Arene Imine Derivatives of Chrysene and of Benzo[g]chrysene: 1a,11c-Dihydrochryseno[5,6-b]azirine and 1a,13c-Dihydrobenzo[11,12]chryseno[5,6-b]azirine

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The syntheses of the K-imines (which are also benzo-bay-region derivatives) of chrysene (**1**) and benzo[g]-chrysene (**2**) are described. The preparation of 1a,11c-dihydrochryseno[5,6-b]azirine (**5**) was accomplished by treatment of 1a,11c-dihydrochryseno[5,6-b]oxirene (**4**) with sodium azide, and the mixture of *trans*-azido-alcohols **6** and **7**, so formed, was either cyclized with triethyl phosphite, or converted into *E*-6-azido-5-chloro-5,6-dihydrochrysene (**8**) followed by lithium aluminium hydride reduction. The synthesis of 1a,13c-dihydrobenzo-[11,12]chryseno[5,6-b]azirine (**12**) included the transformation of the corresponding oxide **11** into a mixture of *E*-9-azido-9,10-dihydrobenzo[g]chrysen-10-ol (**13**) and *E*-10-azido-9,10-dihydrobenzo[g]chrysen-9-ol (**14**), and reaction with tri-*n*-butylphosphine to give a mixture of Staudinger adducts **15** and **16** that underwent thermal decomposition into **12** upon heating in boiling dichloromethane.

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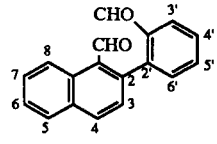
In the course of our program to prepare polycyclic arene imines of authentic structures as probes for metabolites of carcinogenic hydrocarbons, and as standards for cancer research, we have already announced the preparation of several aziridine derivatives of benz[a]anthracene [1-4], benzo[c]phenanthrene [4], benzo[a]pyrene [1], and dibenz[a,h]anthracene [1] [5]. We now report the syntheses of two *stable* aziridine derivatives of chrysene (**1**) [6] and benzo[g]chrysene (**2**) which are not only K-region compounds but also the first examples of benzo-bay-region arene imines.

The initial stage of the synthesis of 1a,11c-dihydrochryseno[5,6-b]azirine (chrysene 5,6-imine, **5**) was the conversion of the parent hydrocarbon into epoxide **4**. Although the latter compound had previously been reported (*e.g.* [7] [8]) we found the ozonolysis of **1** [9] and tris(dimethylamino)phosphine-assisted cyclization of the resulting dialdehyde **3**, to be more convenient than the current methods. Treatment of **4** with sodium azide afforded a mixture of the two *trans*-azido alcohols **6** and **7** in a ratio 7:3. This regioselectivity resembles that observed in nucleophilic oxirane-ring opening by *tert*-butylthiolate [10] [11] and is in agreement with theoretical predictions [10-12]. The conversion of the mixture of **6** and **7** into the imine **5** could be accomplished either by heating with triethyl phospite in dichloromethane [13] or by reaction with thionyl chloride followed by lithium aluminium hydride reduction of the chloro-azide intermediate [14]. It is noteworthy, that the interaction of thionyl chloride with the mixture of both *trans*-azido-alcohols furnished *E*-6-azido-5-chloro-5,6-dihydrochrysene (**8**) as the only stable chloro-azide. The major product in this reaction (68%) was, however, 6-azidochrysene (**9**) (identified by the characteristically low field pmr of H5, H11, H4 and H10 that appear as a singlet, a doublet and two doublets of doublets, respectively). The formation of a single aromatic azide can be rationalized by acid catalyzed dehydration of both **6** and **7** by a similar mechanism to that of boron trifluoride-promoted conversion of *E*-5-[(1,1-dimethylethyl)thio]-5,6-dihydro-6-chrysenol and *E*-6-[(1,1-dimethylethyl)thio]-5,6-dihydro-5-chrysenol into 6-(1,1-dimethylethyl)thiochrysene [11] (*cf.*, also the analogous rearrangement that takes place in the benz[a]anthracene series [10]). In our system a triazole intermediate may be regarded as the cyclic intermediate.

