the cobalt case the rates were about 10^6 times faster.[1] As was expected, the Cr(III)–TPPS is not easily reduced and thus the likelihood of an internal redox mechanism explaining the lability can be ruled out. Thus it appears that the porphyrin ligand labilizes both Cr(III) and Co(III) species by some type of electronic effect which has as its origins the delocalized electronic structure of the complex in which there is very strong mixing of metal-ion orbitals and ligand orbitals causing the metal ion to lose its d^6 or d^3 character. It has recently been found that ruthenium is also labilized in its substitution reactions when complexed to the porphyrin.[13] Other molecular systems in which this type of delocalization may take place, such as in the dithiolene system, can be expected to produce labile Co(III) and Cr(III) complexes.[14]

(13) M. Tsutsui, D. Osteld, and L. Hoffman, *J. Amer. Chem. Soc.*, 93, 1821 (1971).

(14) This work was supported by the National Institutes of Health.

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Specific Alkylation of Polycyclic Hydrocarbons *via* Reductive Alkylation and Oxidative Rearrangement

Sir:

We wish to report a novel and convenient two-step procedure for the introduction of alkyl groups into specific sites of polycyclic aromatic ring systems.

Interaction of methyl bromide with the anionic intermediates from the reaction of lithium metal with biphenyl, 4,5,9,10-tetrahydropyrene and 9,10-dihydrophenanthrene in liquid ammonia affords in excellent yield (>90%) the corresponding monomethyl 1,4-cyclohexadienes **1**, **2**, and **3**,[1] respectively. The latter, upon treatment with trityl fluoroborate[2] in 1,2-dichloroethane, undergo facile simultaneous rearrangement and aromatization to the related monomethyl derivatives (**4**, **5**, and **6** and **7**, respectively) of their hydrocarbon precursors. Compounds **6** and **7** are formed in the ratio 1.6:1, indicative of somewhat greater preference for 1,2 over 1,3 migration of the methyl group. Isomers, other than **4**–**7**, occur to the extent of <1%, if at all. Conversion of **5**, **6**, and **7** to fully aromatic methylpyrene and methylphenanthrenes is smoothly effected upon treatment with excess trityl cation reagent.[3]

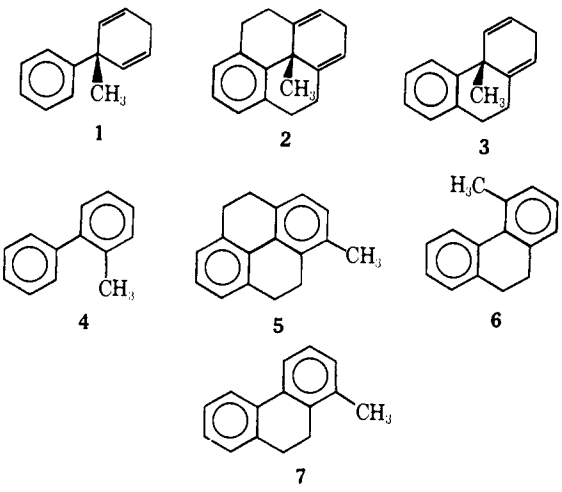
Reactions of the two bridged compounds, **2** and **3**, with trityl fluoroborate are complete within 1 hr at 3–5°, whereas **1** remains unchanged under these conditions. Conversion of **1** is complete, however, in 10 min at reflux temperature.

The intermediate benzenonium ions (*e.g.*, **8**) formed on hydride abstraction from the methyl-1,4-cyclohexadienes are essentially σ complexes. They are unusual, however, in possession of both alkyl and aryl substituents on the tetrahedral carbon atom. The ethylene bridges in the benzenonium ions derived from **2** and **3** may be

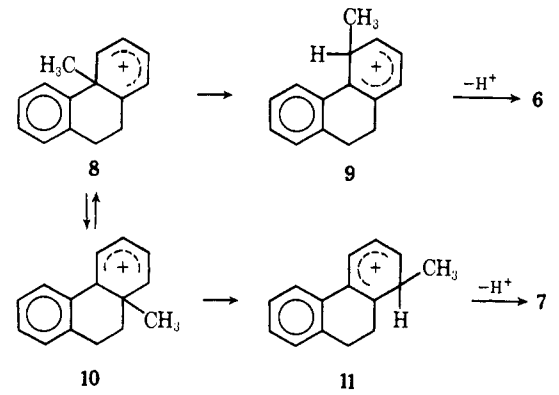
(1) Direct internal alkylation of the pyrene ring system, to our knowledge, has not been previously reported. Synthesis of **3** was reported earlier: P. W. Rabideau and R. G. Harvey, *J. Org. Chem.*, 35, 25 (1970).

