# The Reaction between 2,6- and 2,7-Di-*tert*-butyl-1,4-naphthoquinone and Phenylmagnesium Bromide and Phenyllithium

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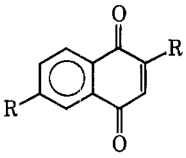
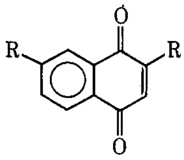
Phenylmagnesium bromide and phenyllithium reacted with 2,6- and 2,7-di-*tert*-butyl-1,4-naphthoquinone to give the expected mono- and diaddition products. Oxidation of the monoaddition products gave *tert*-butylbenzoylbenzoic acids. Two new derivatives, the 3,3-diphenylphthalides and the 3-phenyl-3-anilinophthalides, of each of these acids were prepared. The diaddition products were dehydrated with rearrangement. The two compounds obtained in largest amounts were substituted phthalides, presumably resulting from the oxidation of the 1,2–1,4-diaddition products during isolation. These phthalides reacted with phenylmagnesium bromide, phenyllithium, and lithium aluminum hydride. The 46 new compounds are described.

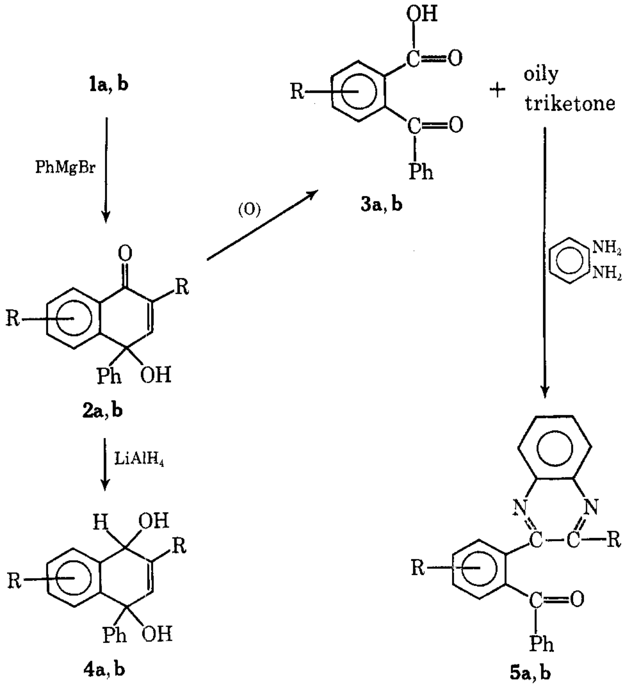
The study[1] of the reactions between quinones and organometallic reagents has been extended to the 2,6- and 2,7-di-*tert*-butyl-1,4-naphthoquinones.

The quinones **1a** and **1b** differ only in the location of the two *tert*-butyl groups on the naphthalene rings. When the reaction products are similar, the "**a**" series will refer to compounds with the *tert*-butyl group in the 6 position and the "**b**" series will refer to the *tert*-butyl group in the 7 position. In all formulas R will be used to represent the *tert*-butyl group and Ph to represent the phenyl group.


**1a**

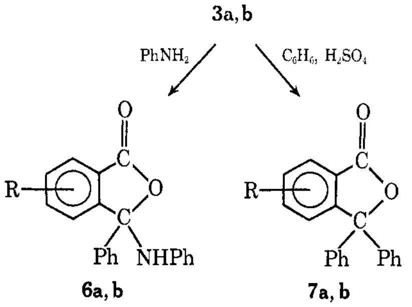

**1b**

More reactions were carried out with the "**a**" series since the 2,6- and 2,7-di-*tert*-butylnaphthalenes are formed in about the ratio of 6:1 and the 2,7 hydrocarbon is very difficult to separate from the complex which it forms with the 2,6 hydrocarbon.



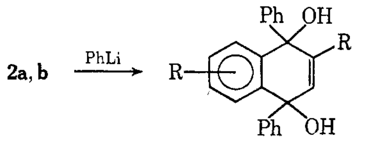
**Monoaddition Products.**—The only monoaddition products isolated were those resulting from the 1,2 addition to the carbonyl group in the 4 position. Oxidation of **2a,b** by chromium trioxide in glacial acetic acid gave the acids **3a,b** and oily triketones which did not crystallize but did react with *o*-phenylenediamine to give the corresponding quinoxalines **5a,b**. The acid **3b** has been prepared before[2] and its formation by the oxidation of various compounds described here establish its structure. The acid **3a** is a new compound which, on treatment with fuming sulfuric acid, gave the same 2-*tert*-butylanthraquinone[2] as **3b**.

Two new derivatives of each of these acids were made by the same procedures used for the preparation of the corresponding derivatives of *o*-benzoylbenzoic acid.[3,4]



The 3,3-diphenylphthalide and the 3-phenyl-3-anilinophthalide were also made from *o*-benzoylbenzoic acid for comparison of their ir spectra with the spectra of **6a,b** and **7a,b**.

**1,2–1,2-Diaddition Products.**—Compounds **2a,b** reacted with phenyllithium to give the diaddition products **8a,b**. **8b** was also obtained in small amounts by the reaction of the quinone **1b** with phenyllithium. It did not lose water spontaneously and too little was available for dehydration experiments. When the quinone **1a** reacted with phenyllithium, a small amount of **2a** was obtained along with compound **9**. Compound **8a** lost water so readily that it could be obtained



**8a, b**

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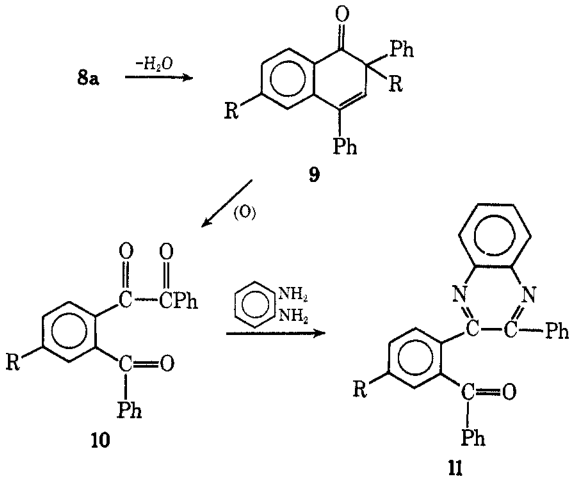
(1) H. M. Crawford, *J. Amer. Chem. Soc.*, **61**, 3310 (1939); **63**, 1070 (1941); **70**, 1081 (1948); *J. Org. Chem.*, **28**, 3082 (1963).

(2) R. B. Contractor and A. T. Peters, *J. Chem. Soc.*, 1314 (1949).

(3) *Beilstein*, 4th ed, **12**, 524 (1929).

