PENTAVALENT ORGANOBISMUTH REAGENTS. PART VI. COMPARATIVE MIGRATORY APTITUDES OF ARYL GROUPS IN THE ARYLATION OF PHENOLS AND ENOLS BY PENTAVALENT BISMUTH REAGENTS⁺

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<u>Abstract</u> - The relative migratory aptitudes of <u>p</u>-substituted aryl groups in moving from intermediates based on pentavalent bismuth to carbon have been investigated for the typical cases of 2-naphthol and 2-carbethoxycyclohexanone. The relative rates for <u>p</u>-OMe, <u>p</u>-Me and <u>p</u>-NO, against <u>p</u>-H (phenyl) as standard have been measured using mixed arylbismuth derivatives. It is concluded that the migration is of the reductive elimination type and that discrete ions or radicals are not involved.

In the preceding parts of this series^{1,2} we showed that pentavalent organobismuth derivatives are efficient reagents for <u>ortho</u> <u>C</u>-phenylation of phenols and <u>C</u>-phenylation of enolic compounds, under well-defined (basic) conditions. The reaction proceeds through a covalent Bi-O intermediate, which is decomposed by reductive elimination to the <u>C</u>-phenylated substrates and a trivalent bismuth compound. We then considered two possible mechanisms for the transformation of the intermediates into <u>C</u>-phenylated products : concerted and radical. The regloselectivity of the reaction as well as the choice of the solvents used to carry out the reaction is better explained by a concerted mechanism. However, <u>a priori</u> the ease of phenylation of some hindered substrates, such as tetraphenylacetone might be better explained through interaction of a phenyl radical with an enolate anion.

In order to obtain evidence about these two possible pathways, we turned our attention to the study of the relative migratory aptitude of a variety of substituted arylbismuth reagents. We now describe our investigations on the synthesis of a series of symmetrical and unsymmetrical pentavalent triarylbismuth reagents and their reaction with a typical phenol and with a representative enolic β -keto-ester.

Synthesis of Symmetrical Triarylbismuth Compounds

Symmetrical triarylbismuths 1, 2 and 3 were prepared by reaction of the appropriate ary Imagnesium bromide with BiCl₂,³ with careful monitoring of the reaction temperature during the addition. In this way, a 65% yield was obtained for tri-p-anisylbismuth 3 instead of the reported 10% yield. 4,5 Tri-p-nitrophenylbismuth 4 was not obtained by this procedure. In recent reviews on organobismuth compounds, ^{6,7} a synthesis of 4 has been attributed to Russian authors;⁸ however, the Russian communication does not claim the synthesis of 4, but of the isomeric tri(m-nitrophenyl)bismuth. Thus, we attempted to prepare 4 by various methods : reaction of p-nitrophenyldiazonium tetrafluoroborate with metallic bismuth prepared according to Nesmeyanov et al.9, or with activated metallic bismuth prepared by Rieke's procedure,¹⁰ gave intractable mixtures. Reaction of p-nitrophenylhydrazine and $BiCl_3$ in the presence of a mixture of $CuCl_2$ and $FeCl_3$, under an atmosphere of oxygen¹¹ also gave complex mixtures. Reaction of p-bromonitrobenzene or p-iodonitrobenzene with Na-Bi alloy¹² was also unsuccessful. Eventually a low yield of $\frac{4}{4}$ was obtained through radical type aryl exchange. Reaction of tri-p-tolylbismuth and p-nitrophenyldiazonium tetrafluoroborate in presence of metallic copper in dimethylformamide at room temperature gave 4 (16%), together with the unsymmetrical derivatives 20 and 21, and the biaryls (4,4'-dimethyl-1,1'-biphenyl, 4-4'-dinitro-1,1'-biphenyl, and 4-methyl-4'-nitro-1,1'-biphenyl).

Ar	Ph	p-Tol	p-An	<u>р</u> -NO ₂ -С ₆ Н
<u> </u>	<u>.</u>		·	
Ar ₃ Bi	<u>1</u>	2	<u>3</u>	<u>4</u>
Ar ₃ BiCl ₂	5	<u>6</u>	7	8
Ar ₃ BiCO ₃	<u>9</u>	<u>10</u>	<u>11</u>	12
Ar ₂ BiCl	<u>13</u>	<u>14</u>	-	
ArBICI2	-	<u>15</u>	-	-

Symmetrical Triarylbismuth Derivatives

Unsymmetrical Triarylbismuth Derivatives

Ar	Ph	p-Tol	p-An	E-NO2-C6H4
Bi				
Tol ₂ ArBi	16	2	<u>18</u>	20
TolAr,Bi	17	2	<u>19</u>	<u>21</u>
Tol, ArBiCi,	22	<u>6</u>	24	26
TolAr,BICI	23	<u>6</u>	25	27
Tol, ArBICO,	<u>28</u>	10	30	32
TolAr2BiCO3	<u>29</u>	<u>10</u>	<u>31</u>	<u>33</u>

Synthesis of Unsymmetrical Triarylbismuth Compounds

Unsymmetrical triarylbismuth compounds are usually prepared by reaction of organo- or diorganobismuth chlorides with Grignard reagents.^{13,14} Diarylbismuth chlorides <u>13</u> and <u>14</u> and <u>p</u>-tolylbismuth dichloride <u>15</u> were prepared by disproportionation between the appropriate triarylbismuth and bismuth trichloride.¹⁵ Pure diarylbismuth chlorides were obtained by very slow addition of bismuth trichloride to a vigorously stirred solution of the triarylbismuth in ether, kept at 0°C. On the other hand, slow addition of a solution of triarylbismuth to a vigorously stirred suspension of BiCl₃ in ether at 0°C gave only arylbismuth dichloride.

Reaction of <u>13</u>, <u>14</u> and <u>15</u> with the appropriate Grignard reagent in ether at 0° C gave the expected unsymmetrical triarylbismuths <u>16</u>, <u>17</u>, <u>18</u> and <u>19</u>. Attempts to improve the yield of <u>19</u> were unsuccessful.

