ene, 54985-30-7; (*E*)-1-phenyl-4-hydroxy-1-hexene, 54985-35-2; tosylhydrazine, 1576-35-8; 3-methyl-2-butanone, 563-80-4; pinacolone, 75-97-8; acetone, 67-64-1; 2-butanone, 78-93-3; cyclohexanone, 108-94-1; phenylacetone, 103-79-7; acetophenone, 98-86-2; cyclopentanone, 120-92-3; cyclopentanone tosylhydrazone, 17529-98-5; ethyl chloroformate, 541-41-3; (*Z*)-2-carboethoxycyclopentanone tosylhydrazone, 64884-90-8; (*E*)-2-carboethoxycyclopentanone tosylhydrazone, 64884-91-9.

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Studies on Selective Preparation of Aromatic Compounds. 15. The Lewis Acid Catalyzed Transalkylation of Some *tert*-Butyldiphenylmethanes and -ethanes in Aromatic Solvents[1]

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The Lewis acid catalyzed transalkylation of *tert*-butyl derivatives of diphenylmethanes (**2a–f**) and -ethanes (**25a–g**) in benzene or toluene was carried out under various conditions. It was found in the transalkylation of **2** that the $AlCl_3$–CH_3NO_2 catalyzed transbenzylation with trans-*tert*-butylation was observed and the $TiCl_4$ transbenzylation of electron-rich *tert*-butyldiphenylmethanes having highly steric crowdedness such as 2,2′,6,6′-tetramethyl- (**2d**) and 2,2′,3,3′-tetramethyldiphenylmethane (**2f**) took place without trans-*tert*-butylation. However, no $AlCl_3$–CH_3NO_2 catalyzed transalkylation of **25** was observed and only trans-*tert*-butylation in benzene took place to afford the desired 2,2′-dimethyl-(**27b**), 2,2′-diethyl-(**27c**), 2,2′-dimethoxy-(**27d**), 2,2′,3,3′-tetramethyl-(**27e**), and 2,2′,6,6′-tetramethyldiphenylethane (**27f**). Based on the above result it could be concluded that *tert*-butyl group can be used as a positional protective group for the preparation of some diphenylethanes but not diphenylmethanes.

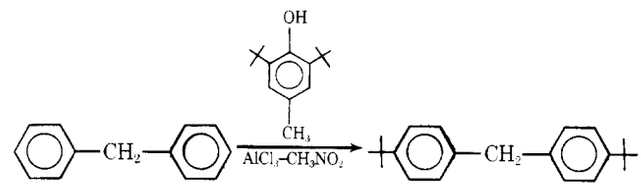
Although $AlCl_3$–CH_3NO_2 does not catalyze the transbenzylation and isomerization of diphenylmethanes,[2-8] it catalyzes transbenzylation of some 4,4′-dihydroxydiphenylmethane derivatives in toluene as was recently reported.[9]

We undertook the present study to obtain more detailed information about factors influencing the above novel transbenzylation of diphenylmethanes and in general to gain a better understanding of the mechanism of transalkylation.

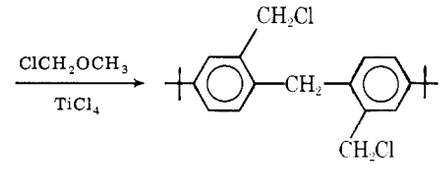
Results and Discussion

Preparation of Some *tert*-Butyldiphenylmethanes. The $AlCl_3$–CH_3NO_2 catalyzed *tert*-butylation of diphenylmethane (**1**) with 2,6-di-*tert*-butyl-*p*-cresol[10] afforded 4,4′-di-*tert*-butyldiphenylmethane (**2a**) in good yield. 4,4′-Di-*tert*-butyl-2,2′-dimethyldiphenylmethane (**2b**) was prepared from **2a** via **3.** The chloromethylation of 4-*tert*-butyltoluene (**4a**) and 5-*tert*-butyl-1,3-dimethyl- (**4b**) and 4-*tert*-butyl-1,2-dimethylbenzene (**4c**) afforded the corresponding 5-*tert*-butyl-2-methyl- (**5a**), 4-*tert*-butyl-2,6-dimethyl- (**5b**), and 5-*tert*-butyl-2,3-dimethylbenzyl chloride (**5c**), respectively, in good yields.

In the $TiCl_4$ catalyzed benzylation of **4a, 4b,** and **4c** with the chlorides, 5,5′-di-*tert*-butyl-2,2′-dimethyl- (**2c**), 4,4′-di-*tert*-butyl-2,2′,6,6′-tetramethyl- (**2d**), 4,5′-di-*tert*-butyl-



1 **2a**



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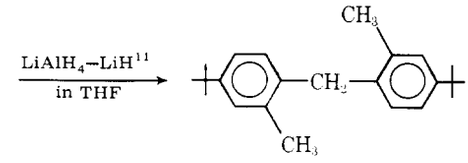
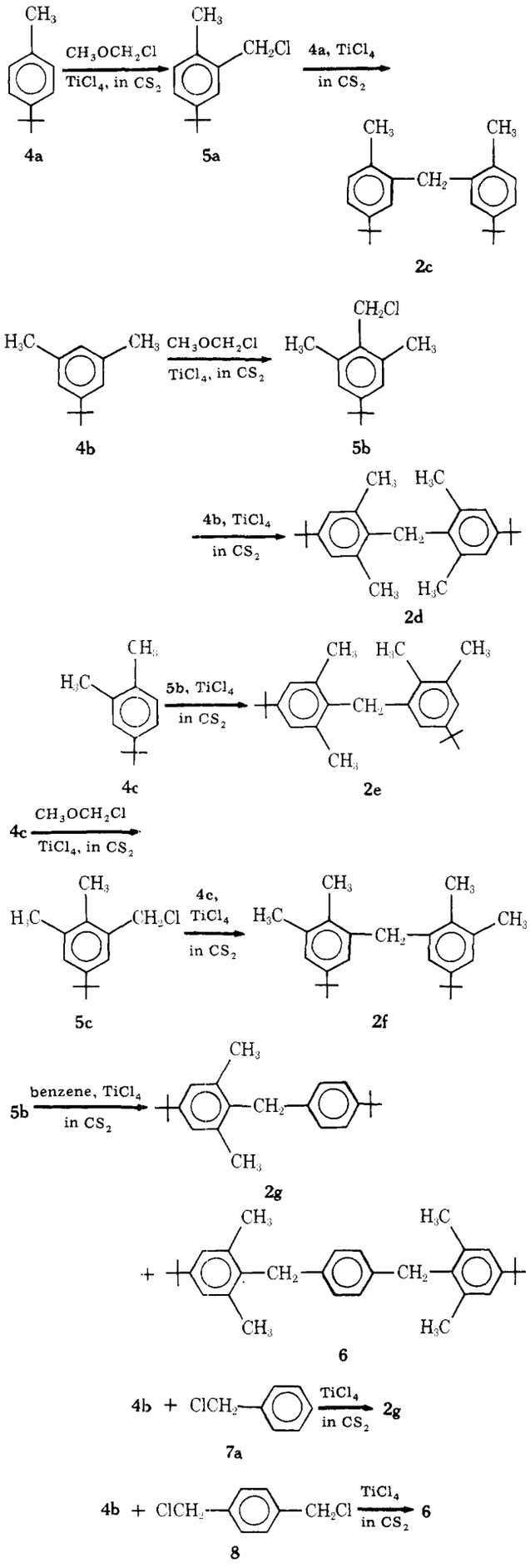


2b

0022-3263/78/1943-1413$01.00/0

Scheme I

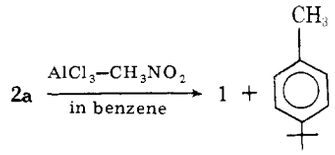


2,2′,3′,6-tetramethyl- (**2e**), and 5,5′-di-*tert*-butyl-2,2′,3,3′-tetramethyldiphenylmethane (**2f**) were obtained in good yields (Scheme I).

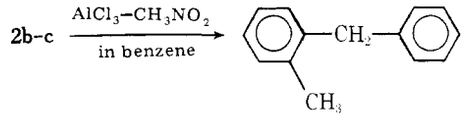
However, the expected product, 4-*tert*-butyl-2,6-dimethyldiphenylmethane (**2g**), in the benzylation of benzene with **5b** was formed in only 43% yield with formation of 1,4-bis(4-*tert*-butyl-2,6-dimethylbenzyl)benzene (**6**) in 50% yield even in excess benzene.

