

TABLE V

Isomer	THE THERMODYNAMIC QUANTITIES FOR THE PERHYDROANTHRACENES							
	$\Delta H^{\circ}_{\text{exp}}$	$\Delta S^{\circ}_{\text{exp}}$	$T\Delta S^{\circ}_{\text{exp}}$	$\Delta G^{\circ}_{\text{exp}}^a$	$\Delta H^{\circ}_{\text{calcd}}$	$\Delta S^{\circ}_{\text{calcd}}$	$T\Delta S^{\circ}$	$\Delta G^{\circ}_{\text{calcd}}^a$
tst	0	0	0	0	0	0	0	0
ct	+2.76	+2.1	+1.14	+1.62	2.62	+2.8	+1.52	+1.10
tat	+4.15	-1.6	-0.87	+5.02	5.86	0	0	+5.86
cac	+5.58	+0.3	+0.16	+5.42	5.56	+1.4	+0.76	+4.80
csc	+8.74	+4.0	+2.18	+6.56	8.13	+2.2	+1.20	+6.93

^a 544 °K.

differences between them are accurate to better than 1 kcal/mol, and the experimental results are in accord with this. Finally, the free energies are given in Table V.

Acknowledgment.—We are indebted to Dr. R. L. Clarke for furnishing us with the samples of the perhydroanthracenes used for identification purposes in this work.

A New Approach to the Synthesis of Dibenzo[*a,l*]pyrenes^{1,2}

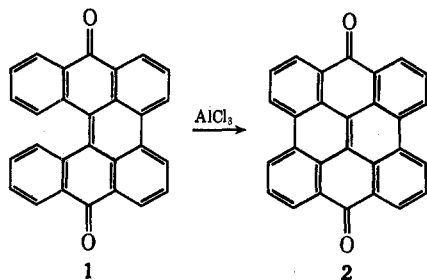
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A new method for the synthesis of dibenzo[*a,l*]pyrene and various derivatives has been achieved through an application of the Scholl reaction. The key to the new approach is to use 1-arylbenz[*a*]anthracenes as the precursors to the desired polycyclic aromatic compounds. The parent hydrocarbon and derivatives containing alkyl, halogen, and alkoxy substituents have been prepared as well as the corresponding TNF adducts.

The Scholl reaction,⁵ which is the elimination of two aryl-bound hydrogen atoms accompanied by the formation of a new aryl-aryl bond under the influence of a Friedel-Crafts catalyst, has been known for some time. This type of reaction was first observed by Friedel and Crafts who reported the formation of biphenyl from benzene in the presence of aluminum chloride; Homer⁶ also reported the formation of dinaphthyl from naphthalene in the presence of aluminum chloride. It was Scholl who, after publishing the synthesis of *meso*-naphthodianthrone (2)⁷ from helianthrone (1) using aluminum chloride as the dehydrogenating catalyst, and the



formation of perylene by three different methods,⁸ recognized the potentiality and generality of this reaction. Subsequent to extensions of the reaction by

Scholl himself,⁹ no important contributions to the Scholl reaction were published until 1950 when Baddely¹⁰ showed that many reactions effected by aluminum chloride and other Friedel-Crafts reagents do not occur in the absence of hydrogen chloride or traces of water. The next and perhaps most significant contribution to the understanding of the Scholl reaction is in the paper of Nenitzescu and Balaban⁵ in which they propose that the reaction takes place in three steps: first, a protonation; second, an electrophilic substitution; and finally, a dehydrogenation to yield the final aromatic product.

The suggestion of Nenitzescu and Balaban⁵ that the first step in the Scholl reaction is a protolytic reaction yielding a σ complex is well supported.¹¹ The fact that Scholl reactions occur readily and in high yield when electron-rich positions are involved but fail when the reaction has to take place at electron-poor positions supports the idea that the second step in Nenitzescu and Balaban's mechanism is one of electrophilic substitution. The cyclodehydrogenation of 8-(1-naphthyl)benz[*a*]anthracene to naphtho[2,1-*a*]perylene¹² proceeds readily and in good yield, presumably because an electron-rich position undergoes electrophilic attack. However, benzophenone does not yield fluorenone^{9a} under Scholl reaction conditions nor does 1,5-dibenzoylnaphthalene^{9e} undergo a Scholl reaction. Both reactions fail presumably because an electrophilic attack would have to occur into a position deactivated by

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(3) Department of Chemistry, Northeast Louisiana University, Monroe, La. 71201.

