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# Studies on Friedel–Crafts Chemistry. 2. The $AlCl_3$–$CH_3NO_2$ Catalyzed Novel Transbenzylation of 4,4′-Dihydroxydiphenylmethanes in Toluene[1]

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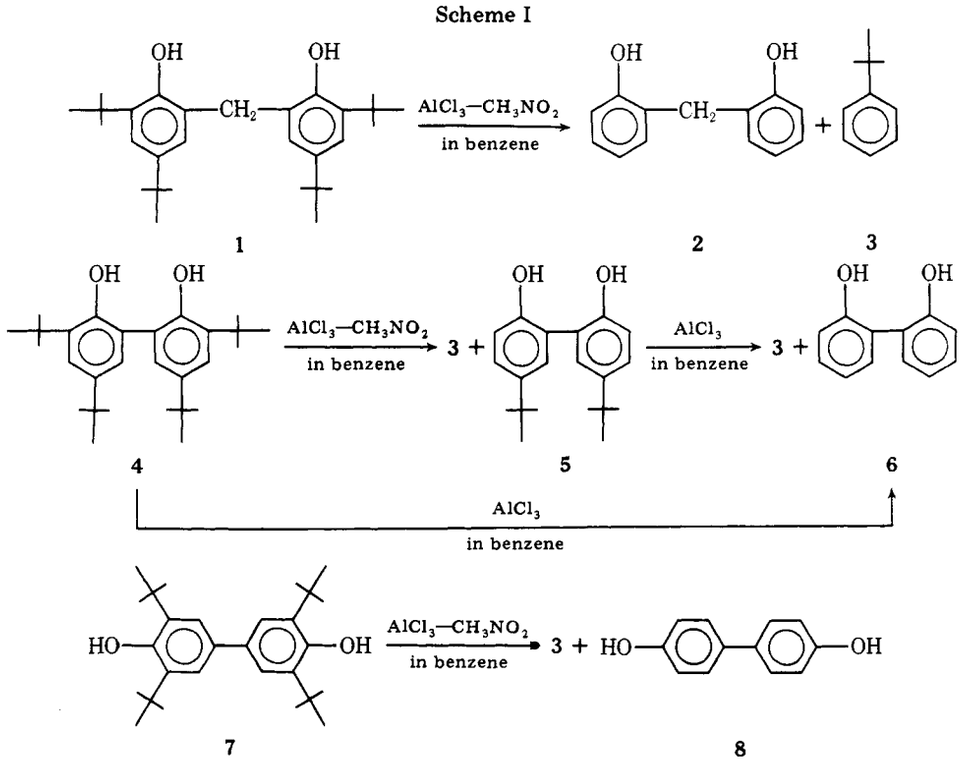
In the $AlCl_3$–$CH_3NO_2$ catalyzed transalkylation of 3,5,3′,5′-tetra-*tert*-butyl- (**9**), 3,3′-di-*tert*-butyl- (**21**), and 3,3′-di-*tert*-butyl-5,5′-dimethyl-4,4′-dihydroxydiphenylmethane (**25**), it was found that not only *tert*-butyl but also benzyl groups were transferred to toluene used as a solvent and an acceptor of the alkyl group, and that the transbenzylation of 3,3′-dimethyl-4,4′-dihydroxy- (**29**), 3,3′-dimethyl-4,4′-dimethoxy- (**31**), and 3,5,3′,5′-tetramethyl-4,4′-dihydroxydiphenylmethane (**34**) took place even under the influence of $AlCl_3$–$CH_3NO_2$ catalyst which has been known to be inactive in the transbenzylation and isomerization of diphenylmethanes. The mechanism of the $AlCl_3$–$CH_3NO_2$ catalyzed transbenzylation is discussed.

It has been previously reported that 2,2′-dihydroxydiphenylmethane (**2**),[2] 2,2′-dihydroxy- (**6**),[3] and 4,4′-dihydroxydiphenyls[3] were easily prepared by the $AlCl_3$–$CH_3NO_2$ or $AlCl_3$ catalyzed transalkylation of the corresponding *tert*-butyl derivatives in benzene as shown in Scheme I.

These results suggest that 4,4′-dihydroxydiphenylmethanes as well as **2**, **6**, and **8** might be prepared by the same manner under the influence of $AlCl_3$–$CH_3NO_2$ catalyst which is known to be active in the transalkylation of the *tert*-butyl group of *tert*-butylbenzenes[2-6] but not in the transalkylation and isomerization of diphenylmethanes.[2,6-11]

We now wish to report the $AlCl_3$–$CH_3NO_2$ catalyzed transalkylation of 3,5,3′,5′-tetra-*tert*-butyl- (**9**), 3,3′-di-*tert*-butyl- (**21**), and 3,3′-di-*tert*-butyl-5,5′-dimethyl-4,4′-dihydroxydiphenylmethane (**25**) and of the related compounds such as 3,3′-dimethyl-4,4′-dihydroxy- (**29**), 3,3′-dimethyl-4,4′-dimethoxy- (**31**), and 3,5,3′,5′-tetramethyl-4,4′-dihydroxydiphenylmethane (**34**) in toluene.

