Kobayashi (*1*)			Stacy et al. (*7*)		
T = 40°C, S = 532 m^2/g			T = 37.8°C, S = 145 m^2/g		
v_m = 5.4 mmol/g			v_m = 1.48 mmol/g		
Pressure, atm	Adsorption, mmmol/g	θ	Pressure, atm	Adsorption, mmol/g	θ
50	2.3	0.43	50	1.1	0.74
100	2.9	0.54	100	2	1.3
140	3.2	0.59	140	3	2.0
Even at −40°C			200	4	2.7
50	4.5	0.83	400	6.5	4.4
100	4.3	0.80	600	8	5.4
140	3.8	0.70			

tainable surface coverage on these adsorbents by any adsorbate gas above its critical temperature (for methane T_c = −82.9°C), and hence can be used for calculating the degree of coverage θ. In Table I the results of Stacy et al. for 37.8°C are compared with those of Gilmer and Kobayashi for 40°C. The adsorption data of Stacy et al. indicate multimolecular adsorption ($\theta > 1$), which is highly improbable so far above the critical temperature of the adsorbate.

It must be emphasized here that the adsorption isotherms of Gilmer and Kobayashi (*1*) at −40°, −20°, and 0°C show clear maxima at pressures of 63, 82, and 96 atm, respectively, while their 20° and 40°C isotherms already level off at 120–40 atm. This behavior of high-pressure adsorption isotherms is normal and expected and has indeed been observed by all previous workers in this field (for a list of work since 1930, see Table 1 in ref. *2*). In contrast to these, the adsorption isotherms of Stacy et al. continuously increase with pressure even at 600–50 atm. This strengthens the suspicion that the gas simply compressed into some unaccounted part of the dead space in their apparatus has masked the true adsorption.

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ORGANIC SECTION

Catalytic Hydrogenation of Polynuclear Hydrocarbons

Products of Partial Hydrogenation of Dibenz(*a,j*)anthracene, Benzo(*ghi*)perylene, Dibenz(*a,c*)anthracene, 3-Methylcholanthrene, 7,12-Dimethylbenz(*a*)anthracene, and Anthanthrene

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The catalytic hydrogenation reactions of the title compounds were studied. A total of 18 products were isolated and characterized. Some of these compounds were products of reduction at noncontiguous carbon atoms, the reactive centers in one case being separated by seven bonds. The mass spectral fragmentation of derivatives of 3-methylcholanthrene and 7,12-dimethylbenz(*a*)anthracene is characterized by a strong tendency to lose methyl groups.

As a result of our interest in the relationship of chemical structure to carcinogenic activity among polynuclear hydrocarbons (*6, 8*), we have recently completed a study (*7, 9*) of the carcinogenicity of a number of partially hydrogenated derivatives of dibenz(*a,j*)anthracene (I), benzo(*ghi*)perylene (II), dibenz(*a,c*)anthracene (III), 3-methylcholanthrene (IV), 7,12-dimethylbenz(*a*)anthracene (V), and anthanthrene (VI). We report the preparation and characterization of those hydrogenation products.

Some of the reactions followed unexpected steric courses. The production of the 1,2,3,7,8,9-hexahydro derivative (VIb) in the hydrogenation of anthanthrene implied that net 1,8- (or greater) addition of hydrogen had occurred. Similarly, IIb and IVc are the products of reduction at noncontiguous carbon atoms.

The mass spectra of the hydrogenated hydrocarbons showed that the added hydrogens were most easily lost so that the peak corresponding to the completely aromatic structure was

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usually prominent. However, the derivatives of 7,12-dimethylbenz(*a*)anthracene and of 3-methylcholanthrene tended to lose the methyl groups first.

The mass spectral data have been deposited with the ACS Microfilm Depository Service.

EXPERIMENTAL

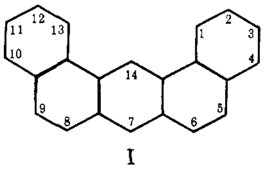
Catalytic Hydrogenation. The hydrogenations were carried out as described (*6*), by adding 300 to 400 mg of hydrocarbon to a platinum catalyst, produced in situ by reduction with H_2 of 60 to 80 mg of PtO_2 suspended in isooctane (2,2,4-trimethylpentane)–acetic acid (1:1). After a suitable volume of H_2 had been taken up (usually 1–4 moles depending on the proportion of saturated to unsaturated molecules desired), the product was poured into water and extracted with benzene.