(4) Abstracted in part from the Doctorate thesis of J. Yanez, presented to the Virginia Polytechnic Institute, 1966.

(5) C. D. Nenitzescu and A. T. Balaban, "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, p. 979.

(6) A. Homer, *J. Chem. Soc.*, 1103 (1907).

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(8) R. Scholl, C. Seer, and R. Weitzenbock, *ibid.*, **43**, 2202 (1910).

(9) (a) R. Scholl and C. Seer, *Justus Liebig's Ann. Chem.*, **394**, 111 (1912);

(b) R. Scholl and C. Seer, *Ber.*, **55**, 109 (1922); (c) R. Scholl and G. Schwarzer, *ibid.*, **55**, 324 (1922); (d) R. Scholl and C. Seer, *ibid.*, **55**, 330 (1922);

(e) R. Scholl and H. Neumann, *ibid.*, **55**, 118 (1922).

(10) B. Baddely, *J. Chem. Soc.*, 994 (1950).

(11) H. C. Brown and H. Pearsall, *J. Amer. Chem. Soc.*, **74**, 191 (1952);

D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951); D. A. McCaulay,

B. H. Schoemaker, and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950); G. A.

Olah and J. J. Kuhn, *J. Amer. Chem. Soc.*, **80**, 6535 (1958); G. A. Olah,

H. W. Quinn, and J. J. Kuhn, *ibid.*, **82**, 426 (1960); P. Kovacic and A. Kyriakis,

ibid., **85**, 454 (1963).

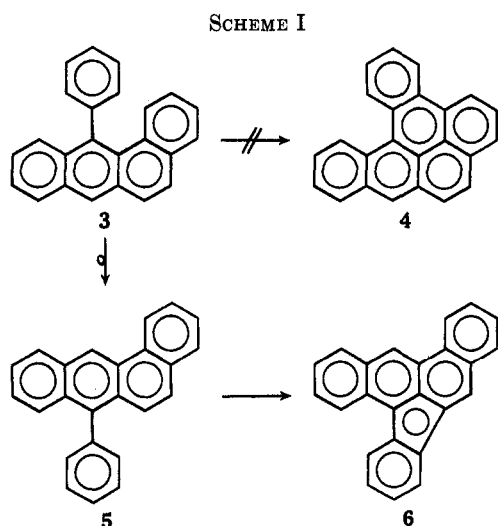
(12) F. A. Vingiello, W. W. Zajac, Jr., and L. G. Mahone, *J. Org. Chem.*,

28, 3253 (1963).

a carbonyl group. Evidence to support the idea that the last step is the actual dehydrogenation step has been difficult to obtain. Indeed, it has been difficult to account for the fate of the hydrogen lost in the Scholl reaction. Since only a small amount of hydrogen is evolved during the reaction,¹³ it is evident that hydrogen is consumed in reductive processes. One interesting example where the dihydro intermediate was isolated is afforded by the Scholl reaction on 7-phenyldibenz[*a,h*]anthracene which gave 10a,10b-dihydrobenzo[*e*]naphtho[1,2-*b*]pyrene which was isolated, characterized, and then dehydrogenated to benzo[*e*]naphtho[1,2-*b*]pyrene.¹⁴

Results

The approach to the synthesis of dibenzo[*a,l*]pyrene (4), using the Scholl reaction, has been to dehydrogenate 12-phenylbenz[*a*]anthracene (3)¹⁵ (Scheme I).



Using Clar's procedure¹⁵ the cyclodehydrogenation of the three isomeric 12-monomethylphenylbenz[*a*]anthracenes¹⁶ and the six 12-dimethylphenylbenz[*a*]anthracenes¹⁶ was performed, and it was concluded that derivatives of dibenzo[*a,l*]pyrene had been synthesized. The structural assignments were based largely on the ultraviolet spectra, which were similar to those reported by Clar¹⁵ for dibenzo[*a,l*]pyrene, and on the elemental analyses. Yields in all the above-mentioned reactions were poor.

