3050–2900, 1500, 1460, 1420, 1080, 1020 (s), 940, 800, 760, 700 cm$^{-1}$. Anal. Calcd for $C_{16}H_{18}OS_3$: C, 59.58; H, 5.62; S, 29.82. Found: C, 59.89; H, 5.57; S, 30.03.

**(d) 2-(Benzylsulfinyl)ethyl Cyclohexyl Disulfide (15).** Cyclohexanethiol (1.16 g, 10.0 mmol) and Na in 10 mL of MeOH reacted with 10 mmol of 17 in MeOH (25 mL) in only 6 min at −15 °C. After the procedure of (a) as usual, chromatography (5.5 × 8 cm column) gave a fraction of $R_f$ 0.53 that yielded 2.20 g (70%) of 15: mp 66–67 °C; NMR δ 7.36 (s, 5 H), 4.04 (s, 2 H), 3.00 (s, 4 H); 2.08–1.00 (m, 11 H); IR (KBr) 3050, 2950 (s), 1600, 1500, 1460 (s), 1420, 1270, 1200, 1030 (s), 940, 750, 700 (s). Anal. Calcd for $C_{15}H_{22}OS_3$: C, 57.28; H, 7.05; S, 30.58. Found: C, 57.23; H, 7.17; S, 30.42.

**(e) 1,4-Bis[[2-(benzylsulfinyl)ethyl]dithio]butane (16).** 1,4-Butanedithiol (1.22 g, 10.0 mmol) and Na (0.46 g, 20 mmol) in 50 mL of MeOH reacted with 7.08 g (20.0 mmol) of 17 in 50 mL of MeOH at −70 °C in 30 min. Delivery into ca. 300 mL of $H_2O$, extraction, and chromatography (5.5 × 8 cm column) as usual then gave a fraction of $R_f$ 0.31 that yielded 2.17 g (42%) of 16: mp 113–115 °C; NMR δ 7.80 (s, 10 H), 4.20–3.88 (t, 4 H), 3.20–2.80 (m, 8 H), 2.80–2.48 (m, 4 H), 1.84–1.56 (m, 4 H); IR (KBr) 2950, 2900, 1600, 1500, 1440, 1400, 1300, 1180, 1140, 1100, 1060, 1030 (s), 940, 760, 740, 700 (s) cm$^{-1}$. Anal. Calcd for $C_{22}H_{30}O_2S_6$: C, 50.93; H, 5.83; S, 37.08. Found: C, 51.05; H, 5.77; S, 37.07.

**Resistance To Change of 8, 11, and 12–16.** The results in columns 1–3 of Table I were obtained at room temperature (ca. 28 °C) using solutions of 0.1 mmol of the disulfide 8, the trisulfide 11, and the unsymmetrical disulfides 12–16 in 10 mL of $CH_2Cl_2$. For column 1 (dark), samples were kept in foil-wrapped containers. Samples for column 2 (ambient light) were treated similarly but were not foil-wrapped. Samples for column 3 (UV) were irradiated in Pyrex flasks (that touched one another in a circle) by a 100-W Hanovia Model 30620 UV lamp placed 18 cm below the flasks; the temperature of the flasks was ca. 28 °C. Each solution was sampled frequently enought to permit estimation within ca. 5–10% of the time at which TLC first showed a spot other than that of the starting material. TLC was done with 100% EtOAc or (8, 11) 15% MeOH in $Me_2CO$. For columns 4 and 5, solutions of 0.1 mmol in either EtOAc (bp 77 °C) or EtOH (bp 78 °C) were heated under reflux in foil-wrapped flasks.

Since only the resistance to change was sought with 8 and 11, the products from 8 and 11 were not studied further (after UV irradiation was well advanced, two new spots were seen for 8 and three for 11). The disulfides 12–16 showed only the three spots expected for disproportionation (plus traces of a fourth spot). That these three spots corresponded to the starting material and the two symmetrical disulfides was confirmed, illustratively, with 12 and 14; after reaction (column 3) was well advanced, TLC comparison with authentic samples showed one spot to be 12 or 14, the second to be 8, and the third to be di-*p*-chlorophenyl or di-*p*-tolyl disulfide.

