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.

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(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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Received May 28, 1971

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

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(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.

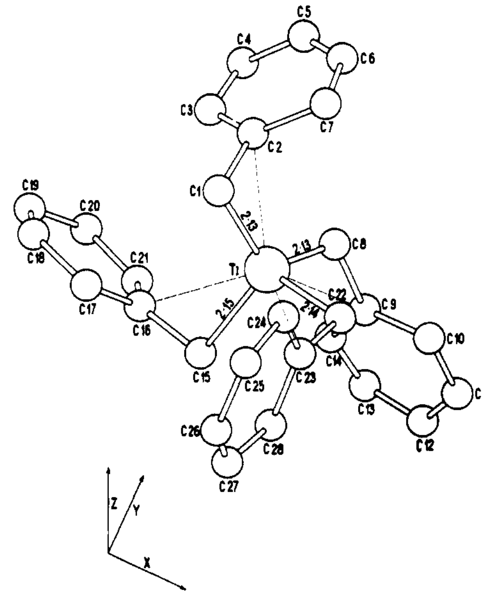

Figure 1. Model of the molecule tetrabenzyltitanium in the crystalline state.

stepwise introduction of the C atoms into the structure factor calculations, their location being derived both on Fourier and on stereochemical grounds. Least-squares refinement was carried out in 16 cycles which were alternately of the block-diagonal and of the full matrix type. Only the Ti atom was assigned anisotropic thermal parameters. The final disagreement factor ($R = \Sigma||F_c| - |F_o||/\Sigma|F_o|$) is 0.128 for the 703 nonzero reflections and 0.176 for all the 1137 reflections subjected to intensity measurement.

The molecular model is shown in Figure 1, while some of the most relevant interatomic distances and bond angles are reported in Table I together with their standard deviations. All C–C bond lengths and C–C–C angles are close to the average values found in other compounds containing similar groups, the difference never being larger than 3σ (average values σ_{C-C} = 0.04 Å, σ_{C-C-C} = 2°). Although the largest distance of the C atoms from the least-squares average planes of their corresponding benzyl groups is 0.07 Å, we do not believe that any deviation from planarity may be claimed. The most interesting structural feature is the apparent existence of Ti–C electronic interactions with the benzyl C atoms in the β position; this is revealed by short Ti–C distances especially with C_2 and C_{16} (in the range 2.6–2.8 Å; see Table I), together with $Ti-C_\alpha-C_\beta$ angles well below the tetrahedral value, and with a rotational orientation of the phenyl ring bringing the $C_\beta \pi$-electron clouds as close as possible to the metal. The last is a common feature of the four benzyl groups, since all dihedral angles between the phenyl rings and the $Ti-C_\alpha-C_\beta$ plane are between 84 and 86°, suggesting that there is probably some degree of overlap between the C_β filled π orbitals and the outer-shell Ti empty orbitals. The carbon-to-metal electron donation may explain the shift to lower field of the C_α proton resonance in the high-resolution nmr spectra of I, with respect to the benzyl derivatives of metals with a similar or higher electronegativity,[3] due to electron draining from C_α to C_β. The $Ti-C_\beta$ interactions, together with steric repulsions between nonbonded atoms, offer a good qualitative explanation of the observed deviations of the $C_\alpha-Ti-C_{\alpha'}$ angles from the tetrahedral value. In particular (see Table I and Figure 1), the largest angle is observed for C_1-Ti-C_8 (123°), consistent with the $C_2-C_1-Ti-C_8$ sequence being in a cis arrangement and with C_2 being the C_β atom closest to Ti. Furthermore, C_1-Ti-C_{15} is the second largest angle (118°), consistent with C_2 and C_{16}, bonded to C_1 and C_{15}, respectively, being the two C_β's closest to Ti.

Table I. The Most Relevant Geometric Parameters of the Molecule Tetrabenzyltitanium in the Crystalline State[a]

Interatomic distances, Å		Bond angles, deg	
$Ti-C_1$	2.13 (3)	C_1-Ti-C_8	123 (1)
$Ti-C_8$	2.13 (3)	C_1-Ti-C_{15}	118 (2)
$Ti-C_{15}$	2.15 (3)	C_1-Ti-C_{22}	102 (1)
$Ti-C_{22}$	2.14 (3)	C_8-Ti-C_{15}	106 (1)
$Ti-C_2$	2.61 (3)	C_8-Ti-C_{22}	100 (1)
$Ti-C_9$	3.16 (3)	$C_{15}-Ti-C_{22}$	107 (1)
$Ti-C_{16}$	2.81 (3)	$Ti-C_1-C_2$	88 (2)
$Ti-C_{23}$	2.95 (3)	$Ti-C_8-C_9$	116 (2)
		$Ti-C_{15}-C_{16}$	98 (2)
		$Ti-C_{22}-C_{23}$	108 (2)

[a] The corresponding esd's are given in units of the last significant digit.

Acknowledgment. We acknowledge the helpful assistance and useful suggestions of Professor P. Corradini and U. Giannini; Professor Giannini also supplied us with the sample.

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(3) U. Zucchini, E. Albizzati, and U. Giannini, *J. Organometal. Chem.*, 26, 357 (1971).

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Received March 20, 1971

The Hydrogen-Bonded (Protonated) Schiff Base of *all-trans*-Retinal[1]

Sir:

As a part of our continuing investigation of the visual pigments,[2,3] we have studied a Schiff base of *all-trans*-retinal. We have obtained a unique result which directly bears upon all previous reports correlating an absorption band to the so-called protonated species. In particular, we have been concerned with the effect of temperature and of a hydrogen bonding (protonating) species upon the *N-all-trans*-retinylidene-*n*-butylamine molecule. The latter is considered to be a model for prelumirhodopsin (*all-trans*-retinal opsin), the first intermediate in the photobleaching of rhodopsin.

Preparation of the imine was similar to that previously reported.[4] Absorption spectra were recorded on a Cary-15 spectrophotometer. Infrared spectra were

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(1) This research was supported by the Atomic Energy Commission, Grant No. ORO-3736-8.

(2) R. S. Becker, K. Inuzuka, and D. E. Balke, *J. Amer. Chem. Soc.*, 93, 38 (1971), and references therein.

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(4) C. S. Irving and P. A. Leermakers, *Photochem. Photobiol.*, 7, 665 (1968).