Later Lavit-Lamy and Buu Hoi¹⁷ showed conclusively that what had been reported as dibenzo[*a,l*]pyrene¹⁵ was actually dibenzo[*a,e*]fluoranthene (6). They synthesized 6 independently and showed it to be identical with what had been reported as 4. They also suggested that the other¹⁸ "dibenzo[*a,l*]pyrenes," since they were made by a similar method, were also in reality dibenzo[*a,e*]fluoranthenes.¹⁸ It was suggested¹⁷ that 3 rearranged to 5 which then gave 6. This suggestion was later verified experimentally.¹⁹

(13) G. D. Buckley, *J. Chem. Soc.*, 561 (1945).

(14) F. A. Vingiello and P. D. Henson, *J. Org. Chem.*, **30**, 2842 (1965).

(15) E. Clar and D. Stewart, *J. Chem. Soc.*, 687 (1951).

(16) F. A. Vingiello and W. W. Zajac, Jr., *J. Org. Chem.*, **26**, 2228 (1961).

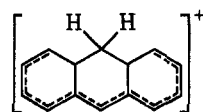
(17) D. Lavit-Lamy and N. P. Buu Hoi, *Chem. Commun.*, 92 (1966).

(18) A manuscript is being prepared wherein experimental data which verify this suggestion will be presented.

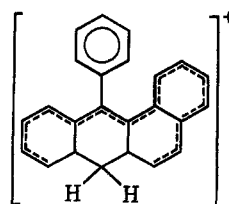
(19) F. A. Vingiello and A. K. Youssef, *Chem. Commun.*, 863 (1967).

A thorough study of literature on the Scholl reaction suggested to us reasons why 3 failed to give 4 and also led us to propose a new route to 4 *via* the Scholl reaction.

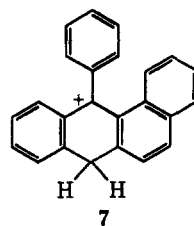
Moist aluminum chloride is able to protonate aromatic systems to form σ complexes.^{11,20} Gold and Tye²¹ and Gold and Long²² confirmed that protonation of anthracene takes place at a meso position and that the σ complex may be represented as follows.



We now suggest, by way of analog, that 3 is protonated by moist aluminum chloride to give a σ complex which may be represented as follows.²³



Although the positive charge is distributed throughout the benz[*a*]anthracene system, its localization at the 12 position is probably favored over the 1 position since this would provide structure 7 in which Kekulé structures could be achieved in the benzene and naphthalene portions of the benz[*a*]anthracene structure. It would



seem then that 3 is a poor precursor for the preparation of 4 *via* a Scholl reaction since (a) the likely intermediate is not favorably disposed to an electrophilic substitution, that is, attack by C-1 of 7 on the phenyl ring; and (b) the phenyl ring in 3 is sterically hindered because of interference between the hydrogen atom at C-1 and the ortho hydrogen atoms on the phenyl ring. These considerations are consistent with the fact that 3 does not give 4 but rearranges to 5, where the phenyl ring is better accommodated, and then gives 6.¹⁷

It appeared to us, based on the above considerations, that 1-phenylbenz[*a*]anthracene (8) would be an excellent precursor for conversion to dibenzo[*a,l*]pyrene *via* a Scholl reaction. On treatment with moist aluminum chloride, 8 would be expected to form the σ complex 8a. The complex in what is probably its most stable form, 8b, is well disposed for an intramolecular

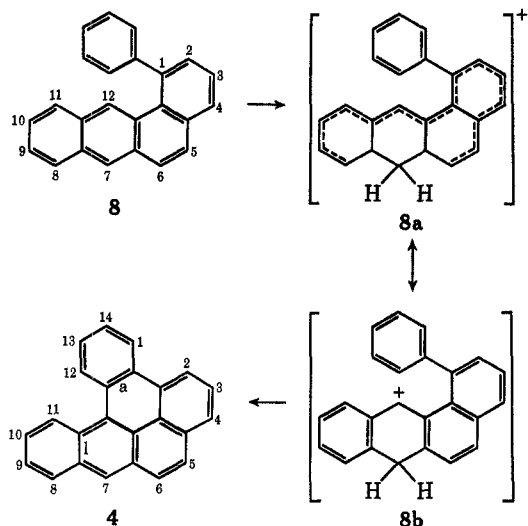
(20) W. E. Truce, *J. Amer. Chem. Soc.*, **74**, 4721 (1952).

(21) V. Gold and F. C. Tye, *J. Chem. Soc., London*, 2172 (1952).

(22) V. Gold and F. A. Long, *J. Amer. Chem. Soc.*, **75**, 4543 (1953).