Scheme I



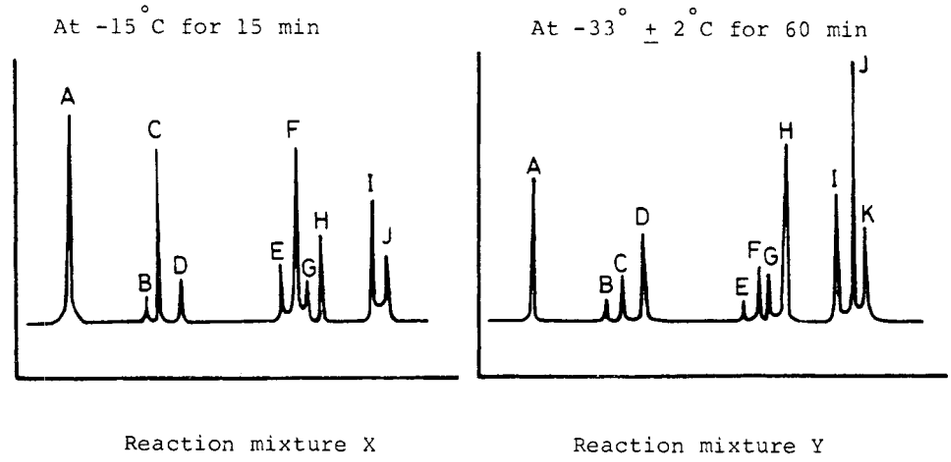



**Figure 1.** Gas–mass spectra of the reaction mixture X and Y.

**Table I. $AlCl_3$–$CH_3NO_2$ Catalyzed Transalkylation of 4,4′-Dihydroxydiphenyl in Toluene[a]**

| Run | Substrate | Temp. °C | Product (%) |
|---|---|---|---|
| 1 | **9** | 30 | **10** (+),[b] **11** (61), **12** (32), **13** (62) |
| 2 | **9** | −15 | **10** (8), **11** (81), **12** (38), **13** (85) |
| 3 | **10** | Reflux | **10** (100) |
| 4 | **21** | 30 | **11** (61), **12** (29), **13** (30) |
| 5 | **25** | 30 | **26** (76), **27** (39), **13** (30) |
| 6[c] | **25** | −35 | **28** (16), **29** (26), **26** (12), **30** (7), **13** (4) |
| 7 | **29** | 30 | **26** (76), **27** (79) |
| 8 | **31** | 30 | **32** (80), **33** (80) |
| 9 | **34** | 30 | **35** (75), **36** (74) |

[a] Reaction time is 1 h unless otherwise indicated. $AlCl_3$/substrate: 1.2 mol/1 mol. [b] Plus sign (+) means a trace amount (less than 1%). [c] Reaction time is 2 h.

## Results and Discussion

The $AlCl_3$–$CH_3NO_2$ catalyzed transalkylations of **9**, **21**, **25**, **29**, **31**, and **34** were carried out in toluene[12] used as a solvent and an acceptor of the alkyl group under various conditions, and the results are summarized in Table I.

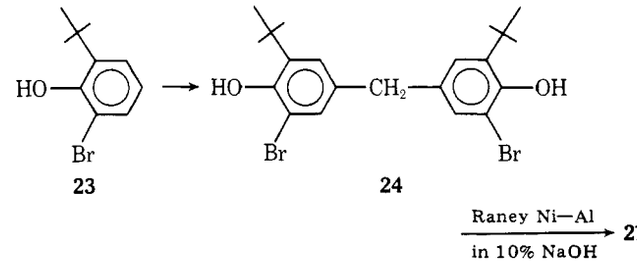
When **9** was treated with $AlCl_3$–$CH_3NO_2$ catalyst in toluene at 30 °C for 1 h, only a trace amount of the expected product 4,4′-dihydroxydiphenylmethane (**10**) was formed but 4-hydroxy-4′-methyldiphenylmethane (**11**, contained 2′ and 3′ isomers) was obtained in 60% yield with formation of phenol (**12**) and *tert*-butyltoluene (**13**).

The yields of the products increased with decreasing reaction temperature (run 2). These results seemed to suggest that **10** might be the intermediate in the formation of **11** and **12**. However, any amount of expected product was not obtained; when **10** was heated with $AlCl_3$–$CH_3NO_2$ catalyst in refluxing toluene, only the starting compound **10** was recovered in quantitative yield. In order to obtain some information about the intermediate preceding the formation of **11** and **12**, the transalkylation of **9** was carried out at −15 °C for 15 min and −33 °C for 60 min and both reaction mixtures (X and Y) were analyzed by gas–mass spectrometer. The results are shown in Figure 1 and Table II.

The above data suggested that the transbenzylation of **9** itself, 3,3′-di-*tert*-butyl- (**21**), and 3,3′,5-tri-*tert*-butyl-4,4′-dihydroxydiphenylmethane (**22**) might afford the corresponding diphenylmethanes such as **17**, **18**, **19**, and **20** which might be the intermediate in the formation of **11**.

