Pentavalent Organobismuth Reagents. Part 3.[1] Phenylation of Enols and of Enolate and other Anions

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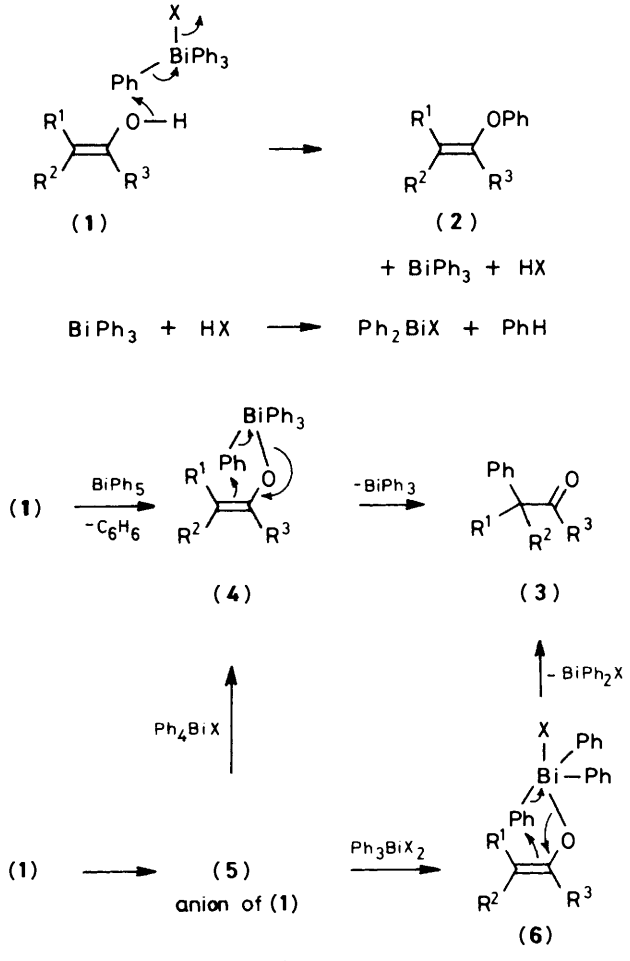
The phenylation of enols and of enolate anions of ketones, β-diketones and keto esters has been studied using a range of Bi reagents. Under basic conditions *C*-phenylation is observed and, even hindered, perphenylated compounds are easily synthesized. Under neutral and acidic conditions ordinary ketones do not react and enolic systems give *O*-phenylation. A number of other anions have been phenylated under basic conditions, including the key compound indole which mainly gave 3-*C*-phenylation. All these reactions can be supposed to have one of two alternative mechanisms, which parallel the two mechanisms proposed for the phenylation of phenols.

In Part 2 of this series[1] we showed that phenols could be smoothly *C*-phenylated in the *ortho*-position using various Bi^V reagents under basic conditions. Such reactions involve a Bi^V intermediate which, in appropriate cases, was isolated and fully characterised. These phenolic Bi^V derivatives are mostly prepared by base-catalysed condensation of Bi^V reagents having electron-withdrawing (leaving) groups with phenolate anions. When a Bi^V intermediate was not formed the same family of phenols was *O*-phenylated, generally in less satisfactory yield.



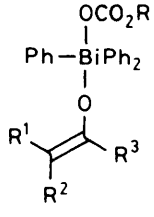
Scheme 1.

The only exception was *p*-nitrophenol which was *O*-phenylated with or without formation of a Bi^V intermediate. This exception is currently under investigation.

If the same analysis of phenylation can be extended to enols and enolate anions then Scheme 1 would be a summary of the reactions to be expected. We have already published a number of preliminary communications on this subject.[2-5]

The reaction of enols (**1**) with organobismuth reagents of the type Ph_4BiX, where X represents an electron-withdrawing group, would be expected to yield the *O*-phenylated product (**2**) by a concerted pathway. In contrast to *O*-phenylation, *C*-phenylation to give (**3**) is expected to occur *via* an intermediate possessing a covalent Bi–O bond. Reaction between pentaphenylbismuth and the enol (**1**) would be expected to give the intermediate (**4**) and benzene. This intermediate (**4**) would also be formed by nucleophilic displacement of an electron-withdrawing substituent from an organobismuth (Ph_4BiX) by the enolate anion (**5**). Breakdown of this intermediate would be predicted to give the *C*-phenylated product (**3**) and triphenylbismuth. The *C*-phenylated product (**3**) could also be obtained *via* the intermediate (**6**). Reaction of the enolate anion (**5**) with organobismuth reagents of the type Ph_3BiX_2 would give (**6**) and would then yield the product (**3**).

We have reported that triphenylbismuth carbonate is a useful reagent for *C*-phenylation of enols (**4**) and enolate anions (**5**)[4,5] to give product (**3**). The mechanism of these transformations are considered to involve intermediates (**7**) or (**8**).



(**7**) R = H
(**8**) R = negative charge

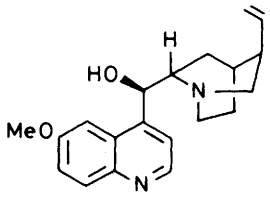
Our investigations of the phenylation of enols and of enolate anions with organobismuth reagents are now described.

Phenylation and Perphenylation of Ketones.—Our investigations of the synthetic utility of triphenylbismuth carbonate as a reagent for the oxidation of alcohols provided, by accident, the first example of the ability of this reagent to function as a

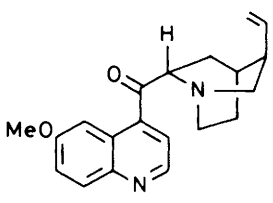
phenylating agent.[4] When quinine (**9**) was treated with triphenylbismuth carbonate (2.5 equiv.) in boiling methylene dichloride solution, a mixture of diastereoisomeric ketones (**11**) (92% yield) was isolated. This ketone (**11**) is produced by the sequence (*i*) oxidation of quinine (**9**) to the quininone (**10**) and (*ii*) phenylation of the quininone (**10**) by triphenylbismuth carbonate. With tri-*p*-tolylbismuth carbonate quinine (**9**) gave a diastereoisomeric mixture of the arylated ketone (**12**) (90% yield). We also noted that deoxybenzoin (**13**) and triphenylbismuth carbonate yielded the oxidised and phenylated product (**14**).

Encouraged by these observations we investigated the synthesis of perphenylated ketones. These highly hindered ketones cannot be easily prepared by alternative routes. We thought that the best method would be by reaction of enolate anions with triphenylbismuth carbonate. Accordingly, a selection of ketones (Table 1) were treated with an excess of potassium hydride and then with triphenylbismuth carbonate. The corresponding perphenylated products were obtained in good yields. We have also found that organobismuth reagents of the type Ph_4BiX can be used as a perphenylating reagents for enolate anions. Thus, cyclohexanone (**21**), potassium hydride, and tetraphenylbismuth toluene-*p*-sulphonate gave 2,2,6,6-tetraphenylcyclohexanone (**22**) (80% yield);[6] and 2,2-diphenylcyclopentanone (**30**), potassium hydride, and tetraphenylbismuth trifluoroacetate gave 2,2,5,5-tetraphenylcyclopentanone (**31**) (74% yield),[6] in accord with mechanistic expectation.

