Synthesis of 1,3,5-Trialkylbenzenes from Anils of Methyl Alkyl Ketones

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Besides the previously observed 2,2,4-trialkyl-1,2-dihydroquinolines, a mixture of 1,3,5-trialkylbenzenes and 1-methyl-2,3,5-trialkylbenzenes was obtained in up to 50% yields when methyl alkyl ketones, aniline, and an acidic catalyst, such as hydrogen chloride, were heated to 180 °C and the water was removed as formed. The reaction is thought to proceed through an $\alpha,\beta,\gamma,\delta$-unsaturated anil intermediate, but the corresponding $\alpha,\beta,\gamma,\delta$-unsaturated imines and aliphatic amines did not give trialkylbenzenes.

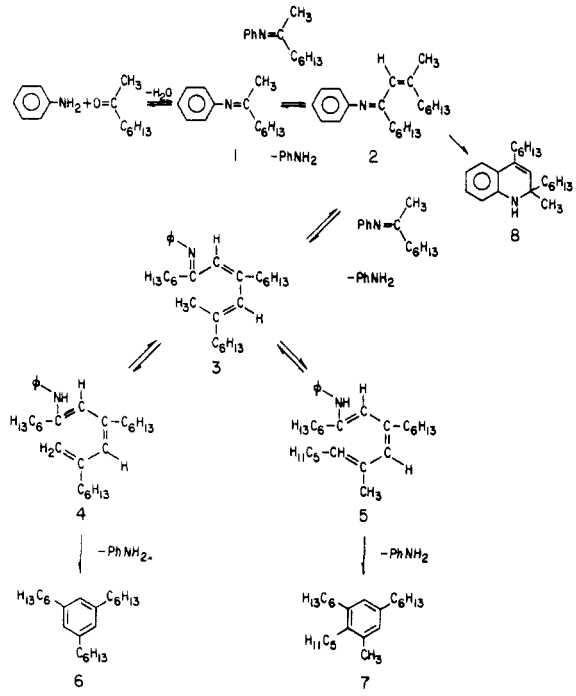
In an effort to obtain new 2,2,4-trialkyl-1,2-dihydroquinolines, we reacted aliphatic ketones with aniline and hydrogen chloride at 180 °C. In spite of the fact that this reaction has been extensively studied,[1,2,3,4] we found that when certain methyl alkyl ketones were used in this reaction, a mixture of 1,3,5-trialkylbenzenes and 1-methyl-2,3,5-trialkylbenzenes (in the approximate ratio of 3:1) was formed in yields up to 40% based on the ketone. The expected products, also formed in this reaction, were 2-methyl-2,4-dialkyl-1,2-dihydroquinolines, 2-methyl-4-alkylquinolines,[5] and ketone anils, as well as their aldol condensation products, and 4,4′-(alkanediyl)bisbenzenamines.[6]

The formation of alkylbenzenes from ketones, such as acetone, methyl ethyl ketone, and cyclohexanone,[7] in the presence of large amounts of strong acids is well-known. However, the formation of alkylbenzenes from ketimines has not been reported. It should be noted that acetophenones are known to give 1,3,5-triarylbenzenes when heated with aniline and aniline hydrochloride.[8] This can be presumed to occur through an anil intermediate. These anomalies prompted us to continue to study the chemical differences between ketones and ketimines.[9]

The formation of alkylbenzenes can be explained by the reactions in Scheme I. Aniline and the methyl ketone react to give the anil **1**, which undergoes an aldol condensation to give **2**. A Michael condensation of **1** and **2**, or perhaps **1** and a ketone, gives the $\alpha,\beta,\gamma,\delta$-unsaturated anil **3**, which has two enamine tautomers, **4** and **5**. These latter conjugated trienes cyclize via a Cope reaction and eliminate aniline to give the observed products, **6** and **7**. Dihydroquinoline (**8**) formation has been reported to occur by the 1,4-addition of aniline to **2**, followed by cyclization and elimination of the aniline.[3]

The alkylbenzenes formed in this reaction require that the methyl group, rather than the methylene group, undergo the required condensation reactions. This is consistent with the preference of the methyl group of ketones to undergo base-catalyzed aldol condensations,[7] and with the report that the acid-catalyzed aldol condensations of ketimines occur regiospecifically at the methyl group.[10] We found that ketones which do not possess a methyl