The p-nitrophenyl derivatives <u>20</u> and <u>21</u> were obtained by reaction of <u>p-nitrophenyldiazonium tetrafluoroborate with tri-p-tolylbismuth in the presence of metallic copper in dimethylformamide. The yields are poor due to the formation of a complex mixture of bismuth derivatives and various biaryls.</u>



Scheme 1

Usually, mixed triarylbismuths are prone to dismutation

$$Ar_2^1Ar^2Bi$$
 \longrightarrow $Ar_1^1Ar_2^2Bi$ \longrightarrow Ar_3^1Bi + Ar_3^2Bi

The method of choice to check the purity of these compounds appeared to be mass spectrometry. Indeed, IR and NMR spectrometry cannot distinguish between the redistribution products, but mass spectrometry can show the presence of these products, as the symmetrical triarylbismuth compounds gave stable molecular ion.

Synthesis of Triarylbismuth Carbonates

The triarylbismuth compounds 1-4 and 16-21 were oxidised to their dichlorides 5-8 and 22-27 by reaction with sulphuryl chloride. Although tri-p-nitrophenylbismuth has not been previously isolated, it must be pointed out that Nesmeyanov et al.⁹ succeeded to prepare tri-p-nitrophenylbismuth dichloride in a very low yield (5.5%), through reaction of p-nitro-

phenyldiazonium tetrafluoroborate with metallic bismuth followed by oxidation of the crude mixture with chlorine. Most of the dichlorides are stable compounds. However, $\frac{25}{26}$, $\frac{26}{26}$ and $\frac{27}{27}$ were relatively unstable and thus were quickly converted to the carbonates $\frac{31}{32}$ and $\frac{33}{33}$. The triarylbismuth carbonates $\frac{9-12}{2}$ and $\frac{28-33}{33}$ were prepared by reacting the dichlorides $\frac{5-8}{3}$ and $\frac{22-27}{10}$ in acetone with aqueous potassium carbonate at room temperature.¹

Reaction of 2-Naphthol <u>34</u> and 2-Carbethoxycyclohexanone <u>39</u> with Symmetrical Triarylbismuth Carbonates

Reaction of 2-naphthol 34 with symmetrical triarylbismuth carbonates gave 1-aryl-2naphthols in good yields (69-84%).

R Substrate	H	СН3	осн _з	NO2	
<u>34</u>	<u>35</u> (76)	<u>36</u> (71)	37 (69)	<u>38</u> (84)	
<u>39</u>	<u>40</u> (86)	<u>41</u> (81)	42 (86)	<u>43</u> (90)	

Table 1. Arylation with Symmetrical Triarylbismuth Carbonates $(\underline{p}-R-C_6H_4)_3BiCO_3$. Yields of Aryl Derivatives (%)

Scheme 2

The reaction with the <u>p</u>-substituted arylbismuth carbonate gave only the <u>p</u>-substituted 1-aryl-2-naphthol. This was strongly suggested by I.R. spectroscopy (v_{max} . 820 cm⁻¹). ¹H-NMR however was not informative. But ¹³C-NMR clearly indicated the <u>para</u> substitution (Table 2). Attribution of the values in the ¹³C-NMR spectra was based on correlation with chemical shifts of the closely related systems : 2-naphthol, ¹⁶ 3-substituted biphenyl.¹⁷ and 4-substituted biphenyl.¹⁸ Table 2. ¹³C-NMR of 1-Aryl 2-Naphthol

C-i R	<u>35</u> : H	<u>з6</u> : СН ₃ а	<u>37</u> : СН ₃ О ^а	<u>38</u> : NO2 ^b
C-1	121.2	121.2	120.8	120.7
C-2	150.3	150.5	150.6	152.7
C-3	117.6	117.5	117.4	119.0
C-4	128.4	129.4	129.4	131.1
C-5	126.6	126.5	126.5	127.8
C-6	123.4	123.3	123.3	124.2
C-7	124.7	124.8	124.8	124.8
C-8	128.2	128.1	128.1	129.2
C-9	133.5	129.2	129.1	134.3
C-10	129.1	с	126.1	129.9
C-1'	134.4	133.7	133.8	148.4
C-2', 6'	131.3	131.2	132.5	133.6
C-3', 5'	129.6	130.4	115.3	124.3
C~4'	129.6	138.4	160.0	145.2
other C	-	21.4	55.5	-

a): in CDCl₂. b): in d₆-acetone. c): not detected.

All four spectra showed three groups of carbon : highest intensity for C-2' and 6' and C-3' and 5', lowest intensity for quaternary carbons. In the case of the p-tolyl derivative of 2-naphthol, it was not possible to detect any signal for C-10, by broad band off-resonance or by spin-echo technique. The relevant signals for C-1, C-2, C-3 and C-4' gave only one peak for compounds <u>36</u>, <u>37</u> and <u>38</u>, indicative of a single isomer, the p-substituted derivative.

Reaction of 2-carbethoxycyclohexanone <u>39</u> with symmetrical triarylbismuth carbonates gave the corresponding 2-aryl 2-carbethoxycyclohexanone <u>40</u> - <u>43</u> in yields better than 80% (Table 1). ¹H-NMR of the p-tolyl derivative showed only one signal for $CH_3-C_6H_4$ - (δ 2.36 ppm) and one signal for $-C_6H_4$ - (δ 6.98 ppm). The methoxy derivative showed one CH_3 -O- signal (δ 3.83 ppm) and an AB system (δ 7.23 and 6.96 ppm). The p-nitro compound showed an AB system (δ 8.28 and 7.45 ppm) for the aromatic protons. These values indicated also only para substitution for the compounds 40 - 43.

Reaction of 2-Naphthol <u>34</u> and 2-Carbethoxycyclohexanone <u>39</u> with Unsymmetrical Triarylbismuth Carbonates

The yields obtained in the previous sets of experiments were not different enough to estimate efficiently the relative migratory aptitudes. A second possible type of experiments would have been the competitive arylation of 34 and 39 with equimolecular mixtures of the different triarylbismuth carbonates. However, two steps are involved in the reaction [(i) formation of a covalent intermediate, (ii) reductive elimination]. Competition reactions could be expected to be influenced by the rates of the two steps. We thus turned our attention to

the use of unsymmetrical triarylbismuth carbonates, avoiding the influence of the first step on the competition studies.