(2) H. Y. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *ibid.*, 25, 1442 (1960).

(3) W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 2773 (1959).



expected to contribute substantially to the stabilization of these intermediates,[4] an effect probably sufficient to account for their greater reactivity relative to **1**. Also, the steady-state concentration of the initial benzenonium ions may be expected to be low relative to that of the trityl cation and to vary in the series **2** > **3** > **1**.[4] In agreement, addition of water to the product of reaction of **1** and the trityl fluoroborate reagent at 3–5° leads to recovery of **1** and trityl alcohol and no detectable quantity of a hydroxy derivative of **1**.



The benzenonium ions (*e.g.*, **9** and **11**) arising on methyl migration to a secondary position must be formed essentially irreversibly. This follows, since other isomers of **4**–**7** are not found, and the rate of proton loss from intermediates **9** and **11** (*i.e.*, aromatization) may reasonably be assumed to greatly exceed the rate of further methyl shift.[5] Product distribution, therefore, is presumably a consequence of the position of the equilibrium between **8** and **10** and the relative rates for the latter to undergo transformation to **9** and **11**, respectively. Predominance of the 4-substituted isomer of 9, 10-dihydrophenanthrene (**6**) is in agreement with the larger partial rate factor for electrophilic substitution in the 4 position compared with the 1 position of this hydrocarbon.[6]

In a typical reductive methylation, a solution of biphenyl (2.5 mmol) in anhydrous ether (75 ml) is added

(4) For a discussion of σ complexes see D. A. McCaulay in "Friedel-Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience, New York, N. Y., 1964.

(5) Methyl migration is considerably more probable than is phenyl migration; see M. J. S. Dewar in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., p 322.

(6) P. B. D. de la Mare, E. A. Johnson, and J. S. Lomas, *J. Chem. Soc.*, 6893 (1965); 5317 (1964).

Table I. Oxidative Rearrangement

Hydrocarbon (mmol)	$Ph_3C^+BF_4^-$, mmol	Solvent[a]	Temp, °C	Time, min	Product	Yield,[b] %
1 (2.5)	2.75	A	3–4	60	**1**	100
1 (2.5)	2.75	A	Reflux	10	**4**[c]	98
2 (2.5)	3.15	A	3–4	60	**5**[d]	100
2 (2.5)	3.1	B	20	60	**5**[e]	100
3 (1.2)	1.2	A	3–4	60	**6**[f]	58 (62)[g]
					7[h]	37 (38)[g]
3 (2.5)	5.45	B	25	60	**6**	71
					7	29
2 (2.0)	5.8	B	Reflux	5	1-Methylpyrene[i]	80
3 (2.5)	6.6	B	Reflux	60	1- and 4-methylphenanthrene[j]	64
					6	28

[a] A = $C_2H_4Cl_2$; B = CH_3CO_2H. [b] Analysis by glpc. [c] Sample collected off glpc had ir spectrum identical with Sadtler spectrum 12194 of 2-methylbiphenyl and nmr (CCl_4) δ 7.30 (s, 5, aromatic), 7.15 (s, 4, aromatic), and 2.24 (s, 3, CH_3)). [d] Nmr (CCl_4) δ 2.78 (s, 8, benzylic), 2.27 (s, 3, CH_3); peaks exhibit a general upfield shift in the presence of triphenylmethane. [e] Includes 10% 1-methylpyrene. [f] Nmr (CCl_4) δ 7.5–7.7 (m, 1, aromatic C-5), 7.0–7.3 (m, 6, aromatic), 2.72 (s, 4, benzylic), 2.62 (s, 3, CH_3). [g] Yields in parentheses obtained after additional 5-min reflux. [h] Nmr (CCl_4) δ 7.45–7.75 (m, 2, aromatic C-4 and C-5), 7.0–7.3 (m, 5, aromatic), 2.81 (s, 4, benzylic), and 2.33 (s, 3, CH_3). [i] Ir and nmr spectra identical with those of the authentic compound. [j] Nmr spectrum identical with that of a 1:1 mixture of the authentic compounds; the methyl resonances at δ 2.71 and 3.10 occur at lower field by ≥10 Hz than those of other isomers.