In analogy to chrysene, benzo[g]chrysene was converted into dialdehyde **10** by ozonolysis [9] that, in turn, was cyclized to the epoxide **11** with the aid of tris(dimethylamino)phosphine. The reaction of **11** with sodium azide yielded a 1:1 mixture of the two *trans*-azido-alcohols **13** and **14**. Attempts to transfer the latter compounds into 1a,13c-dihydrobenzo[11,12]chryseno[5,6-b]azirine (benzo-[g]chrysene 9,10-imine, **12**) by the conventional methods were unsuccessful. Neither heating of the azido alcohols with phosphines [15] or phosphites [13] [16], nor reduction of the corresponding azido chlorides [14] or cyclization of the azido tosylates [17], proved to give solely the expected imine. The only method that furnished pure **12** was a two step synthesis in which the mixture of **13** and **14** was initially treated with a cold etheral solution of tri-*n*-butylphosphine to give the mixture of the Standinger adducts **15** and **16**, (the sparingly soluble adduct **15** was isolated in an analytical state), followed by thermal decomposition in boiling dichloromethane (*cf.* [18]).

The reaction of the mixture of **13** and **14** with phosphites yielded, in the cold, phosphorus containing adducts that could not be transformed to **12**, and gave a mixture of fully aromatized aminobenzo[g]chrysenes in boiling benzene. The reaction of the azido-alcohols with thionyl chloride afforded 46% of 10-azidobenzo[g]chrysene (**19**) together with 35% of a mixture of azido chlorides that con-

sisted mainly of **17** and traces of **18**. Lithium aluminium hydride reduction of the latter compound gave chiefly 9-aminobenzo[*g*]chrysene admixed with <5% of **12**.



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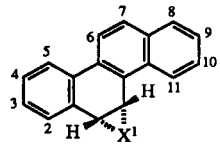

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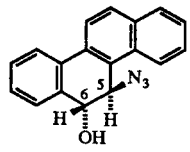
5, X = NH



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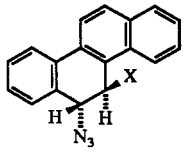
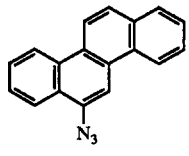


7, X = O
8, X = Cl



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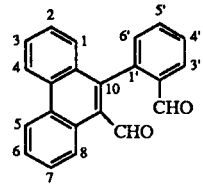

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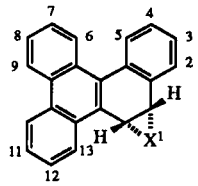
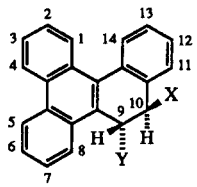
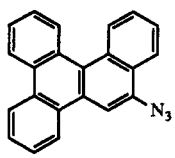


11, X = O
12, X = NH



13, X = OH Y = N_3
14, X = N_3 Y = OH
15, X = OH Y = $N_3P(C_4H_9)_3$
16, X = $N_3P(C_4H_9)_3$ Y = OH
17, X = Cl Y = N_3
18, X = N_3 Y = Cl



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EXPERIMENTAL

2-Phenylnaphthalene-1,2'-dicarboxaldehyde (**3**).