Phenylation and Perphenylation of 1,3-*Dicarbonyl Compounds.*—As we reported[2,4] in preliminary form, enols and enolate anions derived from 1,3-dicarbonyl compounds can be readily phenylated or perphenylated with organobismuth reagents in moderate to good yields (Table 2). The regioselectivity of phenylation, giving *O*- or *C*-phenylated products can be controlled by the choice of the organobismuth reagent. Thus, in accord with mechanistic expectation, *C*-phenylated products were obtained by reaction of 1,3-dicarbonyl compounds with pentaphenylbismuth under neutral conditions,



(**9**)



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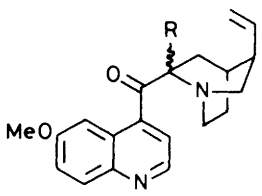


(**11**) R = Ph
(**12**) R = *p*-tolyl

$PhCH_2CHOHPh$

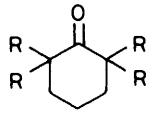
(**13**)

$Ph_2CHCOPh$

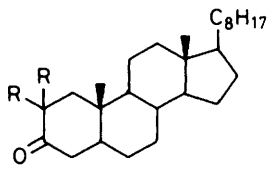
(**14**)

$PhCH_2CH_2OH$ (**15**) Ph_3CCHO (**16**) PhCOMe (**17**) $PhCOCPh_3$ (**18**)

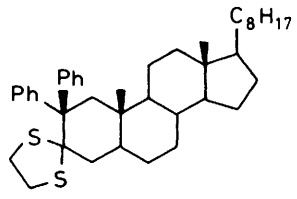
$PhCH_2COCH_2Ph$ (**19**) $Ph_2CHCOCPh_3$ (**20**)



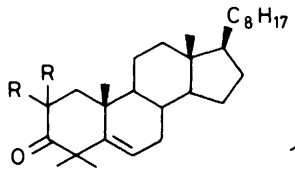
(**21**) R = H
(**22**) R = Ph



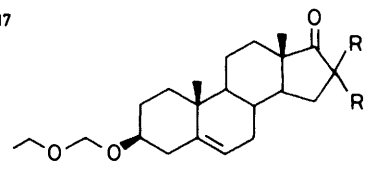
(**23**) R = H
(**24**) R = Ph



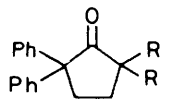
(**25**)



(**26**) R = H
(**27**) R = Ph



(**28**) R = H
(**29**) R = Ph



(**30**) R = H
(**31**) R = Ph

Table 1. Perphenylation of enolate anions of ketones with triphenylbismuth carbonate

Substrate[a]	Product	Product yield (%)	Reaction	
			Time (h)	Temp. (°C)
Acetophenone (**17**)	2,2,2-Triphenylacetophenone (**18**)	69	15	60
Diphenylacetone (**19**)	Pentaphenylacetone (**20**)	60	3	R.t.[b]
Cyclohexanone (**21**)	2,2,6,6-Tetraphenylcyclohexanone (**22**)	93	20	60
Cholestan-3-one (**23**)	2,2-Diphenylcholestan-3-one (**24**)	64	42	60
4,4-Dimethylcholest-5-en-3-one (**26**)	4,4-Dimethyl-2,2-diphenylcholest-5-en-3-one (**27**)	80	22	60
3β-*O*-Ethoxymethoxyandrost-5-en-17-one (**28**)	3β-*O*-Ethoxymethoxy-16,16-diphenylandrost-5-en-17-one (**29**)	68	100	60

[a] Potassium hydride was used to generate the corresponding enolate anion in each case. [b] R.t. = room temperature.

Table 2. Phenylation and perphenylation of 1,3-dicarbonyl compounds

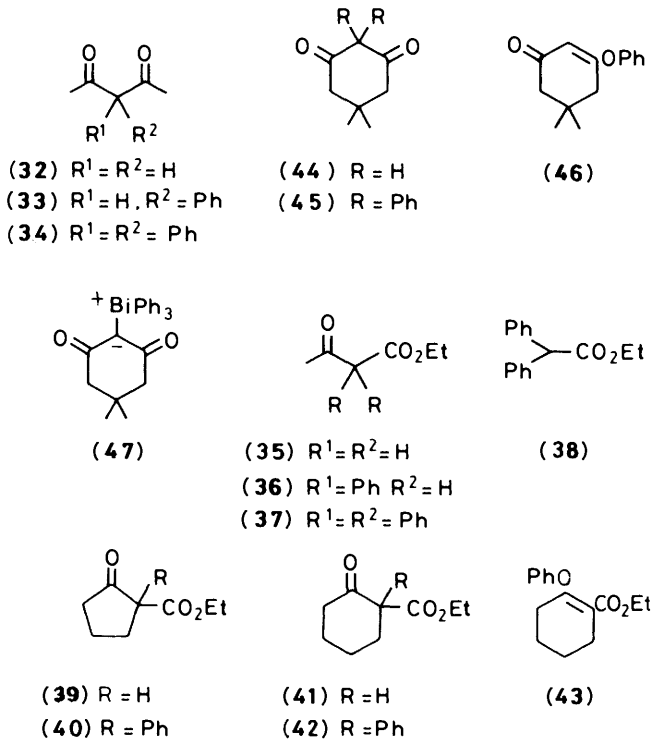
Substrate	Bismuth reagent (equiv.)	Solvent	Temp. (°C)	Time (h)	pH	Products Yield (%)
(**32**)	Ph_3BiCO_3 (2.5)	CH_2Cl_2	40	3.5	N	(**33**) 38, (**34**) 40
(**32**)	Ph_3BiCl_2 (1.0)	Benzene	80	2	B	(**34**) 74[a]
(**32**)	$Ph_4BiOCOCF_3$ (2.0)	Benzene	80	48	N	(**33**) 34, (**32**) 13
(**35**)	Ph_3BiCO_3 (1.0)	CH_2Cl_2	40	20	N	(**36**) 59
(**35**)	Ph_3BiCO_3 (2.1)	CH_2Cl_2	40	20	N	(**37**) 55, (**38**) 21
(**35**)	Ph_3BiCl_2 (2.1)	Benzene	80	2	B	(**37**) 82[a]
(**39**)	Ph_3BiCO_3 (2.0)	CH_2Cl_2	40	24	N	(**40**) 75
(**39**)	Ph_3BiCl_2 (1.0)	Benzene	80	2	B	(**40**) 91[a]
(**41**)	Ph_3BiCO_3 (2.0)	CH_2Cl_2	40	20	N	(**42**) 73
(**41**)	Ph_3BiCl_2 (1.0)	Benzene	80	2	B	(**42**) 75[a]
(**41**)	Ph_5Bi (1.5)	Benzene	r.t.	18	N	(**42**) 89
(**44**)	Ph_3BiCO_3 (1.5)	CH_2Cl_2	40	3	N	(**47**) 75
(**48**)	Ph_3BiCO_3 (1)	THF	67	11	N	(**49**) 53, (**50**) 13, (**48**) 26
(**48**)	Ph_3BiCO_3 (2.5)	THF	67	11	N	(**49**) 18, (**50**) 77
(**48**)	Ph_5Bi (2)	Benzene	r.t.	12	N	(**50**) 32

[a] Triphenylbismuth was also isolated. N: Neutral conditions. B: Tetramethyl-2-t-butylguanidine was used as the base.

Table 3. Phenylation of 2-ethoxycarbonylcyclohexanone (**41**) and of dimedone with esters of tetraphenylbismuth (Ph_4BiX)

2-Ethoxycarbonylcyclohexanone X	Equiv.	pH	(**41**)	(**42**)	(**43**)
$OCOCH_3$	2.4	N	21	47	
	1.7[a]	B		89	
$OCOCF_3$	2[b]	N	50	5	30
	2	B		90	
	1.5	A	26		57
OTs	1.5	N	84		
	1.5	B		72	
	1.5	A	93		
OSO_2CF_3	2	N	90		
	1.5	B		89	
5,5-Dimethylcyclohexane-1,3-dione			(**44**)	(**45**)	(**46**)
$OCOCF_3$	1.4[c]	N			56
	2	B		22	
	1.5	A			88
OTs	1.35	N	51		40
	1.5	B		81	
	1.5	A	26		55
OSO_2CF_3	2	N	70		5
	2	B		80	

All reactions performed in benzene at 60 °C for 24 h unless otherwise stated. [a] Room temperature, 1 h. [b] 80 °C, 18 h. [c] 60 °C, 48 h. N = Neutral. B = Basic; tetramethyl 2-t-butylguanidine. A = Addition of trichloroacetic acid (0.6 mol equiv.).

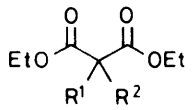


triphenylbismuth carbonate under neutral conditions and triphenylbismuth dichloride under basic conditions. The successful use of triphenylbismuth dichloride as a *C*-phenylating reagent for enolate anions is noteworthy, since all other organobismuth phenylating reagents are prepared in one or more steps from this dichloride. Organobismuth reagents of the type Ph_4BiX have been used for the regioselective phenylation of compounds (**41**) and (**44**) under acidic, neutral, or basic conditions to give either *O*- or *C*-phenylated products (Table 3).