Scheme I



group adjacent to the carbonyl, such as 4-heptanone, undergo aldol condensations very slowly but do not give alkylbenzenes. Cyclohexanone represents a special case. It is a methylene ketone which is known to give the alkylbenzene, triphenylene, when treated with strong acids.[7] When cyclohexanone was heated with aniline and hydrogen chloride, we obtained the anil and aldol condensation products analogous to **2** and **3**. The dihydroquinoline, spiro[cyclohexane-1,6′(5′*H*)-7,8,9,10-tetrahydrobenzo[*c*]-quinoline, was formed in fair yield from the analogue of **2**. But no triphenylene formed from the corresponding analogue of **3**. Small amounts of 4,4′-(cyclohexanediyl)-bisbenzenamine and its aldol condensation products were also formed in this reaction.

Statistically, the tautomers **4** and **5** should form in the ratio of 3:2 and one would expect **6** and **7** to be formed in a similar ratio. The actual ratio of 3:1 was observed when any methyl *n*-alkyl ketone was used in the reaction. This was reasonable since steric factors favor the formation of **6**. With methyl branched-alkyl ketones, such as methyl isobutyl ketone, steric factors became much more important and only **6** formed. Highly hindered ketones, such as methyl *tert*-butyl ketone, are known to form anils which do not undergo further condensations.[10] We also found that they did not form trialkylbenzenes.

In support of this reaction scheme, we have found that alkylbenzenes only formed when primary aromatic amines, which can form anils, were heated with methyl alkyl ketones. Amines which cannot form anils, such as *N,N*-di-

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methylaniline, were not effective in this reaction. Thus, when 2-octanone, *N,N*-dimethylaniline, and hydrogen chloride were heated together for 27 h, less than half of the 2-octanone reacted to give its aldol condensation product, 9-methylpentadec-8-en-7-one. In contrast, the corresponding reaction with aniline gave the theoretical amount of water in 2 h and gave alkylbenzenes in 40% yield. These findings rule out the possibility that the alkylbenzenes were formed directly from the ketone.

We have also found that anils of methyl alkyl ketones readily give alkylbenzenes of the type of **6** and **7** when heated with hydrogen chloride. The usual yields, approximately 30%, were obtained in 2 h, when the aniline was distilled from the reaction as formed. To determine how rapidly the anil was converted into the alkylbenzenes, we reacted *N*-(1-methylheptylidene)benzenamine with aniline hydrochloride at 180 °C. Immediately after the aniline hydrochloride was added to the anil at 180 °C, GC analysis showed that about 50% of the anil (**1**) already had undergone an aldol condensation to **2**, and field desorption mass spectroscopy (FDMS) showed the presence of a trace of **3**. Within 5 min some trialkylbenzenes (**6** and **7**) and dihydroquinoline (**8**) had formed. After 30 min, most of the anil (**2**) had disappeared. FDMS showed the presence of a series of condensation products differing by 110 mass units: *m/e* 203, 313, 423, 533, 643, with **3** (*m/e* 423) predominating. Besides these products, a corresponding series of compounds which contained another aniline moiety were observed: *m/e* 296, 406, 516, 626, 736, 846. After 1.5 h, the reaction mixture was worked up and the distillable materials consisted of dihydroquinoline **8**, trialkylbenzenes **6** and **7** (17% yield), and $\alpha,\beta,\gamma,\delta$-unsaturated anil **3**. These facts indicate that the thermal Cope reaction of the $\alpha,\beta,\gamma,\delta$-unsaturated anil occurs slowly. This was substantiated by heating **3** at 180 °C for 3 h. Approximately 70% of this material was converted into the alkylbenzenes. We made no attempt to measure the actual rates of cyclization of this triene, but this would be a useful extension of this work.