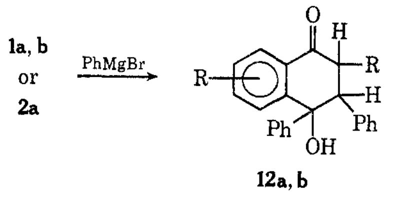
(4) S. D. Ross and M. Schwarz, *J. Amer. Chem. Soc.*, **77**, 3020 (1955).

only by the procedure described in the Experimental Section. Oxidation of **9** by chromium trioxide gave

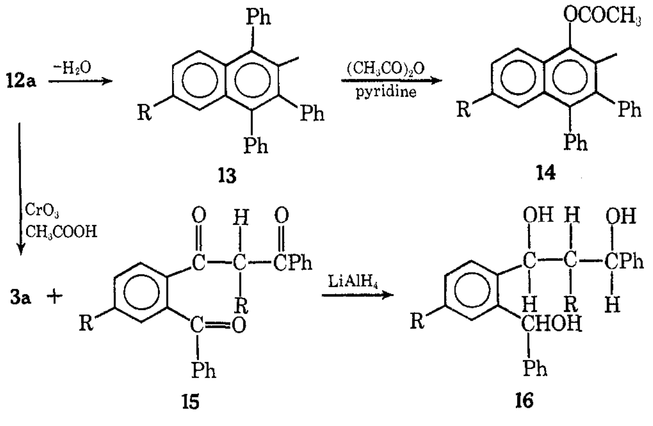


the acid **3a** and the yellow triketone **10** which reacted with *o*-phenylenediamine to give the quinoxaline **11**.

**1,2–1,4-Diaddition Products.**—Compounds of this type were the main products obtained from the reactions of other substituted 1,4-naphthoquinones with phenylmagnesium bromide.[1] In this study, if the same procedure was used, the main solids isolated were the phthalides **17a,b** which will be discussed later. If most of the ether was evaporated as soon as the intermediate magnesium compounds were decomposed, and the mixture was chromatographed on alumina, the expected diaddition products were obtained. The reaction of phenylmagnesium bromide with **2a** also gave **12a**. Both **12a** and **12b** were obtained in two

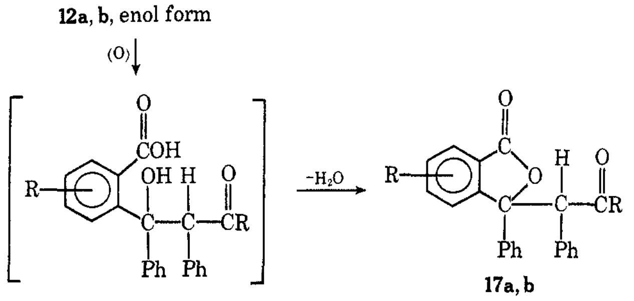


modifications. The two forms of **12a** melted at 198 and 209°, and the two forms of **12b** melted at 146 and 177°. The ir spectra of the four compounds were almost identical, and both forms of **12a** gave the same chemical reactions. Either form of **12a**, or a mixture of the two, could be dehydrated to a naphthol **13**, which on acetylation gave **14**. Either form of **12a**, or a mixture of the two, on oxidation by chromium trioxide



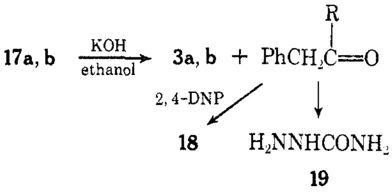
gave the acid **3a** and a triketone **15** which could be reduced to the alcohol **16**.

**Two Phthalides.**—When the ether solution of the products from the reaction of either quinone with phenylmagnesium bromide was allowed to evaporate slowly, the solids obtained were the two phthalides **17a,b**. A possible method for their formation is shown.

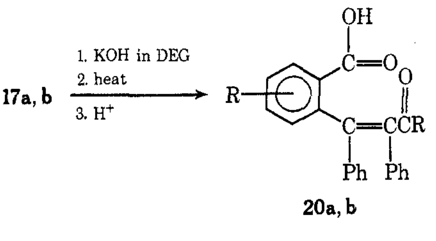


It is well known that compounds of the type written as the intermediate lose water immediately to form phthalides. The reaction of phenylmagnesium bromide with **2a** also gave **17a**.

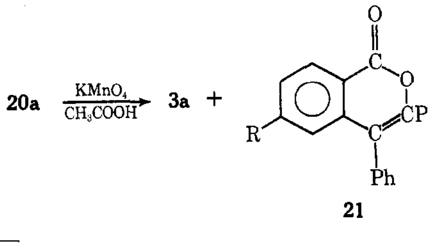
The phthalides both reacted with potassium hydroxide and the products depended on the conditions of the reaction. When they were refluxed with potassium hydroxide in ethanol the products were the corresponding acids **3a,b** and *tert*-butyl benzyl ketone.



The latter was identified as the 2,4-dinitrophenylhydrazone **18** which was identical with a known sample kindly supplied by Dr. House.[5] The semicarbazone **19** was also prepared. When the phthalides were heated to boiling with potassium hydroxide in diethylene glycol, the acids **20a,b** resulted. The acid **20a**, on



oxidation by potassium permanganate in acetic acid, gave the acid **3a** and a neutral compound for which structure **21** is proposed. The phthalides were reduced



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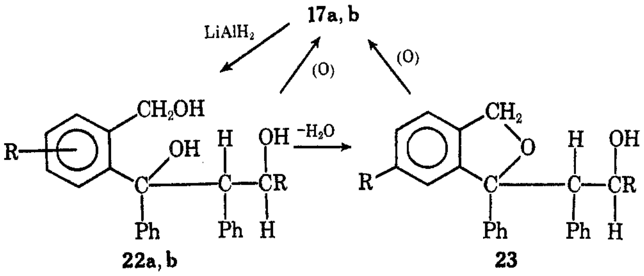
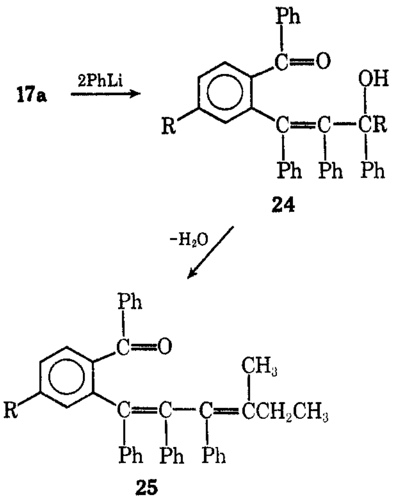
[5] H. O. House and E. J. Grubbs, *J. Amer. Chem. Soc.*, **81**, 4733 (1959).

to the corresponding alcohols **22a,b**, and **22a** was dehydrated to **23**. Oxidation of the alcohols **22a,b** gave

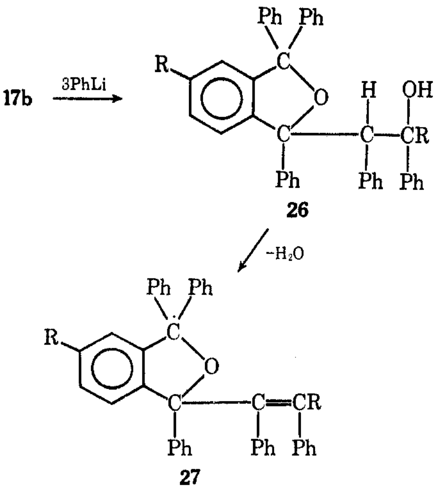


about 70% of the phthalides **17a,b** and small amounts of the acids **3a,b**. Oxidation of **23** also gave 70% of **17a** and some **3a**, which is evidence for the loss of water giving the phthalan rather than an ethylenic structure.