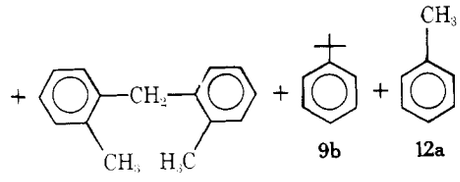
The compounds **2g** and **6** were also obtained by the $TiCl_4$ catalyzed benzylation of **4b** with benzyl chloride (**7a**) and 1,4-bis(chloromethyl)benzene (**8**) in 93 and 60% yields, respectively.

Transalkylation of 2. The Lewis acid catalyzed transalkylation of **2** was carried out under various conditions and the results are summarized in Table I. The *tert*-butyl group is transferred from **2a** to toluene.



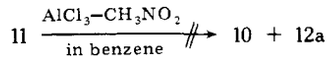
This result suggests that the trans-*tert*-butylation occurred selectively without the transbenzylation as expected from the previous papers.[2-8] However, the $AlCl_3$–CH_3NO_2 catalyzed transalkylation of **2b** and **2c** in benzene afforded 2-methyldiphenylmethane (**10**) and toluene (**12a**) besides the expected products 2,2′-dimethyldiphenylmethane (**11**) and *tert*-butylbenzene (**9b**). These results show clearly that the transbenzylation and trans-*tert*-butylation of **2b** and **2c** took place simultaneously to afford **10** and **11**.

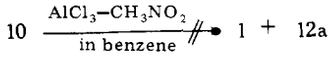




The latter compound **11** seems to be the intermediate in the formation of the former **10** and **12a.**

However, when **11** or **10** was treated under same conditions, only the starting compound **10** or **11** was recovered in quantitative yield.





Although intermediates **13** and **14** could not be isolated when **2b** and **2c** were transalkylated, the reaction pathways in Scheme II might be proposed.

In fact, the $AlCl_3$–CH_3NO_2 catalyzed reaction of **14b,** which was prepared by the benzylation of **4a** with 2-methylbenzyl chloride (**7b**), afforded **10** and **11** in 81.1 and 10.3% yields.

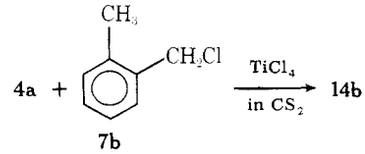
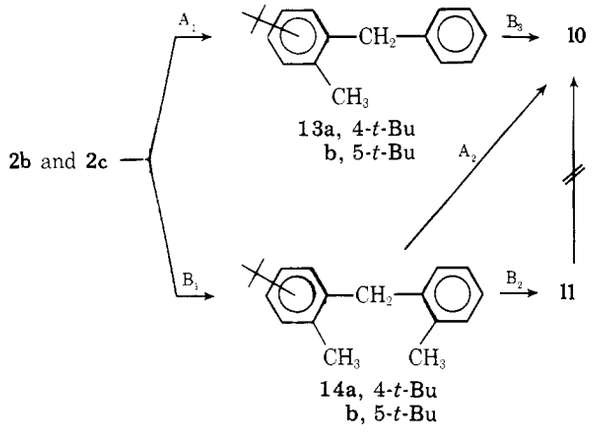


Table I. The Lewis Acid Catalyzed Transalkylation of 2[a]

Run	Substrate	Catalyst[b]	Solvent	Time, h	Product (%)[c]
1	**2a**	A	Toluene	3	**1** (100), **9a** (100)
2	**2a**	B	Toluene	3	No reaction
3	**2b**	A	Benzene	0.5	**10** (75), **11** (25), **9b** (100), **12a** (75)
4	**2b**	B	Benzene	3	No reaction
5	**2c**	A	Benzene	0.5	**10** (40), **11** (60), **9b** (100), **12a** (75)
6	**2c**	B	Benzene	3	No reaction
7	**2d**	A	Benzene	3	**16** (80), **1** (20), **9b** (100), **12b** (80)
8	**2d**	B	Benzene	3	**2g** (89), **4b** (77)
9	**2d**	B	Toluene	2	**18** (93), **4b** (95), **9a** (90)
10	**2d**	B	*m*-Xylene	0.5	**19** (99), **4b** (90)
11	**2d**	C	Toluene	5	No reaction
12	**2d**	C	*m*-Xylene	5	No reaction
13	**2e**	B	Benzene	3	**21** (73), **2g** (23), **4b** (70), **4c** (30)
14	**2f**	A	Benzene	3	**22** (75), **9b** (80), **12b** (78)
15[d]	**2f**	B	Benzene	3	**21** (20), **23** (40), **9a** (38), **4b** (22), 1 (+)[e]
16	**2g**	A	Benzene	1.5	**16** (88), **1** (12), **9b** (100)
17	**14b**	A	Benzene	1	**11** (81), **10** (10), **9b** (100), **12a** (10)
18	**21**	A	Benzene	1.5	**22** (97), **1** (3), **9b** (100)

[a] Reaction temperature, 50 °C; solvent/**2**, 30 mol/l mol; catalyst/**2**, 0.2 mol/l mol. [b] A, $AlCl_3$–CH_3NO_2; B, $TiCl_4$; C, $SnCl_4$. [c] The yields were determined by GC analyses. [d] **2f** was recovered in 40% yield. [e] Plus sign (+) means a trace amount (<1%).

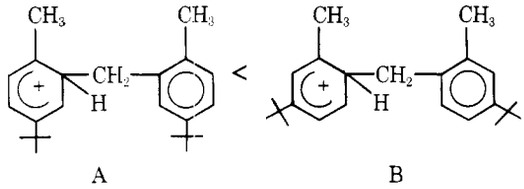
Scheme II



A: transbenzylation
B: trans-*tert*-butylation

The $AlCl_3$–CH_3NO_2 catalyzed transalkylation of **2b** afforded **10** and **11** in 75 and 25% yields, but the reaction of **2c** gave the same products in different yields, that is, 40 and 60% yields, respectively.

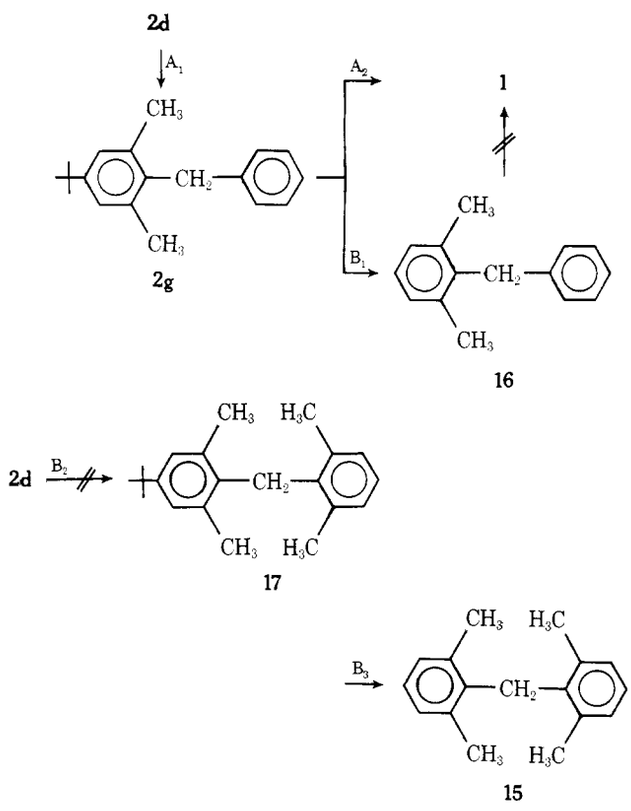
The relative rate of transbenzylation of **2b** and **2c** might be dependent upon the relative stabilities of the corresponding α complex A and B. The latter complex might be more stable than the former one.



In the $AlCl_3$–CH_3NO_2 catalyzed transalkylation of **2d** in benzene, an expected product, 2,2′,6,6′-tetramethyldiphenylmethane (**15**), was not obtained, but 2,6-dimethyldiphenylmethane (**16**), **1**, **9b**, and *m*-xylene (**12b**) were formed.

The transalkylation of **2g** in benzene afforded **1** and **16** in 20 and 80% yields. However, when **16** was treated with the catalyst only starting material was recovered. Based on the above results the reaction pathways in Scheme III are proposed.