Other amines were tried in this reaction. First, we tried ortho-substituted anilines, which form dihydroquinolines more slowly than aniline,[11] in an effort to improve the yield of alkylbenzenes. *o*-Toluidine gave alkylbenzenes in 42% yield. 2,6-Diethylaniline, which cannot form the dihydroquinoline, gave the anil and its condensation products analogous to **2** and **3**, but no alkylbenzene was formed. Apparently steric factors inhibit the Cope cyclization reaction. Primary aliphatic amines, which cannot form dihydroquinolines, did not give alkylbenzenes when heated with methyl alkyl ketones and hydrogen chloride. Imines readily formed and underwent condensations to give analogues of **2** and **3**. In spite of the fact that **3** formed, no trialkylbenzene was detected. This might be rationalized using Carpenter's model for predicting the qualitative effect of substituents on the rate of the thermal Cope reaction.[12] He states that a substituent in the 1-position of hexatrienes, such as **6** and **7**, affects the rate as follows: no substituent > conjugated substituent > polar substituent. Thus the trienes **4** and **5** will undergo cyclization more slowly than unsubstituted trienes. Furthermore, by extending the logic of the molecular orbital theory used to arrive at these conclusions, we would predict that as the Coulomb integral of the substituent at the 1-position increases, the rate of cyclization would decrease. Consequently, one would expect the following order of reactivity: aryl-N > alkyl-N > HO. Since methyl alkyl ketones slowly form trialkylbenzenes in the presence of acids, aliphatic imines would also be expected to give trialkylbenzenes. This requires more study.

The rate of imine formation, tautomerism to the enamine, and aldol condensation are affected by the pK_a of the acid used to catalyze these reactions.[13] We found that the pK_a of the acid also affects the product distribution of this reaction. Using caproic acid as the catalyst for the reaction between 2-octanone and aniline, we found that the anil was the primary product along with some aldol condensation products, but trialkylbenzenes were not formed. When *p*-toluenesulfonic acid was used as the catalyst, a high yield of the dihydroquinoline (**8**) (47%) was obtained. Relatively small amounts of trialkylbenzenes formed even though the condensation products **2** and **3** formed. Methanesulfonic acid gave the trialkylbenzenes in normal yields, some dihydroquinoline, and a fairly large amount of $\alpha,\beta,\gamma,\delta$-unsaturated imine **3**. Phosphoric acid (85%) gave the trialkylbenzenes in good yields (50%). Besides giving high yields of trialkylbenzenes, it also produced very little dihydroquinoline. Some higher boiling products formed but they were not analyzed. Surprisingly, when phosphoric acid was used with methyl isobutyl ketone and aniline, only the anil and its condensation products formed, but neither trialkylbenzene nor dihydroquinoline formed. Sulfuric acid on clay (Retrol) slowly gave the anil and its aldol condensation products but no trialkylbenzene formed. These widely varied results indicate that strong acids ($pK_a < 2$) are required for trialkylbenzene formation. The strongest acids give both the trialkylbenzenes and dihydroquinolines. Acids of moderate strength, $pK_a \sim 2$, give trialkylbenzenes and lesser amounts of dihydroquinolines. Weak acids give only anils and their aldol condensation products. It seems likely that other acids or buffers could be used to catalyze this reaction to improve the yield of trialkylbenzenes.

In view of the above work, it is surprising that mesitylene has never been reported to form in the hydrogen chloride catalyzed reaction between acetone and aniline. We repeated this reaction in three ways. First, the reagents were heated in a sealed bomb for 6 h at 180 °C. GC analysis of this mixture showed that no mesitylene had formed. FDMS showed the primary products to be the dihydroquinoline (*m/e* 173), a series which consisted of two aniline moieties and an increasing number of C_3H_4 units (*m/e* 226, 266, 306, 346, 386), and another series which contained another aniline added to the above series (*m/e*, 319, 359, 399, 439, 479, 519, 559). No attempt was made to assign structures to these products. Similarly, 2-octanone, aniline, and hydrogen chloride, when heated 6 h at 180 °C in a sealed bomb, also failed to give trialkylbenzenes. A second, more commonly used method of reacting acetone and aniline was tried. In this case, acetone was passed through a mixture of aniline and hydrogen chloride at 100 °C according to the procedure of Craig.[2] No mesitylene was found in the product. Finally, the anil, *N*-(1-methylethylidene)benzenamine, was heated with aniline hydrochloride at 180 °C for 1 h. Again GC showed that no mesitylene had formed. The many facets of this reaction are not fully understood and further study of the chemistry of polyaldol condensation products of anils and imines should prove interesting.