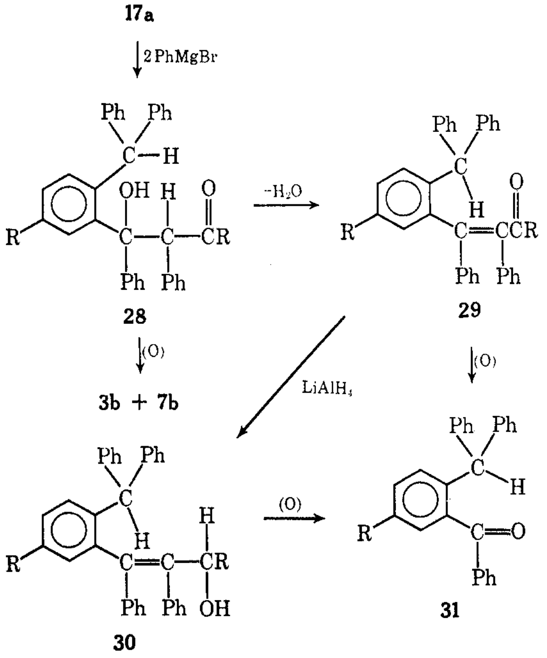
The phthalides reacted with phenyllithium and the products were quite different for the two series. **17a** reacted with 2 mol of phenyllithium to give **24**, which was dehydrated, with rearrangement to give **25**. Oxidation of both **24** and **25** gave methyl ethyl ketone

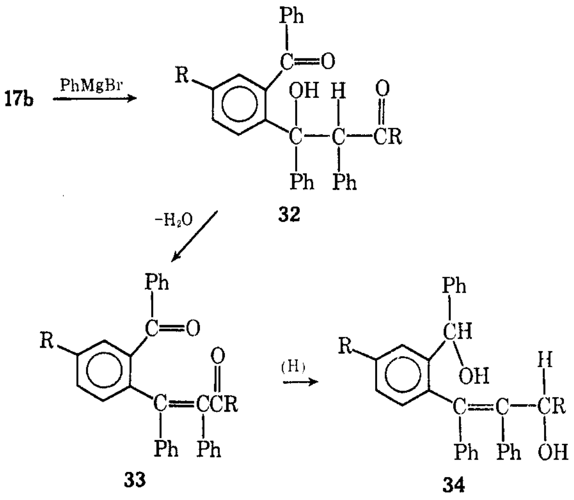


which was identified as the 2,4-dinitrophenylhydrazone. The oxidation of **24** also gave the acid **3b**. **17b** reacted with 3 mol of phenyllithium to give **26** which was dehydrated to give **27**.

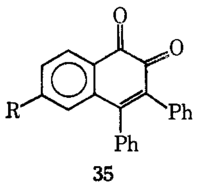


Both phthalides reacted with phenylmagnesiun bromide and again the results were quite different. Oxidation of **28** by chromium trioxide gave the acid **3b** and the phthalide **7b**. Oxidation of both **29** and **30** with chromium trioxide gave **31**. Reductive cleavage of lactones by Grignard reagents has been reported before.[6] The spectra of **31** were very similar to the spectra of a known sample of 2-(diphenylmethyl)benzophenone kindly supplied by Dr. Bradsher.[7] The results of these oxidations established the locations of the phenyl groups. Attempts to oxidize **32** resulted only in the dehydration to **33**.





In reactions of phenylmagnesium bromide with the quinones, after separating as much of the solid products as possible, the thick, dark oils were chromatographed on alumina. This usually gave more of the compounds already obtained. In one case only, the end fractions gave a bright red solid which proved to be the *o*-quinone **35**. Analyses and comparison of its spectra



**35**

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[6] R. C. Fuson and D. E. Brasure, *J. Amer. Chem. Soc.*, **77**, 3131 (1955).

[7] C. K. Bradsher and E. Studley Smith, *ibid.*, **65**, 451 (1943).

with the spectra of the known 3,4-diphenyl-1,2-naphthoquinone kindly furnished by Dr. Smith[8] established its structure. At present no suggestion can be made as to the method of its formation.

In several cases the end fractions from the chromatography gave a yellow compound. It looked and behaved like a *p*-quinone, giving a white diacetate on reductive acetylation. At present no satisfactory structures can be written for these compounds, **36** and **37**.

## Experimental Section

All melting points are uncorrected. All nmr spectra were made in $CDCl_3$ with TMS as reference and are given in $\delta$ values. Most ir spectra were made in $CHCl_3$ or $CS_2$ with a few in KBr, and are given in reciprocal centimeters. The absorption for *tert*-butyl and for mono- and trisubstituted benzenes are not listed as they occur in all compounds.

**Preparation of the Two Quinones (1a,b).**—The quinones were prepared as described earlier[9] by the oxidation of the corresponding hydrocarbons by $CrO_3$ in glacial HOAc. The best yields (70% for **1a** and 60% for **1b**) were obtained when the hydrocarbon was finely divided and the temperature was kept at 35–45° during the addition of the oxidizing agent. The melting point of **1a** was 86–87° and of **1b**, 72–73°. Earlier[9] **1b** was reported as melting at 55–57° but after several years the sample had changed to a higher melting form and all later preparations had the higher melting point. The nmr spectrum for **1a** showed 18 H's at 1.4, 1 vinyl H at 6.9, and 3 aromatic H's at 7.8–8.1.

**Reactions of the Two Quinones.**—The reactions with PhMgBr and with PhLi were carried out as before[1] by adding an ether solution of the reagent to an ether solution of the quinone. A 2.5:1 ratio of the reagent to the quinone usually gave more of the monoaddition products, while a 4:1 ratio gave more of the diaddition products or the phthalides. Reactions of this type are very unpredictable[1] and yields of solid products are usually low and variable. Thick, dark oils account for a large part of the starting material. For these reasons it was best to carry out the reactions on small amounts of the quinones (2.7–5.4 g, 0.01–0.02 mol) rather than on larger amounts. The reaction mixtures were allowed to stand overnight and then decomposed with ice and $NH_4Cl$ solution. The ether solutions were allowed to evaporate slowly and solids were filtered off and recrystallized. After no more solid could be obtained from the dark oils they were chromatographed on alumina. This usually gave more solids. The products obtained in this way (when PhMgBr was the reagent) were **2a,b** and **17a,b**. If most of the ether was distilled off as soon as the reaction mixture was worked up and the solution was then chromatographed on alumina, the products were **2a,b** and **12a,b**. The products obtained when PhLi was the reagent were **8b** or **9**.

**2,6-Di-*tert*-butyl-4-hydroxy-4-phenyl-1(4*H*)-naphthalenone (2a) and 2,7-Di-*tert*-butyl-4-hydroxy-4-phenyl-1(4*H*)-naphthalenone (2b).**—These monoaddition products were formed when PhMgBr reacted with the quinones **1a,b**. The yields were 10–56% for **2a** and 2–50% for **2b**. The faintly yellow **2a** was crystallized from heptane or methanol, mp 164.5–165.5°. **2b** was crystallized from petroleum ether, mp 144–145°. The ir spectra for both showed carbonyl absorption at 1650 and hydroxyl at 3400 $cm^{-1}$. The nmr spectrum for **2a** showed 18 H's at 1.23, 1 H at 3.4, 1 H at 6.8, and 8 H's at 7.0–8.1.

*Anal.* Calcd for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10; mol wt, 348. Found for **2a**: C, 82.5; H, 8.1; mol wt, 345 in benzene. Found for **2b**: C, 83.0; H, 8.18.

