parameters for the nonhydrogen atoms using block-diagonal least squares with unit weights led to an R of 0.094 for the 1567 nonzero reflections observed.

Reaction of 7 with Hg(OAc)$_2$ or HgCl$_2$. The reaction was carried out in a manner identical with that described in the reaction of 1 with HgX$_2$. The mercurials 8a (a, X = OAc) and 8b (b, X = Cl) were readily crystallized from methanol. 8a: 60% yield; mp 116–117 °C; IR (Nujol) 1610, 1480, 1420, 1370, 1295, 1260, 1230, 1200, 1183, 1165, 1155, 1100, 1047, 1015, 1003, 940, 920, 867, 827, 807, 740, 725, 680 cm^{-1}; NMR (100 MHz) δ (CDCl$_3$) 1.75–2.32 (m, 4 H), 2.02 (s, 3 H, OCOCH$_3$), 3.16 (m, 1 H, H$_3$), 3.96 (nearly triplet, 1 H, J = 7.5, H$_{8b}$), 5.55 (dd, 1 H, J = 7.5, 2 Hz and J(^{1}H–^{199}Hg) = 144 Hz, H$_{3a}$), 6.6–7.2 (m, 4 H, phenyl).

Anal. Calcd for C$_{13}$H$_{14}$HgO$_3$: C, 37.27; H, 3.38. Found: C, 37.19; H, 3.37.

8b: 65% yield; mp 164–165 °C; IR (Nujol) 1610, 1480, 1420, 1370, 1295, 1260, 1230, 1200, 1183, 1165, 1155, 1100, 1047, 1015, 1003, 940, 920, 867, 827, 807, 740, 725, 680 cm^{-1}; NMR (100 MHz) δ (CDCl$_3$) 1.5–2.4 (m, 4 H), 3.14 (m, 1 H), 3.96 (nearly triplet, 1 H, J = 7.5 Hz, H$_{8b}$), 5.54 (dd, 1 H, J = 7, 2.5 Hz and J(^{1}H–^{199}Hg) = 144 Hz, H$_{3a}$), 6.6–7.2 (m, 4 H, phenyl).

Anal. Calcd for C$_{11}$H$_{11}$OHgCl: C, 33.42; H, 2.81. Found: C, 33.38; H, 2.85.

Supplementary Material Available: Tables II and III, listing the final positional and thermal parameters for the nonhydrogen atoms, and Tables IV and V, listing the bond distances and bond angles (5 pages). Ordering information is given on any current masthead page.

Registry No.—1, 64252-19-3; **2a**, 64252-20-6; **2b**, 64252-21-7; **2e**, 64252-22-8; **2f**, 64252-23-9; **3a**, 64252-24-0; **3b**, 64252-25-1; **3c**, 64252-26-2; **3d**, 64252-27-3; **3e**, 64252-28-4; **3f**, 64252-29-5; **3g**, 64252-30-8; **3h**, 64252-31-9; **4**, 27124-68-1; **5**, 64252-32-0; **7**, 6627-83-4; **8a**, 64252-33-1; **8b**, 64252-34-2; 3-chlorocyclopentene, 96-40-2; phenol, 108-95-2; Hg(OAc)$_2$, 1600-27-7; HgCl$_2$, 7487-94-7; Hg(NO$_3$)$_2$, 10045-94-0; Hg(ClO$_4$)$_2$, 7616-83-3; Hg(OCOCH$_2$Cl)$_2$, 26719-07-3; Hg(OCOCHCl$_2$)$_2$, 26788-74-9; HgO, 21908-53-2; CCl$_3$COOH, 76-03-9; Hg(OCOCF$_3$)$_2$, 13257-51-7; AgOAc, 563-63-3.

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Addition Reaction of Benzene to α-Substituted Chalcone Derivatives by Means of Palladium(II) Acetate

Kimiaki Yamamura

College of General Education, Kobe University, Tsurukabuto, Nada, Kobe 657, Japan

The reaction of several α-substituted chalcone derivatives with benzene and acetic acid in the presence of palladium(II) acetate was investigated. When the α substituents are bulky and powerfully electron withdrawing, such as benzoyl, nitro, ethoxycarbonyl, and carboxyl groups, the addition of benzene to their carbon–carbon double bond occurs. The formation of the benzene adducts proceeded catalytically with respect to palladium(II) acetate. A mechanism involving the carbanion derived from heterolytic fission of the initially formed intermediate σ-palladium complex is suggested.