A stream of ozone was passed through a suspension of 10 g (43.8 mmoles) of chrysene (**1**) in 400 ml of dichloromethane at −78°. After 2 hours the resulting solution was treated at room temperature for 12 hours with a mixture of 70 g of potassium iodide and 150 ml of acetic acid. The liberated iodine was reduced with aqueous sodium thiosulfate. The organic layer was separated, washed successively with water, 10% aqueous sodium hydroxide and again with water, and dried over magnesium sulfate. The solvent was evaporated and the residue chromatographed on silica gel, using hexane-ether mixtures (from 100 to 50% hexane) as eluent. There was obtained 2.53 g of unreacted **1** and 6.52 g (57% of dialdehyde **3** as pale yellow crystals, mp 50-52°; ir (nujol): 1682 cm^{-1} (C=O); 200 MHz pmr (deuteriochloroform): δ 7.312-7.413 (m, 2H, H4, H5), 7.590-7.725 (m, 4H, H4', H5', H6, H7), 7.946 (dd, 1H, $J_{6,8}$ = 2.3 Hz, $J_{7,8}$ = 7.5 Hz, H8), 8.095 (overlapping dd and d, 2H, $J_{4',6'}$ = 2.6 Hz, $J_{3,4}$ = $J_{5',6'}$ = 7.1 Hz, H3, H6'), 9.275 (dd, 1H, $J_{3',4'}$ = 8.5 Hz, $J_{3',5'}$ = 2.3 Hz, H5'), 9.860 (s, 1H, *H*CO), 10.171 (s, 1H, *H*CO); ms: (70 eV, 80°) m/e (relative intensity) 260 ($M^{+\cdot}$, 9), 232 ($C_{17}H_{12}O^{+\cdot}$, 71), 231 ($C_{17}H_{11}O^{+}$, 100), 203 ($C_{16}H_{11}^{+}$, 70), 202 ($C_{16}H_{10}^{+\cdot}$, 76), 176 ($C_{14}H_8^{+\cdot}$, 26), 126 ($C_{10}H_6^{+\cdot}$, 38), 115 ($C_9H_7^{+}$, 55).

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.00; H, 4.72. Found: C, 82.81; H, 4.65.

1a,11c-Dihydrochryseno[5,6-*b*]oxirene (**4**).

A solution of 2.6 g (15.9 mmoles) of tris(dimethylamino)phosphine in 10 ml of dry benzene was added dropwise under argon at 60° to a stirred solution of 4.0 g (15.3 mmoles) of **3** in 30 ml of the same solvent. The reaction mixture was stirred for 4 hours at 60°, cooled and the solvent removed under reduced pressure. The residue was digested with cold ether and hexane, and the resulting crystals were washed with cold hexane. There was obtained 3.21 g (85%) of colorless **4** that was identical in every respect with an authentic sample prepared according to Harvey *et al.* [7].

E-5-Azido-5,6-dihydrochrysen-6-ol (**6**) and *E*-6-Azido-5,6-dihydrochrysen-5-ol (**7**).

To a mixture of 1.40 g (5.73 mmoles) of **4**, 30 g of sodium azide, 300 ml of acetone and 150 ml of water was added 2 drops of concentrated sulfuric acid. The mixture was stirred under argon at room temperature for 3 days. The acetone was removed under reduced pressure and the resulting azido alcohols extracted into dichloromethane. The organic solution was concentrated and chromatographed on silica gel using ether-hexane mixtures (from 20 to 80% ether) as eluent. There was obtained 1.12 g (68%) of colorless crystals that proved to be a 7:3 mixture of **6** and **7**; mp (**6** + **7**) 123-124°; ir (nujol): 3350 (OH), 2086 cm^{-1} (N_3); 200 MHz pmr (deuteriochloroform): δ 1.693 (br s, 1H, O*H*), 4.825 [d, 0.3H, J = 2.4 Hz, H5 (**6**) affected by deuterium oxide], 4.992 [d, 0.7H, J = 2.6 Hz, H6 (**7**), affected by deuterium oxide], 5.381 [d, 0.7H, J = 2.6 Hz, H5 (**7**)], 5.504 [d, 0.3H, J = 2.4 Hz, H6 (**6**)], 7.371-7.655 (m, 5H, Ar*H*), 7.878-8.060 (m, 4H, Ar*H*), 8.212 [d, 0.7H, J = 8.6 Hz, H12 (**7**)], 8.244 [d, 0.3H, J = 8.5 Hz, H12 (**6**)]; ms: (70 eV, 90°) m/e (relative intensity) 287 ($M^{+\cdot}$, 33), 258 ($C_{18}H_{12}NO^{+}$, 12), 245 ($C_{16}H_{13}O^{+}$, 23), 231 ($C_{17}H_{13}N^{+\cdot}$, 32), 230 ($C_{17}H_{12}N^{+}$, 100), 228 ($C_{17}H_{10}N^{+}$, 16), 215 ($C_{17}H_{11}^{+}$, 16), 202 ($C_{16}H_{10}^{+\cdot}$, 29), 115 ($C_9H_7^{+}$, 8).