Scheme III



A: transbenzylation
B: trans-*tert*-butylation

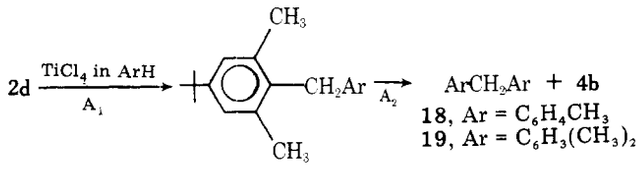
At the first step, transbenzylation (A_1) rather than the trans-*tert*-butylation (B_2) might selectively take place to afford **2g**, which gave **1** by the second transbenzylation (A_2) and **16** by the trans-*tert*-butylation (B_1), respectively. The former reaction (A_2) was less predominant than the latter reaction (B_1).

In contrast to the case of **2a**, **2b**, and **2c**, the $TiCl_4$ catalyzed transalkylation of **2d** in benzene afforded, surprisingly, only **2g** and **4b** in good yields.

$$\mathbf{2d} \xrightarrow[\text{in benzene}]{TiCl_4} \mathbf{2g} + \mathbf{4b}$$

This finding means that only the transbenzylation (A_1) of **2d** occurred selectively without the trans-*tert*-butylation (B_2) under the conditions used, and it also seems to support the proposed reaction pathway of Scheme III.

However, $SnCl_4$ did not show any activity for the transalkylation of **2d.** When toluene and *m*-xylene were used in place of benzene as a solvent and acceptor of alkyl groups in the $TiCl_4$ catalyzed transalkylation of **2d,** ditolylmethanes (**18**) and 2,2′,4,4′-tetramethyldiphenylmethane (**19**) were obtained in good yields, respectively.



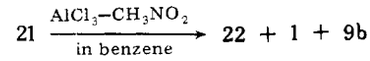
20

In these cases, not only the first-step transbenzylation (A_1) but also the second one (A_2) might easily occur, since toluene and *m*-xylene are stronger Lewis bases than benzene.

In the $TiCl_4$ catalyzed transbenzylation of **2e,** the formation of **2g** and 5-*tert*-butyl-2,3-dimethyldiphenylmethane (**21**) might be expected (Scheme IV). In fact, the reaction afforded **21, 4b, 2g,** and **4c** in 73, 27, 70, and 30% yields. The above result suggests that the transbenzylation A_1 was a more predominant reaction than the A_2, probably because the A_1 should reduce the steric hindrance of **2e** to a higher degree than A_2 should.

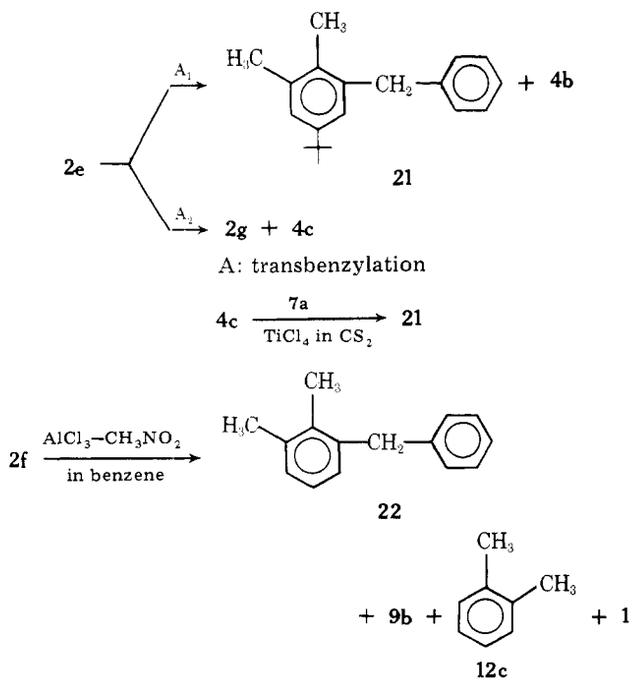
When **2f** was treated with $AlCl_3$–CH_3NO_2 catalyst in benzene, 2,3-dimethyldiphenylmethane (**22**) was obtained in 75% yield with a small amount of **1.**

The $AlCl_3$–CH_3NO_2 catalyzed transalkylation of **21** in benzene afforded **22, 1,** and **9b** in 97.3, 2.7, and 100% yields, respectively.

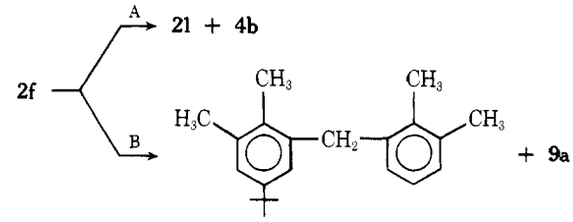


The $TiCl_4$ catalyzed transalkylation of **2f,** as well as **2d** and **2e,** afforded a transbenzylated product **21** and **4b.** However, a considerable amount of **2f** was recovered and the unexpected

Scheme IV



Scheme V



23

A: transbenzylation
B: trans-*tert*-butylation

product, 5-*tert*-butyl-2,2′,3,3′-tetramethyldiphenylmethane (**23**), was also obtained in a low yield (Scheme V).

The crowdedness of the methyl groups of **2f** seems to be less than that of **2d** and **2e.** Consequently the above results might indicate that the steric factor should strongly influence the ease of the transbenzylation of diphenylmethanes.

The results obtained in the above transalkylation of **2** seem to strongly support the mechanisms proposed[9] previously for the transalkylation of 4,4′-dihydroxydiphenylmethanes.

Preparation of *tert*-Butyldiphenylethane (25). The *tert*-butyldiphenylethanes (**25b–g**) with the exception of 4,4′-di-*tert*-butyldiphenylethane (**25a**) were prepared by the coupling reaction[12] using CH_3MgI reagent and the corresponding benzyl chlorides (**5a–g**) (Scheme VI). In some coupling reactions, besides the expected product **25,** *tert*-butylethylbenzenes (**26**) were formed as byproducts. The yields of **25** and **26** are summarized in Table II.

Only **25a** was prepared by the $AlCl_3$–CH_3NO_2 catalyzed *tert*-butylation of diphenylethane (**24**) with 2,6-di-*tert*-butyl-*p*-cresol according to the previously reported method.[10]

The Transalkylation of 25. The Lewis acid catalyzed transalkylation of **25** (Scheme VII) was carried out under various conditions and the results are summarized in Table III.

The $AlCl_3$–CH_3NO_2 and $TiCl_4$ catalyzed transalkylation of **25a** in toluene afforded **24** and 4-*tert*-butyltoluene (**9a**) in good yields. The former catalyst was active for the trans-*tert*-butylation of **2a,** but not the latter one as described above.

The result of the $TiCl_4$ catalyzed trans-*tert*-butylation of **25a** might suggest that the basicity of **25a** should be stronger than that of **2a.**

In contrast to both catalysts, $AlCl_3$ afforded a small amount of ditolylethane (**28**), **24a,** benzene (**12d**), and **9a** with a large amount of resinous material and unidentified compounds.

The result might indicate that $AlCl_3$ was too strong to use as a catalyst for the preparation of **27.** The $AlCl_3$–CH_3NO_2 catalyzed transalkylation of **25b** afforded the expected products **27b** and **9b** in good yields, while the corresponding diphenylmethane derivative gave trans-*tert*-butylated and transbenzylated products as previously described.

Table II. The Coupling Reaction of 1 Using CH_3MgI Reagent in Ether Solution[a]

Run	Chloride	Product (%)
1	**5a**	**25b** (72), **26b** (13)
2	**5d**	**25c** (87), **26c** (17)
3	**5e**	**25d** (63), **26d** (20)
4	**5c**	**25e** (75), **26e** (0)
5	**5b**	**25f** (89), **26f** (11)
6	**5f**	**25g** (70), **26g** (0)
7	**5g**	**25h** (71), **26h** (0)

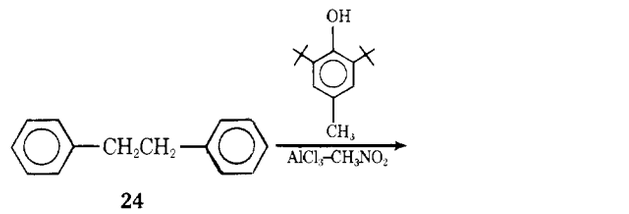
[a] Reaction temperature, reflux; reaction time, 1 h.