Experimental Section

Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. The IR spectra (KBr pellets) were

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(13) M. L. Bender and A. Williams, *J. Am. Chem. Soc.*, **88**, 2502 (1966).

recorded on a Perkin-Elmer 467. Elemental analysis was obtained on a Hewlett-Packard Model 185 CHN-Analyzer. ^1H NMR spectra were obtained on a Varian Model A-60 with Me_4Si as an internal standard, using a 10% solution in deuteriochloroform. A Hewlett-Packard Model 5710A gas chromatograph with 91.4 × 0.476 cm, 10% UCW98 columns was used for GC work.

1,3,5-Trihexylbenzene and 1-Methyl-2-pentyl-3,5-dihexylbenzene. Aniline (93 g, 1.0 mol), 26 g (0.2 mol) of aniline hydrochloride, 154 g (1.2 mol) of 2-octanone, and 50 mL of xylene were refluxed (160–180 °C), and the water was collected as formed in a Dean–Stark trap. In 4 h, the reaction was completed, and the mixture was neutralized with 16 g (0.15 mol) of Na_2CO_3 in 300 mL of water and washed with water. Distillation gave 93.2 g of a yellow oil, bp 105–205 °C (1 mm), and 67 g of pot residue. The distillate was dissolved in 250 mL of benzene and stirred with 100 mL of concentrated sulfuric acid. The benzene layer was separated, washed with water, dried, and concentrated on a rotary evaporator. Distillation gave 37 g (28%) of a mixture of 1,3,5-trihexylbenzene (**6**) and 1-methyl-2-pentyl-3,5-dihexylbenzene (**7**), bp 173–176 °C (0.6 mm), n^{20}_D 1.4810 (lit.[14] n^{20}_D 1.4806), in the ratio of 78:22. This ratio was determined from integrated peak areas of NMR δ 0.88 (CCH_3), 1.35 (CCH_2), 2.28 ($ArCH_3$), 2.67, 2.55, 2.41 ($ArCH_2$), 6.79 (ArH).

Anal. Calcd for $C_{24}H_{42}$: C, 87.19; H, 12.80. Found: C, 87.21; H, 12.97.

The alkylbenzene mixture (10 g) was oxidized with 136 g of $Na_2Cr_2O_7$, 300 mL of water, and 320 mL of concentrated sulfuric acid. A white solid (2 g, 31%) was collected, mp 370–380 °C (lit.[15] mp 380 °C), and the IR spectrum was identical with that of 1,3,5-benzenetricarboxylic acid.

The sulfuric acid layer was neutralized with aqueous sodium hydroxide and then extracted with benzene. The benzene was distilled to leave 43 g of a yellow oil which partially solidified on standing. The solid portion, 4 g, was collected by filtration and recrystallized from hexane to give an analytical sample of 2-methyl-4-hexylquinoline: mp 37–8 °C; NMR δ 0.75–1.80 (m, 11 H, CH_2, CH_3), 2.79 (s, 5 H, $ArCH_3$), 2.83, 2.98, 3.09 (t, 2 H, $ArCH_2$), 7.13–8.13 (m, 5 H, ArH).

Anal. Calcd for $C_{16}H_{21}N$: C, 84.52; H, 9.32; N, 6.16. Found: C, 84.59; H, 9.31; N, 6.13.

The oil remaining after removal of the above solids was distilled, bp 178 °C (0.5 mm), to give 36 g of 2-methyl-2,4-dihexyl-1,2-dihydroquinoline:[8] NMR δ 1.09–1.67 (m, 29 H, CH_2, CH_3), 2.20, 2.31, 2.42 (t, 2 H, $C{=}CCH_2$), 3.31 (s, 1 H, NH), 5.08 (s, 1 H, C=CH), 6.12–7.03 (m, 4 H, ArH).

Anal. Calcd for $C_{22}H_{35}N$: C, 84.28; H, 11.25; N, 4.47. Found: C, 84.36; H, 11.28; N, 4.43.