Chromatography. After evaporating the benzene solution to a small volume, this product was chromatographed on columns of magnesia–Celite (2:1), approximately 500 mg of polynuclear hydrocarbon on a 28 × 8 cm column. Mixtures of hexane–benzene–acetone (8:1:1 or 3:1:1) were the eluting solvents. Bands fluorescent in uv light were cut from the column after extrusion. The adsorbed hydrocarbons were eluted with acetone–benzene–ethanol (*6*). The still impure hydrocarbons were further resolved by repeated chromatography on the same adsorbent or on silica gel, with benzene–hexane (1:9) as eluant, and were crystallized to constant melting point. Further purification was achieved by preparation of a 2,4,7-trinitrofluorenone (TNF) derivative, by adding excess TNF in hot benzene and cooling (*6*). When purified by crystallization, the complex was decomposed by chromatography on magnesia–Celite, and the regenerated hydrocarbon was recrystallized.

Identification of Hydrogenated Derivatives. The structure of each purified product was determined by mass spectrometry at 70 eV (AEI = MS-9 mass spectrometer), using the direct inlet probe, ultraviolet absorption spectrometry in isooctane, λ in nmeters (Cary Model 15), and nuclear magnetic resonance (nmr) spectrometry (Varian HA-100). Data given for each resonance in the nmr spectrum are: chemical shift (or, for multiplets, range covered), multiplicity (s = singlet, d = doublet, t = triplet, and m = multiplet or unresolvable superposition of peaks), number of protons, and assignment (bold face). Chemical shifts are given in τ units, tetramethylsilane having been used in each case as internal reference; coupling constants (J) are given in Hz. Elemental analyses, C and H, in agreement with theoretical values were obtained and submitted for review.

Hydrocarbons. Benzo(*ghi*)perylene (II), 7,12-dimethylbenz(*a*)anthracene (V), and 3-methylcholanthrene (IV) were obtained from Koch-Light Laboratories, Ltd., Colnbrook, England; dibenz(*a,c*)anthracene (III) was obtained from Ruetgerswerke, Darmstadt, Germany; anthanthrene (VI) was prepared by Saber Laboratories, Morton Grove, Ill. Dibenz(*a,j*)anthracene (I) was synthesized by the method of Cook and Stephenson (*2*). The overall yield was quite low, but a total of 5 grams of dibenz(*a,j*)anthracene was obtained, mp 196–7°C.

Hydrogenation of Dibenz(a,j)anthracene (I). A total of 4 grams of dibenz(*a,j*)anthracene was hydrogenated in approximately 250-mg portions until 0.5 mole of hydrogen was taken up. Three major fluorescent bands were separated on magnesia–Celite, the topmost being dibenz(*a,j*)anthracene (50–5% recovered unchanged). The other bands were, in sequence, tetrahydro and dihydro derivatives. The weakly adsorbed material in the filtrate of the columns was a mixture of small quantities of several more saturated derivatives, of which the hexahydro derivative was most prominent.



I

1,2,3,4-TETRAHYDRODIBENZ(*a,j*)ANTHRACENE (Ia). The middle fluorescent zone was eluted and the solvent was evaporated leaving a crystalline solid. A TNF complex was prepared and crystallized to constant melting point (242–3°C). The hydrocarbon was regenerated from the red solid and crystallized from benzene–ethanol; the yield was 200 mg of colorless crystals, mp 112–13°C. The uv absorption spectrum resembled that of benz(*a*)anthracene: λ_{max} (ϵ) 261 (4.61), 271 (4.58), 282 (4.80), 294 (4.89), 303 (4.14), 308 (3.91), 323 (3.92), 342 (3.76), 350 (3.67), 359 (3.56), 367 (3.36), 377 (2.79), 382 (2.56), 387 (3.19).

Nmr spectrum (benzene-d_6): 0.95, s, 1, **14**; 1.29–1.41, m, 1, **13**; 2.02, 3, 1, **7**; 2.30–2.75, m 5, **8**, **9**, **10**, **11**, **12**; 2.59, d (J_{5-6} = 9), 1, **6**; 3.00, d, 1, **5**; 7.00–7.20, m, 2, **1**; 7.26–7.47, m, 2, **4**; 8.25–8.45, m, 4, **2**, **3**. An $A_2'X_2'$ system ($\delta_A = 6.16$, $\delta_X = 5.71$, $J_{AX} \simeq J_{AX'} \simeq 4.3$) found in the spectrum of one sample was assigned to the C-7 and C-14 methylene groups of an impurity, ring C of which was of the 1,4-dihydrobenzene type. This impurity was suspected of being (Ib), confirmed by preparation of the dihydro compound through the disodio derivative (*1*).