Reactions with 2-naphthol $\underline{34}$ were performed in methylene dichloride for 24 hrs at room temperature, while reactions with 2-carbethoxycyclohexanone $\underline{39}$ were performed in 6-8 hrs at reflux.

2-Naphthol with the phenyl p-tolyl derivatives <u>28</u> and <u>29</u> gave mixtures of <u>35</u> and <u>36</u> which were not resolved by preparative t.l.c. or by column chromatography. However, a measure of the ratio was possible by g.l.c. through comparison with authentic samples. Reaction of 2-naphthol with the p-anisyl-p-tolylbismuth derivatives <u>30</u> and <u>31</u> gave similarly a mixture of <u>36</u> and <u>37</u> whose ratio was determined by comparison of the integrals of the <u>CH₃-C₆H₄ (6 2.37 ppm) and <u>CH₃O-C₆H₄ (6 3.77 ppm) in ¹H-NMR. Reaction of 2-naphthol with the p-nitrophenyl-p-tolylbismuth derivatives <u>32</u> and <u>33</u> gave the 1-aryl-2-naphthols <u>36</u> and <u>38</u> which were purified by preparative t.l.c.</u></u>

Reagent Formula		2 3					
	Ar ¹	Ar ² ₂	Overali Yield (%)	Tolyl (%)	Aryi (%)	Ratio ^a Aryl/Tolyl	
28	phenyl	p-tolyl	99	49	51	2.08	
29	P-toly!	phenyl	95	17	83	2,44	
30	<u>p-anisyl</u>	p-tolyl	98	81	19	0.47	
<u>31</u>	p-tolyl	p-anisyl	90	50	50	0.5	
32	<u>p-nitrophenyl</u>	p-tolyl	86	20	80	8	
<u>33</u>	₽-tolyl	p-nitrophenyl	92	6	94	7.8	

Table 3. Arylation of 2-naphthol with Unsymmetrical Triarylbismuth Carbonates $Ar^1Ar_2^2BiCO_3$

a: corrected statistically for the number of aryls on bismuth.

Reaction of <u>39</u> with the phenyl-p-tolyl derivatives <u>28</u> and <u>29</u> produced mixtures of <u>40</u> and <u>41</u> which were estimated by measurement of the ¹H-NMR integrals of C_6H_5 (§ 7.07 ppm) and CH_3 - C_6H_4 (§ 6.93 and 2.3 ppm), and by comparison with measurement on known mixtures of <u>40</u> and <u>41</u>. Reaction of <u>39</u> with the p-anisyl-p-tolylbismuth compounds <u>30</u> and <u>31</u> yielded a mixture of <u>41</u> and <u>42</u>, estimated by the integrals of CH_3 - C_6H_4 (§ 2.3 ppm) and CH_3 O- C_6H_4 (§ 3.73 ppm). Reaction of <u>39</u> with the p-nitrophenyl-p-tolylbismuth derivatives <u>32</u> and <u>33</u> gave mixtures of <u>41</u> and <u>43</u> which were also estimated by the ¹H-NMR integrals of CH_3 - C_6H_4 (§ 6.93 ppm) and $O_2N-C_6H_4$ [§ 8.35-8.13 (2H) and 7.8-7.6 ppm (2H)].

Table 4. Arylation of 2-Carbethoxycyclohexanone with Unsymmetrical Triarylbismuth Carbonates $Ar^1Ar_2^2BiCO_3$

Reagent Formula	Ar ¹	Ar ² ₂	Overall Yield (%)	Tolyl (%)	Aryl (%)	Ratio ^a Aryi/Tolyi
28	phenyl	p-tolyl	87	59	41	1.4
29	p-tolyl	phenyl	91	21	79	1.9
30	p-anisy!	p-tolyl	82	86	14	0.32
31	p-tolyi	<u>p</u> -anisyl	86	49	51	0.52
32	p-nitrophenyl	p-tolyl	76	25	75	6.00
<u>33</u>	p-tolyl	<u>p-nitrophenyl</u>	92	08	92	5.75

a: corrected statistically for the number of aryls on bismuth

Conclusion

The relative migratory aptitudes were thus determined from the ratios Ar-Subst./Ph-Subst. in both sets of experiments and were found to be in the 2-naphthol series (Table 3): $p-NO_2$, 3.55; H, 1; $p-CH_3$, 0.45; $p-CH_3O$, 0.22, and in the 2-carbethoxy-cyclohexanone series (Table 4): $p-NO_2$, 3.55; H, 1; $p-CH_3$, 0.60; $p-CH_3O$, 0.25.

Comparison of these values with those reported for pinacolic transposition¹⁹ discards any cationic mechanism: $p-NO_2 < 0.1$; H, 1; $p-CH_3$, 15.7; $p-CH_3O$, 500. On the other hand, comparison of these values with a radical 1-2 aryl rearrangement^{20,21}, the decarbonylation of β -arylisovaleraldehyde: $p-NO_2$, 31; H, 1; $p-CH_3$, 0.72; $p-CH_3O$, 0.35, indicates that the involvement of free radicals is possible, but not in accord with the $p-NO_2$ result. However, some more closely related systems, such as the unsymmetrical hydroxytetra-arylstiboranes 44, are reported to rearrange to the triarylstibline oxide, via a radical mechanism. In this reaction,²² the relative migratory aptitudes are slightly different $p-NO_2$, 5.6; $p-CH_3O$, 2.6; $p-CH_3$, 1.3; H, 1. A plot of log (migratory aptitude) vs. Hammett σ_p gives a U-shaped curve, and substituted aryl groups have always a greater migratory aptitude than phenyl (Scheme 4).

This was rationalised by a greater stability of the substituted aryl radical compared to the phenyl radical and by a conjugation effect of the substituent on the ease of homolytic cleavage of the C-Sb bond.