Indeed, the expected products, **11**, **12**, and **13**, were obtained in 61, 29, and 30% yields, respectively, when **21**, which was isolated from the reaction mixtures X and Y described above, was treated with $AlCl_3$–$CH_3NO_2$ catalyst in toluene at 30 °C for 60 min.

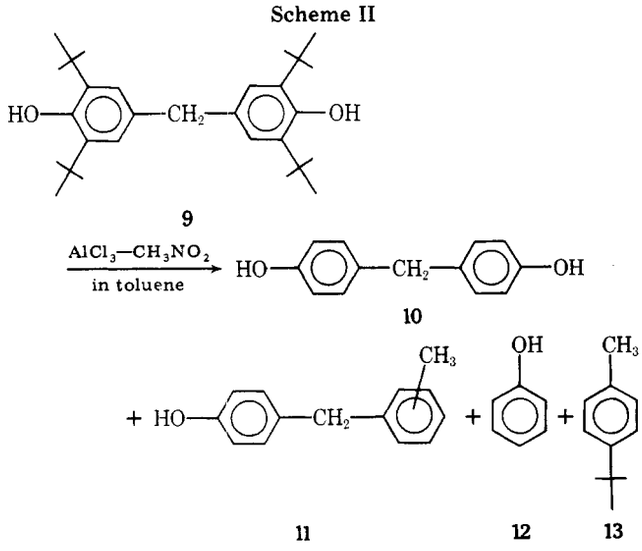
The structure of **21** was confirmed by comparison with the authentic compound which was prepared by the following reactions.[13]