Anal. Calcd. for $C_{18}H_{13}N_3O$: C, 75.25; H, 4.56; N, 14.62. Found: C, 74.93; H, 4.65; N, 14.47.

Reaction of the Mixture of **6** and **7** with Thionyl Chloride.

A mixture of 1.12 g (3.9 mmoles) of the above azido-alcohols, 4 ml of freshly distilled thionyl chloride and 25 ml of dry benzene was stirred under nitrogen at room temperature for 6 hours. After decomposition of the excessive reagent with crushed ice, the layers were separated, and the organic solution was washed with 5% aqueous sodium bicarbonate and with water, dried and concentrated. The residue was chromatographed on silica 60 (benzene as eluent) to give 720 mg (68%) of the pale yellow 6-azidochrysene (**9**) as the first fraction, mp 70-71°; ir (nujol): 2102 cm^{-1} (N_3); 200 MHz pmr (deuteriochloroform): δ 7.571-7.722 (m, 6H, H1, H2, H3, H8, H9, H12), 8.235 (dd, 1H, $J_{7,8}$ = 7.9 Hz, $J_{7,9}$ = 2.3 Hz, H7), 8.323 (s, 1H, H5), 8.515 (d, 1H, J = 9.1 Hz, H11), 8.561-8.713 (two distorted dd, 2H, H4, H10); ms: (70 eV, 100°) m/e relative intensity) 269 ($M^{+\cdot}$, 9), 241 ($C_{18}H_{11}N^{+\cdot}$, 100), 240 ($C_{18}H_{10}N^{+}$, 66), 227 ($C_{18}H_{11}^{+}$, 18), 213 ($C_{17}H_9^{+}$, 11).

Anal. Calcd. for $C_{18}H_{11}N_3$: C, 80.28; H, 4.08. Found: C, 79.95; H, 4.01.

The second fraction consisted of 250 mg (21%) of *E*-6-azido-5-chloro-5,6-dihydrochrysene (**8**), yellow oil; ir (neat) 2096 cm^{-1} (N_3); 200 MHz pmr (deuteriochloroform): δ 5.396 (d, 1H, J = 3.2 Hz, H5 or H6), 5.484 (d, 1H, J = 3.2 Hz, H5 or H6), 7.301-7.53 (m, 5H, Ar*H*), 7.912-8.159 (m, 4H, Ar*H*), 8.18 (d, 1H, J = 7.5 Hz, H11).

Anal. Calcd. for $C_{18}H_{12}ClN_3$: C, 70.71; H, 3.96; N, 13.74. Found: C, 71.02; H, 3.95; N, 13.70.

1a,11c-Dihydrochryseno[5,6-*b*]azirine (**5**).

Method A.

To a boiling solution of 700 mg (28.8 mmoles) of the mixture of azido-alcohols **6** and **7** in 15 ml of dichloromethane, was added under nitrogen 0.5 ml of triethyl phosphite. The mixture was stirred for 3 hours. Then the solvent was removed under reduced pressure. Upon addition of cold ether to the residue colorless crystals separated. Thorough washing with cold hexane afforded 520 mg (74%) of **5**, mp 126-127°; ir (nujol): 3352 cm^{-1} (NH); 200 MHz pmr (deuteriochloroform): δ 3.732 (d, 1H, J = 5.3 Hz, H5), 4.268 (d, 1H, J = 5.3 Hz, H6), 7.401 (m, 2H, H3, H9), 7.572 (dd, 1H, $J_{8,10}$ = 2 Hz, $J_{9,10}$ = 7.2 Hz, H10), 7.611 (d, 1H, $J_{11,12}$ = 8.4 Hz, H11), 7.675 (dd, 1H, $J_{2,4}$ = 1.5 Hz, $J_{3,4}$ = 7.2 Hz, H4), 7.864 (t, 2H, $J_{1,2,3}$ = $J_{7,8,9}$ = 7.2 Hz, H2, H8), 8.182 (m, 2H, H1, H7), 8.467 (d, 1H, $J_{11,12}$ = 8.4 Hz, H12); ms: (70 eV, 150°) m/e (relative intensity) 243 ($M^{+\cdot}$, 100), 242 ($C_{18}H_{12}N^+$, 6), 229 ($C_{18}H_{13}^+$, 10), 215 ($C_{17}H_{11}^+$, 26).