 $Ar^{1}Ar^{2}_{3}SbOH ----> Ar^{1}Ar^{2}_{2}SbO + Ar^{2}_{3}SbO + Ar^{1}H$ <u>44</u> $Ar^{1}Ar^{2}I^{+}BF_{4}^{-} + EtO^{-} ----> Ar^{1}H + Ar^{2}H + Ar^{1}I$

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Scheme 4. Arylation of <u>34</u> and <u>39</u> with triarylbismuth carbonates and thermal decomposition of hydroxytetraarylstiboranes. Migration ratio log (Ar/Ph) vs. $\sigma_{\rm p}$.

In the reaction of unsymmetrical diaryliodonium tetrafluoroborate 45 with sodium ethoxide, ²⁴ a free radical pathway has been invoked and a study of the relative aryl migratory aptitudes gave the series: $\underline{m}-NO_2$, 5.6; $\underline{p}-CH_3$, 1.1; H, 1; $\underline{p}-CH_3O$, 0.8. In this reaction, charged intermediates are involved and the values reflect not only the influence of the bond dissociation energy, but also the stability of the transition states.

In our systems, a plot of log (migratory aptitude) vs. Hammett σ_p shows a similar shape for the curve to the plot $\Delta\delta$ vs. σ_p , (Scheme 5) of the ¹³C-NMR chemical shift for the <u>p</u>-carbon of the corresponding substituted benzene.²⁵

Scheme 5. ¹³C-NMR of monosubstituted benzene.²⁵ Influence of a substituent on the chemical shift of C-4 vs. σ_{p} .

These results, though indicating a possible free-radical mechanism, are better explained as the migratory aptitude being directly related to the electron density of the carbon C-1 (C-Bi bond). The bond dissociation energy would be the main factor in the relative migratory aptitude, as no charged species are involved in that step. In fact, e.s.r. studies and chemical trapping have shown that free radicals are <u>not</u> involved in the <u>C</u>-phenylation reaction. These results will be reported soon.²⁶

Thus <u>C</u>-phenylation of phenols and enolic compounds by pentavalent organobismuth reagents under basic conditions does not involve direct ionic aromatic substitution. In a first step, a covalent Bi-O intermediate is formed by nucleophilic displacement on the bismuth atom.¹ In the second step, phenylation of the substrate occurs through a concerted mechanism, in which *-electrons of the nucleophilic molety attack the <u>ipso</u>-carbon of the Ar-Bi bond, thus inducing phenyl migration and an overall reductive elimination (Scheme 6).

Scheme 6

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. ¹H-NMR spectra were determined for solutions in deuteriochloroform with TMS as internal standard on Varian T-60, Varian EM-360, Bruker WP-80 (80 MHz) and Bruker WM-400 (400 MHz). ¹C-NMR spectra were measured on a Bruker WP-200 SY apparatus. IR spectra were recorded on a Perkin-Elmer 297 instrument. G.l.c. were performed on a Girdel 330 apparatus. Mass spectra were recorded with AEI MS-9 or MS-50 instruments. All solvents and reagents were purified and dried by standard techniques. Chromatographic separations were performed using Merck Kieselgel 60 GF-254 (Preparative t.l.c.), Merck Kieselgel 60H (column chromatography at atmospheric pressure or under light pressure).

Preparation of Organobismuth Reagents

A - Symmetrical Triarylbismuth III Derivatives

Triphenylbismuth (75%), m.p. 78°C, lit.⁵ 77-78°C was prepared by reaction of bismuth trichloride with phenylmagnesium bromide. Tri-p-tolyl bismuth (85%)₅ m.p. 119-120°C, lit. 117-118°C, and tri-p-methoxyphenylbismuth (65%), m.p. 185°C, lit. ' 190°C were similarly prepared.

<u>Tri-p-nitrophenylbismuth.</u> Metallic copper (1.28 g) was added to a stirred solution of tri-p-tolylbismuth. (2.41 g) in anhydrous benzene (5ml). A solution of p-nitrophenyldiazonium tetrafluoroborate (4.74 g) in dry DMF (15 ml) was slowly added at room temperature, and the mixture stirred for 18 hrs. The reaction mixture was then filtered, diluted with cold water and extracted with ether-benzene (1:1) mixtures. Distillation of the solvent followed by column chromatography (eluant: hexane-ether 1:1) yielded tri-p-nitrophenylbismuth, 0.5 g (16%), m.p. 232-235°C, [11t., 121°C, 156°C (but really the m-nitrofsomer)]; 6 (CDCI_3): 8.3-8.1 (6H, d, ortho H) and 7.9-7.7 (6H, d, meta H); m/z 575 (M), 453 (M - C_H_NO_3), 331 (M - 2C_H_NO_2) and 209 (Bi) [Found: C, 38.02; H, 2.30; N, 7.07. $C_{18}H_{12}BiN_3O_6$ requires C, 37.67; H, 2.09; N, 7.30%).

B - Arylbismuth III Mono and Dichlorides

Diphenylbismuth Chloride.- Bismuth trichloride (1.58 g) was added in very small portions over an hour to a vigorously stirred solution of triphenylbismuth (4.402 g) in dry ether (125 ml) at 0°C. The mixture was then stirred at 0°C until completion of the reaction. The precipitate was filtered, washed with ether under an atmosphere of argon and recrystallised from benzene to yield diphenylbismuth chloride (4.8 g, 80%), m.p. 190°C, lit. 184-185°C.

<u>Di-p-tolylbismuth Chloride</u>.- Bismuth trichloride (1.3 g) and tri-p-tolylbismuth (4 g) in dry sther (75 ml) at 0°C gave similarly di-p-tolylbismuth chloride (4.9 g, 92%), m.p. 185°C, lit.²⁵ 181.5°C.

<u>p-Tolylbismuth Dichloride</u>. A solution of tri-<u>p</u>-tolylbismuth (3 g) in dry ether (50 ml) was added at a very slow rate over an hour to a well-stirred suspension of bismuth trichloride (3.92 g) in dry ether (75 ml) at 0°C. The yellow precipitate was filtered, washed with ether and recrystallised from benzene to yield <u>p</u>-tolylbismuth dichloride (4.5 g, 60%), m.p. 209°C, 1it. 20 206-207°C.