In the same way, 2-heptanone gave a mixture of 1,3,5-tripentylbenzene and 1-methyl-2-butyl-3,5-dipentylbenzene,[16] bp 155–158 °C (0.5 mm), in the ratio of 72:28 in 33% yield. 2-Decanone gave 1,3,5-trioctylbenzene and 1-methyl-2-heptyl-3,5-dioctylbenzene,[16] bp 204–208 °C (0.5 mm), in the ratio of 75:25 in 34% yield. Methyl isobutyl ketone gave 1,3,5-trisobutylbenzene, bp 77–80 °C (0.5 mm), in 42% yield.

Anal. Calcd for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.82; H, 12.20.

In the same way, when 112 g (1.2 mol) of aniline, 38 g (0.2 mol) of *p*-toluenesulfonic acid, 192 g (1.5 mol) of 2-octanone, and 50 mL of xylene were refluxed, the reaction was complete in 4 h. Analysis by GC showed that **8** was the predominant product and very little **6** and **7** formed. Distillation gave 129 g of an oil, bp 166–180 °C (0.6 mm), which by GC was a mixture of 106 g (47% yield) of **8** and 23 g (14% yield) of **6** and **7**. The nondistillable portion, 64 g, was shown to be primarily **6** and **7**, *m/e* 423, by field desorption mass spectroscopy (FDMS).

Similarily, when 19.2 g (0.2 mol) of methanesulfonic acid was used as the catalyst, the reaction was complete in 4 h. Distillation gave 84 g of an oil, bp 168–174 °C (0.6 mm), which was determined by GC to contain 44.2 g (15.3%) of **8** and 39.3 g (23.8%) of **6** and **7**, and 67 g (31.7%) of *N*-(1,3-dihexyl-5-methyl-undeca-2,4-dienylidene)benzenamine: bp 210–220 °C (0.4 mm); IR (KBr) 1590, 1610 (N=CC=CC=C), 700 and 750 cm^{-1} (monosubstituted aromatic); atomic composition mass spectrum calcd 423.3865, found 423.3867. A pot residue of 13.7 g was not characterized.

Similarly, 112 g (1.1 mol) of aniline, 192 g (1.5 mol) of 2-octanone, 30 g of "Retrol" (sulfuric acid on clay),[17] and 50 mL of xylene gave the theoretical amount of water in 24 h. Distillation gave 182 g (81%) of *N*-(1-methylheptylidene)benzenamine (**2**), bp 90–110 °C (0.9 mm), and 59 g (17%) *N*-(1-hexyl-3-methyl-2-nonenylidene)benzenamine (**3**), bp 147–151 °C (0.3 mm), IR (KBr) 1640 (N=CC=C), 700 and 750 cm^{-1} (monosubstituted aromatic), and 15 g of pot residue which was not characterized.

Similarly, 93 g (1.0 mol) of aniline, 154 g (1.2 mol) of 2-octanone, 0.5 g of sodium acetate, 2 g of caproic acid, and 50 mL of xylene were refluxed for 5 h to give 154 g (75.8%) of **2**, bp 99 °C (1.0 mm).

Similarly, 112 g (1.2 mol) of aniline, 192 g (1.5 mol) of 2-octanone, 23 g (0.2 mol) of 85% phosphoric acid, and 50 mL of xylene gave the theoretical amount of water in 10 h. Distillation gave 83 g (50%) of **6** and **7**, bp 170–176 °C (0.6 mm), which was pure by GC. The mixture of **6** and **7** were quantitatively recovered after treatment with concentrated sulfuric acid. NMR analysis showed **6** and **7** to be present in the ratio of 75:25. A pot residue of 51 g was not characterized.

When 23 g (0.2 mol) of 85% phosphoric acid, 112 g (1.2 mol) of aniline, 150 g (1.5 mol) of methyl isobutyl ketone, and 50 mL of xylene were refluxed at 150 to 170 °C for 24 h, GC analysis showed that no trialkylbenzenes formed. The usual work up gave 93.5 g of an oil, bp 83–112 °C (0.1 mm), which consisted primarily of the anil, and 67.5 g of an oil, bp 83–112 °C (0.1 mm), which consisted primarily of the anil, and 67.5 g of an oil, bp 129–147 °C (0.7 mm), which was presumed to consist of *N*-4-(2,6,8-trimethyl-5-nonenylidene)benzenamine, *m/e* 257, and *N*-4-[2,8,10-trimethyl-6-(2-methylpropyl)undeca-5,7-dienylidene]benzenamine, *m/e* 339. Neither trialkylbenzenes nor the dihydroquinoline formed in this reaction.