Anal. Calcd. for $C_{18}H_{13}N$: C, 88.86; H, 5.39; N, 5.75. Found: C, 88.53; H, 5.31; N, 5.41.

Method B.

To a suspension of 0.4 g (10.5 mmoles) of lithium aluminium hydride in 5 ml of dry ether was added dropwise at 0° a solution of 210 mg (0.69 mmoles) of **8** in 5 ml of the same solvent. The mixture was stirred under argon for 1 hour, decomposed with cold water, and the resulting solids extracted with benzene. After the usual workup there was obtained 140 mg (84%) of **5** of identical physical properties as the sample obtained by method A.

10-Phenylphenanthrene-2',9-dicarboxaldehyde (**10**).

A solution of 1.0 g (3.6 mmoles) of benzo[*g*]chrysene (**2**) in 50 ml of dichloromethane was treated at −5° with ozone until the entire starting material was consumed and the solution turned greenish-blue (30 minutes). The excessive ozone was removed with a stream of oxygen and the solution was treated with 15 of potassium iodide in 100 ml of acetic acid. After stirring for 3 hours, the iodine was reduced with aqueous sodium thiosulfate. The organic layer was separated, washed with water, 5% aqueous sodium bicarbonate and again with water. The dried solution was concentrated and the residue chromatographed on silica 60, using hexane-ether mixture (containing from 20 to 60% ether) as eluent. There was obtained 721 mg (65%) of **10** as colorless crystals, mp 70-71°; ir (nujol): 1680 cm^{-1} (C=O); 300 MHz pmr (deuteriochloroform): δ 7.310 (dd, 1H, $J_{4',6'}$ = 2.2 Hz, $J_{5',6'}$ = 8.1 Hz, H6'), 7.452 (t, 2H, $J_{3',4',5'}$ = $J_{4',5',6'}$ = 7.6 Hz, H4', H5'), 7.701-7.762 (m, 5H, H2, H3, H6, H7, H8), 8.173 (d, 1H, $J_{1,2}$ = 7.4 Hz, H1), 8.771 (dd, 2H, $J_{2,4}$ = $J_{5,7}$ = 2.4 Hz, $J_{3,4}$ = $J_{5,6}$ = 8 Hz, H4, H5), 9.210 (dd, 1H, $J_{3',4'}$ = 8 Hz, $J_{3',5'}$ = 2.1 Hz, H3'), 9.652 (s, 1H, C*H*O), 10.041 (s, 1H, C*H*O); ms: (70 eV, 120°) m/e (relative intensity) 310 ($M^{+\cdot}$, 10), 282 ($C_{21}H_{14}O^{+\cdot}$, 30), 281 ($C_{21}H_{13}O^+$, 100), 265 ($C_{21}H_{13}^+$, 4), 252 ($C_{20}H_{12}^{+\cdot}$, 30), 181 ($C_{13}H_9O^+$, 22), 176 ($C_{14}H_8^{+\cdot}$, 10), 140 ($C_{11}H_8^{+\cdot}$, 11), 126 ($C_{10}H_6^{+\cdot}$, 14).

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.33; H, 4.85.

1a,13c-Dihydrobenzo[11,12]chryseno[5,6-*b*]oxirene (**11**).