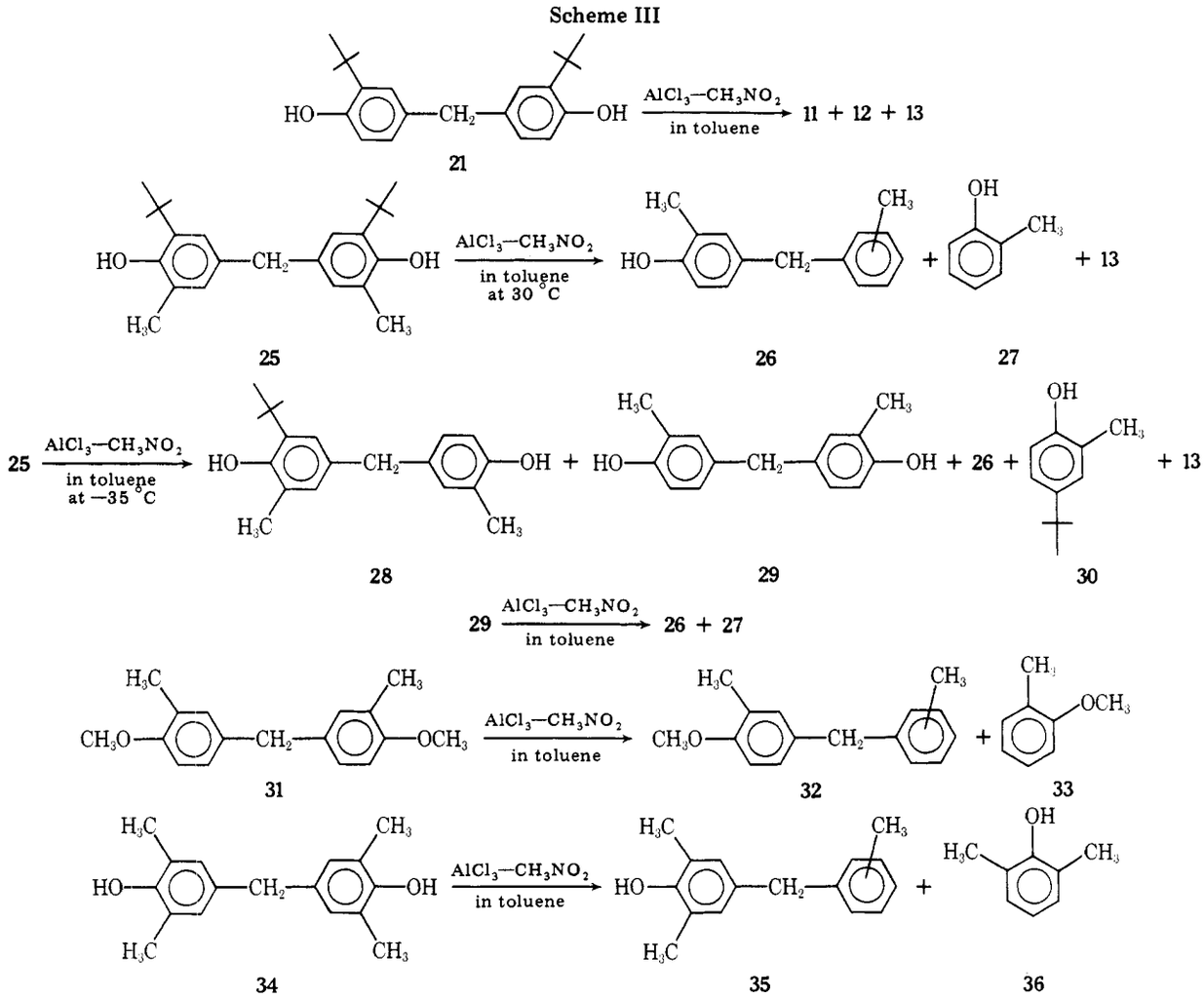

In the $AlCl_3$–$CH_3NO_2$ catalyzed transalkylation of **25** the transbenzylation was also observed as shown in Scheme III. However, at lower reaction temperature, the *tert*-butyl group could be easily transferred before the occurrence of the transbenzylation to afford **28** and **27** with **26**. It was found that **29** was an intermediate in formation of **26** since the treatment of **29** with $AlCl_3$–$CH_3NO_2$ catalyst in toluene at 30 °C afforded **26** and **27** in good yields.

When **31** and **34** were similarly treated as described above, the expected **32** and **35** were obtained with **33** and **36** in good yields, respectively. Also **32** was obtained by the methylation

Scheme II



Scheme III

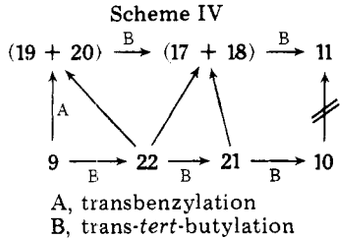


of **26** with dimethyl sulfate in 10% sodium hydroxide solution.

$$\mathbf{26} \xrightarrow[\text{in 10\% NaOH}]{Me_2SO_4} \mathbf{32}$$

Based on the above results, the reaction courses of the $AlCl_3$–$CH_3NO_2$ catalyzed transalkylation of **9** in toluene might be as shown in Scheme IV.

Scheme IV



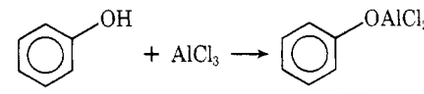
A, transbenzylation
B, trans-*tert*-butylation

It should be noted that the novel $AlCl_3$–$CH_3NO_2$ catalyzed transbenzylation of **9**, **21**, **25**, **29**, **31**, and **34**, which have a 4 and 4′ OH or OMe, in toluene were observed. The transbenzylation of **11**, **26**, **32**, and **35** as well as **10** was not observed.

These results suggest that the electron-rich diphenylmethanes (I) such as **9**, **21**, **25**, **29**, **31**, and **34** might be easily attached by the proton produced from $AlCl_3$–$CH_3NO_2$ catalyst with a small amount of water in these reaction systems to afford $\sigma$ complex (II), and through following formation of $\pi$ complex,[9] $\pi$ outer complex,[9] outer–outer complex (V), and $\sigma$ complex (VII), the product VIII might be formed. The $\sigma$ (IX) and $\pi$ complex (X) might be formed in the reaction by reprotonation of the product VIII (Scheme V).

The substituent R on the ring D can stabilize directly the $\pi$ complex III but not $\sigma$ complex II. These considerations seem to support the observation of the novel transbenzylation in only the electron-rich diphenylmethanes which have at least two electron-donating groups on both ring C and D. It could be concluded that the formation of III would be more important than that of II for the novel transbenzylation to occur. Unobservation of the further transbenzylation of **11**, **26**, **32**, and **35** might show that the methyl group of X could slightly stabilize the complex X.

The hydroxy group should not be regarded as a strong electron-donating group since phenol reacted with $AlCl_3$ to afford dichloroaluminum phenolate (XI).