In the same reaction, *p*-toluenesulfonic acid gave **2**, *m/e* 327, and **3**, *m/e* 437, but no trialkylbenzenes formed.

In the same way, 107 g (1.0 mol) of *o*-toluidine, 154 g (1.2 mol) of 2-octanone, 26 g (0.2 mol) of aniline hydrochloride, and 50 mL of xylene gave the theoretical amount of water in 4 h. Distillation gave 76 g of an oil, bp 165–180 °C (0.9 mm), which when treated with concentrated sulfuric acid gave 55 g (41.6%) of **6** and **7**. A pot residue of 52 g remained.

N-(1-Methylheptylidene)benzenamine (204 g, 1 mol) and 13 g (0.1 mol) aniline hydrochloride were heated from 200 to 290 °C while the aniline was removed by distillation as formed. After 2 h, the distillation of aniline ceased and the reaction was stopped. GC analysis showed the presence of **2**, **3**, **6**, **7**, and **8**. The usual workup gave 33.3 g of **6** and **7** (30.3%) in the ratio of 78:22. When 118 g (0.58 mol) of *N*-(1-methylheptylidene)benzenamine and 16 g (0.117 mol) of aniline hydrochloride were heated together at 180 °C without removing the aniline, the trialkylbenzenes were obtained in 17% yield. Samples were taken at 0, 5, 15, 30, 60, and 95 min to follow the progress of the reaction. FDMS analyses of these samples show that *m/e* 423, **3**, is present in all of the samples, including the 0-min sample. The 30-min sample shows a series of aldol condensation products (*m/e* 203, 313, 423, 533, 643) with the *m/e* 423 predominating. Along with these products, a corresponding series, which contains another aniline moiety added to these aldol condensation products, was also observed (*m/e* 296, 406, 516, 626, 736, 846). The structure of these materials were not characterized but two possibilities exist. One is the Michael addition of aniline to the conjugated unsaturated anils (**2**, **3**, etc.). The other possibility is that the material could be imines of 4,4′-(1-methylheptanediyl)bisbenzenamine.

2-Octanone (194 g, 1.5 mol), 93 g (1.0 mol) of aniline, and 26 g (0.2 mol) of aniline hydrochloride were heated at 180 °C for 6 h in a pressure bomb. GC of the crude mixture showed that 2-octanone, aniline, and the anil (**2**) were the major components along with a number of minor components but no trialkylbenzenes were present. The product was worked up in the usual way to

(14) H. Mueller and H. Friederich, German Patent 890 542, March 7, 1962.

(15) B. Prager and P. Jacobson, Beilsteins Handbuch der Organischen Chemie, Julius Springer, Berlin, 1922, Vol. 5, p 979.

(16) H. J. Peterson, U.S. Patent 3 518 321, June 30, 1970; *Chem. Abstr.*, **73**, p68280g (1970).

(17) Filtrol Corporation, Los Angeles, California 90045.

give an oil, bp 119–147 °C (1.2 mm), which consisted of *m/e* 203, 313, and 423.

2,2,4-Trimethyl-1,2-dihydroquinoline. Acetone (61 g, 1.5 mol), 93 g of aniline, and 26 g (0.2 mol) aniline hydrochloride were heated for 6 h in a pressure bomb. GC analysis of the crude product showed that no mesitylene had formed and that 2,2,4-trimethyl-1,2-dihydroquinoline was the major product. Similarly, FDMS did not detect mesitylene (*m/e* 120). The following ions were present: 173, 226, 266, 306, 346, 302, 342, 382, 399, 439, 479, 519, 559, etc.

2-Propylideneaniline (112 g, 0.84 mol) and 22 g (0.17 mol) of aniline hydrochloride were heated at 180 °C for 1 h. GC analysis showed that no mesitylene had formed and the primary product was the dihydroquinoline. The following compounds were present: *m/e* 93, 173, 226, 266, 306, 346, 386, 320, and 360.