**4-*tert*-Butyl-2-benzoylbenzoic Acid (3a) and 5-*tert*-Butyl-2-benzoylbenzoic Acid (3b).**—**3a** was first obtained in 25% yield by refluxing 1 g of **2a** with 3 g of $K_2Cr_2O_7$ or 2 g of $CrO_3$ in 30 ml of glacial HOAc for 5 min. The solution was diluted with $H_2O$ and neutralized with KOH. (The ether extract of the alkaline solution gave **5a** after treatment with *o*-phenylenediamine.) The alkaline solution was acidified and extracted with ether to give **3a**. This acid was also obtained in small amounts by the oxidation of **9**, **12a**, **20a**, and **23** by $K_2Cr_2O_7$ in glacial HOAc. Oxidation of 2 g of **22a** by refluxing for 25 min with 2 g of $CrO_3$ in 30 ml of glacial HOAc gave 44% of **3a**. Refluxing 3 g of **17a** with 0.5 g of KOH in 75 ml of 95% ethanol for 2 hr gave 44% of **3a**. It was crystallized from benzene and petroleum ether, mp 163–164°. **3b** was prepared by the method of Contractor and Peters,[2] mp 179°. It resulted in small amounts by the oxidation of **2b**, **22b**, and **28** by $CrO_3$ in glacial HOAc. Refluxing 1 g of **17b** with 0.5 g of KOH in 25 ml of 95% ethanol for 2 hr gave 70% of **3b**. The ir spectra for **3a** and **3b** were practically identical, with carbonyl absorptions at 1680 and 1700 $cm^{-1}$ and the broad, merged band of the *tert*-butyl and hydroxyl at 2500–3500 $cm^{-1}$.

*Anal.* Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43; mol wt, 282. Found for **3a**: C, 76.7; H, 6.5; neut equiv, 291.

**Cyclization of 3a.**—The acid (0.6 g) and fuming sulfuric acid (4 ml) were heated on the steam bath for 90 min and then poured into ice water. After washing the ether extract with $NaHCO_3$ solution, the ether was evaporated and the remaining solid crystallized from methanol, mp 102–103°. The ir spectrum, with carbonyl absorption at 1780 $cm^{-1}$, was very similar to the spectrum of anthraquinone. These data identify the cyclization product as 2-*tert*-butylanthraquinone.[2]

**2,6-Di-*tert*-butyl-1,4-dihydro-4-phenyl-1,4-naphthalenediol (4a) and 2,7-Di-*tert*-butyl-1,4-dihydro-4-phenyl-1,4-naphthalenediol (4b).**—These compounds were prepared by the reduction of 1 g of **2a** or **2b** by $LiAlH_4$. **4a** was crystallized from methanol or petroleum ether, mp 128–129°, yield 60%. **4b** was crystallized from petroleum ether, mp 150.5–151°, yield 25%. The ir spectra of both showed hydroxyl absorptions at 3600 $cm^{-1}$. The nmr spectrum of **4b** showed 9 H's at 1.2, 9 H's at 1.4, 3 H's at 2.2–3.2, 1 H at 7.0, and 8 H's at 7.4–8.2.

*Anal.* Calcd for $C_{24}H_{30}O_2$: C, 82.24; H,8.63. Found for **4a**: C, 82.2; H, 8.7. Found for **4b**: C, 81.8; H, 8.7.

**5-*tert*-Butyl-2-(3-*tert*-butyl-2-quinoxalinyl)benzophenone (5a) and 4-*tert*-Butyl-2-(3-*tert*-butyl-2-quinoxalinyl)benzophenone (5b).**—The neutral, greenish fractions from the oxidation of **2a** and **2b** were refluxed for a few minutes with 0.3 g of *o*-phenylenediamine in 10 ml of ethanol. The solids which separated on cooling were crystallized from ethanol. **5a** melted at 156–157° and accounted for 27% of the **2a** used. **5b** melted at 209–210° and accounted for 30% of the **2b**. Both ir spectra showed carbonyl absorption at 1670 $cm^{-1}$.

*Anal.* Calcd for $C_{29}H_{30}N_2O$: C, 82.43; H, 7.16. Found for **5a**: C, 82.1; H, 6.9. Found for **5b**: C, 82.8; H, 7.3.

**5-*tert*-Butyl-3-anilino-3-phenylphthalide (6a) and 6-*tert*-Butyl-3-anilino-3-phenylphthalide (6b).**—These two compounds were made by heating to boiling 0.3 g of the acids **3a,b** with 15 drops of aniline. After crystallization from ethanol **6a** melted at 210–211.5° and **6b** melted at 217–218°. The ir spectra for these compounds and for the known 3-anilino-3-phenylphthalide[3] were identical, except for the *tert*-butyl group, showing carbonyl absorption at 1760 and NH at 3400 $cm^{-1}$.

*Anal.* Calcd for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.49. Found for **6a**: C, 80.7; H, 6.8. Found for **6b**: C, 80.4; H, 6.5.

**5-*tert*-Butyl-3,3-diphenylphthalide (7a) and 6-*tert*-Butyl-3,3-diphenylphthalide (7b).**—These phthalides were prepared from **3a** and **3b** by stirring a mixture of 0.4 g of the acid, 20 ml of benzene, and 15 ml of concentrated $H_2SO_4$ for 2 hr.[4] The mixture was poured into water, and the benzene layer was washed with $Na_2CO_3$ solution and allowed to evaporate. The resulting solids were crystallized for ethanol. **7a** melted at 178.5–179° and **7b** melted at 223–224°. They could also be prepared by treating the acids with $SOCl_2$, followed by benzene and anhydrous $AlCl_3$. **7b** was also obtained in 50% yield by refluxing 2 g of **28** with 5 g of $CrO_3$ in 50 ml of glacial HOAc for 90 min and diluting the mixture with $H_2O$. The ir spectra of **7a**, **7b**, and the known 3,3-diphenylphthalide[4] all showed carbonyl absorption at 1770 $cm^{-1}$. The nmr spectrum of **7b** showed 9 H's at 1.36 and 13 H's at 7.3–8.0.

*Anal.* Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48; mol wt, 342. Found for **7a**: C, 84.0; H, 6.6. Found for **7b**: C, 84.4; H, 6.8; mol wt, 331 in benzene, 340 in camphor.

**2,6-Di-*tert*-butyl-1,4-dihydro-1,4-diphenyl-1,4-naphthalenediol (8a) and 2,7-Di-*tert*-butyl-1,4-dihydro-1,4-diphenyl-1,4-naphthalenediol (8b).**—Attempts to make **8a** by the slow evaporation of the ether solution from the reaction of PhLi with either **1a** or **2a** gave only dark oils and small amounts of **9**. If most of the ether was distilled as soon as the reaction mixture of **2a** and PhLi was worked up, and the remaining solution was chromatographed on alumina, about 10% of **8a** could be obtained. After crystallization from benzene and petroleum ether, it melted at 178–180°. On standing for some time it lost water to form **9**.

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(8) L. I. Smith and H. Hoehn, *J. Amer. Chem. Soc.*, **61**, 2619 (1939).

(9) H. M. Crawford, *ibid.*, **77**, 1046 (1955).

**8b** was obtained once in 69% yield when 1.9 g of **1b** reacted with PhLi, and once in 61% yield when 1 g of **2b** reacted with PhLi. After crystallization from heptane it melted at 195–197°. The ir spectra of **8a** and **8b** were very similar, showing hydroxyl absorption at 3000 cm$^{-1}$.

*Anal.* Calcd for $C_{30}H_{34}O_2$: C, 84.46; H, 8.03. Found for **8a**: C, 84.0; H, 8.4. Found for **8b**: C, 84.2; H, 8.1.