XI

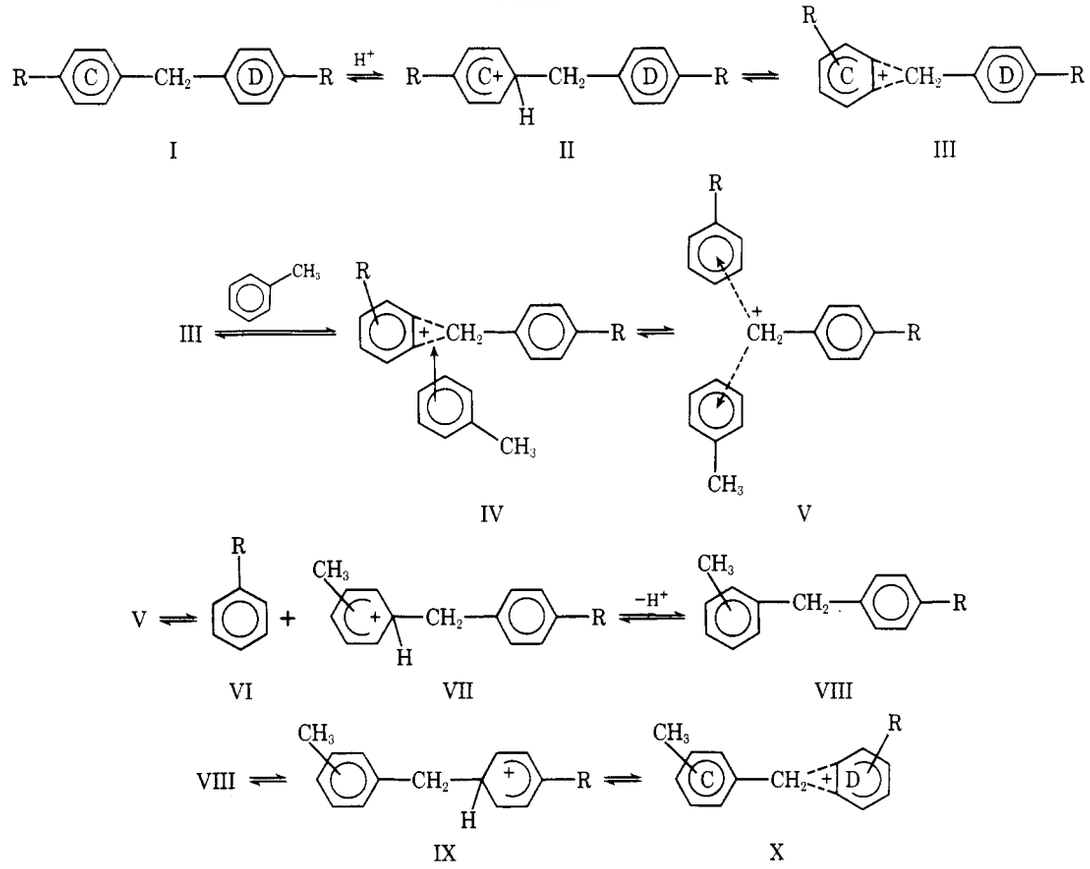
The steric effect of the *o-tert*-butyl group of **9** might inhibit the above reaction and the hydroxy group could act as a strong electron-donating group. In contrast to **9**, **1** might react with aluminum chloride to give the corresponding phenolate, and no transbenzylation was observed as described above.

As mentioned above, the transbenzylation of **9** in benzene used in place of toluene was not observed. This result seems to suggest that benzene does not have enough basicity to form the out complex (IV) with III.

## Experimental Section

All the melting and boiling points are uncorrected. IR spectra were measured as KBr pellets or liquid film on NaCl plates on a Nippon

Scheme V



Bunko IR spectrophotometer and mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet (ionization energy 70 eV). GC–mass spectra were measured on Nippon Denshi JGC-20K, JMS-D 100. NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer with $Me_4Si$ and an internal reference.

**Materials.** 3,5,3′,5′-tetra-*tert*-butyl- (**9**)[14] and 3,5,3′,5′-tetramethyl-4,4′-dihydroxydiphenylmethane (**34**)[15] were prepared according to the reported method. 3,3′-Di-*tert*-butyl-5,5′-dimethyl- (**25**),[16] 3,3′-di-*tert*-butyl-4,4′-dihydroxydiphenylmethane (**21**),[17] and 2-bromo-6-*tert*-butylphenol (**23**)[18] were prepared as previously reported. Aluminum chloride was purified by sublimation just prior to use.

**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, 12 °C/min; carrier gas, helium, 50 ml/min.

**Transalkylation of 3,5,3′5′-Tetra-*tert*-butyl-4,4′-dihydroxydiphenylmethane (9).** To a solution of 2.12 g (5 mmol) of **9** in 25 ml of toluene was added a solution of 1.4 g (11.4 mmol) of $AlCl_3$ in 3 ml of $CH_3NO_2$. After the reaction mixture was stirred at a desired, constant reaction temperature for a specified reaction time, it was quenched with 10% hydrochloric acid. The organic layer was separated and the water layer was extracted with benzene. The organic layer and the benzene solution were combined, dried over sodium sulfate, and evaporated in vacuo to leave the residue which was dissolved in 3 ml of benzene. After a few hours, a small amount of 4,4′-dihydroxydiphenylmethane (**10**)[17] was precipitated. After filtration of **10**, 20 ml of benzene was added into the filtrate, the benzene solution was extracted with 10% sodium hydroxide solution, and the organic layer was separated, dried over sodium sulfate, and evaporated in vacuo to afford **13**.

The sodium hydroxide solution was acidified with 10% hydrochloric acid and extracted with benzene. The benzene solution was dried over sodium sulfate and evaporated in vacuo to leave the residue which was column chromatographed over silica gel using benzene as an eluent to afford **12** and crude **11**. The crude **11** was recrystallized from petroleum ether (bp 30–60 °C) to afford colorless prisms: mp 96.5–98.5 °C; IR (KBr) 3260 $cm^{-1}$ ($\nu_{OH}$); NMR ($CDCl_3$) $\delta$ 2.30 (3 H, s, $CH_3$), 3.84 (2 H, s, $CH_2$), 5.02 (1 H, broad s, OH), and 6.65–7.30 (8 H, m, aromatic protons). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.87; H, 7.34.

Although **11** was found to be identical with the authentic sample of 4-hydroxy-4′-methyldiphenylmethane which was prepared by the reduction of 4-hydroxy-4′-methylbenzophenone, in the crude **11** described above, the formation of a small amount of 4-hydroxy-2′-methyldiphenylmethane (**11′**) was detected by the measurement of its IR spectrum. Unfortunately, an attempt to isolate **11′** was unsuccessful.