The aromatic substitution reaction of olefins by use of palladium(II) salts has received wide attention since Moritani and Fujiwara et al.[1] and Heck et al.[2] independently reported their pioneering work. In the previous work on the Moritani–Fujiwara arylation, the authors reported that electron-withdrawing groups such as a nitro on the olefinic carbon atom affect the arylation very strongly[3] and that β-substituted β-methylstyrenes did not give the usual phenylation compounds, but exclusively the corresponding β-diphenylmethylstyrenes because of a steric effect.[4] In the present paper is described a novel catalytic addition reaction of benzene to the carbon–carbon double bond of some α-substituted chalcones in the

Table I. Reaction of α-Substituted Chalcones with Benzene and Acetic Acid in the Presence of Palladium Acetate

Registry no.	α-Substituted chalcones		Reaction products, Yields, %[a]			
			Benzene adducts		Substituted compounds	
94-41-7	PhCH=CHCOPh	Ia			Ph₂C=CHCOPh	IIIa (74.8)
4023-77-2	PhCH=C(Ph)COPh	Ib			Ph₂C=C(Ph)COPh	IIIb (46.0)[b]
4258-37-1	PhCH=C(Me)COPh	Ic			PhCH=C(CHPh₂)COPh	IIIc (66.2)
6935-75-7	PhCH=C(Br)COPh	Id			Ph₂C=CHCOPh	IIIa (42.6)[c]
5398-64-1	PhCH=C(COPh)₂	Ie	Ph₂CHCH(COPh)₂	IIe (52.5)	Ph₂C=C(COPh)₂	IIIe (8.0)
60999-92-0	PhCH=C(NO₂)COPh	If	Ph₂CHCH(NO₂)COPh	IIf (20.2)	Ph₂C=C(NO₂)COPh	IIIf (5.1)
17451-18-2	PhCH=C(CO₂Et)COPh	Ig	Ph₂CHCH(CO₂Et)COPh	IIg (12.2)	Ph₂C=C(CO₂Et)COPh	IIIg (56.5)
64235-44-5	PhCH=C(CO₂H)COPh	Ih	Ph₂CHCH₂COPh	IIh (36.3)	Ph₂C=CHCOPh	IIIa (7.2)

[a] Yields are of isolated and purified products. [b] A 1.5-fold excess of palladium acetate per mole of Ib was used because palladium acetate was consumed in the cis–trans isomerization of Ib. [c] A small amount of IIIb also was isolated.

presence of palladium(II) acetate. In spite of the extensive studies of arylation by palladium(II) salts, no report dealing with such an addition reaction has appeared.

Results and Discussion

The reactions were carried out with a mixture of the α-substituted chalcone derivatives and an equimolar amount of palladium acetate in the presence of a large excess of benzene and acetic acid. The reaction mixture was refluxed with stirring until precipitation of black metallic palladium ceased. The results obtained are shown in Table I.

Chalcone (Ia) itself and α-phenylchalcone (Ib) gave the usual phenylated products, 1,1-diphenyl-2-benzoylethylene (IIIa) and 1,1,2-triphenyl-2-benzoylethylene (IIIb), respectively. α-Methylchalcone (Ic), as had been reported previously, gave (E)- and (Z)-α-diphenylmethylchalcone (IIIc) exclusively and the formation of these products can be illustrated by the repetition of the normal phenyl substitution.[4] With α-bromochalcone (Id), IIIa was obtained as the main product, together with trace of IIIb. This result can be explained by application of the mechanism for phenylation of β-bromo-β-nitrostyrene,[3] which included the usual phenyl-substitution step, followed by internal rearrangement via a π complex and subsequent elimination of *bromidopalladium acetate*.[5] All of these above four examples can be virtually regarded as phenyl-substitution reactions.

In contrast to these examples, α-benzoylchalcone (Ie) gave a colorless compound, C₂₈H₂₂O₂ (IIe), as a major product, accompanied by a small amount of phenyl-substituted product (IIIe). The structure of IIe was determined to be 1,1-diphenyl-2,2-dibenzoylethane by its NMR, IR, UV, and mass spectra and elemental analyses. IIe is regarded as the benzene adduct of Ie. As far as we know, this is the first example of addition of benzene to a carbon–carbon double bond being brought about by palladium salts. Likewise, α-nitrochalcone (If) and α-ethoxycarbonylchalcone(ethyl α-benzoylcinnamate) (Ig) give the corresponding benzene adducts (IIf and IIg), along with the usual phenyl-substituted products (IIIf and IIIg).