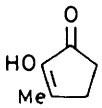
Two complications were encountered during our investigations of the phenylation and perphenylation of 1,3-dicarbonyl compounds. These are now described. Ethyl acetoacetate and triphenylbismuth carbonate (2.1 equiv.) gave, in addition to the expected perphenylated product (**37**), a low yield (21%) of ethyl diphenylacetate (**38**).[4] This is a base catalysed fission product of (**37**) and thus not so unexpected. Dimedone (**44**) and triphenylbismuth carbonate did not give the expected perphenylated product (**45**), but yielded the interesting compound (**47**) possessing a covalent Bi–C bond.

Phenylation and Perphenylation of 2-Hydroxy-3-methylcyclopent-2-en-1-one (**51**).—We have concluded our study of the phenylation and perphenylation of enols and enolate anions by examining the behaviour of a diosphenol, 2-hydroxy-3-methylcyclopent-2-en-1-one (**51**), towards organobismuth phenylating reagents under neutral or basic conditions. Compound (**51**) gave 2-hydroxy-5-methyl-3,5-diphenylcyclopent-2-en-1-one (**52**) with pentaphenylbismuth (30% yield) or triphenylbismuth carbonate (25% yield). In the former case some of compound (**51**) (12% yield) was also recovered. *C*-Phenylated products were also obtained by reaction of the enolate anions of

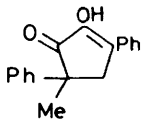
compound (**51**) (generated by addition of sodium hydride) with tetraphenylbismuth toluene-*p*-sulphonate. In this reaction, the diphenylated product (**52**) (44% yield), the monophenylated product (**53**) (10% yield), and the starting material (**51**) (9% yield) were isolated. Compound (**51**) and tetraphenylbismuth



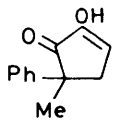
(**48**) $R^1 = R^2 = H$
(**49**) $R^1 = Ph$ $R^2 = H$
(**50**) $R^1 = R^2 = Ph$



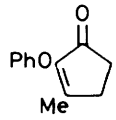
(**51**)



(**52**)



(**53**)

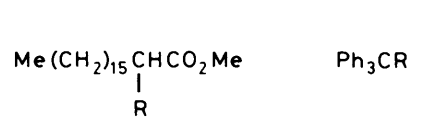


(**54**)

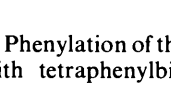
trifluoroacetate gave exclusively the *O*-phenylated product, 3-methyl-2-phenylcyclopent-2-enone (**54**) (84% yield) under neutral conditions.

Phenylation of Stabilised Anions with Triphenylbismuth Carbonate.—We have briefly studied the phenylation of stabilised anions (other than enolates) with triphenylbismuth carbonate. Thus, when 2-nitropropane (**55**) was treated firstly with potassium hydride, and then with triphenylbismuth carbonate, 2-phenyl-2-nitropropane (**56**) (80% yield) was obtained;[7] 2-nitropropane and pentaphenylbismuth also afforded product (**56**) (25% yield). The lithium salt of the ester (**57**) and triphenylbismuth carbonate gave the phenylated product (**58**) (54% yield) directly. Potassium triphenylmethanide could also be phenylated directly with triphenylbismuth carbonate to give tetraphenylmethane (**60**) (40% yield).

(**55**) R = H
(**56**) R = Ph



(**57**) R = H
(**58**) R = Ph

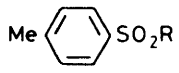


(**59**) R = H
(**60**) R = Ph

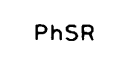
We have also investigated briefly[3] the phenylation of toluene-*p*-sulphinic acid and of its sodium salt. With the latter and triphenylbismuth carbonate, yields of phenyl *p*-tolyl sulphone of up to 50% can be obtained. Even in water, a yield of 27% was obtained at 80 °C and the yield was limited by the instability of the sodium salt, not by that of the carbonate.

A better yield of sulphone (87%) was obtained when toluene-*p*-sulphinic acid was treated with pentaphenylbismuth. The sodium salt with tetraphenylbismuth trifluoroacetate gave 86% of the sulphone, whilst the corresponding sulphinic acid gave a yield of 76%.

Thiols are oxidised by triphenylbismuth carbonate to give good yields of disulphides.[8] In contrast, thiophenol was mainly converted into diphenyl sulphide (70%) with tetraphenylbismuth trifluoroacetate, with the formation of diphenyl disulphide in minor amount (15%). Similarly toluene-*o*-thiol gave *o*-tolyl

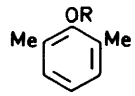


(**61**) R = Na
(**62**) R = H
(**63**) R = Ph

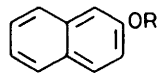


(**64**) R = H
(**65**) R = Ph
(**66**) R = SPh

(**67**) R = H
(**68**) R = Ph



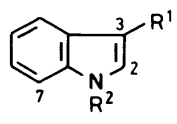
(**69**) R = H
(**70**) R = Ph



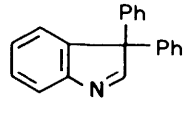
(**71**) R = H
(**72**) R = Ph

phenyl sulphide (80%). By contrast treatment of thiophenylate anion with triphenylbismuth dichloride gave a nearly quantitative yield of the disulphide. The discussion given already[8] adequately explains this result.

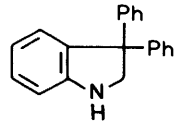
The phenylation of indole (**73**) proved informative. When heated under reflux in benzene for 18 h, indole and tetraphenylbismuth trifluoroacetate, gave 3,*N*-diphenylindole (**74**) (2%), 3-phenylindole (**75**) (43%) (characterised as its *N*-acetyl derivative and by synthesis of an authentic specimen), and unchanged indole (51%). Similar phenylation of indole with tetraphenylbismuth toluene-*p*-sulphonate gave 3-phenylindole (**75**) (36%) and recovered indole (43%).



(**73**) $R^1 = R^2 = H$
(**74**) $R^1 = R^2 = Ph$
(**75**) $R^1 = Ph$, $R^2 = H$
(**76**) $R^1 = Ph$, $R^2 = Ac$



(**77**)



(**78**)

Phenylation of the anion (sodium hydride) of indole (1 mmol) with tetraphenylbismuth toluene-*p*-sulphonate (2 mmol) at room temperature gave 3-phenylindole (5%) and, as the major product, 3,3-diphenyl-3*H*-indole (**77**) (61%) as well as unchanged indole (23%). The indole derivative (**77**) was reduced with cyanoborohydride to the corresponding indoline (**78**).

If these phenylation reactions had involved an N-Bi bonded intermediate, then phenylation would have been at positions 2 or 7 (not seen) or on the nitrogen. The fact that indole is almost exclusively phenylated in the β-position is fully in accord with a bimolecular positive phenyl phenylation of the type discussed above.

Thus the phenylation reactions briefly reported in this section probably do not involve Bi^V intermediates, which undergo α-elimination. A direct phenylation is proposed, the aryl groups on Bi^V being electrophilic in character. Mechanistic studies are in hand.

We must also correct two reported phenylations.[7] We have not been able to repeat the two amide phenylations described earlier.[7]

Again[1] we have not considered radical phenylation as an explanation for the results discussed in this paper. This is because we have strong evidence against this possibility which we will present in due course.

Experimental

General directions. M.p.s. were determined with a Kofler hot-stage apparatus and are uncorrected. N.m.r. spectra were determined for solutions in deuteriochloroform or carbon tetrachloride with $SiMe_4$ as the internal standard on Varian T-60, Varian EM-360, Bruker WP-80 (80 MHz), or Bruker WP-400 (400 MHz) instruments. I.r. spectra were recorded on Perkin-Elmer 257 or 297 instruments. U.v. spectra were recorded on a Jobin-Yvon DUOSPAC 203 spectrometer. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. 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 or Merck Alumina 90 (Column chromatography at atmospheric pressure or under light pressure).

Preparation of Organobismuth Reagents.—Pentaphenylbismuth, tetraphenylbismuth trifluoroacetate, tetraphenylbismuth toluene-*p*-sulphonate, triphenylbismuth dichloride, and triphenylbismuth carbonate were prepared as previously reported.[1] Tri-*p*-tolylbismuth dichloride (88%, m.p. 155—157 °C) and tri-*p*-tolylbismuth carbonate (100%, m.p. 139 °C) were prepared by similar procedures.