A solution of 450 mg (1.45 mmoles) and 250 mg (1.53 mmoles) of tris(dimethylamino)phosphine in 15 ml of dry benzene was refluxed under nitrogen for 5 hours. The solvent was removed under reduced pressure and the oily residue was dissolved in 15 ml of a 2:1 mixture of hexane and ether. After 24 hours in the refrigerator and thorough washing with hexane, there was obtained 351 mg (82%) of **11** as pale yellow crystals, mp 153-154° (literature [19] 155-156°); ir (nujol): 1160 cm^{-1} (C-O); 300 MHz pmr (deuteriochloroform): δ 4.795 (d, 1H, $J_{1a,13c}$ = 4.2 Hz, H1a), 5.295 (d, 1H, $J_{1a,13c}$ = 4.2 Hz, H13c), 7.394-7.179 (m, 7H, H2, H3, H4, H7, H8, H11, H12), 8.244 (d, 1H, $J_{12,13}$ = 7.7 Hz, H13), 8.415 (dd, 1H, $J_{3,5}$ = 3 Hz, $J_{4,5}$ = 9.4 Hz, H5), 8.600 (d, 1H, $J_{6,7}$ = 8.3 Hz, H6), 8.645 (dd, 2H, $J_{7,9}$ = $J_{10,12}$ = 2.3 Hz, $J_{8,9}$ = $J_{10,11}$ = 7.9 Hz, H9, H10); ms: (70 eV, 100°) m/e (relative intensity) 294 ($M^{+\cdot}$, 100), 293 ($C_{22}H_{13}O^+$, 6), 278 ($C_{22}H_{14}^{+\cdot}$, 29), 276 ($C_{22}H_{12}^{+\cdot}$, 15), 263 ($C_{21}H_{11}^+$, 20).

E-9-azido-9,10-dihydrobenzo[*g*]chrysen-10-ol (**13**) and *E*-10-Azido-9,10-dihydrobenzo[*g*]chrysen-9-ol (**14**).

In the same manner as for the preparation of **6** and **7**, 600 mg (2.04 mmoles) of **11** was reacted with 15 g of sodium azide to give 436 mg (63%) of a 1:1 mixture of **13** and **14**, mp (**13** + **14**) 66-67° dec; ir (nujol): 3350 (OH), 2102 cm^{-1} (N_3); 200 MHz pmr (deuteriochloroform): δ 4.791 [d, 0.5H, $J_{9,10}$ = 2.6 Hz, C*H*N_3 (**14**)], 4.862 [br s, 0.5H, upon addition of deuterium oxide changes into d, $J_{9,10}$ = 2.6 Hz, C*H*OH (**13**)], 5.105 [d, 0.5 H, $J_{9,10}$ = 2.6 Hz, C*H*N_3 (**13**), 5.310 [br s, 0.5 H, upon addition of deuterium oxide changes into d, $J_{9,10}$ = 2.6 Hz, C*H*OH (**14**)], 7.342-7.735 (m, 7H, H2, H3, H6, H7, H11, H12, H13), 7.896 (d, 1H, $J_{7,8}$ = 7.7 Hz, H8), 8.255 [dd, 0.5 H, $J_{12,14}$ = 3.1 Hz, $J_{13,14}$ = 7.5 Hz, H14 (**13** or **14**)], 8.335 (dd, 0.5 H, $J_{12,14}$ = 2.8 Hz, $J_{13,14}$ = 6.9 Hz, H14 (**13** or **14**)], 8.554 (dd, 1H, $J_{1,2}$ = 7.2 Hz, $J_{1,3}$ = 2.3 Hz, H1), 8.742 (m, 2H, H4, H5); ms: (70 eV, 145°) m/e (relative intensity) 337 ($M^{+\cdot}$, 91), 309 ($C_{22}H_{15}NO^{+\cdot}$, 37), 308 ($C_{22}H_{14}NO^+$, 36), 295 ($C_{22}H_{15}O^+$, 72), 294 ($C_{22}H_{14}O^{+\cdot}$, 27), 292 ($C_{22}H_{14}N^+$, 11), 282 ($C_{21}H_{14}O^{+\cdot}$, 18), 281 ($C_{21}H_{13}O^+$, 91), 280 ($C_{21}H_{12}O^{+\cdot}$, 100), 278 ($C_{22}H_{14}^{+\cdot}$, 54), 265 ($C_{21}H_{13}^+$, 48), 252 ($C_{20}H_{12}^{+\cdot}$, 72), 140 ($C_{11}H_8^{+\cdot}$, 44), 126 ($C_{10}H_6^{+\cdot}$, 53), 113 ($C_9H_5^+$, 30).

Anal. Calcd. for $C_{22}H_{15}N_3O$: C, 78.32; H, 4.48. Found: C, 78.62; H, 4.78.

Reaction of the Mixture of **13** and **14** with Thionyl Chloride.