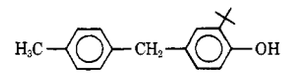
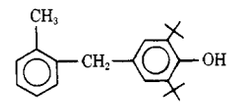
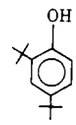
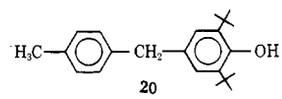
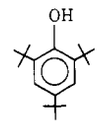
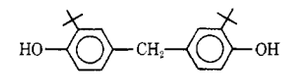
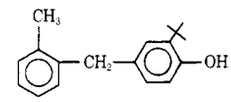
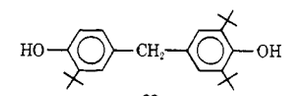
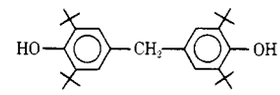
**Making the Sample for Measurement of Gas–Mass Spectra.** Similarly a mixture of 2.12 g (5 mmol) of **9**, $AlCl_3$–$CH_3NO_2$ catalyst (1.5 g/3 ml), and 25 ml of toluene was treated as described above at −15 and −33 °C for 15 and 60 min, respectively. Both reaction mixtures were treated and worked up as described above to afford the reaction mixtures X and Y, respectively. Both reaction mixture X and Y were analyzed by gas–mass spectrometer and the results are shown in Figure 1 and Table II.

**Separation of 3,3′-Di-*tert*-butyl-4,4′-dihydroxydiphenylmethane (21) from the Reaction Mixture X and Y.** Column chromatography of the reaction mixture X and Y over silica gel using benzene as an eluent afforded 3,3′-di-*tert*-butyl-4,4′-dihydroxydiphenylmethane (**21**) in 14 and 16% yields, respectively. The structure of **21** was confirmed by comparison with an authentic sample which was prepared by the reduction of **24** with Raney Ni–Al alloy in 10% sodium hydroxide solution.[13]

**Transalkylation of 3,3′-Di-*tert*-butyl-5,5′-dimethyl-4,4′-dihydroxydiphenylmethane (25). A. At 30 °C.** A solution of 1.7 g (5 mmol) of **25** and $AlCl_3$–$CH_3NO_2$ catalyst (1.5 g/3 ml) in 25 ml of toluene was stirred at 30 °C for 1 h, and the reaction mixture was treated and worked up as described above to afford 0.8 g (76%) of the crude 4-hydroxy-3,4′-dimethyldiphenylmethane (**26**), 0.42 g (77%) of *o*-cresol (**27**), and 1.1 g (74%) of **13**. **26**: colorless needles (petroleum ether); mp 75–76 °C; IR (KBr) 3340 $cm^{-1}$ ($\nu$ OH); NMR ($CDCl_3$) $\delta$ 2.18 (3 H, s, $CH_3$), 2.30 (3 H, s, $CH_3$), 2.82 (2 H, s, $CH_2$), 4.74 (1 H, s, OH), 6.55–7.18 (3 H, m, aromatic protons), and 7.06 (4 H, s, aromatic protons). A small amount of 3,2′-dimethyl-4-hydroxydiphenylmethane (**26′**) was determined by IR spectrum in the crude product, but it could not be isolated.

**B. At −33 °C.** A solution of 3.4 g (10 mmol) of **25** and $AlCl_3$–$CH_3NO_2$ catalyst (3 g/6 ml) in 50 ml of toluene was stirred at −33 ± 2 °C for 1 h, and the reaction mixture was treated and worked up as described above to afford 1.25 g (42%) of **13**, 0.23 g (7%) of 2-methyl-4-*tert*-butylphenol (**30**), 0.26 g (12%) of **26**, 0.4 g (16%) of 3-*tert*-butyl-5,5′-dimethyl-4,4′-dihydroxydiphenylmethane (**28**), and 0.6

Table II. GC–Mass Spectra of the Reaction Mixture

| Peak | M+, m/e | Structure | Peak | M+, m/e | Structure |
|---|---|---|---|---|---|
| A | 148 |  13 | F | 254 |  18 |
| B | 152 |  14 | G | 310 |  19 |
| C | 206 |  15 | H | 310 |  20 |
| D | 262 |  16 | I | 312 |  21 |
| E | 254 |  17 | J | 368 |  22 |
| | | | K | 424 |  9 |

g (26%) of 3,3′-dimethyl-4,4′-dihydroxydiphenylmethane (**29**). **29**: colorless needles, mp 160–161 °C (lit.[17] mp 160–161 °C). **28**: colorless prisms (petroleum ether); mp 171–172 °C; IR (KBr) 3600–3300 $cm^{-1}$ ($\nu$ OH); NMR ($CDCl_3$) $\delta$ 1.40 [(9 H, s, $CH_3$)$_3$], 2.19 (3 H, s, $CH_3$), 2.21 (3 H, s, $CH_3$), 3.77 (3 H, s, $CH_3$), 4.56 (1 H, s, OH), 4.60 (1 H, s, OH), and 6.58–7.00 (5 H, m, aromatic protons). Anal. Calcd for $C_{19}H_{24}O$: C, 80.24; H, 8.51. Found: C, 80.25; H, 8.41.