(23) It should be noted that the phenyl ring is restrained from entering into coplanarity with the benz[*a*]anthracene moiety; see, for example, R. N. Jones, *ibid.*, **67**, 2127 (1945).

electrophilic substitution reaction involving the C-12 atom and an ortho position of the phenyl ring leading finally to dibenzo[*a,l*]pyrene. The phenyl ring in **8** is also less hindered than it is in **3** and should be less prone to migrate. Indeed, when **8** was subjected to Scholl reaction conditions, **4** was easily isolated in excellent



yield. When a methyl group was substituted in the phenyl ring of **8** at position 3 or 4, the resulting compounds easily gave the expected methyl-dibenzo[*a,l*]pyrenes when subjected to Scholl reaction conditions. Attempts to prepare 1-(2-tolyl)-3,4-dihydrobenz[*a*]anthracene for this study met with failure. The Grignard reagent of *o*-bromotoluene does not couple with 1-keto-1,2,3,4-tetrahydrobenz[*a*]anthracene (**9**) because of the steric hindrance of the bulky methyl group which interferes with the OMgBr group. In the Scholl reaction the methyl group probably makes the electrophilic attack by the intermediate carbonium ion on the phenyl ring easier because of its electron-release properties.

When 1- and 4-halophenylbenz[*a*]anthracenes were prepared and subjected to Scholl reaction conditions, substantial evidence was obtained to support the proposed mechanism. The bromine atom in **20** has no appreciable deactivating effect on the position of cyclization. Hence the cyclodehydrogenation occurs in good yield in a reaction time of 5 min. The chlorine atom in **21** deactivates the position of cyclization to a substantial degree by a $-I$ effect. The time needed to effect cyclization of **21** to give **27** is 2 hr. It would appear that the fluorine atom of **22** deactivates the position of cyclization tremendously since the reaction required 12 hr to effect cyclization.²⁴

Attempts at isolating 13-methoxydibenzo[*a,l*]pyrene from **23** under Scholl reaction conditions failed. When the methoxy group lies meta to the point of cyclization, this position is extremely deactivated due to the $-I$ effect. Reaction times of 2 hr or less gave only the starting material **23**. Longer reaction times produced tars, probably because of the fact that the methoxy group is cleaved to the reactive phenolic species.

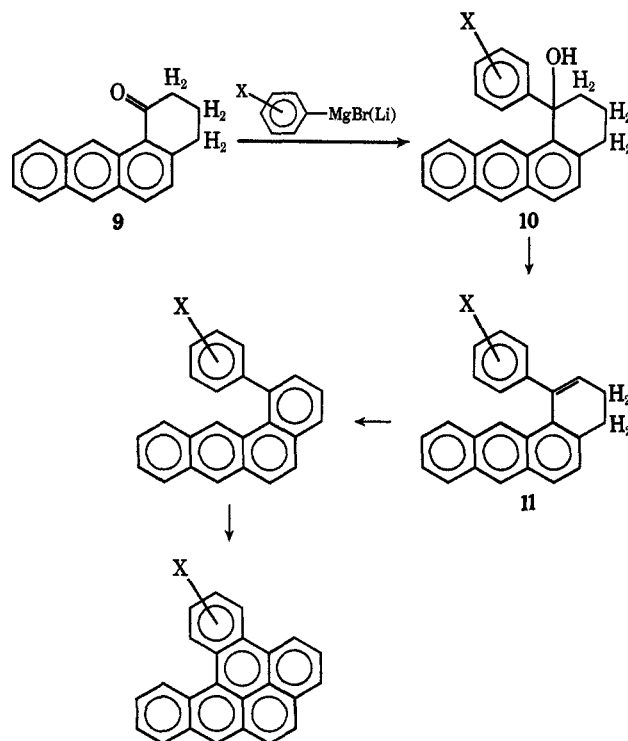
(24) When 1-pyridylbenz[*a*]anthracenes were prepared and subjected to Scholl reaction conditions, no dehydrogenation occurred. Apparently the pyridyl ring presents an extremely electron-poor structure for the carbonium ion to attack and the reaction fails; see ref 4 for details.