C - Unsymmetrical Triarylbismuth III Derivatives

<u>General Procedure</u>.- An ethereal solution of the appropriate Grignard reagent was added dropwise to a well stirred ethereal suspension of diarylbismuth chloride or arylbismuth dichloride at 0°C. After the end of the addition, the reaction mixture was either stirred for l-2 hrs at 0°C, or left at room temperature and stirred for an additional 6 hrs. The mixture was then poured into a large excess of ice-water, quickly filtered over cellte and worked up as usual.

<u>Diphenyl-p-tolylbismuth</u>.- Diphenylbismuth chloride (4.8 g) in dry ether (50 ml) and p-tolylmagnesium browide [from p-bromotoluene (2.05 g) and magnesium (0.3 g) in dry ether (15 ml)] gave, after stirring for 6 hrs, an oil which crystallised on cooling (4.65 g, 85%), m.p. 43-45°C, lit. pil, δ (CDCl₃): 7.64-7.28 (14H, m, ArH) and 2.32 (3H, s, C₆H₄-<u>CH₃</u>); m/z 377 (M⁻ - Ph), 363 (M⁻ - Tol), 300 (M⁻ - 2Ph), 286 (M⁻ - Ph and Tol) and 209 (Bi).

<u>Di-p-tolylphenylbismuth.</u> Di-p-tolylbismuth chloride (4.8 g) in dry ether (50 ml) and phenylmagnesium bromide [from bromobenzene (1.76 g) and magnesium (0.28 g) in dry ether (12 ml)] gave, after stirring for 6 hrs, an oil which crystallised from benzene-methanol (4.45 g, 85%), m.p. $67-69^{\circ}$ C, 6 (CDC1₃): 7.7-7.05 (13H, m, ArH) and 2.32 (6H, s, $C_{6}H_{4}-CH_{3}$); m/z 391 (M - Ph), 300 (M - Ph and Tol), 286 (M - 2 Tol) and 209 (B1).

<u>Di-p-tolyl-p-methoxyphenylbismuth.</u> Di-p-tolylbismuth chloride (4.9 g) in dry ether (50 ml) and p-methoxyphenylmagnesium bromide [from p-bromoanisole (2.41 g) and magnesium (0.30 g) in dry ether (10 ml)] gave, after stirring for 2 hrs at 0°C, the title compound which was recrystallised from benzene-methanol (3.15 g, 65%), m.p. 109-112°C, δ (CDC1₃): 7.52-6.92 (12H, m, Ar-H), 3.73 (3H, s, C₆H₄-O-<u>CH₃</u>) and 2.32 (6H, s, C₆H₄-<u>CH₃</u>); m/z 407 (M⁺ - Tol), 391 (M⁺ -

C,H,OCH₂), 316 (M^+ - 2 To1), 300 (M^+ - To1 and C₆H₄OCH₃) and 209 (B1) [Found: C, 51.00; H, 4.33. C₂₁H₂₁B10 requires C, 50.60; H, 4.22X).

 $\begin{array}{l} \underline{\text{Di-p-methoxyphenyl-p-tolylbismuth.}}_{(60 \text{ ml}) \text{ and } \underline{p-methoxyphenyl-megnesium bromide [from p-bromoanisole (4.42 g) and magnesium (0.54 g) in dry ether (12 ml)] gave, after stirring for l hr at 0°C, the title compound as a solid which was recrystallised from methylene dichloride-methanol (0.9 g, 162), m.p. 130-134°C, & (CDC1_2): 7,58-6.92 (12H, m, ArH), 3.75 (6H, s, C,H,OCH_3) and 2.32 (3H, s, C,H,Me); m/z 514 (M), 423 (M - Tol), 407 (M - C_H,OCH_3), 316 (M - Tol and C_H,OCH_3), 300 (M - 2C_H,OCH_3) and 209 (Bi). [Found: C, 48.81; H, 4.07. C_{21}H_{21}BiO_2 requires C, 49.03; H, 4.09%]. \end{array}$

<u>Di-p-nitrophenyl-p-tolylbismuth</u> and <u>Di-p-tolyl-p-nitrophenylbismuth</u>. These bismuth derivatives were prepared by the same procedure as tri-p-nitrophenylbismuth, by adding a solution of p-nitrophenyldiazonium tetrafluoroborate (2.37 g) in dry DMF (10 ml) to a solution of tri-p-tolylbismuth (2.41 g) in anhydrous benzene (5 ml) in the presence of metallic copper (0.64 g). After work-up, column chromatography of the residue afforded di-p-tolyl-p-nitrophenylbismuth (eluant: hexane) (0.31 g, 12%), m.p. 129-132°C, δ (CDC1_3); 8.14-7.39 (12H, m, ArH) and 2.35 (6H, s, C_H, -CH_3); m/z 513 (M⁺), 422 (M⁺ - p-tolyl), 391 (M⁺ - C_H, NO₂), 331 (M⁺ - 2p-tolyl), 300 (M⁺ - p⁺tolyl⁺) and C_H, MO₂) and 209 (Bi) [Found: C, 47.12; H, 3.6; N, 2.76. C₂₀H₁₈BiNO₂ requires C, 46.78; H, 3.5; N, 2.73%]. Further elution (hexane-ether 95:5) afforded di-p-tolylbismuth (eluant c, H, NO₂), 300 (M⁺ - p-tolyl); m.p. 145-149°C, δ (CDC1₃); 8.17-7.39 (12H, m, ArH) and 2.35 (3H, s, C_H, -CH₃); m/z 544 (M⁺), 453 (M⁺ - p-tolyl), 422° (M⁺ - C_H, NO₂), 331 (M⁻ - p-tolyl and C_H, NO₂), 300 (M⁺ - 2C_H, NO₂) and 209 (Bi) [Found: C, 42.12; H, 2.86; N, 5.22. C₁₉H₁₅BiNO₂ requires C, 41.91; H, 2.76; N, 5.15%].