In the manner described above, 200 mg (0.59 mmole) of the mixture of **13** and **14** was treated under nitrogen with 1 ml of thionyl chloride in 15 ml of dichloromethane for 5 hours at room temperature. The resulting mixture was chromatographed on silica gel (hexane with 10-30% of ether served as eluent) to give in the first fraciton 87 mg (46%) of 10-azidobenzo[*g*]chrysene (**19**), mp 145-146° dec; ir (nujol): 2086 cm^{-1} (N_3); 300 MHz pmr (deuteriochloroform): δ 7.591-7.752 (m, 6H, H2, H3, H6, H7, H12, H13), 8.291 (dd, 1H, $J_{11,12}$ = 7.6 Hz, $J_{11,13}$ = 1.8 Hz, H11), 8.305 (s, 1H, H9), 8.572 (dd, 1H, $J_{6,8}$ = 3.4 Hz, $J_{7,8}$ = 7.8 Hz, H8), 8.630-8.730 (m, 2H, H4, H5), 8.771 (dd, 1H, $J_{1,2}$ = 7.6 Hz, $J_{1,3}$ = 1.5 Hz, H1), 8.902 (dd, 1H, $J_{12,14}$ = 3 Hz, $J_{13,14}$ = 7.6 Hz, H14); ms: (70 eV 150°) m/e (relative intensity) 319 ($M^{+\cdot}$, 15), 291 ($C_{22}H_{13}N^{+\cdot}$, 100), 263 ($C_{21}H_{11}^+$, 12).

The second fraction consisted almost entirely of *E*-9-azido-10-chloro-9,10-dihydrobenzo[*g*]chrysene (**17**), mp 70-72; ir (nujol) 2090 cm^{-1} (N_3); 200 MHz pmr (deuteriochloroform): δ 5.275 (d, 1H, $J_{9,10}$ = 2.5 Hz, H9), 5.345 (d, 1H, $J_{9,10}$ = 2.5 Hz, H10), 7.430-7.777 (m, 7H), 7.978 (d, 1H, J = 8 Hz), 8.195 (dd, 1H, J_o = 7 H, J_m = 3.4 Hz), 8.585 (d, 1H, 8.1 Hz), 8.745-8.814 (m, 2H).

Neither **17** nor **19** could be obtained in an analytically pure state.

Reaction of the Mixture of **13** and **14** with Tributylphosphine.

To a stirred solution of 100 mg (0.296 mmole) of **13** + **14** in 10 ml of dry ether was added under nitrogen at room temperature 65 mg (0.321 mmoles) of freshly distilled tributylphosphine. After 20 minutes a heavy colorless precipitate started to separate. The mixture was stirred further for 15 minutes, cooled to 0° and filtered. The solid (23 mg) was washed with cold ether and proved to be pure *E*-9,10-dihydro-10-[3-tributylphosphoranylidene)-1-triazenyl]-10-benzo[*g*]chrysenol (**15**); mp 101° dec; 300 MHz pmr (deuteriochloroform): δ 0.873 (t, 9H, J = 7 Hz, C*H*$_3$), 1.339 (sextet shape, 6H, J = 7 Hz, C*H*$_2$CH$_3$), 1.468 (m, 6H, C*H*$_2$CH$_2$CH$_3$), 1.832 (m, 6H, PC*H*$_3$), 5.073 (d, 1H, $J_{9,10}$ = 2.3 Hz, H10), 5.924 (d, 1H, $J_{9,10}$ = 2.3 Hz, H9), 7.205-7.732 (m, 7H, Ar*H*), 7.841 (dd, 1H, J_o = 7.4 Hz, J_m = 2.4 Hz), 8.295 (d, 1H, J = 8 Hz), 8.615 (d, 1H, J = 8 Hz), 8.675 (d, 1H, J = 7.4 Hz), 8.745 (d, 1H, J = 8 Hz); 81 MHz ^{31}P nmr (deuteriochloroform-phosphoric acid): 45.630 ppm; ms: (70 eV, 95°) m/e (relative intensity) 293 ($C_{22}H_{15}N^{+\cdot}$, 100), 292 ($C_{22}H_{14}N^+$, 64), 279 ($C_{21}H_{13}N^{+\cdot}$, 19), 265 ($C_{21}H_{13}^+$, 144), 189 ($C_{15}H_9^+$, 89), 176 ($C_{14}H_8^{+\cdot}$, 15), 162 ($C_{13}H_6^{+\cdot}$, 47).