Reaction of Quinine (**9**) *with Triphenylbismuth Carbonate.*—A mixture of quinine (**9**) (0.5 g) and triphenylbismuth carbonate (1.93 g) in methylene dichloride (5 ml) was heated under reflux (24 h) under an atmosphere of argon. The mixture was filtered through Celite and the filtrate evaporated. Column chromatography using ether–hexane gradient elution, afforded a mixture of diastereoisomeric ketones (**11**) (0.564 g, 92%) as a yellow glass, $\lambda_{max.}$ (EtOH) 344 nm (ε 3 690); $\nu_{max.}$ ($CHCl_3$) 1 685 and 1 620 cm^{-1}; δ ($CDCl_3$; 400 MHz) 8.64 (1 H, m, 2′-H), 7.91 (0.6 H, d, *J* 5 Hz, 3′-H), 7.79 (1 H, d, *J* 10 Hz, 8′-H), 7.46—7.00 (7.4 H, m, 3′-H, 5′-H, 7′-H, Ph), 5.96 (0.6 H, m, 10-H), 5.58 (0.4 H, m, 10-H), 5.09—4.82 (2 H, m, 11-H), 3.81 (1.2 H, s, OMe), and 3.71 (1.8 H, s, OMe); $[\alpha]_D^{20}$ + 101.0° (*c* 0.68, EtOH); *m/z* 398 (M^+), 212 ($C_{15}H_{18}N^+$), and 158 ($M^+ - C_{16}H_{18}NO$) (Found: 398.2014. $C_{26}H_{26}N_2O_2$ requires 398.1994).

Reaction of Quinine (**9**) *with Tri-*p*-tolylbismuth Carbonate.*—A mixture of quinine (**9**) (0.162 g) and tri-*p*-tolylbismuth carbonate (0.91 g) in methylene dichloride (3 ml) was heated under reflux (6 h) under an atmosphere of argon. The mixture was filtered through Celite, the filtrate evaporated, and the residue chromatographed over neutral alumina (grade IV) using ether–hexane gradient elution to afford a mixture of diastereoisomeric ketones (**12**) (0.145 g, 92%) as a yellow glass, $\nu_{max.}$ (CH_2Cl_2) 1 690 and 1 620 cm^{-1}; δ($CDCl_3$) 3.80 and 3.75 (3 H, 2 × s, OMe) and 2.31 and 2.20 (3 H, 2 s, ArMe); *m/z* 412 (M^+), 227 ($C_{16}H_{21}N^+$), 226 ($C_{16}H_{20}N^+$), and 158 ($M^+ - C_{17}H_{20}NO$) (Found: 412.2149. $C_{27}H_{28}N_2O_2$ requires 412.2151).

Reaction of 1,2-*Diphenylethanol* (**13**) *with Triphenylbismuth Carbonate.*—A mixture of 1,2-diphenylethanol (**13**) (0.198 g) and triphenylbismuth carbonate (0.750 g) in methylene dichloride was heated under reflux for 12 h. The mixture was filtered, the filtrate evaporated, and the residue purified by preparative thick layer chromatography using hexane–ethyl acetate (9:1) as the eluant to afford 2,2-diphenylacetophenone (**14**) (0.190 g, 70%), m.p. 135—136 °C (methanol) (lit.,[9] 136—137 °C).

Reaction of 2-*Phenylethanol with Pentaphenylbismuth.*—A solution of 2-phenylethanol (**15**) (0.049 g) and pentaphenylbismuth (1.19 g) in anhydrous benzene (3 ml) was stirred overnight at room temperature under argon. The mixture was evaporated and the residue purified by thick layer chromatography using pentane–ether (4:1) as the eluant. A non-polar mixture of triphenylbismuth and aldehyde (**16**) was recovered. Treatment of the ethereal solution with trichloroacetic acid (1 g) for 2 h under reflux, followed by column chromatography using hexane as the eluant, afforded triphenylacetaldehyde (**16**) as white needles (0.076 g, 69%), m.p. 102—104 °C (ethanol) [lit.,[10] 106—107 °C (ethanol)].

Phenylation of Enolate Anions with Triphenylbismuth Carbonate. General Method.—A solution of the ketone and potassium hydride (1.1—12 equiv.) in anhydrous THF (5 ml $mmol^{-1}$ of substrate) was stirred under argon at room temperature for 15 to 30 min. After addition of triphenylbismuth carbonate (2—8 equiv.) the mixture was stirred until the reaction was complete, (time and temperature indicated in Table 1). The reaction mixture was filtered through Celite, the filtrate evaporated, and the residue purified by preparative thick layer chromatography or column chromatography. (*a*) Acetophenone (**17**) (0.060 g), potassium hydride (0.090 g) and triphenylbismuth carbonate (1.150 g) [eluant hexane–ether (95:5)] gave 2,2,2-triphenylacetophenone (**18**) (0.122 g, 69%), m.p. 175—180 °C (benzene) (lit.,[11] 181 and 204—205 °C). (*b*) 1,3-Diphenylacetone (**19**) (0.210 g), potassium hydride (0.480 g), and triphenylbismuth carbonate (3 g) [eluant pentane–ether (98:2)] gave pentaphenylacetone (**20**) (0.263 g, 60%), m.p. 180—181 °C (ether) (lit.,[12] 180—181 °C). (*c*) Cholestan-3-one (**23**) (0.193 g), potassium hydride (0.075 g), and triphenylbismuth carbonate (1 g) (column chromatography, ether–hexane gradient elution) gave 2,2-diphenylcholestan-3-one (**24**) (0.172 g, 64%), m.p. 70 °C (methanol); $\lambda_{max.}$ (CH_2Cl_2) 300 nm (ε 134); $\nu_{max.}$ ($CHCl_3$) 1 700, 1 600, and 1 400 cm^{-1}; δ ($CDCl_3$) 7.29—6.69 (10 H, m, ArH) and 3.09—1.03 (44 H, m, aliphatic H); $[\alpha]_D^{25}$ + 69.5° (*c* 2.26, $CHCl_3$); *m/z* 538 (M^+). Compound (**24**) (0.160 g), ethane-1,2-dithiol (0.5 ml) and boron trifluoride–diethyl ether (0.5 ml) gave 2,2-*diphenylcholestan*-3-*one ethylenedithioacetal* (**25**) (0.147 g, 80%), m.p. 183—184 °C (methanol); $\nu_{max.}$ ($CHCl_2$) 1 600, 1 400, and 1 250 cm^{-1}; δ($CDCl_3$) 7.74—6.57 (10 H, m, ArH), 3.40—0.89 (39 H, m, aliphatic H), 0.89 (3 H, s, Me), 0.57 (3 H, s, Me), and 0.17 (3 H, s, Me); $[\alpha]_D^{25}$ + 200° (*c* 0.24, CH_2Cl_2); *m/z* 614 (M^+) and 522 ($M^+ - C_2H_4S_2$) (Found: C, 79.7; H, 9.4; S, 10.7. $C_{41}H_{58}S_2$ requires C, 80.07; H, 9.50; S, 10.43%). (*d*) 4,4-Dimethylcholest-5-en-3-one (**26**) (0.824 g), potassium hydride (0.4 g) and triphenylbismuth carbonate (2 g) (column chromatography, ether–hexane gradient elution) gave 4,4-*dimethyl*-2,2-*diphenylcholest*-5-*en*-3-*one* (**27**) (0.925 g, 80%), m.p. 190—193 °C (ether); $\lambda_{max.}$ (CH_2Cl_2) 315 nm (ε 20); $\nu_{max.}$ ($CHCl_3$) 1 700 and 1 600 cm^{-1}; δ($CDCl_3$) 7.00 (10 H, s, ArH), 5.46—5.26 (1 H, m, 6-H), and 1.74—0.6 (47 H, m, aliphatic H); $[\alpha]_D^{25}$ + 20.7° (*c* 2.8, CH_2Cl_2); *m/z* 564 (M^+) (Found: C, 86.75; H, 9.85; O, 3.2. $C_{41}H_{58}O$ requires C, 87.17; H, 9.91; O, 2.83%). (*e*) *Synthesis of* 3β-*ethoxymethoxyandrost*-5-*en*-17-*one* (**28**). Chloromethyl ethyl ether (1.8 ml) was added to a cooled suspension of 3β-hydroxyandrost-5-en-17-one (1 g) and di-isopropylethylamine (4 ml) in methylene dichloride. The reaction was stirred for 20 min at room temperature, after which time the solvent was distilled off and methanol and water were added. Compound (**28**) was obtained after crystallisation from methanol (0.95 g, 81%), m.p. 119—121 °C (methanol); $\nu_{max.}$ (CH_2Cl_2) 1 730 cm^{-1}; δ($CDCl_3$) 5.47—5.23 (1 H, m, 6-H), 4.70 (2 H, s, OCH_2), 3.80—3.30 (1 H, m, 3-H), 3.55 (2 H, q, *J* 7 Hz, OCH_2 Me), 2.83—1.33 (19 H, m, aliphatic H), 1.33 (3 H, s, Me), 1.20 (3 H, t, *J* 7 Hz, OCH_2*Me*), and 0.83 (3 H, s, Me); $[\alpha]_D^{25}$ + 2.6° (*c* 4.23, CH_2Cl_2); *m/z* 270 ($M^+ - C_3H_8O_2$). *Phenylation of compound* (**28**). 3β-Ethoxymethoxyandrost-5-en-17-one (**28**) (0.5 g), potassium hydride (0.219 g) and triphenylbismuth carbonate (2.8 g and 1 g after 48 h)