5,6-DIHYDRODIBENZ(a,*j*)ANTHRACENE (Ic). The lowest fluorescent zone of the column chromatogram was eluted, and the solvent was evaporated, leaving a white crystalline solid. After crystallization from benzene–ethanol, 1.01 grams of crystals were obtained, melting at 155.5–156.5°C. The uv absorption spectrum resembled that of a phenylphenanthrene: λ_{max} (ϵ): 235 (4.39), 257 (4.63), 271 (4.72), 289 (4.30), 307 (4.45), 322 (4.44), 344 (3.35), 361 (3.16).

Nmr spectrum (benzene-d_6): 1.05, s, 1, **14**; 1.39–1.51, m, 1, **13**; 2.06–2.20, m, 1, **1**; 2.53, s, 1, **7**; 2.25–3.00, m, 8, **2**, **3**, **4**, **8**, **9**, **10**, **11**, **12**; 7.34, s (broad; $\delta_5 \neq \delta_6$), 4, **5**, **6**.

1,2,3,4,8,9-HEXAHYDRODIBENZ(*a,j*)ANTHRACENE (Id). Reduction of 300 mg of 5,6-dihydrodibenz(*a,j*)anthracene was carried out until 1 mole of hydrogen was taken up. The product was chromatographed on magnesia–Celite. A blue fluorescent zone on the column was unchanged dihydrodibenzanthracene. The nonfluorescent filtrate was evaporated, and a TNF complex was prepared. The red complex was crystallized to constant melting point (192–3°C) and the polynuclear hydrocarbon was regenerated. The colorless compound from the filtrate was crystallized from benzene–ethanol in 102-mg yield, mp 132–3°C.

The uv spectrum was similar to that of 2-phenylnaphthalene [and to that of the hexahydro derivative of dibenz(*a,h*)anthracene (*6*) of similar structure]; λ_{max} (ϵ): 227 (4.29), 236 (4.24), 249 (4.42), 259 (4.60), 268 (4.65), 290 (3.92), 306 (4.10), 316 (4.08), 348 (2.96).

Nmr spectrum (benzene-d_6): 1.72, s, 1, **14**; 2.03–2.16, m, 1, **13**; 2.58, *d*, (J_{5-6} = 9), 1, **6**; 2.62, s, 1, **7**; 2.70–2.95, m, 3, **10**, **11**, **12**; 3.00, d, 1, **5**; 7.05–7.23, m, 2, **1**; 7.23–7.48, m, 6, **4**, **8**, **9**; 8.20–8.50, m, 4, **2**, **3**.

From the filtrates of the various column chromatograms, several minor hydrogenation products were isolated by a combination of chromatography on silica gel and fractional crystallization of the TNF complexes. The physical data on which their identifications were based are given below.

5,6,8,9-TETRAHYDRODIBENZ(*a,j*)ANTHRACENE (Ie). Uv spectrum: λ_{max} (ϵ): 257 (4.68), 263 (4.78), 313 (3.84), 323 (3.79); mp 160–160.5°C.

Nmr spectrum (CCl_4): 1.98, s, 1, **14**; 2.19–2.31, m, 2. **1**, **13**; 2.68–2.94; m, 6, **2**, **3**, **4**, **10**, **11**, **12**; 3.01, s, 1, **7**; 7.18, s, 8, **5**, **6**, **8**, **9**.

1,2,3,4,4a,5,6,14b-OCTAHYDRODIBENZ(*a,j*)ANTHRACENE (If). Mp 93–94°C. Uv spectrum is similar to phenanthrene: λ_{max} (ϵ): 248 (4.54), 256 (4.68), 273 (4.20), 280 (4.14), 287 (3.98), 300 (3.98), 320 (2.59), 326 (2.51), 335 (2.60), 344 (2.38), 351 (2.46).

Nmr spectrum (dilute in CCl_4; chemical shifts are imprecise, as the C1024 computer used in data collection was not calibrated): 1.43–1.56, m, 1, **13**; 1.73, s, 1, **14**; 2.20–3.05 m, 6, **7**, **8**, **9**, **10**, **11**, **12**; 6.80–7.15, m, 3, **6**, **14b**; 7.70–8.50, m, 11, **1**, **2**, **3**, **4**, **4a**, **5**.

1,2,3,4,4a,5,6,8,9,9a,10,11,12,13,13a,14b-HEXADECAHYDRODIBENZ(*a,j*)ANTHRACENE (Ig). Uv spectrum [almost identical with hexadecahydrodibenz(*a,h*)anthracene (*6*)]: λ_{max} (ϵ): 226 (3.87), 268 (3.00), 273 (3.22), 277 (3.17), 283 (3.34).