to 150 ml of refluxing liquid ammonia in a Morton flask equipped with a dewar condenser. General precautions, previously described,[7] for the exclusion of air, moisture, and other impurities are scrupulously observed. Lithium wire (6 mg-atoms) is added to the resulting stirred suspension giving a red solution. After 15 min, gaseous methyl bromide is introduced relatively rapidly to decolorize the solution in approximately 1 min, and reaction is quenched with solid ammonium chloride (20 g). Products are isolated by partition between ether and water utilizing conventional procedures. Glpc analysis on a 6 ft × 0.25 in. 5% FFAP on Varaport 30 column at 110° gives **1** (93%) and recovered biphenyl (4%). The structure of **1** is supported by microanalysis and by the nmr spectrum (CCl_4) which shows δ 7.17 (m, 5, aromatic), 5.61 (s, 4, vinylic), 2.62 (broad s, 2, allylic), 1.43 (s, 3, CH_3). Analogous reductive alkylation[8] of biphenyl with ethyl bromide, isopropyl bromide, methylene chloride, and 1,2-dichloroethane furnished the corresponding 1-alkyl-1,4-dihydrobiphenyl in 96, 99, 52, and 62% yields, respectively.

Oxidative rearrangements (Table I) are conducted under nitrogen, by addition of solid trityl fluoroborate to a solution of the hydrocarbon. After an appropriate interval, reaction is quenched with a large excess of water, and the product is partitioned between hexane and water and isolated by conventional procedures. Triphenylmethane is conveniently and completely removed by treatment with sodamide and air in liquid ammonia[9] and passage through a column of alumina.

It is clear that the net overall sequence of reactions described herein represents a singularly effective method for the specific alkylation of the aromatic ring systems concerned. In principle, this approach is readily adaptable to the synthesis of alkyl derivatives of numerous other hydrocarbons containing either a biphenyl or a *phene* structural unit, *e.g.*, chrysene, benz[*a*]anthracene, fluoranthene, perylene, fluorene, 1- and 2-phenylnaphthalene, etc. In particular, it holds promise for the synthesis of carcinogenic hydrocarbons, or their analogs, previously available only *via* tedious multistep syntheses from smaller ring systems.[10] Investigations along these lines are currently in progress.

(7) R. G. Harvey, *Synthesis*, 161 (1970); R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *J. Amer. Chem. Soc.*, **91**, 4535 (1969).

(8) Experiments with ethyl and isopropyl bromide were conducted at −78° with THF as cosolvent; those with methylene chloride and 1,2-dichloroethane were done without cosolvent and with sodium as the metal.

(9) This process is reported to lead to trityl peroxide according to C. A. Kraus and R. Rosen, *J. Amer. Chem. Soc.*, **47**, 2739 (1925).

(10) J. Pataki, C. Duguid, P. Rabideau, H. Huisman, and R. G. Harvey, *J. Med. Chem.*, in press.

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Crystal Structure of an Organometallic Complex with Titanium–Carbon σ Bonds. Tetrabenzyltitanium

Sir:

Tetrabenzyltitanium (I) is a catalyst for the polymerization of ethylene as well as of α olefins.[1] Furthermore, it appears as the most stable of the Ti–alkyl compounds reported hitherto. In addition, no Ti complex containing Ti–C σ bonds has yet been reported. Although the X-ray results presently obtained by us at room temperature are somewhat inaccurate because of the high value of the average thermal parameter ($B \simeq 10$ Å^2), we believe it interesting to discuss the prominent features of the structure in this preliminary account. A low-temperature X-ray investigation is now being started by one of us (I. W. B.).

X-Ray single-crystal equiinclination photographs of I were taken with an automated Stoe Weissenberg diffractometer (Cu Kα). The space group was unequivocally determined as $P2_12_12_1$ ($a = 19.28 \pm 0.10$, $b = 13.03 \pm 0.07$, $c = 9.26 \pm 0.05$ Å, $Z = 4$). The Ti coordinates were derived from the three-dimensional Patterson map; since $y_{Ti} \simeq 0.25$ (see ref 2), the Fourier synthesis phased on Ti alone revealed a double image of the molecule. Image separation was achieved by

(1) U. Giannini, U. Zucchini, and E. Albizzati, *J. Polym. Sci., Part B*, **8**, 405 (1970).

(2) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, p 105.