D - Triarylbismuth Dichloride Derivatives

<u>General Procedure.</u> Sulphuryl chloride (1 equiv.) in methylene dichloride solution (2-4 mH/10 ml) was added dropwise to a cooled (-78°C) stirred methylene dichloride triarylbismuth (2-3 mH/10 ml). The reaction mixture was further stirred for 15-30 mins at -78°C. Distillation of the solvent at room temperature under reduced pressure and recrystallisation of the solid residue from methylene dichloride or a mixture benzene-methanol afforded the corresponding following triarylbismuth dichlorides : (1) Triphenylbismuth dichloride (96%), m.p. 167-169°C, 11t. 159-160°C; (11) Tri-p-tolylbismuth dichloride (98%), m.p. 147-149°C, 11t. 147°C; (111) Tri-p-methoxyphenylbismuth dichloride (85%), m.g. 135°C, 11t. 133°C; (1v) Tri-p-nitro-phenylbismuth dichloride (95%), m.p. 165°C, 11t. 160-161°C; (v) Diphenyl-p-tolylbismuth dichloride (95%), m.p. 121-123°C, 11t. 109-110°C [Found: C, 43.08; H, 3.31; Cl, 13.38. C_1H, BfCl_ requires C, 43.42; H, 3.25; cl, 13.52X]; (yi) Di-p-tolylphenylbismuth dichloride (95%), m.p. 120-123°C, 503 (M' - Cl), 391 (M' - 2Cl), 377 (M' - 2Cl and p-tolyl), 337, 335 (M' - Cl) and p-tolyl), 323, 321 (M' - Cl and 2p-tolyl), 300 (M' - 2Cl, Ph and p-tolyl), 316 (M' - 2Cl and 2p-tolyl) and 209 (Bi); (vii) Di-p-tolyl-p-methoxyphenyl-bismuth dichloride (89%), m.p. 120-122°C, & (CDCl_1): 8.28-8.03 (6H, m, ArH), 7.25-6.8 (6H, m, ArH), 3.75 (3H, s, C_H, -OCH) and 2.32 (6H, s, C_H, -CH); m/z 533, 533 (M' - Cl), 407 (M' - 2Cl and p-anisyl), 316 (H' - 2Cl and 2p-tolyl), 300 (M' - 2Cl, p-tolyl and 2.32 (6H, s, C_H, -CH); m/z 533, 533 (M' - Cl), 407 (M' - 2Cl and p-anisyl), 316 (H' - 2Cl and 2p-tolyl), 316 (H' - 2Cl, m/z 533, 533 (M' - Cl), 407 (M' - 2Cl, p-tolyl and p-anisyl), 316 (H' - 2Cl, and 2p-tolyl), 300 (M' - 2Cl, p-tolyl and p-anisyl), 316 (H' - 2Cl and 2p-tolyl), 300 (M' - 2Cl, p-tolyl and p-anisyl), 316 (H' - 2Cl and 2p-tolyl), 300 (M' - 2Cl, p-tolyl and p-anisyl), 316 (H' - 2Cl and 2p-tolyl), 300 (M' - 2Cl, p-tolyl and p-anisyl), 316 (H' - 2Cl and 2p-tolyl), 300 (M' - 2Cl, p-tolyl) and p-anisyl) and

E - Triarylbismuth Carbonates

Triarylbismuth carbonates were prepared from the corresponding triarylbismuth dichlorides by the previously reported method. (1) <u>Tri-p-methoxyphenylbismuth carbonate</u> (997), m.p. 140-145°C (dec.) [Pound: C, 44.37; H, 3.58. $C_{22}H_{21}BiO_{5}$ requires C, 44.74; H, 3.56%]; 11) Tri-p-nitrophenylbismuth carbonate (85%), m.p. 170-176°C; (111) <u>Diphenyl-p-tolylbismuth</u> <u>carbonate</u> (96%), m.p. 142-146°C [Found: C, 46.73; H, 3.58. $C_{20}H_{18}BiO_{5}$ requires C, 46.60; H, 3.50%); (iv) <u>Di-p-tolylphenylbismuth carbonate</u> (95%), m.p. 134-136°C³[Found: C, 48.16; H, 3.73. $C_{21}H_{10}BiO_{3}$ requires C, 47.73; H, 3.60%); (v) <u>Di-p-tolyl-p-methoxyphenylbismuth</u> carbonate (95%), m.p. 110-115°C [Found: C, 47.59; H, 4.13. $C_{22}H_{21}BiO_{4}$ requires C, 47.31; H, 3.77%]; (vi) <u>Di-p-methoxyphenyl-p-tolylbismuth carbonate</u> (80%), m.p. 118-121°C [Found: C, 45.53; H, 3.77. $C_{27}H_{18}BiO_{5}$ requires C, 45.97; H, 3.66%]; (vii) Di-p-tolyl-p-nitrophenylbismuth carbonate (85%), m.p. 108-112°C; (viii) <u>Di-p-tolyl-p-nitrophenyl-p-tolylbismuth</u> carbonate (85%), m.p. 126-134°C.

Arylation of 2-Carbethoxycyclohexanone by Symmetrical Triarylbismuth Carbonates.