**Transalkylation of 3,3′-Dimethyl-4,4′-dihydroxydiphenylmethane (29).** Similarly a solution of 1.14 g (5 mmol) of **29** and $AlCl_3$–$CH_3NO_2$ catalyst (1.5 g/3 ml) in 35 ml of toluene was treated at 30 °C for 1 h and worked up as described above to afford 0.4 g (79%) of **27** and 0.8 g (76%) of **26**.

**Preparation of 3,3′-Dimethyl-4,4′-dimethoxydiphenylmethane (31).** To a solution of 2.45 g (11 mmol) of **29** in 20 ml of 10% sodium hydroxide was added 3 ml of dimethyl sulfate at room temperature. After the reaction mixture was warmed on a water bath for 1 h, it was cooled to room temperature and extracted with benzene. The benzene solution was dried over sodium sulfate and evaporated in vacuo to leave resinous material which was column chromatographed over silica gel using an eluent to give 1.9 g (70%) of pale yellow, viscous, oily product. **31**: NMR ($CDCl_3$) $\delta$ 2.12 (6 H, s, $CH_3$), 3.70 (8 H, s, $OCH_3$ and $CH_2$), 6.44–6.86 (6 H, m, aromatic protons). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.64; H, 7.75.

**Transalkylation of 3,3′-Dimethyl-4,4′-dimethoxydiphenylmethane (31).** A solution of 1 g (4 mmol) of **31** and $AlCl_3$–$CH_3NO_2$ catalyst (1.2 g/2.5 ml) in 20 ml of toluene was treated at 30 °C for 1 h and worked up as described above to afford 0.38 g of **33** and 0.71 g (80%) of a mixture of dimethyl-4-methoxydiphenylmethanes [3,4′-dimethyl isomer (**32**) was the main product which was also prepared by methylation of **26**]. **32**: pale yellow, viscous oil; NMR ($CCl_4$) $\delta$ 2.12 (3 H, s, $CH_3$), 2.17 (3 H, s, $CH_3$), 2.26 (3 H, s, $CH_3$), 3.69 (3 H, s, $OCH_3$), 3.74 (2 H, s, $CH_2$), 3.78 (2 H, s, $CH_2$), and 6.47–7.10 (7 H, m, aromatic protons). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.89; H, 8.18.

**Preparation of 32 from 26.** To a solution of 0.5 g (2.4 mmol) of **26** in 20 ml of 10% sodium hydroxide was added 2 ml of dimethyl sulfate at room temperature. The reaction mixture was heated at 100 °C for 30 min and worked up as described above to give 0.48 g (90%) of **32**.

**Transalkylation of 3,5,3′,5′-Tetramethyl-4,4′-dihydroxydiphenylmethane (34).** A mixture of 10 g (40 mmol) of **34**, $AlCl_3$–$CH_3NO_2$ catalyst (11.5 g/25 ml), and 500 ml of toluene was treated at 30 °C for 1 h and worked up as described above to afford 3.53 g (74%) of 2,6-dimethylphenol (**36**) and 0.21 g (75%) of crude 2,6,4′-trimethyl-4-hydroxydiphenylmethane (**35**). **35**: colorless needles (petroleum ether); mp 89–89.5 °C; IR (KBr) 3400 $cm^{-1}$ ($\nu$ OH); NMR ($CDCl_3$) $\delta$ 2.15 (6 H, s, $CH_3$), 2.27 (3 H, s, $CH_3$), 3.76 (2 H, s, $CH_2$), 4.45 (1 H, s, OH), 6.76 and 7.05 (2 H and 4 H, each s, aromatic protons). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.91; H, 7.96.

Although formation of a small amount of 3,5,2′-trimethyl-4-hydroxydiphenylmethane (**35′**) was detected by measurement of the IR spectrum of crude **35**, it could not be isolated.

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**Registry No.**—**9**, 118-82-1; **11**, 28994-46-9; **21**, 32861-23-7; **25**, 96-65-1; **26** isomer A, 37559-11-8; **26** isomer B, 61377-16-0; **28**, 61377-14-8; **29**, 2467-25-6; **31**, 61377-15-9; **32** isomer A, 37559-10-7; **32** isomer B, 61377-17-1; **34**, 5384-21-4; **35** isomer A, 55563-86-5; **35** isomer B, 61377-18-2; $AlCl_3$, 7446-70-0; $CH_3NO_2$, 75-52-5; toluene, 108-88-3; dimethyl sulfate, 77-78-1.