**2,6-Di-*tert*-butyl-2,4-diphenyl-1(2*H*)-naphthalenone (9).**—This compound was formed in 20% yield by the reaction of PhLi with 2.7 g of **1a**, by the spontaneous loss of water from **8a**, and in 37% yield by the reaction of PhLi with 3.7 g of **2a**. When crystallized from heptane or ethanol, it melted with decomposition at 140°. The ir spectrum showed carbonyl absorption at 1675 cm$^{-1}$. The nmr spectrum showed 18 H's at 1.2, 1 H at 6.8, and 13 H's at 7.1–8.2.

*Anal.* Calcd for $C_{30}H_{32}O$: C, 88.19; H, 7.90; mol wt, 400. Found: C, 88.1; H, 8.0; mol wt, 389 in benzene.

**4-*tert*-Butyl-2-benzoylbenzil (10).**—This yellow triketone was formed in 40% yield by the oxidation of 1 g of **9** by $K_2Cr_2O_7$ in glacial HOAc. It melted at 147–147.5° after crystallization from ethanol and ethyl acetate. The ir spectrum showed carbonyl absorption at 1675 cm$^{-1}$. The nmr spectrum showed 9 H's at 1.2 and 13 H's at 6.9–8.0.

*Anal.* Calcd for $C_{25}H_{22}O_3$: C, 81.05; H, 6.0; mol wt, 370. Found: C, 81.0; H, 6.1; mol wt, 344 in benzene.

**5-*tert*-Butyl-2-(3-phenylquinoxalinyl)benzophenone (11).**—This compound was formed in 50% yield when 0.37 g of **10** and 0.15 g of *o*-phenylenediamine were refluxed for 30 min in 15 ml of ethanol. After crystallization from methanol or hexane and benzene it melted at 153–154°. The ir spectrum showed carbonyl absorption at 1670 cm$^{-1}$ and was very similar to the spectra of **5a,b**. The nmr spectrum showed 9 H's at 1.35 and 17 H's at 7.0–8.2.

*Anal.* Calcd for $C_{31}H_{26}N_2O$: C, 84.13; H, 5.92. Found: C, 84.0; H, 6.2.

**2,6-Di-*tert*-butyl-4-hydroxy-3,4-diphenyl-(2,3*H*)-naphthalenone (12a) and 2,7-Di-*tert*-Butyl-4-hydroxy-3,4-diphenyl-(2,3*H*)-naphthalenone (12b).**—The quinones **1a,b** were treated with an excess (4:1) of PhMgBr and allowed to stand overnight. The reaction mixture was decomposed with $NH_4Cl$ solution and most of the ether was removed by distillation. A little benzene was added and the solution chromatographed on alumina. This gave 54% of solid material **12a** which was separated by fractional crystallization from ethanol and ethyl acetate into the two isomeric forms melting at 198–199 and 209–210°. Both isomers were also formed (61%) when the reaction mixture from **2a** and PhMgBr was treated in the same way. By the same procedure, **1b** and PhMgBr gave 70% of two isomers which melted at 146–147 and 177–178°. The ir spectra for these four isomers were very similar showing carbonyl absorption at 1670 and hydroxyl at 3500 cm$^{-1}$. The nmr spectrum of the 198° compound showed 9 H's at 0.9, 9 H's at 1.22, 1 H each at 2.2, 3.2, and 3.8, and 13 H's at 6.95–7.9.

*Anal.* Calcd for $C_{30}H_{34}O_2$: C, 84.46; H, 8.03; mol wt, 427. Found for **12a** (198°): C, 84.2; H, 8.3; mol wt, 400 in benzene. Found for **12a** (209°): C, 84.7; H, 8.1; mol wt, 406 in benzene. Found for **12b** (146°): C, 84.9; H, 8.0. Found for **12b** (177°): C, 84.4; H, 8.2; mol wt, 404 in benzene.

**6-*tert*-Butyl-3,4-diphenyl-1-naphthol (13).**—Either form of **12a** could be dehydrated by heating with $I_2$ in glacial HOAc or *p*-toluenesulfonic acid in benzene. The naphthol darkened on standing and no satisfactory solvent for crystallization could be found. Dehydration of 2 g of the 209° isomer by refluxing for 90 min with 1 g of *p*-toluenesulfonic acid in 15 ml of benzene, washing the benzene with water, distilling about half of the solvent, and diluting with petroleum ether gave 1.7 g (80%) of a pale pink solid melting at 142–146°. The ir spectrum showed hydroxyl absorption at 3600 cm$^{-1}$. Acetylation gave **14**.

**6-*tert*-Butyl-3,4-diphenyl-1-naphthol Acetate (14).**—The acetate was made from 1 g of the crude naphthol **13** by refluxing for 1 hr with 5 ml of $Ac_2O$ in 15 ml of pyridine. The solution was diluted with water. The resulting solid crystallized from ethanol as long, shiny white needles, mp 124–125°. The ir spectrum showed carbonyl absorption at 1750 cm$^{-1}$. The nmr spectrum showed 9 H's at 1.2, 3 H's at 2.4, and 13 H's at 7.0–8.0.

*Anal.* Calcd for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64. Found: C, 85.2; H, 6.7.

**2-*tert*-Butyl-3-phenyl-1-(4-*tert*-butyl-2-benzoylphenyl)-1,3-propanedione (15).**—This compound was formed in 25–30% yield by refluxing either form of **12a**, or a mixture of the two, with $CrO_3$ in glacial HOAc. After crystallization from ethanol, it melted at 163–164°. The ir spectrum showed carbonyl absorption at 1675 and 1730 cm$^{-1}$. The nmr spectrum showed 9 H's at 1.05, 9 H's at 1.3, 1 H at 5.25, and 13 H's at 7.3–8.0.

*Anal.* Calcd for $C_{30}H_{32}O_3$: C, 81.78; H, 7.32; mol wt, 441. Found: C, 81.5; H, 7.6; mol wt, 429 in benzene.

**2-*tert*-Butyl-3-phenyl-1-[4-*tert*-butyl-2-(hydroxyphenylmethyl)-phenyl]-1,3-propanediol (16).**—Compound **15** (1 g) was refluxed for 1 hr with 1 g of $LiAlH_4$ in 25 ml of ether. After decomposing the excess $LiAlH_4$ with ethyl acetate and dilute HCl, the ether solution gave a white solid (70%) which was crystallized from petroleum ether and acetone and melted at 196–197°. The ir spectrum showed hydroxyl absorption at 3500 cm$^{-1}$.

*Anal.* Calcd for $C_{30}H_{38}O_3$: C, 80.68; H, 8.58. Found: C, 80.6; H, 8.8.

**5-*tert*-Butyl-3-phenyl-3-(α-pivaloylbenzyl)phthalide (17a) and 6-*tert*-Butyl-3-phenyl-3-(α-pivaloylbenzyl)phthalide (7b).**—These phthalides were the main products isolated from the slow evaporation of the ether solutions from the reactions of **1a,b** with PhMgBr. Yields varied, with a maximum of 52% for **17a** and 32% for **17b**. After crystallization from ethyl acetate **17a** melted at 222–223° and **17b** at 213–214°. Neither of these could be oxidized by refluxing with $CrO_3$ in glacial HOAc. The ir spectra for both showed carbonyl absorptions at 1700 and 1750 cm$^{-1}$. The nmr spectra for both showed 9 H's at 0.8, 9 H's at 1.4, 1 H at 5.23, 12 H's at 7.0–7.8, and 1 H at 8.5.