<u>Ceneral Procedure</u>.- A stirred mixture of 2-carbethoxycyclohexanone (0.5 mmole) and triarylbismuth carbonate (0.75 mmol) in methylene dichloride (2 ml) was heated under reflux under an atmosphere of argon until reaction was complete (6-8 hrs). The reaction mixture was filtered over celite, evaporated, and the residue purified by preparative t.l.c₃₁ (eluant: hexane-ether 7:3). (1) 2-Carbethoxy-2-phenylcyclohexanone (81%), colourless oil, δ (CDCl₃): 6.93 (4H, s, ArH), 4.15 (2H, q, J 7Hz, O-CH₂-CH₃), 2.73-2.37 (4H, m, cyclic CH₂), 2.3 (3H, g, C_H₄-p-CH₃), 2.21-1.16 (4H, m, cyclic CH₂) and 1.23 (3H, t, J 7Hz, O-CH₂-CH₃); m/z 260 (M) [Found: C, 73.94; H, 7.68; O, 18.60. $C_{1,6}H_{2,0}O_{3}$ requires C, 73.85; H, 7.69; O, 18.46%]; (111) <u>2-Carbethoxy-2-p-methoxyphenylcyclohexanome</u> (86%), colourless oil, δ (CDC1₃): 7.08-6.68 (4H, AB system, $C_{0,H_{2}}-DCH_{3}$), 4.15 (2H, q, J 7Hz, O-CH₂-CH₃), 3.73 (3H, s, $C_{0,H_{2}}-DCH_{3}$), 2.73-2.37 (4H, m, cyclic CH₂), 2.1-1.16 (4H, m, cyclic CH₂) and 1.23 (3H, t, J 7Hz, O-CH₂-CH₃); m/z 276 (H') [Pound: C, 69.85; H, 7.17; O, 23.32. $C_{1,H_{2,0}O_{4}}$ requires C, 69.57; H, 7.24; O, 23.19%]; (iv) 2-Carbethoxy-2-p-nitrophenylcyclohexanome (90%), pale yellow oil, δ (CDC1₃): 8.25 (2H, d, ArH), 7.45 (2H, d, ArH), 4.15 (2H, q, J 7Hz, O-CH₂-CH₃), 2.73-2.37 (4H, m, cyclic CH₂) and 2.1-1.6 (4H, m, cyclic CH₂).

Competitive Arylation of 2-Carbethoxycyclohexanone by Unsymmetrical Triarylbismuth Carbonates.

<u>General Procedure</u>.- The reaction was performed as above, on 0.5 mmol (0.085 g) of 2-carbethoxycyclohexanone. Preparative t.l.c. afforded a mixture of the 2-aryl-2-carbethoxycyclohexanones, which was not resolved by chromatography. Thus, the ratios were determined by H-MRM analysis of the mixtures. (1) Diphenyl-p-tolylbismuth carbonate gave a mixture (0.106 g, 91%) of 2-carbethoxy-2-phenylcyclohexanone (79%) and 2-carbethoxy-2-p-tolylcyclohexanone (21%); (11) Di-p-tolylphenylbismuth carbonate gave a mixture (0.110 g, 87%) of 2-carbethoxy-2-phenylcyclohexanone (41%) and 2-carbethoxy-2-p-tolyloyclohexanone (59%); (111) Di-p-tolylp-mathoxyphenylbismuth carbonate gave a mixture (0.108 g, 82%) of 2-carbethoxy-2-p-methoxyphenylcyclohexanone (14%) and 2-carbethoxy-2-p-tolylcyclohexanone (86%); (iv) Di-p-methoxyphenylcyclohexanone (51%) and 2-carbethoxy-2-p-tolylcyclohexanone (49%); (v) Di-p-tolyl-pnitrophenylbismuth carbonate gave a mixture (0.107 g, 76%) of 2-carbethoxy-2-p-mitrophenylcyclohexanone (75%) and 2-carbethoxy-2-p-tolylcyclohexanone (25%); (vi) Di-p-tolyl-pnitrophenylbismuth carbonate gave a mixture (0.107 g, 76%) of 2-carbethoxy-2-p-nitrophenylcyclohexanone (92%) and 2-carbethoxy-2-p-tolylcyclohexanone (25%); (vi) Di-p-nitrophenyl-ptolylbismuth carbonate gave a mixture (0.13 g, 92%) of 2-carbethoxy-2-p-nitrophenyl-phexanone (92%) and 2-carbethoxy-2-p-tolylcyclohexanone (8%);

Arylation of 2-Naphthol by Symmetrical Triarylbismuth Carbonates

<u>General Procedure.</u> A mixture of 2-naphthol (0.072 g, 0.5 mmol) and triarylbismuth carbonate (0.75 mmol) in methylene dichloride (2 ml) was stirred at room temperature under an atmosphere of argon until reaction was complete (24-36 hrs). The reaction mixture was filtered over celite, evaporated and the residue purified by pregrative t.l.c. (eluant: hexane-ether 7:3). (1) 1-Phenyl-2-naphthol (767), m.p. 85-86°C, 1it. 81-83°C; (11) 1-p-Tolyl-2-naphthol (712), m.p. 62-64°C, $_{6}$ (CDC1₃): 7.95-6.95 (10H, m, ArH), 5.05 (1H, s, <u>OH</u>) and 2.37 (3H, s, C.H.-<u>CH</u>₃); m/z 234 (M) [Found: C, 86.85; H, 6.0. C₁-H₁O requires C, 87.18; H, 5.98%); (111) 1-<u>p-Methoryphenyl-2-naphthol</u> (69%), m.p. 108-110°C, $_{6}$ (CDC1₃): 7.83-6.91 (10H, m, ArH), 5.05 (1H, s, <u>OH</u>) and 3.77 (3H, s, C.H.-<u>OCH</u>₃); m/z 250 (M) [Found: C, 81.69; H, 5.56; 0, 12.67. C₁-H₁O requires C, 81.69; H, 4.51; N, 5.26%).

Competitive Arylation of 2-Naphthol by Unsymmetrical Triarylbismuth Carbonates

<u>General Procedure</u>.- A mixture of 2-naphthol (0.072 g, 0.5 mmol) and unsymmetrical triarylbiamuth carbonate (0.75 mmol) in methylene dichloride (2 ml) was stirred at room temperature under an atmosphere of argon until reaction was complete (24-36 hrs). The usual work-up followed by preparative t.l.c. (eluant: hexane-ether 9:1) afforded either the pure products or a mixture, which was analysed either by g.l.c. or by H-N.M.R. (i) Diphenyl-p-tolylbiamuth carbonate afforded a mixture (0.105 g, 95%). The ratio was determined by g.l.c. (column: SE 30, 5%): 1-phenyl-2-naphthol (83%) and 1-p-tolyl-2-naphthol (17%); (ii) Di-p-tolyl-phenylbiamuth carbonate afforded a mixture (0.113 g, 98%) of 1-phenyl-2-naphthol (51%) and 1-p-tolyl-2-naphthol (49%); (i11) Di-p-tolyl-p-methoxyphenyl-2-naphthol (19%) and 1-p-tolyl-2-naphthol (81%); (iv) Di-p-methoxyphenyl-p-tolybiamuth carbonate gave a mixture (0.107 g, 98%) of 1-p-methoxyphenyl-2-naphthol (50%); (v) Di-p-tolyl-2-naphthol (81%); (iv) Di-p-methoxyphenyl-2-naphthol (50%); (v) Di-p-tolyl-2-naphthol (50%); (v) Di-p-tolyl-2-naphthol (50%); (v) Di-p-tolyl-2-naphthol (0.0915 g, 69%) and 1-p-tolyl-2-naphthol (0.0915 g, 69%) and 1-p-tolyl-2-naphthol (0.020 g, 17%); (vi) Di-p-nitrophenyl-2-naphthol (0.006 g, 5%).