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# Selective Oxidation of the Side Chain at C-3 of Indoles

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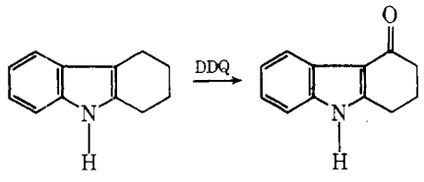
Treatment of 1,2,3,4-tetrahydrocarbazole (**1**) with dichlorodicyanobenzoquinone (DDQ) in aqueous tetrahydrofuran at 0 °C readily gave 1,2,3,4-tetrahydrocarbazol-4-one (**2**) in a high yield. This selective oxidation of C-3 side chains of indoles was extended to cycloalkan[*b*]indoles (**8–11**) to afford the corresponding ketones (**12–15**). The oxidation of *N*-methyl (**17**) and *N*-benzyl (**18**) derivatives also proceeded smoothly. 2,3-Dimethylindoles (**23**) gave 2-formylindole (**25**) as well as the expected 3-formylindole (**24**), but the yield of **25** was lower in tetrahydrofuran containing acetic acid. Oxidation of 3-ethyl-2-methylindole (**26**) gave again only a 3-acyl product (**27**). 3-Monosubstituted indoles (**35–40**) under similar conditions gave the corresponding 3-acylindoles including a β-keto derivative of tryptophan (**46**). Oxidation of methyl 1-benzylindole-3-propionate (**49**) in anhydrous tetrahydrofuran gave methyl 1-benzylindole-3-acrylate (**50**) in a high yield.

Despite numerous reports on the oxidation of indole derivatives,[1] no general method for the selective oxidation of side chains at C-3 is so far available. Thus, oxidation of 3-substituted and 2,3-disubstituted indoles usually occurs on the pyrrole ring and at the 2 substituent, not at the 3 substituent. This is because most oxidizing agents act as electrophiles and first attack C-3 of the indole ring leading to the oxidation of the pyrrole portion and to the formation of 2-acylindoles. Among many oxidative reactions of phenols with dichlorodicyanobenzoquinone (DDQ), Becker[2] showed that the selective benzylic oxidation of suitable phenols proceeded smoothly in methanol. This reaction was successfully extended to an alternative synthesis of tetralones from tetralins.[3] In the present paper, we describe an application of the DDQ oxidation to indoles for a convenient and selective oxidation of C-3 side chains in indoles.

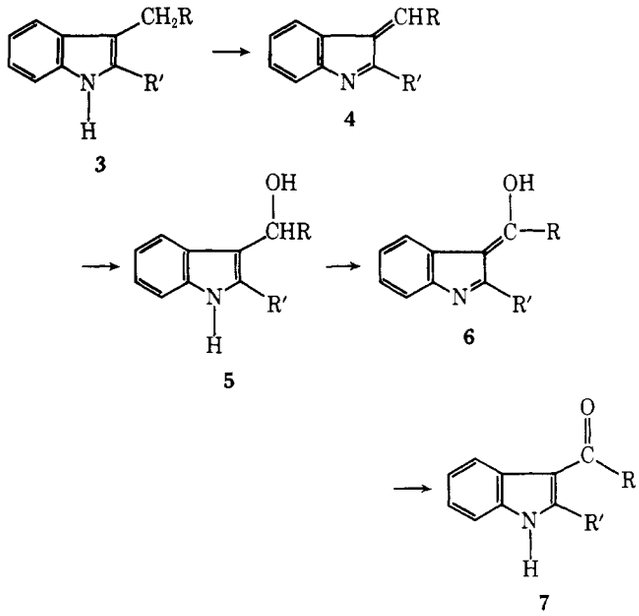
Treatment of tetrahydrocarbazole (**1**) with 2 equiv of DDQ in methanol at 20 °C under nitrogen or argon led to a blue-colored solution, but the color rapidly changed to pale yellow. Tetrahydrocarbazol-4-one (**2**) was isolated from the reaction




**1** **2** (83%)

mixture as a single oxidation product, but only in 22% yield. The yield improved slightly at 0 °C (27%). However, in aqueous tetrahydrofuran the oxidation proceeded quite rapidly and **2** was isolated in 70% yield when reacted at 20 °C and in 83% yield at 0 °C.

No detectable formation of 1,2,3,4-tetrahydrocarbazol-1-one, which was synthesized selectively from **1** with several oxidizing agents,[4] was observed in these conditions. This selective oxidation can be explained by four consecutive reactions (from **3** to **7**), dehydrogenation, addition of water, another dehydrogenation, and isomerization as shown in the following scheme. Since DDQ is known to be a strong electron acceptor, the initial step in the oxidation of electron-donative indoles by DDQ must be the formation of charge-transfer complexes, which readily change to **4** and 2,3-dichloro-5,6-dicyanohydroquinone (DDH).[2,3]




**3** **4** **5** **6** **7**

Several cycloalkan[*b*]indoles (**8–11**) were oxidized under similar conditions to afford the corresponding ketones (**12–15**) as the sole products,[5] and their structural establishment rested on spectral data. In particular, the distinction between the ketones (**12–15**) and **16** was provided by UV spectra. Shioiri[8] reported that a series of **16** and 2-acylindoles have two characteristic strong bands at about 240 and 310 nm, whereas the DDQ oxidation products have three strong bands at 240–250, 260–270, and 290–300 nm, which are characteristic of 3-acylindoles.