(column chromatography, ether–hexane gradient elution) afforded 3β-*ethoxymethoxy*-16,16-*diphenylandrost*-5-*en*-17-*one* (**29**) (0.48 g, 68%), m.p. 83—84 °C (ether); $\nu_{max.}$ (CH_2Cl_2) 1 730 and 1 600 cm^{-1}; δ($CDCl_3$) 7.49—7.00 (10 H, m, ArH), 5.47—5.23 (1 H, m, 6-H), 4.63 (2 H, s, OCH_2O), 3.77—3.33 (1 H, m, 3-H), 3.53 (2 H, q, *J* 7 Hz, OCH_2Me), 2.83—1.41 (17 H, m, aliphatic H), 1.23 (3 H, t, *J* 7 Hz, $-OCH_2Me$), 1.06 (3 H, s, Me), and 0.97 (3 H, s, Me); $[\alpha]_D^{25}$ + 7.6° (*c* 1.44, CH_2Cl_2); *m*/*z* 498 (M^+), 422 ($M^+ - C_3H_8O_2$), and 394 ($M^+ - C_4H_8O_3$) (Found: C, 81.64; H, 8.45; O, 9.76. $C_{34}H_{42}O_3$ requires C, 81.89; H, 8.49; O, 9.62%).

Phenylation and Perphenylation of 1,3-*Dicarbonyl Compounds: General Methods.—Method A: neutral conditions.* A solution of the substrate in anhydrous benzene or methylene dichloride [5 ml $mmol^{-1}$ of substrate] was stirred under an atmosphere of argon in the presence of the bismuth reagent (see Tables 2 and 3 for reaction time and temperature), until the reaction was complete. The reaction mixture was filtered through Celite, the filtrate evaporated, and the residue purified by preparative thick layer chromatography or column chromatography.

Method B: basic conditions. A solution of the substrate and tetramethyl-2-t-butylguanidine (1.2—2.5 equiv.) in anhydrous benzene [5 ml $mmol^{-1}$ of substrate] was stirred for 30 min. at room temperature under an atmosphere of argon. The bismuth reagent (1—2.5 equiv.) was added and the mixture stirred until the reaction was complete (see Tables 2 and 3 for reaction time and temperature). The mixture was evaporated and the residue fractionated by preparative thick layer chromatography. In some cases, triphenylbismuth identical with an authentic sample was also isolated.

Method C: acidic conditions. A solution of the substrate in anhydrous benzene [5 ml $mmol^{-1}$ of substrate] and trichloroacetic acid (0.6 equiv.) was stirred under an atmosphere of argon in the presence of the bismuth reagent at 60 °C for 24 h. The reaction mixture was worked up as above in Method A to afford the phenylated products (Table 3).

(*a*) Acetylacetone (0.15 g) and triphenylbismuth carbonate (1.9 g) (eluant pentane) gave 3-phenylpentane-2,4-dione (**33**) (0.100 g, 38%), m.p. 55—57 °C (methanol), (lit.,[13] 56—60 °C) and 3,3-diphenylpentane-2,4-dione (**34**) (0.150 g, 40%), m.p. 88—90 °C (methanol) (lit.,[14] 88—92 and 95—96 °C). (*b*) Acetylacetone (0.087 g), tetramethyl-2-t-butylguanidine (0.4 g) and triphenylbismuth dichloride (1 g) gave triphenylbismuth (0.138 g, 36%) and 3,3-diphenylpentane-2,4,-dione (**34**) (0.163 g, 74%) as a white solid, m.p. 94—95 °C. (*c*) Acetylacetone (0.098 g) and tetraphenylbismuth trifluoroacetate (0.630 g) gave 3-phenylpentane-2,4-dione (**33**) (0.052 g, 34%) and recovered acetylacetone (**32**) (0.013 g, 13%). (*d*) Ethyl acetoacetate (0.476 g) and triphenylbismuth carbonate (1.80 g) (column chromatography, ether–hexane gradient elution) gave ethyl 3-oxo-2-phenylbutanoate (**36**) (0.449 g, 59%) as an oil, identical with an authentic sample.[15] (*e*) Ethyl acetoacetate (0.261 g) and triphenylbismuth carbonate (2.1 g) [column chromatography, eluant hexane–ether (98:2)] gave *ethyl* 2,2-*diphenyl*-3-*oxobutanoate* (**37**) (0.316 g, 55%) as a colourless oil, $\nu_{max.}$ ($CHCl_3$) 1 735, 1 720, and 1 600 cm^{-1}; δ($CDCl_3$) 7.17 (10 H, s, ArH), 4.13 (2 H, q, *J* 6 Hz, OCH_2Me), 2.07 (3 H, s, *Me*CO), and 1.13 (3 H, t, *J* 6 Hz, OCH_2Me); *m*/*z* 282 (M^+) and 209 ($M^+ - C_3H_5O_2$) (Found: C, 76.4; H, 6.4; O, 16.8. $C_{18}H_{18}O_3$ requires C, 76.57; H, 6.43; O, 17.0%) and ethyl 2,2-diphenylacetate (**38**) (0.105 g, 21%), m.p. 56 °C (ethanol) (lit.,[16] 58 °C). (*f*) Ethyl acetoacetate (0.137 g), tetramethyl-2-t-butylguanidine (0.4 g) and triphenylbismuth dichloride (1.1 g) [column chromatography, eluant hexane–ether (98.2)] afforded triphenylbismuth (0.145 g, 32%) and ethyl 2,2-diphenyl-3-oxobutanoate (**37**) (0.244 g, 82%) as a colourless oil, identical with an authentic sample. (*g*) 2-Ethoxycarbonylcyclopentanone (**39**) (0.156 g) and triphenylbismuth carbonate (1 g) [eluant pentane–ether (95:5)] gave 2-ethoxycarbonyl-2-phenylcyclopentanone (**40**) (0.175 g, 75%) as a colourless oil,[17] $\nu_{max.}$ (CCl_4) 3 050, 2 980, and 1 720 cm^{-1}; δ(CCl_4) 7.34—6.85 (5 H, m, ArH), 4.0 (2 H, q, OCH_2Me), 3.0—1.67 (6 H, m, CH_2), and 1.17 (3 H, t, OCH_2Me); *m*/*z* 232 (M^+). (*h*) 2-Ethoxycarbonylcyclopentanone (**39**) (0.147 g), tetramethyl-2-t-butylguanidine (0.2 g) and triphenylbismuth dichloride (0.5 g) afforded triphenylbismuth (0.087 g, 21%) and 2-ethoxycarbonyl-2-phenylcyclopentanone (**40**) (0.198 g, 91%) as a colourless oil, identical with an authentic sample. (*i*) 2-Ethoxycarbonylcyclohexanone (**41**) (0.230 g) and triphenylbismuth carbonate (1.33 g) [eluant pentane–ethyl acetate (9:1)] gave 2-ethoxycarbonyl-2-phenylcyclohexanone (**42**) (0.243 g, 73%) as a colourless oil,[18] $\nu_{max.}$ ($CHCl_3$) 3 020, 2 920, 1 720, and 1 705 cm^{-1}; δ(CCl_4) 7.07 (5 H, m, $W_{\frac{1}{2}}$ 2 Hz, ArH), 4.0 (2 H, q, *J* 7 Hz, OCH_2), 2.8—2.27 (4 H, m, 3-H and 6-H), 2.1—1.57 (4 H, m, 4-H and 5-H), and 1.17 (3 H, t, *J* 7 Hz, OCH_2Me); *m*/*z* 246 (M^+) and 201 ($M^+ - C_2H_5O$). (*j*) 2-Ethoxycarbonylcyclohexanone (**41**) (0.175 g), tetramethyl-2-t-butylguanidine (0.2 g), and triphenylbismuth dichloride (0.53 g) afforded triphenylbismuth (0.085 g, 19%) and 2-ethoxycarbonyl-2-phenylcyclohexanone (0.190 g, 75%). (*k*) 2-Ethoxycarbonylcyclohexanone (**41**) (0.085 g) and pentaphenylbismuth (0.45 g) gave 2-ethoxycarbonyl-2-phenylcyclohexanone (**42**) (0.110 g, 89%). (*l*) 5,5-Dimethylcyclohexane-1,3-dione (**44**) (0.140 g) and triphenylbismuth carbonate (0.75 g) (column chromatography, ether–hexane gradient elution gave *triphenylbismuthonio*-4,4-*dimethyl*-2,6-*dioxocyclohexan*-1-*ide* (**47**) (0.436 g, 75%) as a gum, $\nu_{max.}$ ($CHCl_3$) 1 590, 1 570, and 1 525 cm^{-1}; δ($CDCl_3$) 7.90—7.27 (15 H, m, ArH), 2.40 (4 H, s, CH_2), and 1.13 (6 H, s, Me); *m*/*z* 578 (M^+), 501 (M^+–Ph), 286 ($M^+ - C_{20}H_{20}O_2$), and 209 ($M^+ - C_{26}H_{25}O_2$) (Found: C, 53.9; H, 4.45; O, 5.5. $C_{26}H_{25}BiO_2$ requires C, 53.98; H, 4.37; O, 5.53%). (*m*) Diethyl malonate (**48**) (0.246 g) and triphenylbismuth carbonate (0.75 g, 1 equiv.) [eluant hexane–ethyl acetate (9:1)] gave diethyl 2,2-diphenylmalonate (**50**) (0.062 g, 13%), m.p. 56—58 °C (methanol) (lit.,[19] 56—57 °C, diethyl 2-phenylmalonate (**49**) (0.188 g, 53%) as a colourless oil, identical with an authentic sample[20] and recovered (**48**) (0.064 g, 26%). (*n*) Diethyl malonate (**48**) (0.110 g) and triphenylbismuth carbonate (0.85 g, 2.5 equiv.) gave diethyl 2,2-diphenylmalonate (**50**) (0.163 g, 77%) and diethyl 2-phenylmalonate (**49**) (0.028 g, 18%), identical with authentic samples. (*o*) Diethylmalonate (**48**) (0.086 g) and pentaphenylbismuth (0.6 g) gave diethyl 2,2-diphenylmalonate (**50**) 0.050 g, 32%).