R = COC₆H₅, NO₂, COOC₂H₅
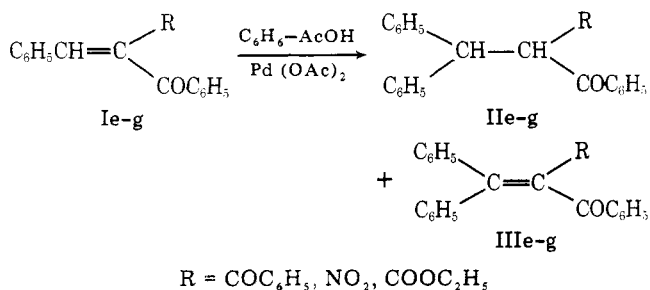
With α-carboxylchalcone(α-benzoylcinnamic acid) (Ih), the decarboxylated benzene adduct and phenyl-substituted compound, 1,1-diphenyl-2-benzoylethane (IIh) and IIIa, were

obtained. These products might be produced by decarboxylation of an initially formed benzene adduct (IV) and phenyl-substituted compound (V), since V, obtained by hydrolysis of IIIg, gave IIIa under the reaction conditions.[6]
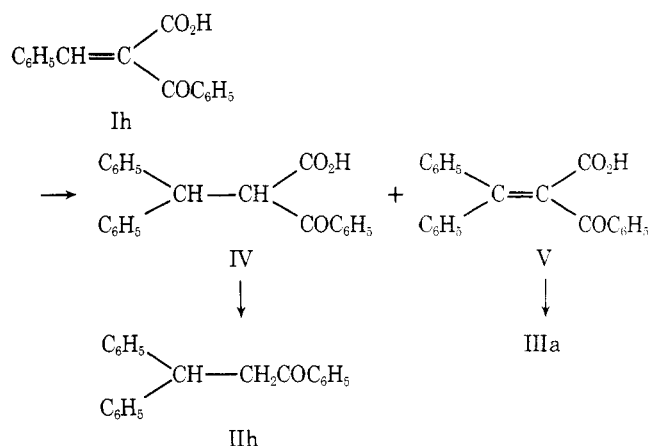
Similar decarboxylation with palladium salts was reported by Sakakibara et al. in the phenylation of cinnamic acid.[7] IIe–h could be regarded both as the benzene adducts of Ie–h and the reduction products of the corresponding usual phenyl-substituted compounds (IIIe–g and IIIa). However, reduction of the carbon–carbon double bond of IIIe–g and IIIa under the reaction conditions used seems unlikely, since IIIe was recovered unchanged when treated to the reaction conditions. Moreover, when Ie was treated with C₆D₆ and CH₃CO₂D under similar conditions, the hexadeuterio compound (II′e) was obtained instead of IIe.[8] The formation of
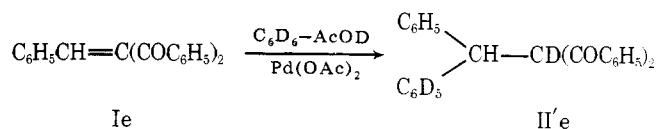

II′e indicated that fission of the olefinic hydrogen–carbon bond of Ie does not occur during the reaction. These findings suggest that the benzene adducts (IIe–h) were not derived from the usual phenyl-substituted compounds (IIIe–g and IIIa) but were formed by another type of reaction.

Heck has proposed a mechanism for arylation using palladium acetate and arylmercury compounds, in which the first step is cis addition of *arylpalladium acetate* to the olefinic double bond, this being followed by cis elimination of *hydridopalladium acetate*.[9] When this reaction mechanism is applied to the benzene addition reactions, the following reaction pathway can be proposed.

The initially formed intermediate σ complex (VI) derived from cis addition of *phenylpalladium acetate* to I is shown as A and/or B (for (E)-isomer of I). For cis elimination of *hydridopalladium acetate*, the favorable conformations of VI

Table II. The Catalytic Benzene Addition to Ie

Ie, mol	Pd(OAc)₂, mol	Yields of IIe, %
0.01	0.01	52.5 (52.5)[a]
0.01	0.005 (½)	53.5 (107)
0.01	0.0025 (¼)	54.4 (216)
0.01	0.00125 (⅛)	41.3 (330)
0.01	0.00063 (1/16)	33.4 (534)

[a] Based upon palladium acetate.