*Anal.* Calcd for $C_{30}H_{32}O_3$: C, 81.78; H, 7.32; mol wt, 441. Found for **17a**: C, 81.7; H, 7.2; mol wt, 426 in benzene. Found for **17b**: C, 81.4; H, 7.4; mol wt, 436 in benzene.

**2,4-Dinitrophenylhydrazone of *tert*-Butyl Benzyl Ketone (18).**—This compound resulted when the neutral fraction, from the reaction of either **17a** or **17b** with KOH in ethanol, was treated with 2,4-dinitrophenylhydrazine. It melted at 140–141° and was not depressed when mixed with a known sample.$^5$

**Semicarbazone of *tert*-Butyl Benzyl Ketone (19).**—The semicarbazone was prepared in the usual way from the neutral fraction from the reaction of **17a** with KOH in ethanol. After crystallization from 10% ethanol it melted at 149–150°.

*Anal.* Calcd for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.21. Found: C, 66.7; H, 8.3.

**4-*tert*-Butyl-2-(4,4-dimethyl-1,2-diphenyl-1-penten-3-onyl)benzoic Acid (20a) and 5-*tert*-Butyl-2-(4,4-dimethyl-1,2-diphenyl-1-penten-3-onyl)benzoic Acid (20b).**—These acids were formed when the phthalides (1 g) were heated to boiling with KOH (0.3 g) in 7.5 ml of diethylene glycol. The solution was poured on ice and the clear solution acidified. The heavy, white precipitate was filtered and crystallized from ethanol. The yield of **20a** was 90% and it melted at 178–180°. It was unchanged by heating to 250°, and oxidation by $CrO_3$ gave 44% of **3a**. The yield of **20b** was very small and it melted at 176–177°. The ir spectra were very similar showing the broad, merged band of the acid hydroxyl and the *tert*-butyl groups at 2500–3500 cm$^{-1}$, and the carbonyl groups at 1680 and 1740 cm$^{-1}$. The nmr spectrum for **20b** showed 9 H's at 0.8, 9 H's at 1.2, 13 H's at 6.8–7.8, and the acid H at 11.0. The acid H disappeared after $D_2O$ exchange.

*Anal.* Calcd for $C_{30}H_{32}O_3$: C, 81.78; H, 7.32; mol wt, 441. Found for **20a**: C, 81.8; H, 7.4; mol wt, 453 in camphor; neut equiv, 431. Found for **20b**: C, 81.8; H, 7.4.

**6-*tert*-Butyl-3,4-diphenylisocoumarin (21).**—The acid **20a** (1 g) was refluxed for 10 min with $KMnO_4$ (0.5 g) in 5 ml of glacial HOAc and then poured on ice. The solution was decolorized by $NaHSO_3$ and filtered, and the precipitate was dissolved in ether and extracted with $NaHCO_3$ solution. After evaporating the ether, the solid was crystallized from ethanol and ethyl acetate, mp 175–176°, yield 25%. The ir spectrum showed carbonyl absorption at 1760 cm$^{-1}$. The nmr spectrum showed 9 H's at 1.1 and 13 H's at 7.2–8.0.

*Anal.* Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 84.8; H, 6.5.

**4,4-Dimethyl-1,2-diphenyl-1-(2-hydroxymethyl-5-*tert*-butylphenyl)-1,3-pentanediol (22a) and 4,4-Dimethyl-1,2-diphenyl-1-(2-hydroxymethyl-4-*tert*-butylphenyl)-1,3-pentanediol (22b).**—Reduction of **17a** (4 g) by refluxing for 45 min with $LiAlH_4$ (3 g) in 100 ml of ether gave 95% of **22a**. After crystallization from ethanol it melted at 225–227°. Reduction of 2 g of **17b** in the same way gave 66% of **22b**. It was crystallized from benzene and melted at 198–199°. The ir spectra of both showed hydroxyl absorption at 3400 cm$^{-1}$ and no carbonyl. The nmr spectra showed 9 H's at 0.8, 9 H's at 1.4, 2 H's at 2.0, 5 H's at 3.8–4.7, and 13 H's at 6.9–7.8.

*Anal.* Calcd for $C_{30}H_{38}O_3$: C, 80.68; H, 8.58; mol wt, 447. Found for **22a**: C, 80.8; H, 8.8; mol wt, 425 in bromoform. Found for **22b**: C, 80.7; H, 8.22.

**5-*tert*-Butyl-3-(3,3-dimethyl-1-phenyl-2-butanolyl)-3-phenylphthalan (23)**.—The dehydration of **22a** (0.7 g) was carried out by refluxing for 2 hr with *p*-toluenesulfonic acid (1 g) in 20 ml of benzene. The benzene solution was washed with $H_2O$ and the solvent was allowed to evaporate. Crystallization from ethanol gave 60% of **23**, mp 155–156°. The ir spectrum showed hydroxyl absorption at 3500 $cm^{-1}$ and a broad ether band at 1100 $cm^{-1}$. The nmr spectrum showed 9 H's at 0.7, 9 H's at 1.4, 2 H's at 3.7, 1 H at 4.1, 2 H's at 5.2, and 13 H's at 6.9–7.65.

*Anal.* Calcd for $C_{30}H_{36}O_2$: C, 84.07; H, 8.47. Found: C, 84.0; H, 8.7.

**4,4-Dimethyl-1,2,3-triphenyl-1-(2-benzoyl-5-*tert*-butylphenyl)-1-penten-3-ol (24)**.—This compound resulted from the reaction of PhLi with the phthalide **17a** in yields of 50–80%. It was crystallized from ethyl acetate, mp 198–199°. Oxidation of 1 g by refluxing for 15 min with $CrO_3$ (2 g) in 30 ml of glacial HOAc gave the acid **3b** (100%) and a neutral fraction from which the 2,4-dinitrophenylhydrazone of methyl ether ketone was isolated. The ir spectrum showed hydroxyl absorption at 3400 and carbonyl at 1650 $cm^{-1}$. The nmr spectrum showed 9 H's at 0.8, 9 H's at 1.1, 1 H at 6.0, and 23 H's at 6.5–7.8.

*Anal.* Calcd for $C_{42}H_{42}O_2$: C, 87.14; H, 7.32; mol wt, 579. Found: C, 87.0; H, 7.4; mol wt, 562 in camphor.

**4-Methyl-1,2,3-triphenyl-1-(2-benzoyl-5-*tert*-butylphenyl)-1,3-hexadiene (25)**.—Compound **24** (1.3 g) was refluxed for 90 min with 20 ml of Lucas reagent and 20 ml of benzene. The benzene layer was washed with water and evaporated, and the resulting solid was crystallized from ethanol and ethyl acetate. It melted at 158–160° and the yield was 75%. Oxidation by $CrO_3$ gave only benzoic acid from the acid fraction and the 2,4-dinitrophenylhydrazone of methyl ethyl ketone from the neutral fraction. The ir spectrum showed carbonyl absorption at 1670 $cm^{-1}$. The nmr spectrum showed 17 H's at 0.82–1.6 and 23 H's at 6.2–8.2.

*Anal.* Calcd for $C_{42}H_{40}O$: C, 89.95; H, 7.19. Found: C, 89.9; H, 7.3.