9-Methylpentadec-8-en-7-one. *N,N*-Dimethylaniline (145 g, 1.2 mol), 16 mL (0.2 mol) of concentrated hydrochloric acid, and 50 mL of xylene were refluxed and the water removed in a Dean–Stark trap. The mixture was cooled, 192 g (1.5 mol) of 2-octanone was added, and refluxing was continued. In 24 h, only 27% of the theoretical amount of water had formed. No trialkylbenzenes were detected by GC analysis. Distillation gave 43 g (44%) of 9-methylpentadec-8-en-7-one: bp 102–104 °C (0.4 mm); n^{20}_D 1.4565 (lit. n^{20}_D 1.4563).[18]

***N*-(1-Methylheptylidene)-2,6-diethylbenzenamine.** 2,6-Diethylaniline (179 g, 1.2 mol), 154 g (1.2 mol) of 2-octanone, 7.3 g of (0.2 mol) HCl, and 100 mL of xylene were refluxed for 5 h to collect the theoretical amount of water. GC analysis showed that no trialkylbenzenes had formed. Distillation gave 136 g (43.8%) of *N*-(1-methylheptylidene)-2,6-diethylbenzenamine, bp 124–8 °C (0.8 mm).

Anal. Calcd for $C_{18}H_{29}N$: C, 83.33; H, 11.27; N, 5.40. Found: C, 83.42; H, 11.33; N, 5.48.

N-(1-Hexyl-3-methyl-2-nonenylidene)-2,6-diethylbenzenamine (37 g, 17.6%) was also collected by distillation: bp 196–202 °C (0.8 mm); IR (KBr) 1640 cm^{-1} (N=CC=C). Anal. Calcd for $C_{26}H_{43}N$: C, 84.48; H, 11.73; N, 3.79. Found: C, 84.55; H, 11.69; N, 3.83.

***N*-(1-Methylheptylidene)cyclohexylamine.** 2-Octanone (158 g, 1.23 mol), 122 g (1.23 mol) of cyclohexylamine, 7 g (0.2 mol) of HCl, and 100 mL of xylene were refluxed together. The theoretical amount of water was collected in 2 h. GC and FDMS showed that no trialkylbenzenes had formed. Distillation gave 139 g of *N*-(1-methylheptylidene)cyclohexylamine [bp 95–100 °C (0.4 mm); IR (KBr) 1635 cm^{-1} (N=CC=C); mass spectrum, *m/e* 209] and *N*-(1-hexyl-3-methyl-2-nonenylidene)cyclohexylamine [21 g; bp 144–149 °C (0.4 mm); mass spectrum, *m/e* 319], and the NMR spectrum was also consistent with this structure and showed that the compound exists as the cis and trans and syn and anti isomers about the olefinic and iminic double bonds, respectively.

Anal. Calcd for $C_{22}H_{41}N$: C, 82.68; H, 12.93; N, 4.38. Found: C, 82.55; H, 12.88; N, 4.33. Also formed in the reaction were compounds with molecular weights of 429 and 539. No attempt was made to assign a structure to these compounds. The same results were obtained by using 85% phosphoric acid as the catalyst in this reaction.

(18) J. L. Guthrie and N. Rabjohn, *J. Org. Chem.*, **22**, 176 (1957).

***N*-(1-Propylbutylidene)-4-methylbenzenamine.** *p*-Toluidine (107 g, 1.0 mol), 29 g (0.2 mol) of *p*-toluidine hydrochloride, 171 g (1.5 mol) of 4-heptanone, and 50 mL of xylene were refluxed to give the theoretical amount of water in 8 h. GC analysis showed that the anil was the major product and that no trialkylbenzenes had formed. Distillation gave 170 g (83%) of *N*-(1-propylbutylidene)-4-methylbenzenamine: bp 175–180 °C (14 mm); IR (KBr) 1660 cm^{-1} (CN).

Anal. Calcd for $C_{14}H_{22}N$: C, 82.29; H, 10.85; N, 6.86. Found: C, 82.18; H, 10.89; N, 6.81.