**Registry No.** 5, 3878-41-9; 6, 4332-51-8; 7, 54623-96-0; 8, 101544-07-4; **9a**, 101544-08-5; 10, 3753-27-3; 11, 101544-09-6; 12, 101544-10-9; 13, 101544-11-0; 14, 101544-12-1; 15, 101544-13-2; 16, 101544-14-3; 17, 101544-06-3; *p*-chlorobenzenethiol, 106-54-7; thiophenol, 108-98-5; *p*-toluenethiol, 106-45-6; cyclohexanethiol, 1569-69-3; 1,4-butanedithiol, 1191-08-8.

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# Selective, Oxophilic Imination of Ketones with Bis(dichloroaluminum) Phenylimide[1]

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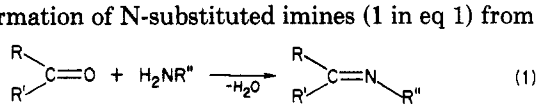
Bis(dichloroaluminum) phenylimide, which can be readily prepared from ethylaluminum dichloride and aniline, is shown to be a highly selective iminating agent for aldehydes, ketones, and acid chlorides. Especially the transformation of α,β-unsaturated ketones into anils can be achieved exclusively, without any detectable amount of the usual conjugate addition of the amine to the C═C linkage. This oxophilic iminating agent functions in the complete absence of water and thus obviates the tendency of α,β-unsaturated ketimines to rearrange, in the presence of water, into the corresponding β-aminoalkyl ketones. The reasons for the failure of previous attempts to synthesize chalcone anil from chalcone and aniline are analyzed in terms of kinetic and thermodynamic factors.



(1)

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The formation of N-substituted imines (1 in eq 1) from primary amines and aldehydes or ketones plays a pivotal role in chemical transformations as diverse as the synthesis of azaaromatic heterocycles[2] and the biosynthesis of amino acids.[3] The preparation of imines in vitro becomes progressively more difficult as one passes from aldehydes to ketones and as one employes aromatic, rather than aliphatic, amines.[4] Over 120 years ago, Schiff showed that aldimine formation from aromatic amines is base-catalyzed.[5] For the most difficult case, ketimines bearing two or more aromatic groups (1: R,R″ = aromatic), Reddelien found that a combination of proton and Lewis acids $ArNH_2$–HCl–$ZnCl_2$) proved to be an effective iminating catalyst.[6] The use of acidic or basic catalysis, however, coupled with the slower rates of ketiminations, can lead to extensive side reactions, such as aldol condensations or competitive 1,4-additions to α,β-unsaturated ketones. Under Reddelien's conditions of imination, for example, acetophenone and aniline produce a large proportion of dypnone anil (2, eq. 2)[7] while chalcone (3) yields only one

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[1] Part 5 of the series "Rearrangements of Heterocyclic Compounds". Part 4: Eisch, J. J.; Noels, A. F. *J. Org. Chem.* **1976**, *41*, 1461.

[2] Joule, J. A.; Smith, G. F. "Heterocyclic Chemistry", 2nd ed.; Van Nostrand Reinhold: New York, 1978, pp 74–80.

[3] Snell, E. E.; Braunstein, A. E.; Severin, E. S.; Torchinsky, Yu. M. "Pyridoxal Catalysis: Enzymes and Model Systems"; Wiley: New York, 1968.

[4] Layer, R. W. *Chem. Rev.* **1963**, *63*, 493.

[5] Schiff, H. *Ann. Chem. Pharm.* **1864–5**, *131*, 118.

[6] Reddelien, G. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 2721.

[7] Eisch, J. J., unpublished studies, 1976.

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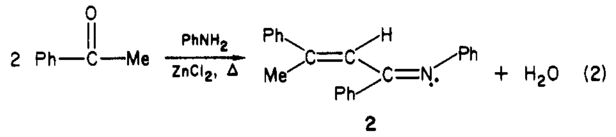
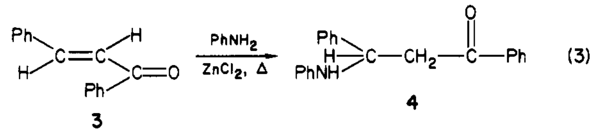
conjugate adduct (4, eq. 3):[7,8]