**5-*tert*-Butyl-1-(3,3-dimethyl-1,2-diphenyl-2-butanolyl)-1,3,3-triphenylphthalan (26)**.—The phthalide **17b** reacted with 3 mol of PhLi to give 42% of **26**. After crystallization from ethanol and benzene it melted at 226–227°. The ir spectrum showed hydroxyl absorption at 3500 and the broad ether band at 1000–1200 $cm^{-1}$. The nmr spectrum showed 18 H's at 1.1, 1 H at 3.5, 1 H at 4.9, and 28 H's at 6.5–7.7.

*Anal.* Calcd for $C_{48}H_{48}O_2$: C, 87.76; H, 7.37; mol wt, 657. Found: C. 87.5; H, 7.3; mol wt, 631 in camphor.

**5-*tert*-Butyl-1-(3,3-dimethyl-1,2-diphenyl-1-butenyl)-1,3,3-triphenylphthalan (27)**.—This compound was formed in 50% yield by the dehydration of **26** (0.4 g) by refluxing for 2 hr with *p*-toluenesulfonic acid (0.2 g) in 10 ml of benzene. After crystallization from $CHCl_3$ it melted, with decomposition, at 236–238°. The ir spectrum showed the wide ether band at 1075–1200 $cm^{-1}$. The nmr spectrum showed 9 H's at 0.9, 9 H's at 1.1, and 28 H's at 6.8–7.5.

*Anal.* Calcd for $C_{48}H_{46}O$: C, 90.24; H, 7.26. Found: C, 90.4; H, 7.0.

**4,4-Dimethyl-1,2-diphenyl-1-[5-*tert*-butyl-2-(diphenylmethyl)-phenyl]-1-pentanol-3-one (28)**.—The phthalide **17a** reacted with 2 mol of PhMgBr to give 50–80% of **28**. After crystallization from benzene it melted at 252–253°. The ir spectrum showed carbonyl absorption at 1652 and hydroxyl at 3400 $cm^{-1}$. The nmr spectrum showed 9 H's at 1.0, 9 H's at 1.4, 1 H at 2.2, and 25 H's at 6.7–7.5.

*Anal.* Calcd for $C_{42}H_{44}O_2$: C, 86.83; H, 7.64; mol wt, 581. Found: C, 86.8; H, 7.3; mol wt, 592 in bromoform.

**4,4-Dimethyl-1,2-diphenyl-1-[5-*tert*-butyl-2-(diphenylmethyl)-phenyl]-1-penten-3-one (29)**.—This compound was obtained (62%) by refluxing **28** (2.5 g) for 1 hr with *p*-toluenesulfonic acid (1 g) in 25 ml of glacial HOAc. The solution was diluted and filtered, and the resulting solid was crystallized from ethyl acetate, mp 266–267°. **28** also lost water when refluxed with $I_2$ in HOAc or with Lucas reagent or *p*-toluenesulfonic acid in benzene, but the yields were lower and the compound was more difficult to purify. The ir spectrum showed carbonyl absorption at 1670 $cm^{-1}$. The nmr spectrum showed 9 H's at 0.4, 9 H's at 0.9, 1 H at 2.17, and 23 H's at 6.55–7.7.

*Anal.* Calcd for $C_{42}H_{42}O$: C, 89.62; H, 7.52. Found: C, 89.8; H, 7.2.

**4,4-Dimethyl-1,2-diphenyl-1-(5-*tert*-butyl-2-diphenylmethyl)-phenyl-1-penten-3-ol (30)**.—Reduction of **29** (0.7 g) by $LiAlH_4$ in ether gave 90% of **30**. After crystallization from ethyl acetate and $CHCl_3$, it melted at 281–282°. The ir spectrum showed hydroxyl absorption at 3550 $cm^{-1}$.

*Anal.* Calcd for $C_{42}H_{44}O$: C, 89.30; H, 7.85. Found: C, 89.1; H, 7.8.

**5-*tert*-Butyl-2-(diphenylmethyl)benzophenone (31)**.—This compound was formed by the oxidation of either **29** (50%) or **30** (31%) by refluxing with $CrO_3$ in glacial HOAc. In both cases small amounts of benzoic acid were formed. After crystallization from hexane it melted at 140–141°. The ir spectrum showed carbonyl absorption at 1670 $cm^{-1}$. The nmr spectrum showed 9 H's at 1.34, 1 H at 2.2, and 18 H's at 7.0–8.5. Both the ir and the nmr spectra showed close agreement with a sample of 2-benzoyltriphenylmethane kindly supplied by Dr. Bradsher.[7]

*Anal.* Calcd for $C_{30}H_{28}O$: C, 89.07; H, 6.98, mol wt, 405. Found: C, 89.0; H, 6.6; mol wt, 383 in benzene.

**4,4-Dimethyl-1,2-diphenyl-1-(4-*tert*-butyl-2-benzoylphenyl)-1-pentanol-3-one (32)**.—The phthalide **17b** reacted with 1 mol of PhMgBr to give 58% of **32**. Solutions that were left over the summer gave only the dehydration product **33**. Crystallization of **32** from acetic acid or petroleum ether gave a melting point of 181–182°. The ir spectrum showed carbonyl absorption at 1700 and hydroxyl at 3400 $cm^{-1}$. The nmr spectrum showed 9 H's at 0.95, 9 H's at 1.37, 1 H at 5.2, 1 H at 5.8, and 18 H's at 7.2–8.2.

*Anal.* Calcd for $C_{36}H_{38}O_3$: C, 83.36; H, 7.39. Found: C, 83.4; H, 7.6.

**4,4-Dimethyl-1,2-diphenyl-1-(4-*tert*-butyl-2-benzoylphenyl)-1-penten-3-one (33)**.—This compound was formed by spontaneous loss of water from **32**. After crystallization from benzene and petroleum ether, it melted at 222–223°. The ir spectrum showed carbonyl absorption at 1700 $cm^{-1}$.

*Anal.* Calcd for $C_{36}H_{36}O_2$: C, 86.36; H, 7.25; mol wt, 501. Found: C, 86.9; H, 7.6; mol wt, 527 in benzene.

**4,4-Dimethyl-1,2-diphenyl-1-[4-*tert*-butyl-2-(α-hydroxybenzyl)-phenyl]-1-penten-3-ol (34)**.—Reduction of **33** (0.4 g) by $LiAlH_4$ gave 78% of **34**. Crystallization from ethanol and ethyl acetate gave a melting point of 197–198°. The ir spectrum showed hydroxyl absorption at 3400 $cm^{-1}$. The nmr spectrum showed 9 H's at 0.6, 9 H's at 1.23, 1 H at 2.17, 1 H at 3.65, 1 H at 4.35, and 18 H's at 6.9–8.1.

*Anal.* Calcd for $C_{36}H_{40}O_2$: C, 85.67; H, 7.99. Found, C, 85.6; H, 7.8.

**6-*tert*-Butyl-3,4-diphenyl-1,2-naphthoquinone (35)**.—This bright red compound was isolated from the end fractions after chromatographing mixtures from the reaction of PhMgBr with the quinone **1a**. It melted at 183–184° after crystallization from ethanol. The ir spectrum showed carbonyl absorption at 1670 $cm^{-1}$ and was very similar to the spectrum of a sample of 3,4-diphenyl-1,2-naphthoquinone kindly supplied by Dr. Smith.[8] The nmr spectrum showed 9 H's at 1.2 and 13 H's at 6.9–7.7.