Phenylation of 2-*Ethoxycarbonylcyclohexanone with Tetraphenylbismuth Esters:* (*Table* 3).—(*a*) 2-Ethoxycarbonylcyclohexanone (**41**) (0.1 g) and tetraphenylbismuth acetate [from pentaphenylbismuth (0.825 g) and acetic acid (0.084 g)] [eluant hexane–ether (95:5)] gave 2-ethoxycarbonyl-2-phenylcyclohexanone (**42**) (0.068 g, 47%) and unchanged (**41**) (0.021 g, 21%). (*b*) Compound (**41**) (0.1 g) tetramethyl-2-t-butylguanidine (0.121 g) and tetraphenylbismuth acetate [from pentaphenylbismuth (0.594 g) and acetic acid (0.060 g)] gave (**42**) (0.130 g, 89%). (*c*) Compound (**41**) (0.085 g) and tetraphenylbismuth trifluoroacetate (0.630 g) gave *ethyl* 2-*phenoxycyclohex*-1-*enecarboxylate* (**43**) (0.037 g, 30%) as a colourless oil, $\nu_{max.}$ (CCl_4) 3 050, 2 900, 1 720, 1 700, 1 600, 1 280, 1 250, and 1 210 cm^{-1}; $\lambda_{max.}$ (EtOH) 224 and 218 nm (ε 11 660 and 11 280); δ(CCl_4) 7.4—6.6 (5 H, m, ArH), 3.95 (2 H, q, *J* 8 Hz, OCH_2), 2.7—2.0 (4 H, m, 3-H and 6-H), 1.9—1.5 (4 H, m, 4-H and 5-H), and 1.0 (3 H, t, *J* 8 Hz, OCH_2Me); *m*/*z* 246 (M^+), 217 ($M^+ - C_2H_5$), 201 ($M^+ - OC_2H_5$), 173 ($M^+ - C_3H_5O_2$), and 169 ($M^+ - C_6H_6$) (Found: C, 73.15; H, 7.4. $C_{15}H_{18}O_3$ requires C, 73.15; H, 7.37%), 2-ethoxycarbonyl-2-phenylcyclohexanone

(**42**) (0.006 g, 5%) and unchanged (**41**) (0.042 g, 50%). (*d*) Compound (**41**) (0.128 g) tetramethyl-2-t-butylguanidine (0.171 g) and tetraphenylbismuth trifluoroacetate (1 g) gave cyclohexanone (**42**) (0.165 g, 90%). (*e*) Compound (**41**) (0.050 g) tetraphenylbismuth trifluoroacetate (0.28 g) and trichloroacetic acid (0.029 g, 0.6 equiv.) gave the cyclohexene (**43**) (0.041 g, 57%), and unchanged (**41**) (0.013 g, 26%). (*f*) Compound (**41**) (0.085 g), tetramethyl-2-t-butylguanidine (0.130 g) and tetraphenylbismuth toluene-*p*-sulphonate (0.516 g) gave compound (**42**) (0.088 g, 72%). (*g*) Compound (**41**) (0.050 g) tetramethyl-2-t-butylguanidine (0.060 g) and tetraphenylbismuth trifluoromethanesulphonate (0.3 g) gave compound (**42**) (0.064 g, 89%).

Phenylation of 5,5-*Dimethylcyclohexane*-1,3-*dione* (**44**) *with Tetraphenylbismuth Esters:* (*Table* 3).—(*a*) 5,5-Dimethylcyclohexane-1,3-dione (**44**) (0.070 g) and tetraphenylbismuth trifluoroacetate (0.430 g) [eluant hexane–ether (3:1)] gave 5,5-dimethyl-3-phenoxycyclohex-2-en-1-one (**46**), m.p. 82 °C (pentane–ether) (lit.,[21] 80—82 °C); $\nu_{max.}$ ($CHCl_3$) 3 450, 1 650, and 1 615 cm^{-1}; δ($CDCl_3$) 7.4—6.8 (5 H, m, ArH), 5.1 (1 H, s, 2-H), 2.5 (2 H, s, CH_2), 2.2 (2 H, s, CH_2), and 1.15 (6 H, s, Me); *m/z* 216 (M^+) and 160 ($M^+ - Me_2CCH_2$). (*b*) Dione (**44**) (0.035 g), tetramethyl-2-t-butylguanidine (0.052 g) and tetraphenylbismuth trifluoroacetate (0.3 g) gave 5,5-dimethyl-2,2-diphenylcyclohexane-1,3-dione (**45**) (75%), m.p. 175—176 °C (ethanol) (lit.,[21] 175—176 °C); $\nu_{max.}$ ($CHCl_3$) 3 050, 2 950, 1 720, and 1 690 cm^{-1}; δ(CCl_4) 7.4—7.0 (6H, m, *m*- and *p*-ArH), 6.76—6.5 (4 H, m, *o*-ArH), 2.6 (4 H, s, CH_2), and 1.08 (6 H, s, Me); *m/z* 292 (M^+) and 194 ($M^+ - CH_2CMe_2CH_2CO$). (*c*) The dione (**44**) (0.050 g), trichloroacetic acid (0.035 g), and tetraphenylbismuth trifluoroacetate (0.34 g) gave the cyclohexenone (**46**) (0.068 g, 88%). (*d*) The dione (**44**) (0.078 g) and tetraphenylbismuth toluene-*p*-sulphonate (0.516 g) gave compound (**46**) (0.048 g, 40%) and recovered (**44**) (0.040 g, 51%). (*e*) The dione (**44**) (0.035 g), tetramethyl-2-t-butylguanidine (0.085 g), and tetraphenylbismuth toluene-*p*-sulphonate (0.344 g) gave (**45**) (0.059 g, 81%). (*f*) The dione (**44**) (0.035 g), trichloroacetic acid (0.024 g), and tetraphenylbismuth toluene-*p*-sulphonate (0.25 g) gave (**46**) (0.041 g, 55%) and recovered (**44**) (0.009 g, 26%). (*g*) The dione (**44**) (0.035 g) tetramethyl-2-t-butylguanidine (0.086 g), and tetraphenylbismuth trifluoromethanesulphonate (0.333 g) gave the dione (**45**) (0.061 g, 80%).