In more recent work, $TiCl_4$ has been used to promote the formation of ketimines from substituted cyclohexanones,[9] and employing a molar equivalent of $n$-$Bu_2SnCl_2$ has been suggested for the same purpose.[10] Likewise, $ZnCl_2$ has shown to catalyze the preparation of ketimines from ketones and *N*,*N*-bis(trimethylsilyl)amines.[11] Other indirect routes to ketimines include the reactions of ketones with iminophosphoranes,[12] of *N*-dialkylaluminoimines with primary amines,[13] and of $\alpha$-iminophosphonium methylides with aldehydes.[14] But of the foregoing syntheses of ketimines, the former Lewis acid catalyzed methods do not resolve the issue of possible side reactions (e.g. eq 2 and 3), and the latter indirect methods involve multistep processes.

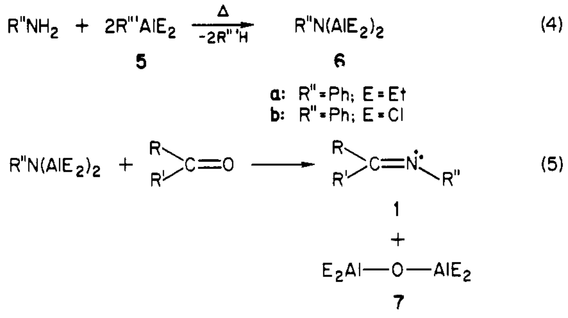
Therefore, in the present study we sought to find a potent iminating agent for both aldehydes and ketones, which would selectively and irreversibly attack the carbonyl group of even $\alpha,\beta$-unsaturated types (a selectivity that can be termed oxophilicity). Furthermore, the desired reagent should be effective at moderate temperatures and acidities, so as to minimize condensation reactions. After some orienting experiments we have identified bis(dichloroaluminum) imides as just such an iminating agent.

## Results

A suitable iminating agent meeting the aformentioned requirements could not involve the formation of any free $H_2O$, because the ketimines of $\alpha,\beta$-unsaturated ketones were found to hydrolyze easily and rearrange to the $\beta$-amino ketone (cf. Scheme III). Accordingly, the dialuminum salt of a primary amine (6) was an attractive reagent, since reaction with a ketone would irreversibly form a highly stable dialuminoxane (7, in Scheme I).[15]

As our test amine, we chose aniline ($R'' = Ph$) and as the aluminum reagent 5, we initially tried triethylaluminum (5: $R'''$, $E = Et$). Indeed, the iminating agent, bis(diethylaluminum) phenylimide (6a: $R'' = Ph$; $E = Et$), was smoothly formed upon heating (eq 3).[15] This reagent proved capable of iminating ketones (eq 5), but the conversions were only modest at lower temperatures (15–60%) and at higher temperatures the residual Et–Al groups in

**Scheme I**



**Scheme II**

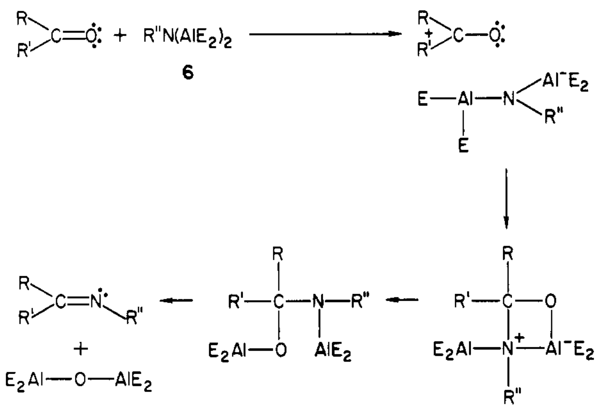


Table I. Preparation of Imines with Bis(dichloroaluminum) Phenylimide

| carbonyl compound | yield of imine, % | mp (bp), °C |
|---|---|---|
| cyclohexanone | 95 | (140–142/20 mm) |
| acetophenone | 46[a] | (175/13 mm) |
| cinnamaldehyde | 75 | 105–106 |
| benzophenone | 92 | 110–112 |
| benzalacetophenone (chalcone) | 80 | 99–101[b] |
| fluorenone | 93 | 79–81 |

[a] Some 20–30% of unreacted ketone and about 10% of dypnone anil accompanied the main product. [b] The literature melting point is almost 10 °C higher (ref 14), but our highly purified anil melted no higher than 101 °C. Our letter of inquiry to the original authors has not been answered.