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References

 Part II: D.H.R. Barton, N.Y. Bhatnagar, J.-C. Blazejewski, B. Charpiot, J.-P. Finet, D.J. Lester, W.B. Motherwell, M.T.B. Papoula, and S.P. Stanforth, <u>J. Chem. Soc., Perkin Trans</u> <u>I</u>, in press (1985).
 Part III: D.H.R. Barton, J.-C. Blazejewski, B. Charpiot, J.-P. Finet, W.B. Motherwell, M.T.B. Papoula, and S.P. Stanforth, <u>J. Chem. Soc., Perkin Trans I</u>, in press (1985).

- 2. We designate Part IV as : D.H.R. Barton, B. Charpiot, E.T. Huu Dau, W.B. Motherwell, C. Pascard, and C. Pichon, <u>Helv. Chim. Acts</u>, <u>67</u>, 586 (1984) and Part V as : D.H.R. Barton, B. Charpiot, K.U. Ingold, L.J. Johnston, W.B. Motherwell, J.C. Scaiano, and S.P. Stanforth, J. Am. Chem. Soc., 107, 3607 (1985).
 P. Pfeiffer, Ber. Dtsch. Chem. Ges., 37, 4620 (1904).
 J. Supniewski, <u>Roczniki Chem., 6</u>, 97 (1926).
 J. Supniewski and R. Adams, J. Am. Chem. Soc., 48, 507
 P.G. Harrison, Organometal. Chem. Rev., A5, 183 (1970).
- 3.
- 4.
- 5. 507 (1926).
- 6.
- M. Wieber, Gmelin Handbuch der Anorganischen Chemie, 7. Band 47, Bismut-Organische Verbindungen, Springer-Verlag, Berlin, 91 (1977).
- 0.A. Ptitsyna, 0.A. Reutov and Y.S. Ovodov, Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk., 638 8. (1962); Chem. Abstr., 57, 15147 (1962). A.N. Nesmeyanov, T.P. Tolstaya and L.S. Isaeva, Dokl. Akad. Nauk. SSSR, 122, 614 (1958).
- 9.

- R.D. Ricke, Acc. Chem. Res., 10, 301 (1977).
 R.D. Ricke, Acc. Chem. Res., 10, 301 (1977).
 A.B. Bruker and K.H. Malkov, Dokl. Akad. Nauk. SSR, 128, 948 (1959).
 A. Gillmeister, Ber. Dtsch. Chem. Ges., 30, 2843 (1897).
 F. Challenger, J. Chem. Soc., 105, 2210 (1914); 1bid, 109, 250 (1916).
 H. Gilman and H.L. Yablunky, J. Am. Chem. Soc., 63, 207 (1941).
 H. Gilman and A.C. Svigoon, J. Am. Chem. Soc., 61, 3586 (1939).
 K. Kitching M. Bullnitt D. Cartchore W. Addock, T.C. Ehor. D. Doddy. 16. W. Kitching, M. Bullpitt, D. Gartshore, W. Adcock, T.C. Khor, D. Doddrell, and I.D. Rae,
- J. Org. Chem., 42, 2411 (1977). 17.
- S.G. Baram, O.P. Shkurko and V.P. Mamaev, Izv. Akad. Nauk. SSSR, Ser. Khim., 294 (1983). E.M. Schulman, K.A. Christensen, D.N. Grant, and C. Walling, J. Org. Chem., 39, 2686 18. (1974).
- Molecular Rearrangements, P. de Mayo Ed., Interscience, New York, 1964, Vol. 1, p. 22 and 19. references cited.
- Ibid, Vol. 1, p. 429. 20.
- 21. C. Ruechardt, Chem. Ber., 94, 2609 (1961).
- F.L. Chupka, J.W. Knapczyk, and W.E. McEwen, J. Org. Chem., 42, 1399 (1977).
 C. Hansch, A. Leo, S.H. Unger, K.H. Kim, D. Nikaitani, and E.J. Lien, J. Med. Chem., 16, 1207 (1973).
- J.J. Lubinkowski, C.G. Arrieche, and W.E. McEwen, J. Org. Chem., 45, 2076 (1980).
 E. Breitmaier and W. Voelter, ¹C NMR Spectroscopy, <u>Monographs in Modern Chemistry</u>, Verlag Chemie, Weinheim, New York, Vol. 5, 1978, p. 185 and references cited.
 D.H.R. Barton, J.-P. Finet, C. Giannotti, and F. Halley, publication in preparation.
- D.H.R. Barton, J.-P. Finet, G. Glannotti, and T. S. Starkey, J. Am. Chem. Soc., 59, 1479 (1937).
 F. Challenger and C.F. Allpress, J. Chem. Soc., 119, 913 (1921).
 G. Golland H.S. Prasad, Can. J. Chem., 48, 2488 (1970).

- R.G. Goel and H.S. Prasad, <u>Can. J. Chem., 48</u>, 2488 (1970).
 A. Michaelis and A. Marquardt, <u>Liebigs Ann. Chem., 251</u>, 323 (1889).
- F.M. Beringer and P.S. Forgione, <u>J. Org. Chem.</u>, <u>28</u>, 714 (1963).
 R. Huisgen, L.A. Feiler, and P. Otto, <u>Chem. Ber.</u>, <u>102</u>, 3405 (1969).