R = COC₆H₅, NO₂, CO₂C₂H₅, (CO₂H)
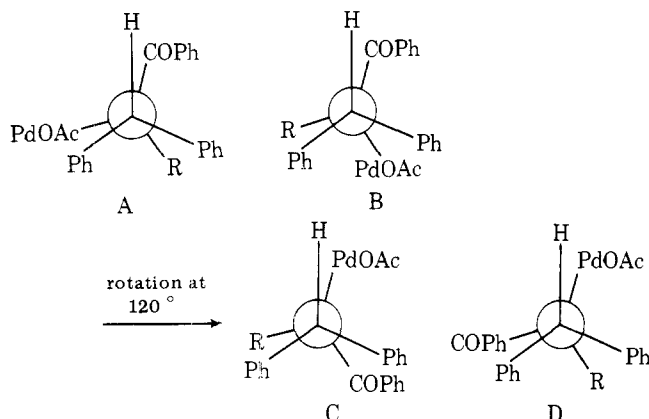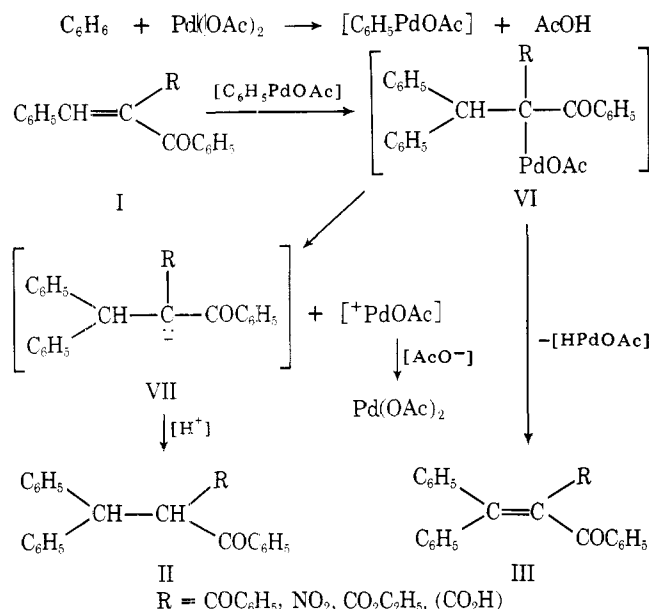
rotation at 120°

are C and/or D. For converting the former (A and/or B) into the latter (C and/or D) the rotation about the carbon–carbon bond of 120° is required. This rotation appears to be somewhat sterically restricted. Furthermore, it can be seen that the conformations shown in C and D are unstable because of severe steric hindrance. These steric factors would make the cis elimination of *hydridopalladium acetate* from VI to III difficult. Consequently, the heterolytic fission of the carbon–palladium σ bond to give a carbanion (VII)[10] and palladium acetate cation occurs in competition with cis elimination of *hydridopalladium acetate*. Attack of the solvent cation, H⁺, on the carbanion (VII) gives the benzene adduct (II), while the attack of the solvent anion, OAc⁻, on the palladium acetate cation results in regeneration of palladium acetate. If this mechanism is correct, palladium acetate should act catalytically in the formation of the benzene adduct (II), although palladium acetate must be consumed stoichiometrically for the generation of III and biphenyl,[11] forming metallic palladium. To confirm this possibility, Ie was treated with varying amounts of palladium acetate under similar conditions and the yields of IIe are shown in Table II. These experimental results indicate that about ¼ mol equiv of palladium acetate

relative to Ie is sufficient to allow this reaction to reach completion. A further consideration may be the possibility of homolytic fission of the carbon–palladium σ bond[12] of VI and attack of the produced radical on solvent to give II. However,
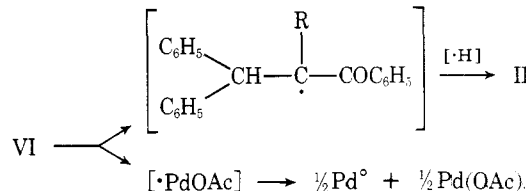
the fact that the yield of IIe based upon palladium acetate is over 200% is not explained by this mechanism.[13] Although the reduction of VI by *hydridopalladium acetate,* generated in the formation of III, is considered,[14] this mechanism can also be ruled out by the fact of the overwhelming formation of IIe compared with IIIe from Ie.[13]

Inoue et al. reported that when some benzocycloalkenes were treated with *phenylpalladium chloride* in protic solvent the phenyl group and an anion part of the solvent added to the olefins simultaneously, because of steric inhibition for cis elimination of *hydridopalladium chloride* (oxyphenylation).[15] In contrast with the oxyphenylation found by Inoue et al., the benzene addition reaction can be attributed to both steric and electronic factors.