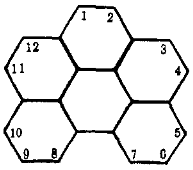
Nmr spectrum (CCl_4): 3.31, s, 1, **7**(?); 3.40, s, 1, **14**(?); 7.15–7.60, m, 6, **6**, **8**, **13a**, **14b**; 7.80–8.90, m, 18, **1**, **2**, **3**, **4**, **4a**, **5**, **9**, **9a**, **10**, **11**, **12**, **13**.

7,14-DIHYDRODIBENZ(*a,j*)ANTHRACENE (Ib). Approximately 1 gram of powdered sodium was added to 96 mg of dibenz (*a,j*)-anthracene dissolved in 10 ml of toluene and 100 ml of ether. The mixture was stirred magnetically in a closed flask for 4 hr, and the deep blue suspension was poured into 100 ml of methanol. Benzene, 50 ml, was added, followed by 400 ml of water. The upper layer was separated and dried with anhydrous sodium sulfate, and the solvent was removed. The residue was chromatographed on 5 TLC plates of magnesium hydroxide, with benzene as developer (*5*). Above the major fluorescent band, consisting of unchanged dibenz(*a,j*) anthracene, was a weaker fluorescent band. The latter was cut out and eluted, and the hydrocarbon in it was crystallized from benzene–ethanol. The yield was 18 mg, mp 160–1°C.

The uv absorption spectrum was similar to that of 7,14-dihydrodibenz(*a,h*)anthracene (*6*); λ_{max} (ϵ): 215 (4.97), 228 (4.88), 233 (5.01), 249 (4.15), 258 (4.17), 274 (4.10), 285 (4.21), 292 (4.14), 297 (4.25), 314 (3.45), 322 (3.55), 333 (3.13), 348 (2.82).

Nmr spectrum (benzene-d_6): 1.96–2.10, m, 2, **1**,**13**; 2.25–2.97, m, 10, **2**, **3**, **4**, **5**, **6**, **8**, **9**, **10**, **11**, **12**; 5.56, 6 ($J_{7-14} = 4$), 2, **14**; 6.04, t, 2, **7**.

Hydrogenation of Benzo(ghi)perylene (II). Two grams of benzo(*ghi*) perylene was hydrogenated in 500-mg portions until 1.5–2 moles of H_2 were taken up (uptake of hydrogen was extremely slow). The crude reduction product was crystallized from hot benzene to remove unreduced benzoperylene (1.4 grams). The benzene mother liquor was chromatographed on magnesia–Celite. There were three fluorescent zones on the column, and a slightly fluorescent filtrate. The upper, strongly fluorescent zone was benzoperylene.



II

3,4-DIHYDROBENZO(*ghi*)PERYLENE (IIa). The middle fluorescent zone was eluted and the solvent was removed. A TNF complex was prepared from the residual solid and crystallized *to constant melting point* (264–5°C). The hydrocarbon was regenerated from the TNF complex and crystallized from benzene–methanol, yielding 60 mg, mp 210–10.5°.

The uv spectrum resembled that of benzo(*e*)pyrene: λ_{max} (ϵ): 218 (4.65), 225 (4.72), 241 (4.44), 246 (4.40), 262 (4.39), 272 (4.46), 283 (4.59), 295 (4.65), 310 (4.15), 323 (4.33), 338 (4.52), 360 (2.96), 364 (2.98), 370 (2.82), 381 (2.75).

Nmr spectrum (CCl_4): 1.25–1.37, m, 1, **8** (**or 7**); 1.45–1.58, m, 1, **7** (**or 8**); 1.95–2.75, m, 8, **1**, **2**, **5**, **6**, **9**, **10**, **11**, **12**; 6.51, s, 4, **3**, **4**.

5,6,7,8,9,10-HEXAHYDROBENZO(*ghi*)PERYLENE (IIb). The lower fluorescent zone was eluted and evaporated to dryness. The crude crystalline material was converted to the TNF complex and crystallized to constant melting point (219–20°C). The hydrocarbon was regenerated and crystallized from benzene–methanol, giving 140 mg, mp 169–170°C.

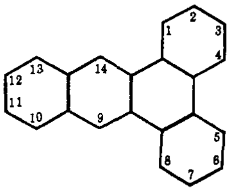
The uv absorption spectrum was that of a substituted pyrene: λ_{max} (ϵ): 238 (4.67), 247 (4.87), 259 (4.16), 269 (4.52), 280 (4.81), 306 (3.70), 318 (4.14), 334 (4.52), 350 (4.66), 362 (3.65), 377 (2.88), 384 (3.25).