Table III. The Lewis Acid Catalyzed Transalkylation of 25[a]

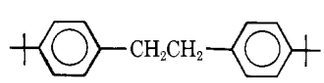
Run	Substrate	Catalyst[b]	Solvent	Time, h	Product (%)[c]
1[d]	**25a**	A	Toluene	3	**24** (84),[g] **9a** (90)
2[e]	**25a**	B	Toluene	6	**24** (80),[g] **9a** (95)
3[f]	**25a**	C	Toluene	0.5	**28** (12), **12c** (31), **24a** (5), **9a** (52)
4	**25b**	A	Benzene	2	**27b** (90),[g] **9b** (100)
5	**25c**	B	Benzene	8	**27b** (11), **9b** (35)
6	**25d**	A	Benzene	5	**27c** (70),[g] **9b** (80)
7	**25d**	A	Benzene	6	**27d** (63),[g] **9b** (88)
8	**25d**	B	Benzene	9	No reaction
9	**25e**	A	Benzene	1	**27e** (99),[g] **9b** (100)
10	**25e**	B	Benzene	3	**27e** (100),[g] **9b** (100)
11	**25f**	A	Benzene	1	**27f** (95),[g] **9b** (100)
12	**25f**	B	Benzene	3	**27f** (96),[g] **9b** (100)
13	**25g**	A	Benzene	5	No reaction
14	**25g**	C	Benzene	0.25	**27g** (97),[g] **9b** (100)

[a] Reaction temperature, 50 °C; catalyst/**25**, 0.2 mol/l mol. [b] A, $AlCl_3$–CH_3NO_2; B, $TiCl_4$; C, $AlCl_3$. [c] The yields were determined by gas chromatographic analyses unless otherwise indicated. [d] **25a** was recovered in 16% yield. [e] **25a** was recovered in 20% yield. [f] The large amount of resinous materials and unidentified compounds were formed. [g] The yields isolated are shown.

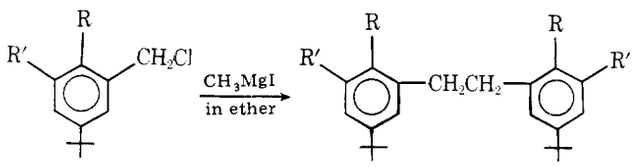
Scheme VI



24



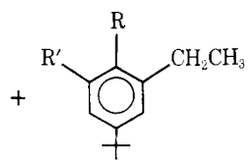
25a



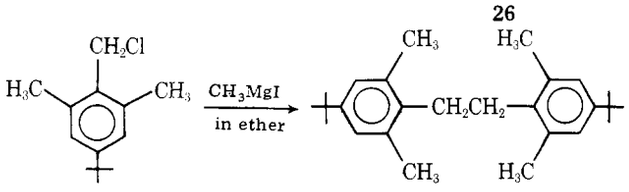
5 **25**

5a, R′ = H; R = CH_3
c, R′ = R = CH_3
d, R′ = H; R = C_2H_5
e, R′ = H; R = OCH_3
f, R′ = H; R = Cl
g, R′ = H; R = Br

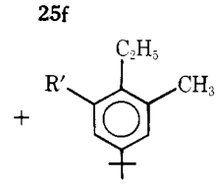
b, R′ = H; R = CH_3
c, R′ = H; R = C_2H_5
d, R′ = H; R = OCH_3
e, R′ = R = CH_3
g, R′ = H; R = Cl
h, R′ = H; R = Br



26



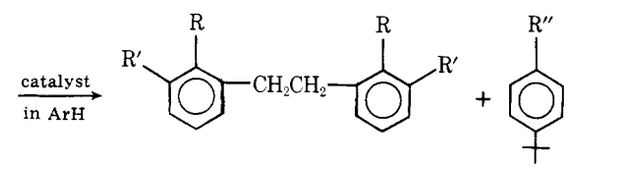
5b **25f**



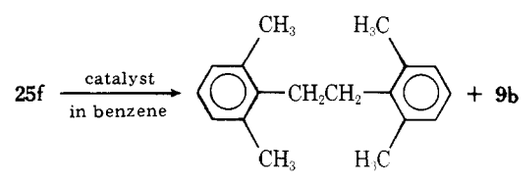
26f

Scheme VII

25a–e and **25g–h**

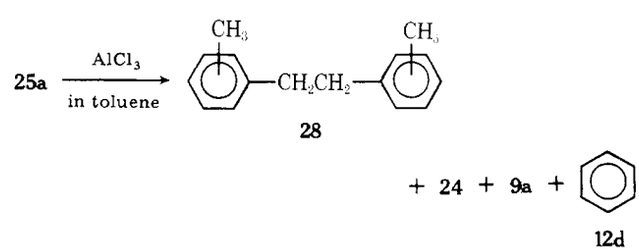


27a, R′ = R = H (**24**) **9a**, R″ = CH_3
b, R′ = H; R = CH_3 **b**, R″ = H
c, R′ = H; R = C_2H_5 **c**, R″ = 2,4-$(CH_3)_2$
d, R = H; R = OCH_3
e, R′ = R = CH_3
g, R′ = H; R = Cl
h, R′ = H; R = Br



27f

The $TiCl_4$ catalyzed transalkylation of **25b** gave also **27b** and **9b** in low yields, but the catalyst was not active for the transalkylation of **2c**.



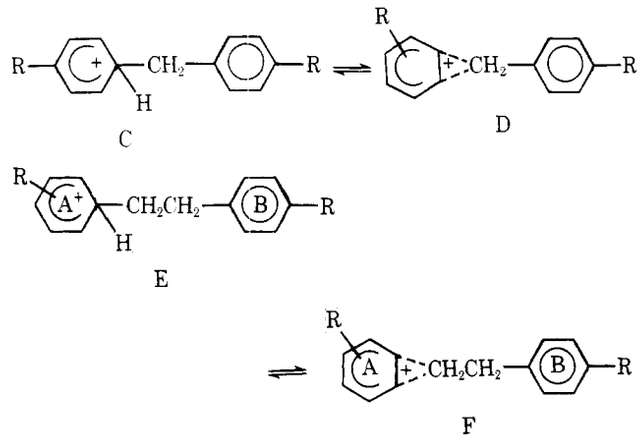
28 **12d**

The $AlCl_3$–CH_3NO_2 catalyzed reactions of **25c, 25d, 25e,** and **25f** as well as **25a** and **25b** afforded the expected products **27c, 27d, 27e,** and **27f,** respectively.

However, in the case of **25d,** a large amount of the catalyst had to be used in order to obtain **27d** in good yield. The catalyst might react with the methoxy group of **25d** and **27d** to form a complex which reduce the catalytic activity and the basicity of **25d.** No observation of the $TiCl_4$ catalyzed transalkylation of **25d** might be explained for the same reason, since the $TiCl_4$ seems to be a weaker catalyst than $AlCl_3$–CH_3NO_2.

It should be noted that although $TiCl_4$ catalyzed the transalkylation of **2d** as mentioned above, the same reaction of **25f** gave only trans-*tert*-butylated product **27f.** In addition, the $AlCl_3$–CH_3NO_2 catalyzed transalkylation of **25f** gave also **27f** without the formation of any amount of the transaralkylated product. The above results might support, although not directly, the previous proposed mechanisms[9] of the transbenzylation of 4,4′-dihydroxydiphenylmethanes; that is, the intermediate D would be more important than the intermediate C for the occurrence of transbenzylation reaction.

However, even in the electron-rich diphenylethanes such as **27e** and **27f,** the substituent R on the ring B could not stabilize the σ-complex E and even π-complex F, in which the screen effect of the methylene group might take a negative role for the stabilization in contrast to D.



The $AlCl_3$–CH_3NO_2 catalyzed transalkylation of the electron-poor diphenylethane such as **25g** and **25h** did not afford any product, but the starting materials were recovered in almost quantitative yields. However, the $AlCl_3$ catalyzed transalkylation of **25g** afforded **27g** in good yield. In contrast to the case of **25g,** the $AlCl_3$ catalyzed transalkylation of **25h** gave only a small amount of **27h,** which could be detected by GC analyses but not isolated.

Based on the results obtained in the present study it could be concluded that: (i) the $AlCl_3$–CH_3NO_2 catalyzed transbenzylation of the electron-rich diphenylmethanes such as **2b–f** was observed; (ii) the transbenzylation of the electron-rich *tert*-butyldiphenylmethane having highly steric hindrance was easily catalyzed by even a weak catalyst like $TiCl_4$ without the trans-*tert*-butylation but not by $SnCl_4$; (iii) the $AlCl_3$–CH_3NO_2 catalyzed transalkylation of the electron-rich diphenylmethanes in benzene solution afforded only the first-step transbenzylated compound as a main product; (iv) however, when toluene and *m*-xylene were used as a solvent and acceptor in the transbenzylation of the electron-rich diphenylmethanes, the completely transbenzylated product was formed; (v) the $AlCl_3$–CH_3NO_2 catalyzed transbenzylation of the electron-poor diphenylmethanes was not observed; (vi) the alkyl, methoxy, and chloro substituted diphenylethanes such as **27b–g** could be prepared by using the *tert*-butyl group as a positional protective group; (vii) in contrast to diphenylmethanes, even the electron-rich diphenylethanes did not afford any transaralkylated product under the influence of $AlCl_3$–CH_3NO_2 catalyst; (viii) *tert*-butyldiphenylethanes seem to be higher basic compounds than *tert*-butyldiphenylmethanes, so that the former might be easily protonated by the weak Lewis acid such as $TiCl_4$ catalyst to afford the trans-*tert*-butylated product.