*Anal.* Calcd for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 85.6; H, 6.1.

**Yellow Quinone (36)**.—This compound was obtained several times in chromatographing the residues from the reaction of PhMgBr with the quinone **1a**. It crystallized from ethanol as soft, cottony, yellow needles melting at 204–205°. The ir spectrum showed carbonyl absorption at 1675 $cm^{-1}$. The nmr spectrum showed 9 H's at 1.4 and 13 H's at 6.8–8.3. These data suggest a *tert*-butyldiphenyl-1,4-naphthoquinone, but the percentages of carbon and hydrogen are too low.

*Anal.* Calcd for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05, mol wt, 366. Calcd for $C_{26}H_{22}O_3$; C, 81.65; H, 5.8; mol wt, 382. Found: C, 81.6; H, 5.9; mol wt, 373 in bromoform.

**Diacetate of 36 (37)**.—Compound **36** (1.5 g) was refluxed for 10 min with Zn powder (5 g), anhydrous NaOAc (1 g), and 15 ml of $(CH_3CO)_2O$. The clear, colorless solution was poured on ice and most of the acid neutralized with KOH, and the solution was extracted with ether. Evaporation of the solvent gave an oil which solidified when rubbed with petroleum ether. The white solid was crystallized from hexane and melted at 125–127°, yield 80%. Later this material changed to a form melting at 144–145°. The spectra and analyses were the same for both forms. The ir spectra showed carbonyl absorption at 1770 $cm^{-1}$. The nmr spectra showed 9 H's at 1.35, 3 H's at 1.95, 3 H's at 2.05, and 13 H's at 6.5–7.9.

*Anal.* Calcd for $C_{30}H_{28}O_4$: C, 79.6; H, 6.24; mol wt, 452. Calcd for $C_{30}H_{28}O_5$: C, 76.90; H, 6.02; mol wt, 468. Found: C, 76.6; H, 6.1; mol wt, 453 in benzene.

**Registry No.**—**1a**, 31592-22-0; **1b**, 10239-91-5; **2a**, 31592-24-2; **2b**, 31592-25-3; **3a**, 31592-26-4; **3b**, 31592-27-5; **4a**, 31592-28-6; **4b**, 31592-29-7; **5a**, 31592-30-0; **5b**, 31592-31-1; **6a**, 31592-32-2; **6b**, 31592-33-3; **7a**, 31592-34-4; **7b**, 31592-35-5; **8a**, 31592-36-6; **8b**, 31592-37-7; **9**, 31592-38-8; **10**, 31592-39-9; **11**, 31592-40-2; **12a**, 31592-41-3; **12b**, 31592-42-4; **13**, 33189-77-4; **14**, 33189-78-5; **15**, 31592-45-7; **16**, 31592-46-8; **17a**, 31592-47-9; **17b**, 31592-48-0; **18**, 31592-49-1; **19**, 31592-50-4; **20a**, 31592-51-5; **20b**, 31662-33-6; **21**, 31592-52-6; **22a**, 31592-53-7; **22b**, 31592-54-8; **23**, 31592-55-9; **24**, 31592-56-0; **25**, 31592-57-1; **26**, 31592-58-2; **27**, 31592-59-3; **28**, 31592-60-6; **29**, 31592-61-7; **30**, 31592-62-8; **31**, 31592-63-9; **32**, 31592-64-0; **33**, 31592-65-1; **34**, 31592-66-2; **35**, 31592-67-3; phenylmagnesium bromide, 100-58-3; phenyllithium, 591-51-5.

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# Reaction of Nitriles with Hydrazine Hydrate and Raney Nickel[1]

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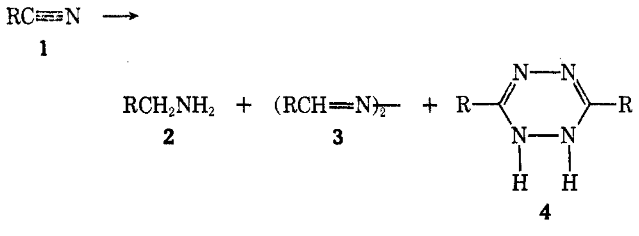
The reaction of ethanolic solutions of nitriles with hydrazine hydrate and catalytic amounts of Raney nickel was investigated as a possible general synthesis of aldehydes (isolated as the aldazines). The types of nitriles investigated were mono-, di-, and trisubstituted acetonitriles, carbocyclic nitriles, aromatic nitriles, α,β-unsaturated nitriles, and some heterocyclic nitriles. Depending upon the structure of the nitrile, it was found that either a primary amine, an aldazine, or a 3,6-disubstituted 1,2,4,5-tetrazine derivative was the major product. The reaction of α,β-unsaturated nitriles is further complicated by reactions of the double bond. Some experiments aimed at elucidating the reaction path were also performed. As a general aldehyde synthesis, the reaction appears to be limited to benzonitrile and substituted benzonitriles.

Hydrazine hydrate and Raney nickel are an effective combination for the reduction of aromatic nitro compounds to amines.[3] These same reagents have been employed by Pietra and Trinchera[4] for the partial reduction of 20 substituted benzonitriles to the corresponding aldazines which upon hydrolysis affords the corresponding aldehydes. We extended the hydrazine–Raney nickel reducing system to 2-(arylmethyl)benzonitriles and obtained aldazines which upon heating with acid give excellent yields of polynuclear aromatic hydrocarbons.[5] Terent'ev, *et al.*,[6] reported that phenylacetonitrile, 3-indoleacetonitrile, and 5-methoxy-2-methyl-1-benzyl-3-indoleacetonitrile are reduced to the primary amines with hydrazine and Raney nickel. In another investigation using these reducing agents, Dallacker[7] reported that the three isomeric cyanopyridines and 3,4-methylenedioxybenzonitrile yield the corresponding 3,6-disubstituted 1,2-dihydro-1,2,4,5-tetrazines. However, it was later reported by Butte and Case[8] that Raney nickel is not necessary for the formation of the tetrazines as had been reported by Dallacker.

In view of the results of the various studies, we undertook an examination of the effect of structure in determining the nature of the product from the reaction of nitriles with hydrazine hydrate and catalytic amounts of Raney nickel.



The results of the reactions of the 34 nitriles studied are tabulated in Table I.

Some nonkinetic methods of investigation were also used to study the course of the reduction of nitriles with hydrazine and Raney nickel. Preparatively, benzaldazine is obtained from benzonitrile by evaporation of the solvent from the reaction mixture followed by addition of aqueous acid to the residual oil. The oil was thought to be either the impure hydrazone or aldazine or a mixture of both. The ultraviolet spectrum of this oil (before acidification) was found to be consistent with that which would be obtained from a mixture of benzaldehyde hydrazone and benzaldazine. The presence of benzaldehyde hydrazone was confirmed by acidifying the oil, thus converting the hydrazone to benzaldazine, and this was observed spectroscopically. The presence of benzylamine (15%) and benzonitrile (a trace) was confirmed by vapor phase chromatograms of the reaction mixture both before and after conversion of the hydrazone to the aldazine.

Robinson and Brown[9] had found that hydrazine–Raney nickel effected the cleavage of N,N′-diacylated hydrazines to produce the corresponding amides. This suggested that the benzylamine found in the reaction

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(2) Abstracted in part from the M.S. theses of J. F. Siuda, 1964, M. J. Nolan, 1964, and T. M. Santosusso, 1966, Villanova University.

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