It may be concluded that two bulky, electron-withdrawing groups (benzoyl and other groups) on the same carbon atom make the benzene addition reaction possible and that the reaction may proceed through the carbanion derived from an initially formed σ-palladium complex.

Experimental Section

All the melting points are uncorrected. IR spectra were recorded on a Nihonbunko DS-701G spectrometer, and NMR spectra were determined with a Hitachi R-24A spectrometer in CDCl₃ using Me₄Si as an internal reference.

Materials. Palladium acetate was prepared according to the method of Stephenson et al.[16] Chalcone (Ia) was commercially available. α-Phenylchalcone (Ib),[17] α-methylchalcone (Ic),[18] α-bromochalcone (Id),[19] α-benzoylchalcone (Ie),[20] α-nitrochalcone (If),[21] and α-ethoxycarbonylchalcone (Ig)[22] were prepared as described in the literature. α-Carboxylchalcone (Ih) and β,β-diphenyl-α-benzoylacrylic acid (V) were obtained by hydrolysis of Ig and IIIg, respectively; Ih: mp 158 °C; V: mp 144 °C.

General Procedure for the Reaction of α-Substituted Chalcone with Benzene and Acetic Acid in the Presence of Palladium Acetate. A mixture of the α-substituted chalcone (0.01 mol) and palladium acetate (0.01 mol) in 150 mL of benzene and 40 mL of acetic acid was refluxed with stirring until the precipitation of metallic palladium ceased. After filtration of the palladium metal, the mixture was washed with water and the solvent was evaporated in vacuo. The residue was chromatographed on silica gel. Elution with hexane gave a small amount of biphenyl; subsequent elution with hexane–benzene (1:1) gave the phenylated compounds. The structures of IIIa and IIIb were confirmed by comparison with authentic samples. The physical data for IIIc have been reported in a previous paper.[4] The physical properties of IIe, IIf, IIh, IIIe, IIIf, and IIIg are given below.

IIe: mp 227 °C; IR (KBr) 1693, 1662, 1599, 1449, 1265, 749, 700 cm⁻¹; NMR (CDCl₃) δ 8.05–7.00 (m, 20 H, phenyl), 6.34 (d, 1 H, methine, *J* = 12 Hz), 5.33 (d, 1 H, methine). Found: C, 86.21; H, 5.60.

IIf: mp 145 °C; IR (KBr) 1680, 1553, 1453, 1358, 1297, 767, 701 cm⁻¹; NMR (CDCl₃) δ 8.00–7.00 (m, 15 H, phenyl), 7.04 (d, 1 H, methine, *J* = 12 Hz), 5.30 (d, 1 H, methine). Found: C, 76.13; H, 5.14; N, 4.26.

IIg: mp 139 °C; IR (KBr) 1739, 1675, 1445, 1212, 1150, 737, 701 cm⁻¹; NMR (CDCl₃) δ 8.05–7.00 (m, 15 H, phenyl), 5.42 (d, 1 H, methine, *J* = 6 Hz), 5.06 (d, 1 H, methine), 3.90 (q, 2 H, methylene, *J* = 6 Hz), 0.91 (t, 3 H, methyl). Found: C, 80.22; H, 6.24.

IIh: mp 95 °C; IR (KBr) 1672, 1593, 1492, 1447, 1375, 748, 701 cm⁻¹; NMR (CDCl₃) δ 8.00–7.14 (m, 15 H, phenyl), 4.80 (t, 1 H, methine, *J* = 7.0 Hz), 3.69 (d, 2 H, methylene). Found: C, 88.18; H, 6.30.

IIIe: mp 158 °C; IR (KBr) 1663, 1633, 1597, 1445, 1253, 900, 695 cm⁻¹; NMR (CDCl₃) δ 8.00–7.16 (m, 20 H, phenyl). Found: C, 86.40; H, 5.30.

IIIf: mp 122 °C; IR (KBr) 1643, 1595, 1522, 1445, 1344, 780, 690 cm^{-1}; NMR (CDCl$_3$) δ 7.90–7.08 (m, 15 H, phenyl). Found: C, 76.70; H, 4.58; N, 4.20.