Experimental Section^{25,26}

1-Phenyl-3,4-dihydrobenz[*a*]anthracene (11, X = H).—By using 15.7 g (0.10 mol) of bromobenzene in 125 ml of anhydrous ether and 2.4 g (0.10 g-atom) of magnesium turnings, a Grignard reagent was formed in the usual way. After the magnesium had been consumed, the ether was replaced by anhydrous benzene; the resulting benzene solution was cooled to ice bath temperature. A solution of 2.5 g (0.010 mol) of 1-keto-1,2,3,4-tetrahydrobenz[*a*]anthracene (**9**) in 50 ml of anhydrous benzene was added slowly to the cold solution. The resulting solution was stirred for 36 hr. The reaction mixture was then hydrolyzed with 50 ml of 10% HCl. The layers were separated; the aqueous layer was extracted once with 50 ml of benzene. The combined benzene layers were washed twice with 50-ml portions of water and dried over magnesium sulfate. The dry solution was concentrated to about 25 ml; an infrared spectrum of the solution showed the presence of a hydroxyl function. The solvent was removed completely and the resulting oil heated at 70° in a vacuum oven for 18 hr. The oil was dissolved in benzene; an infrared spectrum of the solution showed that the hydroxyl band had disappeared. Addition of ethanol to the solution caused crystallization to occur, 2.0 g (67% yield). Recrystallization gave yellow needles, mp 145–148°. The crystals were dissolved in a small amount of benzene and absorbed on an acid alumina column. A colorless, blue fluorescing band was removed using a 1:4 benzene-petroleum ether solution. Upon concentration of this first fraction, a yellow oil resulted which was crystallized from a benzene-ethanol mixture as yellow needles. Recrystallization from benzene-ethanol gave yellow needles, mp 145–147°.

The remaining new 1-phenyl-3,4-dihydrobenz[*a*]anthracenes were prepared essentially as was compound 11 as illustrated in Scheme II. The data are shown in Table I.

SCHEME II



1-Phenylbenz[*a*]anthracene (8).—A solution of 1.0 g (0.003 mol) of 1-phenyl-3,4-dihydrobenz[*a*]anthracene in 75 ml of anhydrous benzene was added to 1.0 g of 2,3-dichloro-5,6-dicyanobenzoquinone which had been placed in a 100-ml round-bottom flask equipped with a reflux condenser. The reaction mixture was allowed to reflux for 4 hr. The cold solution was extracted with 10% sodium hydroxide solution until most of the

(25) All melting points were taken on a Fisher-Johns melting point block and are corrected.

(26) Analyses for C, H, and N were performed in this laboratory; halogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

TABLE I
 NEW 1-PHENYL-3,4-DIHYDROBENZ[a]ANTHRACENES^a

Compd	Yield, %	Mp, °C
1-Phenyl-3,4-dihydrobenz[a]-anthracene (11)	67	145-147
1-(4-Tolyl)-3,4-dihydrobenz[a]-anthracene (12)	62	166-168
1-(3-Tolyl)-3,4-dihydrobenz[a]-anthracene (13)	40	135-137
1-(4-Bromophenyl)-3,4-dihydrobenz[a]anthracene (14) ^b	40	228.5-229.5
1-(4-Chlorophenyl)-3,4-dihydrobenz[a]anthracene (15)	66	223.5-224
1-(4-Fluorophenyl)-3,4-dihydrobenz[a]anthracene (16)	68	184.5-185.5
1-(4-Methoxyphenyl)-3,4-dihydrobenz[a]anthracene (17)	61	185-186

^a All compounds in Tables I-IV (except compound 31) gave satisfactory C and H analytical data (± 0.4). In addition, compounds in Tables I-IV which contain halogen gave satisfactory halogen analyses and all compounds in Table IV (except compound 31) gave satisfactory N analyses. All analytical data were made available to the editors and the referees. ^b Prepared by the reaction of *p*-bromophenyllithium with 1-keto-1,2,3,4-tetrahydrobenz[a]anthracene.

yellow color had disappeared. The solution was then washed with water and dried over anhydrous magnesium sulfate. The dry benzene solution was concentrated to about 10 ml and 25 ml of 95% ethanol was added. The resulting solution was then concentrated until crystals began to appear; then enough benzene was added to dissolve the crystals. The product crystallized as long white needles and was isolated in 90% yield (0.90 g), mp 157-158°.

The remaining new 1-phenylbenz[a]anthracenes were prepared essentially as was compound 8. The data are shown in Table II.