Anal. Calcd. for $C_{34}H_{42}N_3OP$: C, 75.67; H, 7.84; N, 7.78. Found: C, 75.81; H, 7.98; N, 7.63.

The mother liquor and the ether washings were united and the solvent evaporated under reduced pressure at 20°. The resulting oil was triturated with cold ether to give (after washing with cold hexane) pale yellow crystals of a 3:7 mixture of **15** and **16**; mp 85-87° dec. The total yield of **15** and **16** was 122 mg (80%); ir (nujol): 3250 cm^{-1} (OH), no free N_3 band; 300 MHz pmr (deuteriochloroform of **15** + **16**): δ 0.873 (t, 9H, J = 7 Hz, C*H*$_3$), 1.339 (sextet shape, 6H, J = 7 Hz, C*H*$_2$CH$_3$), 1.468 (m, 6H, C*H*$_2$CH$_2$CH$_3$), 1.832 (m, 6H, PCH$_2$), 5.073 [d, 0.3H, $J_{9,10}$ = 2.3 Hz, H10 (**15**)], 5.195 [d, 0.7H, $J_{9,10}$ = 2.4 Hz, H9 (**16**)], 5.332 [d, 0.7H, $J_{9,10}$ = 2.4 Hz, H10 (**16**)], 5.924 [d, 0.3H, J = 2.3 Hz, H9 (**15**)], 7.305-7.732 (m, 7H, Ar*H*), 7.841 (dd, 1H, J_o = 7.4 Hz, J_m = 2.4 Hz), 8.295 (d, 0.3H, J = 8 Hz (**15**)], 8.435 [dd, 0.7H, J_o = 8.7 Hz, J_m = 3.3 Hz, (**16**)], 8.542-8.766 (m, 3H, Ar*H*).

1a,13c-Dihydrobenzo[11,12]chryseno[5,6-*b*]azirine (**12**).

A solution of 30 mg (5.84 × 10^{-2} mmoles) of the mixture of **15** and **16** in 10 ml of dichloromethane was refluxed under nitrogen for 5 hours. The solvent was removed under reduced pressure at room temperature and the oily residue digested with cold hexane. After *ca.* 1 hour a heavy precipitate separated. The solid was washed several times with cold hexane till the washings were phosphorus free. There was obtained 12.4 mg (72%) of **12** as pale yellow crystals, mp 85-86°; ir (nujol) 3350 cm^{-1} (NH); 300 MHz pmr (deuteriochloroform): δ 3.921 (br s, 1H, changes into d upon addition of deuterium oxide, $J_{1a,13c}$ = 4.6 Hz, H1a), 4.282 (br s, 1H, changes into d upon addition of deuterium oxide, $J_{1a,13c}$ = 4.6 Hz, H13c), 7.381-7.715 (m, 7H, Ar*H*), 8.273 (dd, 1H, $J_{11,13}$ = 2.3 Hz, $J_{12,13}$ = 8.9 Hz, H13), 8.515 (d, 1H, $J_{4,5}$ = 6.6 Hz, H5), 8.615 (d, 1H, $J_{6,7}$ = 8 Hz, H6), 8.750 (dd, 2H, $J_{7,9}$ = $J_{10,12}$ = 2.4 Hz, $J_{8,9}$ = $J_{10,11}$ = 8 Hz, H9, H10); ms: (70 eV, 100°) m/e (relative intensity) 293 ($M^{+\cdot}$, 50), 278 ($C_{22}H_{14}^{+\cdot}$, 100), 265 ($C_{21}H_{13}^+$, 15), 200 ($C_{16}H_8^{+\cdot}$, 7), 139 ($C_{11}H_7^+$, 27), 100 ($C_8H_4^{+\cdot}$, 17).

Anal. Calcd. for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.77. Found: C, 89.85; H, 5.25; N, 4.77.

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