IIIg: mp 116 °C; IR (KBr) 1731, 1645, 1449, 1233, 1107, 778, 700 cm^{-1}; NMR (CDCl$_3$) δ 7.95–7.10 (m, 15 H, phenyl), 4.03 (q, 2 H, methylene, J = 7 Hz), 0.93 (t, 3 H, methyl). Found: C, 80.95; H, 5.60.

Registry No.—IIe, 60999-93-1; IIf, 60999-95-3; IIg, 60999-96-4; IIh, 606-86-0; IIIe, 60999-94-2; IIIf, 60999-97-5; IIIg, 61024-39-3; V, 64235-45-6; benzene, 71-43-2; Pd(OAc)$_2$, 3375-31-3.

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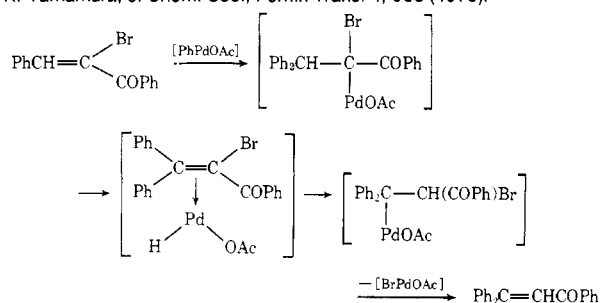
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(14) According to this mechanism (vida infra), the yield of the saturated compounds should be lower than those of the olefinic compounds.

$$RCH_2CH_2M \rightarrow RCH\!=\!CH_2 + [M\text{-}H]$$

$$RCH_2CH_2M + [M\text{-}H] \rightarrow RCH_2CH_3 + 2M$$
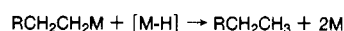
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A Synthesis of *trans*-15-*n*-Butyl-16-methyldihydropyrene. Synthetic Access to 1,2,3-Trisubstituted Benzene Derivatives via Direct Alkylation of 1,3-Bis(4',4'-dimethyl-2'-oxazolinyl)benzene

Thomas D. Harris, Brent Neuschwander, and Virgil Boekelheide*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

A convenient general synthesis of 15,16-dihydropyrenes requires easy access to 1,2,3-trisubstituted benzene derivatives having appropriate functionality. It is now shown that isophthalic acid on conversion to 1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene (1), followed by alkylation of the corresponding anion, gives the 2-alkyl derivatives 3 and 4 in high yield. Similarly, alkylation of the anion of 2,6-bis(4',4'-dimethyl-2'-oxazolinyl)toluene (3) occurs smoothly to give 2-substituted 1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene derivatives (8 or 9). The hydrolysis of 2-*n*-butyl-1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene (8) to 2-*n*-butylisophthalic acid and its subsequent conversion to dithiacyclophane 13 followed by a Wittig rearrangement and a Hofmann elimination to give *trans*-15-*n*-butyl-16-methyldihydropyrene (15) are described.

The route involving synthesis of dithiacyclophanes,[1-4] followed by elimination of sulfur to give cyclophanes,[5-9] cyclophanedienes,[10-12] and dihydropyrenes,[1] has proved to be an extremely useful method. The general application of this method, though, requires the availability of 1,2,3-trisubstituted benzene derivatives with appropriate functionality as starting materials. For the important case requiring 2,6-bis(bromomethyl)toluene, this starting compound can be made in a reasonable fashion from commercial chemicals. However, for other examples, where the internal substituents of the target dihydropyrenes are varied, the synthesis of the requisite starting materials is a tedious chore.[13] We now describe a method of alkylating aromatic rings which provides 1,2,3-trisubstituted benzene derivatives conveniently and in high yield.

Metalation of anisoles followed by reaction with an electrophile has been a useful synthetic procedure and recent developments of this method have been summarized in a series of papers by Slocum.[14] The extensive studies of Meyers on aryloxazolines led to the discovery that the reaction of *o*-methoxyaryloxazolines with Grignard reagents and organolithium compounds results in the displacement of the methoxyl by alkyl or aryl substituents.[15] Gschwend and Hamdan showed that the reaction of simple aryloxazolines with alkyllithium reagents followed by treatment with an electrophile leads to introduction of the electrophilic substituent ortho to the oxazoline group.[16] Furthermore, *o*-methylaryloxazolines on reaction with *n*-butyllithium followed by reaction with an electrophile generates a product in which the electrophilic substituent is attached to the methyl group. Subsequently, Gschwend et al. extended this method to show that *N,N*-dimethylbenzamides can be readily converted to ortho-substituted aryl ketones.[17]

It appeared to us that the oxazoline ring served two func-