Experimental Section

All melting and boiling points are uncorrected. Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet (isomerization energy 70 eV). NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with Me_4Si and internal references and IR spectra were measured as KBr pellets or liquid film on NaCl plates on a Nippon Bunko IR-S spectrometer.

Analytical Procedure. The analyses were carried out by gas chromatography using a Yanagimoto gas chromatograph, Yanaco YR-101; 30% high vacuum silicon grease, 2 m, increase rate of column temperature, 15 °C/min; carrier gas, helium, 50 mL/min.

Preparation of 4,4′-Di-*tert*-butyldiphenylmethane (2a). To a solution of 120 g (542 mmol) of 2,6-di-*tert*-butyl-4-methylphenol and 70 g (417 mmol) of diphenylmethane (1) in 200 mL of nitromethane was added at 15 °C $AlCl_3$–CH_3NO_2 catalyst [$AlCl_3$ (107.3 g, 813 mmol)/nitromethane (200 mL)] over a period of 5 min. After the reaction mixture was stirred for 20 min more, it was poured into a large amount of ice–water. The organic layer was extracted with benzene and the benzene solution was dried over sodium sulfate and evaporated in vacuo to leave the residue which was washed with 10% NaOH aqueous solution affording 96.6 g (82.7%) of **2a:** colorless needles (from EtOH); mp 70–71 °C; NMR (CCl_4) δ 1.31 [18 H, s, $-C(CH_3)_3$], 7.38 (8 H, s, aromatic protons); IR (KBr) 2960, 1510, 1360, 1270, 1110, 1025, 865, 820 cm^{-1}. Anal. Calcd for $C_{21}H_{28}$: C, 89.94; H, 10.06. Found: C, 90.03; H, 101.4. The washed 10% sodium hydroxide solution was acidified with 10% hydrochloric acid to give 56.3 g (96.2%) of *p*-cresol.

Chloromethylation of 2a. To a solution of 35 g (125 mmol) of **2a** and 80.5 g (100 mmol) of $ClCH_2OCH_3$ in 150 mL of CS_2 was added at −5 °C 20 mL (150 mmol) of $TiCl_4$. After the reaction mixture was stirred at −5 °C for 1 h, it was poured into 300 mL of ice–water. The organic layer was extracted with benzene. The benzene extract was dried over sodium sulfate and evaporated in vacuo to afford 36 g (76.4%) of 2,2′-dichloromethyl-4,4′-di-*tert*-butyldiphenylmethane (**3**): colorless plates (EtOH); mp 90–91 °C; NMR ($CDCl_3$) δ 1.30 [18 H, s, $-C(CH_3)_3$], 4.18 (2 H, s, $-CH_2-$), 4.50 (4 H, s, $-CH_2Cl$), 6.78–7.30 (6 H, m, aromatic protons); IR (KBr) 2960, 1500, 1260, 1200, 842, 740 cm^{-1}. Anal. Calcd for $C_{23}H_{30}Cl_2$: C, 73.20; H, 8.02. Found: C, 73.58; H, 8.03.

Preparation of 2b. According to Johnson's method,[11] a $LiAlH_4$–LiH reductive agent was prepared from 0.987 g of $LiAlH_4$ and 2.39 g of LiH in 500 mL of THF. To the agent was added a solution of 37.7 g (100 mmol) of **3** in 20 mL of THF under gently refluxing conditions over a period of 40 min. After the reaction mixture was refluxed for an additional 1 h, it was quenched with 25 mL of a mixture of water and THF (60:40 volume) at below 20 °C. The mixture was poured into a large amount of ice–water containing 20 mL of concentrated H_2SO_4 with stirring and was extracted with ether. The ether solution was dried over sodium sulfate and evaporated in vacuo to give 24.9 g (81%) of 4,4′-di-*tert*-butyl-2,2′-dimethyldiphenylmethane (**2b**): colorless plates (EtOH); mp 51–52 °C; NMR ($CDCl_3$) δ 1.30 [18 H, s, $-C(CH_3)_3$], 2.27 (6 H, s, $-CH_3$), 3.84 (2 H, s, $-CH_2-$), 6.70–7.30 (6 H, m, aromatic protons); IR (KBr) 2960, 1500, 1430, 1280, 850, 820 cm^{-1}. Anal. Calcd for $C_{23}H_{32}$: C, 89.55; H, 10.45. Found: C, 89.33; H, 10.43.

Preparation of 2c. To a solution of 4.95 g (25 mmol) of **5a** and 3.7 g (25 mmol) of **4a**[10] in 40 mL of CS_2 was gradually added 2 mL of $TiCl_4$ at 5 °C. After the reaction mixture was stirred at 5 °C for 90 min, it was treated and worked up as described above to afford 7.7 g (86.2%) of 5,5′-di-*tert*-butyl-2,2′-dimethyldiphenylmethane (**2c**): colorless liquid; bp 162–163 °C (3 mm); NMR (CCl_4) δ 1.20 [18 H, s, $-C(CH_3)_3$], 2.18 (6 H, s, $-CH_3$), 3.80 (2 H, s, $-CH_2-$), 6.80–6.96 (6 H, m, aromatic protons). Anal. Calcd for $C_{33}H_{32}$: C, 89.55; H, 10.45. Found: C, 89.59; H, 10.39.

Preparation of 2d. To a solution of 21.05 g (100 mmol) of **5b** and 16.23 g (100 mmol) of **4b**[10] in 100 mL of CS_2 was added 4 mL of $TiCl_4$ at 5 °C. After the reaction mixture was stirred for an additional 2 h, it was treated and worked up as described above to give 28 g (88.3%) of **2d:** colorless needles (EtOH); mp 135–136 °C; NMR ($CDCl_3$) δ 1.30 [18 H, s, $-C(CH_3)_3$], 2.14 (12 H, s, $-CH_3$), 4.02 (2 H, s, $-CH_2-$), 1.98 (4 H, s, aromatic protons). Anal. Calcd for $C_{25}H_{36}$: C, 89.22; H, 10.78. Found: C, 89.18; H, 10.71.

Preparation of 2e. To a solution of 21.5 g (100 mmol) of **5b** and 16.23 g (100 mmol) of **4c**[10] in 100 mL of CS_2 was added 4 mL of $TiCl_4$. After the reaction mixture was stirred for 3 h, it was treated and worked up as described above to afford 31.6 g (94%) of 4,5′-di-*tert*-butyl-2,2′,3′,6-tetramethyldiphenylmethane (**2e**): colorless needles (EtOH); mp 122–123 °C; IR (KBr) 2960, 1550, 1460, 1360, 870 cm^{-1}; NMR ($CDCl_3$) δ 1.09 [9 H, s, $-C(CH_3)_3$], 2.18 (6 H, s, $-CH_3$), 2.28 (3 H, s, $-CH_3$), 2.32 (3 H, s, $-CH_3$), 3.89 (2 H, s, $-CH_2-$), 6.37 (1 H, s), 7.00 (1 H, s) and 7.09 (2 H, s, aromatic protons). Anal. Calcd for $C_{25}H_{36}$: C, 89.22; H, 10.78. Found: C, 89.13; H, 10.76.

Preparation of 2f. A solution of 21.05 g (100 mmol) of **5c** and 16.23 g (100 mmol) of **4c** in 100 mL of CS_2 was treated and worked up as

described above to afford 26.88 g (90%) of **2f:** colorless needles (EtOH); mp 86.5–87.5 °C; IR (KBr) 2960, 1480, 1440, 1360, 880, 870, 725 cm^{-1}; NMR ($CDCl_3$) δ 1.18 [18 H, s, $-C(CH_3)_3$], 2.13 (6 H, s, $-CH_3$), 2.30 (6 H, s, $-CH_3$), 3.93 (2 H, s, $-CH_2-$), 6.77–7.10 (4 H, m, aromatic protons). Anal. Calcd for $C_{25}H_{36}$: C, 89.22; H, 10.78. Found: C, 89.03; H, 10.88.