6 tended to eliminate ethylene.[17] The resulting Al–H bonds then caused a competing reduction of the ketone.

To obviate this difficulty, an analogous iminating reagent, bis(dichloroaluminum) phenylimide (6b: $R'' = Ph$; $E = Cl$) was prepared from ethylaluminum dichloride (5: $R''' = Et$; $E = Cl$). This reagent proved capable of converting aldehydes and a variety of aliphatic and aromatic ketones into ketimines in generally high yields within a reaction temperature range of 25–65 °C. (Table I). In addition, 6 reacted with aroyl chlorides at room temperature to give amides. It is especially noteworthy that benzalacetophenone (chalcone) yielded only its ketimine and no detectable amount of its conjugate adduct 3. Modest amounts of aldol condensation still were observed with acetophenone but the conversion to the anil was higher than that with Reddelien's method.[7] Although these results were principally obtained with the imide from aniline, the method has also been shown to be applicable to other primary aromatic amines. Evaluation of the

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(8) Abraham, T.; Eisch, J. J., unpublished studies, 1975.

(9) Weingarten, H.; Chupp, J. P.; White, W. A. *J. Org. Chem.* **1967**, *32*, 3246.

(10) Stein, C.; DeJeso, B.; Pommier, J. C. *Synth. Commun.* **1982**, *12*, 495.

(11) Duffaut, N.; Dupin, J. P. *Bull. Soc. Chim. Fr.* **1966**, 3205.

(12) Gambaryan, N. P.; Rokhlin, E. M.; Zeifman, Y. V. *Angew. Chem., Int. Ed. Eng.* **1966**, *5*, 947.

(13) Bogdanovic, G.; Konstantinovic, S. *Justus Liebigs Ann. Chem.* **1970**, *738*, 202.

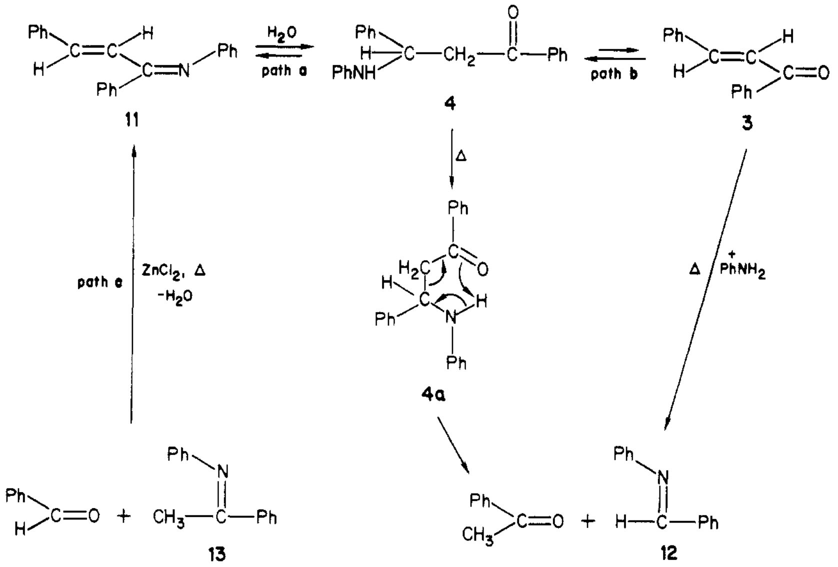
(14) Oshida, H. Y.; Ogata, T. *Synthesis* **1977**, 626.

(15) (a) Boleslawski, M.; Serivatowski, J.; Pasynkiewicz, S. *J. Organomet. Chem.* **1978**, *161*, 279. (b) Tani, H.; Oguni, N. *J. Polymer Sci.* **1965**, *B3*, 123.

(16) Laubengayer, A. W.; Wade, K.; Lengnik, G. *Inorg. Chem.* **1962**, *1*, 632.

(17) Lehmkuhl, H.; Ziegler, K.; Gellert, H. G. In "Houben-Weyl Methoden der Organischen Chemie"; Miller, E., Ed.; Georg Thieme: Stuggart, 1970; Vol. 13/4, 34.