Nmr spectrum (benzene-d_6): 2.14, d ($J_{3-4} = 8$), 2, **3**, **12**; 2.19, s, 2, **1**, **2**; 2.43, d, 2, **4**, **11**; 6.96, 6 ($J_{5-6} = 6$), 4, **5**, **10**; 7.18, t ($J_{6-7} = 6.5$), 4, **7**, **8**; 8.10, m (approximates a quintet), 4, **6**, **9**.

3,4,11,12-TETRAHYDROBENZO(*ghi*)PERYLENE (IIc). The filtrate of the initial chromatographic column was evaporated, the residue was dissolved in benzene, and TNF was added. The TNF complex was crystallized to constant melting point, 190–1°C, and the hydrocarbon was regenerated. The melting point was 147–8°C. The uv absorption spectrum was similar to that of triphenylene: λ_{max} (ϵ): 238 (4.25), 259 (4.75), 268 (4.93), 291 (4.17), 323 (3.15), 329 (3.15), 339 (3.21), 345 (3.18).

Nmr spectrum (dilute in CCl_4; chemical shifts are imprecise): 1.65–1.78, m, 2, **7**, **8**; 2.40–2.80, m, 4, **5**, **6**, **9**, **10**; 2.80, s, 2, **1**, **2**; 6.82, s, 8, **3**, **4**, **11**, **12**.

Hydrogenation of Dibenz(a,c)anthracene (III). One gram of dibenz(*a,c*)anthracene was hydrogenated in 500-mg portions until 2 moles H_2 were taken up. The reduction product was chromatographed on magnesia–celite. Two fluorescent bands were present, separated by a nonfluorescent band. The upper fluorescent band was unchanged dibenz(*a, c*)anthracene.



III

10, 11, 12, 13-TETRAHYDRODIBENZ(*a,c*)ANTHRACENE (IIIa). The nonfluorescent band was eluted and the residue, after evaporation to dryness, was a colorless solid, mp 191–2°C. A TNF complex was prepared and recrystallized from benzene; the light orange crystals melted at 228–30°C. The hydrocarbon was regenerated and crystallized from benzene–ethanol yielding 600 mg of colorless crystals, mp 198–198.5°C.

The uv spectrum resembled that of triphenylene: λ_{max} (ϵ): 253 (4.88), 262 (5.13), 277(4.26), 289 (4.20), 316 (2.93), 324 (2.73), 331 (2.90), 339 (2.58), 347 (2.76).

Nmr spectrum (benzene-d_6): 1.50–1.70, m, 4, **1**, **4**, **5**, **8**; 1.85, s, 2, **9**, **14**; 2.52–2.72, m, 4, **2**, **3**, **6**, **7**; 7.13–7.34, m, 4, **10**, **13**; 8.22–8.44, m, 4, **11**, **12**.

1,2,3,4,10,11,12,13-OCTAHYDRODIBENZ(*a,c*)ANTHRACENE (IIIb). The lower fluorescent zone was eluted, the solvent was evaporated, and a TNF complex was prepared from the residue. After crystallization from benzene, the complex melted 214–16°C. The hydrocarbon was regenerated and crystallized from benzene–ethanol, yielding 200 mg of colorless crystals, mp 108.5–110°C.

The uv spectrum resembled that of phenanthrene: λ_{max} (ϵ): 230 (4.35), 252 (4.64), 259 (4.78), 278 (4.38), 285 (4.25), 292 (4.10), 305 (4.02), 323 (2.74), 331 (2.62), 339 (2.80), 347 (2.51), 356 (2.70).

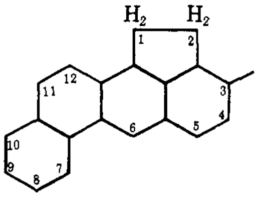
Nmr spectrum (benzene-d_6): 1.37–1.56, m (closely approximates the B part of an $A_2'B_2'$ pattern), 1, **5**; 2.38, s, 1, **14**; 2.48–2.67, m (A part of an $A_2'B_2'$ system), 2, **6**, **7**; 7.02–7.30, m, 8, **1**, **4**, **10**, **13**; 8.15–8.45, m, 8, **2**, **3**, **11**, **12**.

9,14-DIHYDRODIBENZ(*a,c*)ANTHRACENE (IIIc). A solution of 118 mg of dibenz(*a,c*)anthracene was reduced with 1 gram of powdered sodium, as for Ib. The dihydro compound had a higher R_f on magnesium hydroxide (*5*) than dibenz(*a,c*)-anthracene, and was sharply separated. The yield of dihydro compound crystallized from benzene–methanol was 45 mg, mp 191–2°C.