Phenylation of 2-*Hydroxy*-3-*methylcyclopent*-2-*en*-1-*one* (**51**).—(*a*) 2-Hydroxy-3-methylcyclopent-2-en-1-one (**51**) (0.112 g) and triphenylbismuth carbonate (0.5 g) in THF was stirred at 40 °C for 12 h. Triphenylbismuth carbonate (0.5 g) was added and the mixture stirred for a further 12 h. After a third addition of triphenylbismuth carbonate (0.5 g) the mixture was stirred for a further 12 h at 40 °C, after which it was filtered, and the filtrate evaporated; the residue was fractionated by column chromatography using ether–pentane gradient elution to afford 2-*hydroxy*-5-*methyl*-3,5-*diphenylcyclopent*-2-*en*-1-*one* (**52**) (0.064 g, 25%), m.p. 160—161 °C (hexane–ether); $\lambda_{max.}$ (cyclohexane) 317, 304, and 290 nm (ε 32 210, 45 410, and 38 810); $\nu_{max.}$ ($CHCl_3$) 3 450, 3 050sh, 2 900, 1 680, and 1 620 cm^{-1}; δ($CDCl_3$) 8.0—7.8 (2 H, m, *o*-ArH), 7.63—7.13 (8 H, m, ArH), 7 (1 H, m, OH), 3.15 (2 H, dd, J_{AB} 13 Hz, CH_2), and 1.63 (3 H, s, Me); *m/z* 264 (M^+) and 118 (PhCHCO) (Found: C, 82.05; H, 6.3. $C_{18}H_{16}O_2$ requires C, 81.79; H, 6.1%). (*b*) Compound (**51**) (0.112 g) and pentaphenylbismuth (0.9 g) in dry benzene (5 ml) was stirred for 3 h at room temperature under an atmosphere of argon. Further pentaphenylbismuth (0.9 g) was added, and the reaction stirred for 1 h. The solvent was evaporated and the residue fractionated by preparative t.l.c. using hexane–ether (9:1) as the eluant to afford (**52**) (0.080 g, 30%) and recovered (**51**) (0.014 g, 12.5%). (*c*) Compound (**51**) (0.224 g) and sodium hydride (50% suspension in oil, washed with pentane; 0.144 g) in anhydrous THF were stirred for 30 min under an atmosphere of argon at room temperature. Tetraphenylbismuth toluene-*p*-sulphonate (2.1 g) was added and the mixture stirred for 36 h at room temperature. After the addition of aqueous concentrated HCl, the THF was distilled off and the residue extracted with ether. After evaporation, the residue was fractionated by column chromatography using ether–hexane gradient elution to afford the cyclopentenone (**52**) (0.232 g, 44%), 2-*hydroxy*-5-*methyl*-5-*phenylcyclopent*-2-*en*-1-*one* (**53**) (0.037 g, 10%) as a white solid, m.p. 110—113 °C (hexane–ether); $\lambda_{max.}$ (cyclohexane) 255 and 250 nm (ε 5 440 and 5 300); $\nu_{max.}$ (CH_2Cl_2) 3 500, 2 900, 2 850, 1 700, and 1 650 cm^{-1}; δ($CDCl_3$) 7.2 (5 H, m, $W_{\frac{1}{2}}$ 2 Hz, ArH), 6.6 (1 H, t, $J_{3,4}$ 3 Hz, 3-H), 2.7 (2 H, 2 × dd, J_{AB} 13 Hz, $J_{3,4}$ 3 Hz, 4-H), and 1.55 (3 H, s, Me); *m/z* 188 (M^+) (Found: C, 76.4; H, 6.45. $C_{12}H_{12}O_2$ requires C, 76.57; H, 6.43%), and recovered (**51**) (0.020 g, 9%). (*d*) A solution of compound (**51**) (0.112 g) and tetraphenylbismuth trifluoroacetate (0.700 g) in anhydrous benzene (5 ml) was heated for 5 h under reflux under an atmosphere of argon. After distillation of the solvent, the residue was fractionated by column chromatography (using ether–hexane gradient elution) to afford 3-*methyl*-2-*phenoxycyclopent*-2-*en*-1-*one* (**54**) (0.150 g, 84%) as a white solid, m.p. 57—58 °C (hexane–ether); $\lambda_{max.}$ (ethanol) 243 nm (ε 14 310); $\nu_{max.}$ (CH_2Cl_2) 2 900, 1 700, 1 650, 1 600, 1 200, 1 150, and 1 100 cm^{-1}; δ($CDCl_3$) 7.5—6.7 (5 H, m, ArH), 2.6 (4 H, m, 4-H and 5-H), and 2 (3 H, s, Me); *m/z* 188 (M^+) (Found: C, 76.45; H, 6.45; O, 16.85. $C_{12}H_{22}O_2$ rquires C, 76.57; H, 6.43; O, 17%).

Phenylation of 2-*Nitropropane* (**55**).—(*a*) 2-Nitropropane (**55**) (0.1 g) and pentaphenylbismuth (1.78 g) in anhydrous benzene gave after 24 h at room temperature under an atmosphere of argon, followed by preparative t.l.c. [pentane–methylene dichloride (9:1)] α-nitrocumene (**56**) (0.047 g, 25%) as an oil,[22] $\nu_{max.}$ (CH_2Cl_2) 1 540 and 1 350 cm^{-1}; δ($CDCl_3$) 7.20 (5 H, s, ArH) and 1.90 (6 H, s, Me); *m/z* 165 (M^+) and 119 ($M^+ - NO_2$). (*b*) A solution of 2-nitropropane (**55**) (0.671 g) in THF (5 ml) was added to a suspension of potassium hydride (20% suspension in oil; 0.6 g) in anhydrous THF, under an atmosphere of argon. The mixture was stirred for 30 min at room temperature after which triphenylbismuth carbonate (7.5 g) was added. The mixture was heated under reflux for 3 h after which it was filtered through Celite and the filtrate evaporated. The residue was purified by column chromatography using ether–hexane gradient elution, to afford α-nitrocumene (**56**) (0.990 g, 80%) as an oil. Reduction of (**56**) by Zn–HCl in ethanol gave α-aminocumene, characterised as its *N*-benzoyl derivative, m.p. 159—160 °C (ethanol) (lit.,[23] 159 °C).

Phenylation of Methyl Octadecanoate (**57**) *with Triphenylbismuth Carbonate.*—Methyl octadecanoate (**57**) (0.57 g) was added at room temperature to a solution of lithium hexamethyldisilazide[24] [prepared from BuLi (1.6M solution in hexane; 2.5 ml) and hexamethyldisilazane (0.82 ml)], and the mixture stirred for 30 min at room temperature. Triphenylbismuth carbonate (2.5 g) was added and the mixture heated at 40 °C for 2 days. After work-up and column chromatography using ether–hexane gradient elution, *methyl*-2-*phenyloctadecanoate* (**58**) was obtained (0.385 g, 54%), m.p. 42—43 °C (decomp.) (CH_2Cl_2); $\nu_{max.}$ ($CHCl_2$) 1 720 cm^{-1}; δ($CDCl_3$) 7.30 (5 H, m, ArH), 3.75 (3 H, s, Me), and 2.65—0.65 (34 H, m, aliphatic H and Me); *m/z* 374 (M^+), 342 (M^+ – Me), and 267 ($M^+ - C_7H_8O$).