Preparation of 2g. To a solution of 32.4 g (200 mmol) of **4b** and 37.95 g (300 mmol) of benzyl chloride (**7a**) in 100 mL of CS_2 was added at 5 °C 8 mL (40 mmol) of $TiCl_4$. After the reaction mixture was stirred at 5 °C for 4 h, it was treated and worked up as described above to afford 33.72 g (69%) of 4-*tert*-butyl-2,6-dimethyldiphenylmethane (**2g**): colorless needles (EtOH); mp 43–45 °C; bp 132–134 °C (3 mmHg); IR (KBr) 2660, 1600, 1490, 1450, 1200, 1040, 880, 715, 700 cm^{-1}; NMR ($CDCl_4$) δ 1.30 [9 H, s, $-C(CH_3)_3$], 2.20 (6 H, s, $-CH_2-$), 6.82–7.20 (7 H, m, aromatic protons). Anal. Calcd for $C_{19}H_{24}$: C, 90.24; H, 9.58. Found: C, 90.34; H, 9.53.

Preparation of 5a. To a solution of 100 g (676 mmol) of **4a** and 136 g (1.7 mmol) of $ClCH_2OCH_3$ in 200 mL of CS_2 was added at 5 °C 23 mL (140 mmol) of $TiCl_4$. After the reaction mixture was stirred for 90 min, it was poured into 300 mL of ice–water and extracted with ether. The ether extract was dried over sodium sulfate and evaporated in vacuo to leave a residue which was distilled under reduced pressure to afford 9.1 g (9.1%) of **4a** and 95.5 g (71.1%) of **5a:** colorless liquid; bp 94–95 °C (3 mm); IR (NaCl) 2970, 1500, 1360, 1250, 825, 740 cm^{-1}; NMR (CCl_4) δ 1.30 [9 H, s, $-C(CH_3)_3$], 2.35 (3 H, s, $-CH_3$), 4.55 (2 H, s, $-CH_2-$), 7.00–7.31 (3 H, m, aromatic protons).

Preparation of 5b. To a solution of 50 g (308 mmol) of **4b** and 49.6 g (616 mmol) of $ClCH_2OCH_3$ in 150 mL of CS_2 was added at 5 °C 14 mL (70 mmol) of $TiCl_4$. The reaction mixture was stirred at 5 °C for 1 h and treated as described above to afford 60.54 g (93.3%) of 4-*tert*-butyl-2,6-dimethylbenzyl chloride (**5b**) with 2.15 g (4.1%) of **2d.** **5b:** colorless liquid; bp 95–96 °C (3 mm) [lit.[13] bp 135–136 °C (10 mm)]; IR (KBr) 2960, 1460, 1260, 870, 730, 680 cm^{-1}; NMR ($CDCl_3$) δ 1.30 [9 H, s, $-C(CH_3)_3$], 2.41 (6 H, s, $-CH_3$), 4.62 (2 H, s, $-CH_2-$), 7.07 (2 H, s, aromatic protons).

Preparation of 5c. A mixture of 50 g (308 mmol) of **4c** and 49.6 g (616 mmol) of chloromethyl ether was treated with 14 mL (70 mmol) of $TiCl_4$ and worked up as described above to afford 50 g (77.1%) of 5-*tert*-butyl-2,3-dimethylbenzyl chloride (**5c**) and 8.28 g (16%) of **2f.** **5c:** colorless needles; mp 45–47 °C (lit.[13] mp 48.5–49.0 °C); bp 117–118 °C (3 mm); IR (KBr) 2960, 1480, 1460, 1360, 1260, 880, 740, 690 cm^{-1}; NMR ($CDCl_4$) δ 1.30 [9 H, s, $-C(CH_3)_3$], 2.27 (6 H, s, $-CH_3$), 4.58 (2 H, s, $-CH_2-$), 7.16 (2 H, s, aromatic protons).

Preparation of 5d. To a solution of 100 g (0.616 mol) of 4-*tert*-butylethylbenzene[10] and 99.2 g (1.23 mol) of $ClCH_2OCH_3$ in 300 mL of CS_2 was added at 5 °C 28 mL (0.14 mol) of $TiCl_4$. After the reaction mixture was stirred for 2 h, it was poured into 500 mL of ice–water and extracted with ether. The ether solution was dried over sodium sulfate and evaporated to leave the residue, which was distilled under reduced pressure to afford 80.94 g (62.4%) of 5-*tert*-butyl-2-ethylbenzyl chloride (**5d**) and 27.13 g of the starting compound [bp 57–58 °C (3 mm)]. **5d:** colorless liquid; bp 102–102 °C (3 mm); NMR (CCl_4) δ 1.30 [9 H, s, $-C(CH_3)_3$ and 3 H, t, $-CH_3$], 2.70 (2 H, q, $-CH_2-$), 4.51 (2 H, s, $-CH_2CH_2-$), 7.10–7.30 (3 H, m, aromatic protons).

Preparation of 5e. After a mixture of 109.3 g (0.674 mol) of 4-*tert*-butylanisole,[10] 10 g (0.33 mol) of paraformaldehyde, and 104 g of 31% hydrochloric acid was stirred vigorously at 55 °C for 7 h, it was cooled to room temperature and extracted with benzene. The benzene solution was washed with 10% sodium carbonate solution, dried over sodium sulfate, and evaporated in vacuo to leave the residue, which was distilled under reduced pressure to afford 39.9 g (28.1%) of 5-*tert*-butyl-2-methoxybenzyl chloride (**5e**) and 60 g of the starting compound [bp 73–74 °C (3 mm)]. **5e:** colorless liquid; bp 117–118 °C (3 mm); NMR (CCl_4) δ 1.26 [9 H, s, $-C(CH_3)$], 3.72 (3 H, s, $-CH_3$), 4.51 (2 H, s, $-CH_2-$), 6.59–7.25 (3 H, m, aromatic protons). When the $TiCl_4$ catalyzed chloromethylation of 4-*tert*-butylanisole with $ClCH_2OCH_3$ was carried out, **5e** was not obtained but only large amount of resinous material was formed.

Preparation of 5f. To a solution of 51.9 g (0.308 mol) of 4-*tert*-butylchlorobenzene[14] and 49.6 g (0.616 mol) of $ClCH_2OCH_3$ in 75 mL of CS_2 was added at 5 °C 14 mL of $TiCl_4$. After the reaction mixture was stirred for 10 h, it was treated and worked up as described above to afford 31.4 g (47.0%) of 5-*tert*-butyl-2-chlorobenzyl chloride (**5f**) and 22.43 g of the starting compound [bp 58 °C (3 mm)]. **5f:** colorless liquid; bp 105–107 °C (3 mm); NMR (CCl_4) δ 1.30 [18 H, s, $-C(CH_3)_3$], 4.95 (2 H, s, $-CH_2-$), 7.10–7.45 (3 H, m, aromatic protons).

Preparation of 5g. Similarly a solution of 131.2 g (0.616 mol) of 4-*tert*-butylbromobenzene,[14] 99.2 g (1.23 mol) of $ClCH_2OCH_3$, and 28 mL of $TiCl_4$ in 150 mL of CS_2 was treated and worked up as described above to afford 70.3 g (52.7%) of 5-*tert*-butyl-2-bromobenzyl chloride (**5g**) and 44.3 g of the starting compound. **5g:** colorless liquid; bp 130–132 °C (5 mm); NMR (CCl_4) δ 1.30 [18 H, s, $-C(CH_3)_3$], 4.60 (2 H, s, $-CH_2$), 7.27–7.54 (3 H, m, aromatic protons).

The $TiCl_4$ Catalyzed Benzylation of Benzene with 5b. To a solution of 21.04 g (0.1 mol) of **5b** in 120 mL of benzene 4 mL of $TiCl_4$ was gradually added at room temperature. After the reaction mixture was stirred for 1 h, it was treated and worked up as described above to afford 10 g (50%) of **6** and 11 g (43%) of **2g.**

Preparation of 6. To a solution of 16.2 g (100 mmol) of **4b** and 8.75 g (50 mmol) of 1,4-bis(chloromethyl)benzene (**8**) in 5 mL of CS_2 was added 4 mL (10 mmol) of $TiCl_4$ at 5 °C. After the reaction mixture was stirred for 3 h, it was treated and worked up as described above to afford 12 g (59.1%) of 1,4-bis(4-*tert*-butyl-2,6-dimethylbenzyl)-benzene (**6**): colorless prisms (EtOH); mp 196–198 °C; IR (KBr) 2960, 1485, 1450, 1360, 880 cm^{-1}; NMR ($CDCl_3$) δ 1.30 [18 H, s, $-C(CH_3)_3$], 2.20 (12 H, s, $-CH_3$), 3.94 (4 H, s, $-CH_2-$), 6.88–7.08 (8 H, m, aromatic protons). Anal. Calcd for $C_{32}H_{42}$: C, 90.08; H, 9.92. Found: C, 89.52; H, 9.86.