The uv absorption spectrum was similar to that of phenanthrene: λ_{max} (ϵ): 248 (4.69), 255 (4.80), 272 (4.29), 286 (4.21), 298 (4.08), 320 (2.87), 326 (2.84), 333 (2.90), 350 (2.80).

Nmr spectrum ($CDCl_3$): 1.20–1.34, m, 2, **4**, **5**; 1.72–1.90, m, 2, 1, **8**; 2.25–2.45, m, 4, **2**, **3**, **6**, **7**; 2.50–2.80, m, 4, **10**, **11**, **12**, **13**; 5.49, s, 4, **9**, **14**.

Hydrogenation of 3-Methylcholanthrene (IV). A total of 1.2 grams of methylcholanthrene was hydrogenated in 400-mg portions until 1.5 grams of H_2 were taken up. The product was chromatographed on magnesia–Celite and three blue fluorescent bands were present; the filtrate was nonfluorescent. The topmost band was unchanged methylcholanthrene (580 mg).



IV

7,8,9,10-Tetrahydro-3-methylcholanthrene (IVa). The middle fluorescent zone was eluted, the solvent was removed and a TNF complex was prepared, mp 212–14°C after recrystallization. Decomposition of this complex, with regeneration of the hydrocarbon, gave colorless crystals crystallized from benzene–ethanol, mp 164–5°C.

The uv spectrum resembled that of anthracene: λ_{max} (ϵ): 230 (3.90), 257 (4.89), 265 (5.20), 323 (3.23), 340 (3.48), 358 (3.69), 378 (3.77), 398 (3.75).

Nmr spectrum (CCl_4): 1.98, s, 1, **6**; 2.48, d [J_{11-12} (or J_{4-5}) = 9], 1, **12** (**or 5**); 2.53, d [J_{4-5} (or J_{11-12}) = 8.5], 1, **5** (or **12**); 2.92, d, 1, **4** (**or 11**); 3.04, d, 1, **11** (**or 4**); 6.32–6.53, m, 2, **1**; 6.61–6.94, m, 4, **2**, 7; 7.04–7.25, m, 2, **10**; 7.65, s, 3, **3**; 7.95–8.24, m, 4, **8**, **9**.

11,12-Dihydro-3-methylcholanthrene (IVb). The lower blue fluorescent band was eluted and the solvent was removed. The crude colorless crystals (250 mg) were crystallized from benzene–ethanol, yielding 213 mg, mp 153–4°C.

The uv spectrum resembled that of hexahydrodibenz(*a*,*h*)-anthracene (*6*): λ_{max} (ϵ): 221 (4.44), 236 (4.28), 263 (4.70), 272 (4.75), 310 (4.12).

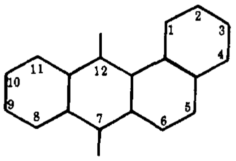
Nmr spectrum (benzene-d_6): 2.00, s, 1, **6**; 2.09–2.22, m, 1, 7; 2.46, d (J_{4-5} = 8.5), 1, **5**, 2.68–2.93, m, 4, **4**, **8**, **9**, **10**; 7.13, s, 4- **1**, **2**; 7.32, s, 4, **11**, **12**; 7.81, s, 3, **3**.

6,7,8,9,10,12b-Hexahydro-3-methylcholanthrene (IVc). This preparation roughly follows that given by Fieser and Hershberg (*3*) for hexahydromethylcholanthrene. Methylcholanthrene (0.7 gram) was dissolved in 600 ml of *n*-butanol, and 18 grams of sodium were added in small pieces during the course of 1 hr. Water was added slowly to decompose the alkoxide, and water and butanol were removed by distillation under reduced pressure. The hydrocarbon in the residue was extracted with benzene and crystallized from benzene–ethanol to constant melting point. The nmr spectrum indicated the presence of only traces of impurity, so the hydrocarbon was not purified further. The yield was 307 mg of colorless crystals, mp 152–3°C.

The uv absorption spectrum showed the presence of 3% of the 7,8,9,10-tetrahydro compound.

Nmr spectrum (CCl_4): 3.09, d (J = 8), 1, **4**, **5**, **11**, or **12**; 3.16, s, 2, **11 and 12** (**or 4 and 5**); 3.18, d, 1, **4**, **5**, **11 or 12**; 5.96–6.70, m, 3, assignments uncertain; 6.97–7.37, m, 7, **7**, **10**, and three other protons; 7.78, s, 3, **3**; 7.89–8.43, m, 5, **8**, **9**, and one other proton.