 TABLE II
 NEW 1-PHENYLBENZ[a]ANTHRACENES

Compd	Yield, %	Mp, °C
1-Phenylbenz[a]anthracene (8)	90	157-158
1-(4-Tolyl)benz[a]anthracene (18)	86	152-153
1-(3-Tolyl)benz[a]anthracene (19)	80	131-132
1-(4-Bromophenyl)benz[a]-anthracene (20)	78	168.5-169.5
1-(4-Chlorophenyl)benz[a]-anthracene (21)	83	164-165
1-(4-Fluorophenyl)benz[a]-anthracene (22)	88	158-159
1-(4-Methoxyphenyl)benz[a]-anthracene (23)	85	140.5-141.5

Dibenzo[a,l]pyrene (4).—To a refluxing mixture of 25 ml of anhydrous benzene, 0.6 g of aluminum chloride, and 0.5 g of stannic chloride was added a hot solution of 0.30 g of 1-phenylbenz[a]anthracene in 25 ml of anhydrous benzene. The reaction mixture which immediately turned green was allowed to reflux for 5 min. The reaction mixture was slowly poured into 500 ml

of 10% hydrochloric acid. The layers were separated; the acid layer was extracted with 50 ml of benzene. The combined benzene solutions were washed with water and dried over anhydrous magnesium sulfate. The dry solution was concentrated to about 5 ml. The addition of 95% ethanol precipitated a tan solid. The solid, 0.20 g (66% yield), melting at 160-163°, was recrystallized from a benzene-ethanol mixture as pale yellow plates, mp 162-163°.

The remaining new dibenzo[a,l]pyrenes were prepared essentially as was compound 4. The data are shown in Table III.

 TABLE III
 NEW DIBENZO[a,l]PYRENES

Compd	Yield, %	Mp, °C
Dibenzo[a,l]pyrene (4)	66	162-163
13-Methyldibenzo[a,l]pyrene (24)	57	180-181
14-Methyldibenzo[a,l]pyrene (25)	66	164-165
13-Bromodibenzo[a,l]pyrene (26)	52	216-217
13-Chlorodibenzo[a,l]pyrene (27)	54 ^a	212-213
13-Fluorodibenzo[a,l]pyrene (28)	58 ^b	185-186

^a After 2-hr reaction time. ^b After 12-hr reaction time.

2,4,7-Trinitrofluorenone Adduct of Dibenzo[a,l]pyrene (29).—A hot solution of 0.050 g (0.00016 mol) of dibenzo[a,l]pyrene in 5 ml of benzene was added to a hot solution of 0.0504 g (0.00016 mol) of 2,4,7-trinitrofluorenone (TNF) in 10 ml of ethanol. The mixture darkened immediately; brown-green needles began to form as soon as the solution began to cool. The product was recrystallized from a benzene-ethanol mixture, mp 218-219°.

The remaining TNF adducts were prepared essentially as was compound 29. The data are shown in Table IV.

 TABLE IV
 NEW TNF ADDUCTS OF DIBENZO[a,l]PYRENES
 (NEW DIBENZO[a,l]PYRENE-TNF ADDUCTS)

Compd	Color	Mp, °C
Dibenzo[a,l]pyrene-TNF adduct (29)	Brown-green	218-219
13-Methyldibenzo[a,l]pyrene-TNF adduct (30)	Brown	220-221
14-Methyldibenzo[a,l]pyrene-TNF adduct (31)	Green	
13-Bromodibenzo[a,l]pyrene-TNF adduct (32)	Brown	226.5-227.5
13-Chlorodibenzo[a,l]pyrene-TNF adduct (33)	Brown	226-227
13-Fluorodibenzo[a,l]pyrene-TNF adduct (34)	Brown	205-205.5

Registry No.—4, 191-30-0; 8, 10383-87-6; 11, 29568-49-8; 12, 29568-50-1; 13, 29568-51-2; 14, 29568-52-3; 15, 29568-53-4; 16, 29568-54-5; 17, 29584-23-4; 18, 29584-24-5; 19, 29584-25-6; 20, 29584-26-7; 21, 29584-27-8; 22, 29584-28-9; 23, 29584-29-0; 24, 5950-67-4; 25, 5950-66-3; 26, 29584-32-5; 27, 29584-33-6; 28, 29584-34-7; 29, 29584-35-8; 30, 29584-36-9; 32, 29584-37-0; 33, 29584-38-1; 34, 29584-39-2.