Synthesis of Tetraphenylmethane (**60**).—A mixture of triphenylmethane (**59**) (0.5 g) and potassium (0.4 g) in 1,2-dimethoxyethane was stirred for 16 h at room temperature under an atmosphere of argon after which triphenylbismuth carbonate (3 g) was added to it and stirring continued for 12 h at

room temperature and then 24 h at 80 °C. Further triphenylbismuth carbonate (3 g) was added and the mixture stirred for 24 h at 80 °C. After work-up and preparative t.l.c., tetraphenylmethane (**60**) (0.261 g, 40%), m.p. 272 °C (benzene) (lit.,[25] 282 °C), and unchanged (**59**) (0.227 g, 45%) were obtained.

Phenylation of Toluene-p-sulphinic Acid Sodium Salt.—(*a*) *With triphenylbismuth carbonate.* (*i*) A mixture of sodium toluene-*p*-sulphinate, monohydrate (**61**) (0.196 g) and triphenylbismuth carbonate (0.750 g) in DMF (5 ml) was heated at 60 °C for 24 h. The mixture was filtered through Celite and evaporated. Preparative t.l.c. afforded phenyl *p*-tolyl sulphone (**63**) (0.115 g, 50%) as a white powder, m.p. 125 °C (hexane–methylene dichloride) (lit.,[26] 124—125 °C). (*ii*) Compound (**61**) (0.196 g) and triphenylbismuth carbonate (1 g) in H_2O (5 ml) heated at 80 °C for 48 h afforded the sulphone (**63**) (0.062 g, 27%).

(*b*) *With tetraphenylbismuth trifluoroacetate.* A solution of compound (**61**) (0.098 g) and tetraphenylbismuth trifluoroacetate (0.470 g) in THF (3 ml) was heated under an atmosphere of argon, at 60 °C for 24 h. Work-up gave compound (**63**) (0.100 g, 86%).

*Phenylation of Toluene-*p*-sulphinic Acid.*—(*a*) *With pentaphenylbismuth.* A solution of toluene-*p*-sulphinic acid (**62**) (0.078 g) and pentaphenylbismuth (0.600 g) in benzene (4 ml) was stirred under an atmosphere of argon at 40 °C for 24 h. Usual work-up and preparative t.l.c. gave (**63**) (0.101 g, 87%). (*b*) *With tetraphenylbismuth trifluoroacetate.* A solution of (**62**) (0.078 g) and tetraphenylbismuth trifluoroacetate (0.630 g) in benzene (4 ml) was stirred under argon at 60 °C for 24 h to yield after preparative t.l.c., compound (**63**) (0.088 g, 76%). (*c*) *With triphenylbismuth carbonate.* A mixture of (**62**) (0.078 g) and triphenylbismuth carbonate (0.500 g) stirred under an atmosphere of argon at 40 °C for 24 h, gave after work-up and preparative t.l.c., compound (**63**) (0.036 g, 31%).

Reactions of Arylthiols.—(*a*) A solution of thiophenol (**64**) (0.110 g) and tetraphenylbismuth trifluoroacetate (0.945 g) in benzene (5 ml) was heated under an atmosphere of argon at 60 °C for 24 h. Distillation of the solvent and preparative t.l.c. of the residue gave a mixture of diphenyl sulphide (**65**) and diphenyl disulphide (**66**) as a yellow oil (0.196 g). An ethereal solution of the mixture of (**65**) and (**66**) was stirred with lithium aluminium hydride (0.040 g) at room temperature for 4 h. After hydrolysis, and extraction with aqueous 15% sodium hydroxide, the ethereal phase gave diphenyl sulphide (**65**) (0.130 g, 70%) as an oil, δ(CCl_4) 7.15 (s, $W_{\frac{1}{2}}$ = 4 Hz); *m/z* 186 (M^+). (*b*) A solution of toluene-*o*-thiol (**67**) (0.062 g) and tetraphenylbismuth trifluoroacetate (0.480 g) in benzene (4 ml) was treated under an atmosphere of argon at 60 °C for 18 h. Work-up as above gave phenyl *o*-tolyl sulphide (**68**) (0.080 g, 80%) as an oil, δ(CCl_4) 7.1 (9 H, s, ArH) and 2.3 (3 H, s, Me); *m/z* 200 (M^+), 122 (M^+ − PhH) and 91 ($C_7H_7^+$). (*c*) A mixture of thiophenol (0.110 g), sodium hydride (50% suspension in oil, washed with pentane; 0.050 g) in anhydrous THF was stirred under an atmosphere of argon at room temperature for 0.5 h. After the addition of triphenylbismuth dichloride (0.570 g) the mixture was heated at 60 °C for 18 h. Work-up and preparative t.l.c. (eluant hexane) of the residue, gave diphenyl disulphide (**66**) as a white solid (0.124 g, 99%), m.p. 57—59 °C (ethanol) (lit.,[27] 61 °C). After treatment with lithium aluminium hydride, no diphenyl sulphide was detected in the organic phase.

Phenylation of Indole by Tetraphenylbismuth Trifluoroacetate under Neutral Conditions.—Indole (0.117 g) and tetraphenylbismuth trifluoroacetate (0.950 g) in benzene (3 ml) were heated under reflux for 18 h. There was no apparent evolution of the reaction after 5 h. Chromatography using ether–hexane gradient elution gave Ph_3Bi (15%) *N*,3-diphenylindole (**74**) (2%), m.p. 99—101 °C (lit.,[28] m.p. 103—104 °C); δ($CDCl_3$) 7.9 (1 H, m, 2-H) and 7.5—7.0 (14 H, m, ArH); *m/z* 269 (M^+), indole (**73**) (51%) and 3-phenylindole (**75**) (43%), m.p. 88—89 °C (hexane) (lit.,[29] 88—89 °C) δ($CDCl_3$) 8.2—7.75 (1 H, m, 2-H), 7.6—6.6 (10 H, m, ArH and NH), *m/z* 193 (M^+). Acetylation with an excess of acetic anhydride and a trace of DMAP at room temperature overnight gave the *N*-acetyl derivative (**76**), m.p. 136—137 °C (hexane–CH_2Cl_2) (lit.,[30] 138—139 °C).

An authentic sample of 3-phenylindole (**75**) was synthesized by the Fischer procedure.[31] This indole, and its *N*-acetyl derivative were identical with the compounds mentioned above.

*Phenylation of Indole by Tetraphenylbismuth Toluene-*p*-sulphonate under Neutral Conditions.*—Indole (0.059 g) in benzene (2 ml) was heated in presence of tetraphenylbismuth toluene-*p*-sulphonate (1 g) at 60 °C for 24 h. Preparative t.l.c. [hexane–ether (9:1)] gave recovered indole (43%) and 3-phenylindole (**75**) (36%). There was almost no observable reaction when the above procedure was performed at room temperature; after 24 h the yield of compound (**75**) was only 6%.

*Phenylation of Indole under Basic Conditions using Tetraphenylbismuth Toluene-*p*-sulphonate.*—Indole (0.117 g) in tetrahydrofuran (4 ml) was agitated in the presence of sodium hydride (2.5 mmol) for 30 min. Tetraphenylbismuth toluene-*p*-sulphonate (1.4 g) was added and the agitation was continued at room temperature for 24 h. Column chromatography of the product using ether–hexane gradient elution gave triphenylbismuth (0.900 g, 97%), unchanged indole (23%), 3-phenylindole (**75**) (5%), and then 3,3-diphenyl-3*H*-indole (**74**) (61%), m.p. 90—93 °C (hexane–ether) (lit.,[32] m.p. 93—94 °C); δ($CDCl_3$) 8.32 (1 H, s, 2-H), 7.75—7.55 (1 H, m, 4-H), and 7.45—6.9 (13 H, m, ArH); *m/z* 269 (M^+) and 165 (PhN=C). Reduction at 15 °C using an excess of sodium cyanoborohydride gave (quantitatively) 3,3-diphenylindoline, m.p. 91 °C (hexane–ether) (lit.,[32] m.p. 91—92 °C).

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