Hydrogenation of 7,12-Dimethylbenz(*a*)*anthracene* (V). Two grams of dimethylbenz(*a*)anthracene (DMBA) was hydrogenated until approximately 1 mole H_2 had been taken up. The product was chromatographed on magnesia–Celite, the chromatogram showing two blue fluorescent bands. The upper fluorescent zone was unreduced DMBA, eluted, and crystallized from 95% ethanol. The crystalline substance was almost colorless and melted at 122–3°C. Chromatography, nmr, and mass spectrometry showed the material to be of high purity and free of the halogenated and other impurities that constitute as much as 5–10% of the commercial product. The yield was 1.1 grams.



V

8,9,10,11-Tetrahydro-7,12-dimethylbenz(*a*)anthracene (Va). The lower blue fluorescent zone was eluted, the solvent was evaporated, and a TNF derivative was prepared from the residue, mp 174–5°C after recrystallization. The hydrocarbon was regenerated and crystallized from ethanol, giving 600 mg of colorless crystals, mp 114–16°C.

Uv spectrum: λ_{max} (ϵ): 230 (4.21), 264 (4.75), 290 (3.96), 302 (4.03), 314 (4.04), 344 (2.56).

Nmr spectrum (benzene-d_6): 1.43–1.62, m, 1, **1**; 2.21, d (J_{5-6} = 9.5), 1, **6** (**or 5**); 2.22–2.37, m, 1, **4**; 2.53, d, 1, **5** (**or 6**); 2.60–2.75, m, 2, **2**, **3**; 7.41, s, 3, **12**; 7.30–7.55, m, 4, **8**, **11**; 7.71, s, **3**, **7**; 8.25–8.52, m, 4, **9**, **10**.

5,6-Dihydro-7,12-dimethylbenz(*a*)anthracene (Vb). This was prepared according to the published method (*4*) by reduction of 500 mg of DMBA. The hydrocarbon was regenerated from the TNF complex (mp 168–70°C) and was crystallized from methanol. The yield was 310 mg of colorless crystals, mp 109–11°C.

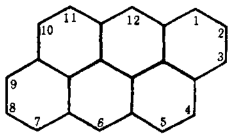
Uv spectrum was similar to that of IVb: λ_{max} (ϵ): 222 (4.40), 258 (4.67), 267 (4.73), 300 (4.07), 343 (2.85).

Nmr spectrum ($CDCl_3$): 1.91–2.14, m, 2, **8**, **11** (?); 2.48–2.71, m, 3, **1**, **9**, **10** (?); 2.74–2.96, m, 3, **2–4** (?); 7.19, s, 3, **12**; 7.05–7.40, m, ($A_2'B_2'$), 4, **5**, **6**; 7.45, s, 3, **7**.

7,12-Dihydro-7,12-dimethylbenz(*a*)anthracene (Vc). This compound was prepared by stirring a solution of 7,12-dimethylbenz(*a*)anthracene in ether with powdered sodium and decomposing the deep blue sodium salt with methanol. The 7,12-dihydro compound was separated on thin layer chromatography (TLC) plates of magnesium hydroxide from unchanged dimethylbenz(*a*)anthracene. The product was an oil which failed to crystallize.

Nmr spectrum (CCl_4): 1.85–1.99, m, 1 assignment uncertain; 2.20–2.95, m, 9, *remaining aromatic protons;* 5.27, quartet (J = 7), 1, *12-methinyl proton;* 5.88, quartet (J = 7), 1, *7-methinyl proton;* 8.40 and 8.44, superposition of doublets, 6, *methyl groups.*

Hydrogenation of Anthanthrene (VI). The anthanthrene as received contained several percent of impurity. The hydrocarbon, purified by crystallization from benzene, was hydrogenated in two 400-mg portions until 1.5 moles H_2 had been taken up. The product was chromatographed on magnesia–Celite. Three fluorescent bands were seen; the topmost had a green fluorescence and was unreacted anthanthrene (230 mg).



VI

4,5-Dihydroanthanthrene (VIa). The middle fluorescent zone (blue) was eluted, and the hydrocarbon was rechromatographed to remove anthanthrene. The main fluorescent zone was again eluted and the residue after evaporation of the solvent had an mp 202–203.5°C. A TNF complex was prepared and crystallized from benzene, giving green crystals, mp 227–9°C. The hydrocarbon was regenerated and crystallized from benzene. The yield of yellow-green crystals was 180 mg, mp 203–4°C.