Preparation of 14b. To a solution of 14.5 g (0.1 mol) of CS_2 was added 8 mL of $TiCl_4$ at 5 °C. After the reaction mixture was stirred at 5 °C for 2 h, it was treated and worked up as described above to give 13.28 g (53%) of **14b:** colorless liquid; bp 139–142 °C (3 mm); IR (NaCl) 2960, 1460, 1360, 820, 740 cm^{-1}; NMR (CCl_4) δ 1.20 [9 H, s, $-C(CH_3)_3$], 2.14 (3 H, s, $-CH_3$), 2.22 (3 H, s, $-CH_3$), 3.80 (2 H, s, $-CH_2-$), 6.60–7.10 (7 H, m, aromatic protons). Anal. Calcd for $C_{19}H_{24}$: C, 90.24; H, 9.58. Found: C, 89.98; H, 9.59.

Preparation of 21. A solution of 32.4 g (200 mmol) of **4c** and 37.95 g (300 mmol) of **7a** in 100 mL of CS_2 was treated and worked up as described above to afford 24.36 g (48.2%) of **21** with 10 g of starting compound **4c. 21:** colorless liquid; bp 137–139 °C (3 mm); IR (NaCl) 2960, 1600, 1500, 1450, 1360, 880, 735, 700 cm^{-1}; NMR (CCl_4) δ 1.27 [9 H, s, $-C(CH_3)_3$], 2.00 (3 H, s, $-CH_3$), 3.90 (2 H, s, $-CH_2-$), 6.70–7.20 (7 H, m, aromatic protons); mass spectrum *m/e* 252 (M^+). Anal. Calcd for $C_{19}H_{24}$: C, 90.24; H, 9.58. Found: C, 90.50; H, 9.45.

General Procedure of the Transalkylation of 2. After a mixture of 30 equiv of benzene (or toluene, *m*-xylene), 0.2 equiv of the catalyst/equiv of **2,** and 1 mol of **2** had been maintained at a desired, constant temperature and a specified reaction time with stirring, the reaction mixture was separated and dried over sodium sulfate. A definite amount of the benzene solution was analyzed by gas chromatography. After the analyses, the products were isolated and purified by distillation and/or recrystallization, respectively. The reaction conditions and the yields are summarized in Table I.

11: colorless liquid; bp 110–112 °C (3 mm); IR (NaCl) 3020, 2960, 1600, 1055, 740 cm^{-1}; NMR (CCl_4) δ 2.18 (6 H, s, $-CH_3$), 3.78 (2 H, s, $-CH_2-$), 6.70–7.20 (8 H, m, aromatic protons). Anal. Calcd for $C_{15}H_{16}$: C, 91.79; H, 8.22. Found: C, 91.33; H, 8.29. **16:** colorless liquid; bp 107–109 °C (3 mm); IR (NaCl) 3040, 3970, 2940, 1600, 1450, 735, 700 cm^{-1}; NMR (CCl_4) δ 2.10 (3 H, s, $-CH_3$), 2.23 (3 H, s, $-CH_3$), 3.83 (2 H, s, $-CH_2-$), 6.85–7.20 (8 H, m, aromatic protons). Anal. Calcd for $C_{15}H_{16}$: C, 91.79; H, 8.22. Found: C, 91.76; H, 8.16.

22: colorless liquid; bp 123 °C (33 mm); IR (NaCl) 3070, 3040, 2920, 1600, 1500, 1450, 790, 730, 700 cm^{-1}; NMR (CCl_4) δ 2.13 (6 H, s, $-CH_3$), 3.79 (2 H, s, $-CH_2$), 6.30–7.20 (8 H, m, aromatic protons). Anal. Calcd for $C_{15}H_{16}$: C, 91.79; H, 8.22. Found: C, 91.74; H, 8.19.

23: colorless liquid; IR (NaCl) 2960, 1480, 1360, 860, 750 cm^{-1}; mass spectrum *m/e* 280 (M^+); NMR (CCl_4) δ 1.10 [9 H, s, $-C(CH_3)$], 1.98 (3 H, s, $-CH_3$), 2.10 (3 H, s, $-CH_3$), 2.22 (6 H, s, $-CH_3$). This compound **23** was separated by using separative gas chromatography.

Preparation of 25a. To a solution of 54.8 g (0.3 mol) of diphenylethane (**24**) and 86 g (0.39 mol) of 2,6-di-*tert*-butyl-*p*-cresol in 120 mL of nitromethane was added at 15 °C a $AlCl_3$–CH_3NO_2 solution [67 g (0.507 mol) of $AlCl_3$/120 mL of CH_3NO_2]. After the reaction mixture was stirred for 5 min, it was poured into a large amount of ice–water and the organic layer was extracted with benzene. The benzene solution was dried over sodium sulfate and evaporated in vacuo to leave the residue in which benzene was added again. The benzene solution was extracted with 10% sodium hydroxide. The benzene was washed with water, dried over sodium sulfate, and evaporated in vacuo to afford 79 g (90%) of **25a:** colorless plates (EtOH); mp 154–155 °C; NMR (CCl_4) δ 1.30 [18 H, s, $-C(CH_3)_3$], 2.83 (4 H, s, $-CH_2CH_2-$), 6.95–7.30 (8 H, aromatic protons). Anal. Calcd for $C_{22}H_{30}$: C, 89.73; H, 10.27. Found: C, 89.48; H, 10.27. *p*-Cresol was obtained almost quantitatively from the 10% sodium hydroxide extract by acidification with 10% hydrochloric acid.

Preparation of 25b. To a solution of CH_3MgI (prepared from 150 g of methyl iodine and 25 g of magnesium) in 400 mL of ether was gradually added a solution of **5a** in 1 h under the condition of reflux. After the reaction mixture was refluxed for an additional 2 h, it was quenched with 10% hydrochloric acid and extracted with ether. The

ether extract was dried over sodium sulfate and evaporated in vacuo to leave the residue, in which a small amount of ethanol was added to afford 45 g (72%) of 5,5′-di-*tert*-butyl-2,2′-dimethyldiphenylethane (**25b**) as a colorless crystal, and the filtrate afforded 9.1 g (13.4%) of 4-*tert*-butyl-2-ethyltoluene (**26b**). **25b:** colorless needles (EtOH); mp 55–56 °C; NMR (CCl_4) δ 1.25 [18 H, s, $-C(CH_3)_3$], 2.15 (6 H, s, $-CH_3$), 2.81 (4 H, s, $-CH_2CH_2-$), 6.96 (6 H, s, aromatic protons). Anal. Calcd for $C_{24}H_{34}$: C, 89.39; H, 10.62. Found: C, 89.35; H, 10.66. **26b:** colorless liquid; bp 69–71 °C (3 mm).

Preparation of 25c. To a solution of methylmagnesium iodide (from 60 g of methyl iodide and 10 g of magnesium) in 150 mL of ether was added a solution of 32.7 g (0.155 mol) of **5d** in 50 mL of ether. The reaction mixture was treated and worked up as described above to afford 23.4 g (86.5%) of 5,5′-di-*tert*-butyl-2,2′-diethyldiphenylethane (**25c**) and 4.2 g (16.6%) of 2-ethyl-4-*tert*-butylethylbenzene (**26c**). **25c:** colorless liquid; bp 79–82 °C (3 mm); NMR (CCl_4) δ 1.22 (6 H, t, $-CH_3$), 1.25 [18 H, s, $-C(CH_3)_3$], 2.56 (4 H, q, $-CH_2CH_2-$), 7.03 (6 H, s, aromatic protons). Anal. Calcd for $C_{26}H_{38}$: C, 89.08; H, 10.92. Found: C, 88.78; H, 10.94. **26c:** colorless liquid; bp 78–82 °C (3 mm).