Spiro[cyclohexane-1,6′(5′*H*)-7,8,9,10-tetrahydrobenzo[*c*]quinoline]. Aniline (112 g, 1.2 mol), 26 g (0.2 mol) of aniline hydrochloride, 147 g (1.5 mol) of cyclohexanone, and 50 mL of xylene were refluxed to give the theoretical amount of water in 9 h. Distillation gave 46 g of lower boiling anils, which were not characterized. A second cut, bp 162–213 °C (0.1 mm), gave 68 g of an oil which by GC contained 87% of spiro[cyclohexane-1,6′(5′*H*)-7,8,9,10-tetrahydrobenzo[*c*]quinoline] and 13% of 4,4′-(cyclohexanediyl)bisbenzenamine [mass spectrum, *m/e* 253 and 266; IR (KBr) 3400 (NH), 740 cm^{-1} (1,2-disubstituted aromatic ring)]; the product was not changed on boiling with aqueous hydrochloric acid, and the atomic composition mass spectrum established its molecular formula (calcd 253.1830, found 253.1833), and the NMR spectrum was also consistent with this structure. A third cut, bp 217–257 °C (0.1 mm), was analyzed by FDMS and found to contain primarily *m/e* 333, probably *N*-{2-[(2-cyclohexylidene)cyclohexylidene]cyclohexylidene}benzenamine, and *m/e* 266, 4,4′-(cyclohexanediyl)bisbenzenamine. Also present were *m/e* 335, 344, 348, 413, and 426, all of which can be ascribed to the imines and their aldol condensation products of both aniline and 4,4′-(cyclohexanediyl)bisbenzenamine.

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Registry No. 2, 61285-56-1; **3**, 78870-38-9; **6**, 29536-28-5; **7**, 78890-47-8; **8**, 65811-13-4; aniline, 62-53-3; 2-octanone, 111-13-7; 1,3,5-benzenetricarboxylic acid, 554-95-0; 2-methyl-4-hexylquinoline, 78870-39-0; 2-heptanone, 110-43-0; 1,3,5-tripentylbenzene, 78870-40-3; 1-methyl-2-butyl-3,5-dipentylbenzene, 78870-41-4; 2-decanone, 693-54-9; 1,3,5-trioctylbenzene, 7694-77-1; 1-methyl-2-heptyl-3,5-dioctylbenzene, 78870-42-5; methyl isobutyl ketone, 108-10-1; 1,3,5-triisobutylbenzene, 1460-02-2; *N*-4-(2,6,8-trimethyl-5-nonylenylidene)benzenamine, 61285-54-9; *N*-4-[2,8,10-trimethyl-6-(2-methylpropyl)undeca-5,7-dienylidene]benzenamine, 78870-43-6; *N*-(1-methylheptylidene)benzenamine, 61285-50-5; acetone, 67-64-1; 2,2,4-trimethyl-1,2-dihydroquinoline, 147-47-7; 2-propylideneaniline, 1124-52-3; *N,N*-dimethylaniline, 121-69-7; 9-methylpentadec-8-en-7-one, 72552-21-7; *N*-(1-methylheptylidene)-2,6-diethylbenzenamine, 78870-44-7; *N*-(1-hexyl-3-methyl-2-nonenylidene)-2,6-diethylbenzenamine, 78870-45-8; cyclohexylamine, 108-91-8; *N*-(1-methylheptylidene)cyclohexylamine, 53626-91-8; *N*-(1-hexyl-3-methyl-2-nonenylidene)cyclohexylamine, 78870-46-9; *p*-toluidine, 106-49-0; 4-heptanone, 123-19-3; *N*-(1-propylbutylidene)-4-methylbenzenamine, 78870-47-0; cyclohexanone, 108-94-1; spiro[cyclohexane-1,6′(5′*H*)-7,8,9,10-tetrahydrobenzo[*c*]quinoline], 78870-48-1; 4,4′-(cyclohexanediyl)bisbenzenamine, 78870-49-2; 2-[(2-cyclohexylidene)cyclohexylidene]cyclohexylidenebenzenamine, 78870-50-5; 2,6-diethylaniline, 579-66-8; 4-methylpentyl-2-idenebenzenamine, 61285-47-0.