The uv spectrum was similar to that of benzo(*a*)pyrene: λ_{max} (ϵ): 224 (4.52), 232 (4.69), 267 (4.68), 279 (4.54), 291 (4.72), 303 (4.81), 335 (3.70), 351 (4.10), 370 (4.44), 384 (4.38), 389 (4.53), 407 (3.55).

Nmr spectrum (benzene-d_6): 1.75, s, 1, **12**; 1.93–2.74, m, 9, **1**, **2**, **3**, **6**, **7**, **8**, **9**, **10**, **11**; 6.82, s, 4, **4**, **5**.

1,2,3,7,8,9-Hexahydroanthanthrene (VIb). The lowest, violet-fluorescent band was eluted and rechromatographed. The main band was again eluted and crystallized from benzene, but appeared not to be pure. A TNF complex was prepared and recrystallized from benzene, giving dull blue crystals, mp 212–13°C. The hydrocarbon was regenerated from the complex and crystallized three times from benzene, giving 220 mg of colorless crystals, mp 208–10°C.

The uv spectrum was that of a substituted pyrene: λ_{max} (ϵ): 238 (4.53), 247 (4.80), 257 (4.09), 268 (4.46), 279 (4.73), 317 (4.03), 332 (4.39), 349 (4.55), 364 (3.74), 376 (3.04), 384 (3.75).

Nmr spectrum (benzene-d_6): 2.12, d ($J_{4-5} = 7.5$), 2, **5**, **11**; 2.42, d, 2, **4**, **10**; 2.42, s, 2, **6**, **12**; 6.97, t ($J_{2-3} = 6$), 4, **3**, **9**; 7.03 broad triplet ($J_{1-2} = 6$), **1**, **7**; 8.11, quintet, 4, **2**, **8**.

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Chemistry of Sulfur Compounds[1]

Selectivity of Addition of Thiyl Radicals to Terminal Olefins

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The free radical addition of thiols to terminal olefins of the type $CH_2{=}CHCH_2X$ produced a small amount of the Markovnikov-type addition product along with a high yield of the expected anti-Markovnikov adduct. The yield in the Markovnikov adduct depended on the nature of X and the thiyl radical. A possible mechanism involving the addition of positively polarized radicals to a polarized double bond is proposed to explain the formation of the ionic-type adduct.

It is generally considered that the addition of radicals X to olefins of the type $RCH{=}CH_2$ occurs by an exclusive initial attack at the terminal carbon (*9*). This specificity is explained on the basis of the greater stability of the secondary radical $R(CH\cdot)CH_2X$ compared with the primary radical $RCHXCH_2\cdot$. The polar and the steric factors were considered to be of less importance (*15*). The relative unimportance of the polarization of the double bond in $RCH{=}CH_2$ where R is a CF_3, $C{\equiv}N$, Cl, F, or CO_2CH_3 group in determining the position of attack of trifluoromethyl and bromine radicals was demonstrated earlier (*4*). The addition of thiols to substrates with heteroatoms or heteroatom groups in an allylic position was also reported to follow the Kharasch rule. In some cases, allyl sulfides were formed by β elimination (*9*). The stereoselectivity of the addition of thiols to substituted cyclohexenes and the fast isomerization of 2-butene by a small amount of methanethiol were observed (*13*, *17*), but the presence of Markovnikov-type adduct has not been indicated. However, it was shown in a previous publication that the free radical addition of methane thiol to allyl alcohol gave 3-methylthio-1-propanol along with a small amount of 2-methylthio-1-propanol (*3*).

The addition to diallylmaleate also produced a small yield of the Markovnikov-type addition product (*14*). More recently the reaction mixtures resulting from the addition of different mercaptans to various terminal olefins in presence of uv light were examined to identify the type of adducts formed. The purpose of this paper is to report and discuss the results thus obtained. The Kharasch-type adduct will be referred to as type [A] compound and the Markovnikov-type adduct will be referred to as type [B] compound.

The addition of methyl mercaptan to vinyl acetate or to isopropenyl acetate, the addition of *t*-butylmercaptan to allyl alcohol, and the addition of thiophenol to vinyl acetate, acrylonitrile, or 3,3′-dimethyl-1-butene gave a single adduct of the type [A] (Table I). On the other hand, the addition of thiophenol, *p*-chlorothiophenol, and benzylmercaptan to allyl alcohol gave both isomers [A] and [B]. Two isomers were also formed when thiophenol was added to allyl chloride, phenyl allyl ether, allyl benzene, allyl cyanide, or allyl *n*-propionate (Ta-

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