Preparation of 25d. An ether solution of methylmagnesium iodide (CH_3I, 60 g; Mg, 10 g) was treated with a solution of 32.7 g (0.155 mol) of **5e** in 50 mL of ether and the reaction mixture was worked up as described above to afford 17 g (62.6%) of 5,5′-di-*tert*-butyl-2,2′-dimethoxydiphenylethane (**25d**) and 6 g (20.3%) of 4-*tert*-butyl-2-ethylanisole (**26d**). **25d:** colorless needles (EtOH); mp 92–93 °C; NMR ($CDCl_4$) δ 1.20 [18 H, s, $-C(CH_3)_3$], 2.82 (4 H, s, $-CH_2CH_2-$), 3.71 (6 H, s, $-CH_3$), 6.54–7.12 (6 H, m, aromatic protons). Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.31; H, 9.67. Found: C, 81.05; H, 9.71. **26d:** colorless liquid; bp 83–85 °C (3 mm).

Preparation of 25e. Similarly 32.7 g (0.155 mol) of **5c** was treated with methylmagnesium iodide (CH_3I, 60 g; Mg, 10 g) in the same manner as described above to afford 20.4 g (75.2%) of 5,5′-di-*tert*-butyl-2,2′,3,3′-tetramethyldiphenylethane (**25e**): colorless needles (EtOH); mp 87–88 °C; NMR (CCl_4) δ 1.23 [18 H, s, $-C(CH_3)_3$], 2.08 (6 H, s, $-CH_3$), 2.21 (6 H, s, $-CH_3$), 2.80 (4 H, s, $-CH_2-$), 6.80–7.00 (4 H, m, aromatic protons). Anal. Calcd for $C_{26}H_{38}$: C, 89.08; H, 10.92. Found: C, 89.03; H, 10.88.

Preparation of 25f. Similarly 24.1 g (89.8%) of 4,4′-di-*tert*-butyl-2,2′,6,6′-tetramethyldiphenylethane (**25f**) and 3.07 g (10.5%) of 4-*tert*-butyl-2,6-dimethylethylbenzene (**26f**) were obtained from 32.7 g (0.155 mol) of **5b** in same manner as described above. **25f:** colorless needles (EtOH); mp 220–221 °C (lit.[13] mp 216–217 °C); NMR (CCl_4) δ 1.30 [18 H, s, $-C(CH_3)_3$], 2.42 (12 H, s, $-CH_3$), 2.78 (4 H, s, $-CH_2-$), 7.05 (4 H, m, aromatic protons). Anal. Calcd for $C_{26}H_{38}$: C, 89.08; H, 10.92. Found: C, 88.99; H, 10.86. **26f:** colorless liquid.

Preparation of 25g. To a solution of methylmagnesium iodide (30 g of CH_3I, 5 g of Mg) in 75 mL of ether was added a solution of 16.82 g (77.5 mmol) of **5f** in 25 mL of ether. After the reaction mixture was refluxed for 3 h, it was treated and worked up as described above to afford 9.5 g (70%) of 5,5′-di-*tert*-butyl-2,2′-dichlorodiphenylethane (**25g**): colorless needles (EtOH); mp 113–114 °C; NMR (CCl_4) δ 1.30 [18 H, s, $-C(CH_3)_3$], 2.94 (4 H, s, $-CH_2-$), 7.10–7.30 (6 H, m, aromatic protons). Anal. Calcd for $C_{22}H_{28}Cl_2$: C, 72.72; H, 7.77. Found: C, 72.43; H, 7.75.

Preparation of 25h. To a solution of methylmagnesium iodide (30 g of CH_3I, 5 g of Mg) in 75 mL of ether was added a solution of 20.3 g (77.5 mmol) of **5g** in 25 mL of ether over a period of 30 min. The reaction mixture was refluxed for 3 h and was treated and worked up as described above to afford 12.5 g (71.3%) of 5,5′-di-*tert*-butyl-2,2′-dibromodiphenylethane (**25h**): colorless needles (EtOH); mp 92–93 °C; NMR (CCl_4) δ 1.30 [18 H, s, $-C(CH_3)_3$], 2.95 (4 H, s, $-CH_2-$), 7.15–7.50 (6 H, m, aromatic protons). Anal. Calcd for $C_{22}H_{28}Br_2$: C, 58.42; H, 6.24. Found: C, 58.31; H, 6.20.

The Transalkylation of 25. After a mixture of 30 equiv of benzene (or toluene, *m*-xylene), 0.2 equiv of the catalyst/equiv of **25**, and 1 mol of **25** had been maintained at a desired, constant temperature and a specified reaction time with stirring, the reaction mixture was quenched with 10% hydrochloric acid. The layer was separated and dried over sodium sulfate. A definite amount of benzene solution was analyzed by gas chromatography. After the analyses, the products were isolated and purified by distillation and/or recrystallization, respectively. The reaction conditions and the yields are summarized in Table III.

27b: colorless needles (EtOH); mp 65–66 °C; NMR (CCl_4) δ 2.23 (6 H, s, $-CH_3$), 2.79 (4 H, s, $-CH_2CH_2-$), 7.02 (8 H, s, aromatic protons). Anal. Calcd for $C_{16}H_{18}$: C, 91.04; H, 8.63. Found: C, 91.23; H, 8.62.

27c: colorless plates (EtOH); mp 26–28 °C; NMR (CCl_4) δ 1.20 (6 H, t, $-CH_3$), 2.63 (4 H, q, $-CH_2-$), 2.85 (4 H, s, $-CH_2CH_2-$), 7.18 (8 H, s, aromatic protons). Anal. Calcd for $C_{18}H_{22}$: C, 90.07; H, 9.30. Found: C, 90.67; H, 9.26.

27d: colorless needles (EtOH); mp 80–82 °C; NMR (CCl_4) δ 2.82 (4 H, s, $-CH_2CH_2-$), 3.77 (6 H, s, $-OCH_3$), 6.60–7.10 (6 H, m, aromatic protons). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.30; H, 7.54.

27e: colorless needles (EtOH); mp 110–111 °C; NMR (CCl_4) δ 2.19 (6 H, s, $-CH_3$), 2.25 (6 H, s, $-CH_3$), 2.80 (4 H, s, $-CH_2-$), 6.92 (6 H, s, aromatic protons). Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 89.02; H, 9.35.

27f: colorless needles (EtOH); mp 123–125 °C; NMR (CCl_4) δ 2.21 (12 H, s, $-CH_3$), 2.75 (4 H, s, $-CH_2-$), 6.87 (6 H, s, aromatic protons). Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.33; H, 9.38.

27g: colorless needles; mp 57–58 °C; NMR (CCl_4) δ 3.00 (4 H, s, $-CH_2-$), 7.00–7.40 (8 H, m, aromatic protons). Anal. Calcd for $C_{14}H_{12}Cl_2$: C, 66.95; H, 4.82. Found: C, 66.89; H, 4.79.

Registry No.—1, 101-81-5; **2a,** 19099-48-0; **2b,** 65276-21-3; **2c,** 65276-22-4; **2d,** 65338-71-8; **2e,** 65276-23-5; **2f,** 65276-24-6; **2g,** 65276-25-7; **3,** 65276-26-8; **4a,** 98-51-1; **4b,** 98-19-1; **4c,** 7397-06-0; **5b,** 19387-83-8; **5c,** 28162-13-2; **5d,** 65276-27-9; **5e,** 22252-73-9; **5f,** 65276-28-0; **5g,** 65276-29-1; **6,** 65276-30-4; **7a,** 100-44-7; **7b,** 552-45-4; **8,** 623-25-6; **11,** 1634-74-8; **14b,** 65276-31-5; **16,** 28122-29-4; **21,** 65276-32-6; **22,** 62155-16-2; **23,** 65276-33-7; **24,** 103-29-7; **25a,** 22927-07-7; **25b,** 65276-09-7; **25c,** 65276-10-0; **25d,** 65276-11-1; **25e,** 65276-12-2; **25f,** 65276-13-3; **25g,** 62576-14-4; **25h,** 65276-15-5; **26b,** 65276-16-6; **26c,** 65276-17-7; **26d,** 65276-18-8; **26f,** 65276-19-9; **27b,** 952-80-7; **27c,** 27499-60-1; **27d,** 14310-34-0; **27e,** 65276-20-2; **27f,** 25115-79-1; **27g,** 6639-40-3; 2,6-di-*tert*-butyl-4-methylphenol, 128-37-0; $ClCH_2OCH_3$, 107-30-2; 4-*tert*-butylethylbenzene, 7364-19-4; 4-*tert*-butylanisole, 5396-38-3; hydrochloric acid, 7647-01-0; 4-*tert*-butylchlorobenzene, 3972-56-3; 4-*tert*-butylbromobenzene, 3972-65-4.

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