**Scheme III**

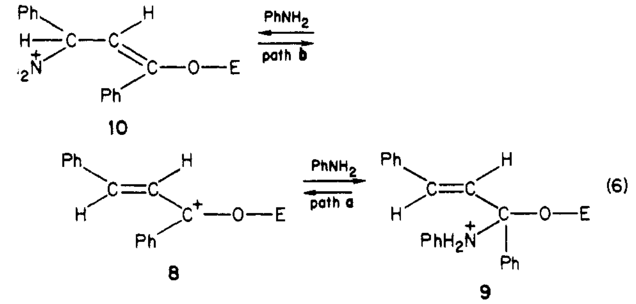


suitability of primary aliphatic amines is in progress.

## Discussion

The facility and specificity with which bis(dichloroaluminum) phenylimide attacks the carbonyl group of these substrates is consistent with the heightened Lewis acidity of geminal dialumino groups of the type $(R_2Al)_2E$, where E = O or $CR_2$.[15] The thermodynamic driving force for these iminations (eq 5) is clearly the formation of two Al-O bonds from two weaker Al-N bonds.[18] As a mechanism, one could therefore propose an electrophilic attack of **6** on the carbonyl oxygen, followed by Al-N bond heterolysis and the β-elimination of the dialuminoxane (Scheme II).

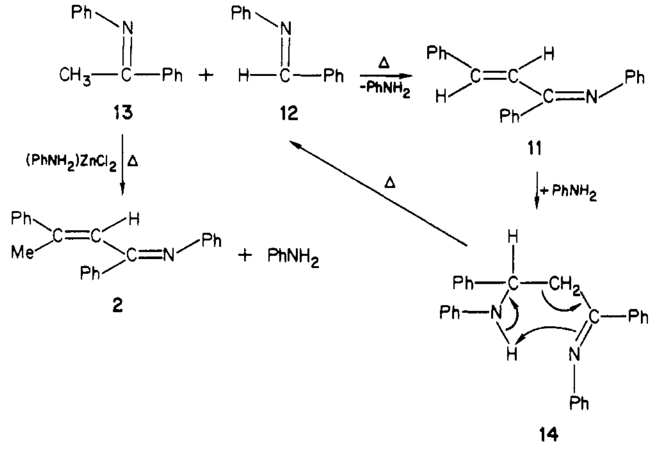
The electrophilic (oxophilic) attack of **6** on chalcone merits being contrasted with the acid-catalyzed reaction of chalcone with free aniline. Under the latter conditions, it is apparent that aniline would initiate nucleophilic attack on complex **8** (E = H or $ZnCl_2$), either at the carbonyl carbon (eq 5, path a, **9**) or at the β-carbon (**10**, path b):



(6)

The failure to isolate the anil of the ketone under these conditions seems to be due to the facile reversibility of step a and the ease with which **10** can ketonize to form the more stable amino ketone **4**. Support for the rapid reversibility of path a has been gained by treating chalcone anil (**11**) with water at 25 °C. Under these conditions, the anil was smoothly converted into the amino ketone **4** (Scheme III). Even path b proved to be reversible, albeit at higher temperatures. For example, heating the amino ketone **4** with catalytic amounts of acid ($p$-$C_6H_4SO_3H$) or base (KOH) at 80 °C led to the elimination of aniline.

**Scheme IV**



Since chalcone reacts reversibly with aniline at higher temperatures (paths a and b, eq 5), an attempt was made to prepare chalcone anil (**11**) by dehydrating **4**. However, at >150 °C **4** underwent fragmentation instead (possibly via **4a**), to produce acetophenone and benzalaniline (**12**, Scheme III). Finally, when an attempt was made to prepare **11** by the acid-catalyzed condensation of acetophenone anil (**13**) with benzaldehyde, again only the amino ketone **4** could be isolated (path c, Scheme III).

Thus, three potential routes to chalcone anil (paths, a, b, c, Scheme III) all failed because of the presence of $H_2O$. In the presence of $H_2O$, the anil **11** is clearly the least thermodynamically stable product, when compared with (a) amino ketone **4**, (b) a mixture of chalcone and aniline, and (c) a mixture of acetophenone and benzalaniline (**12**). All these reaction products are accessible from **11**, when $H_2O$ is present to generate intermediate **9** (E = H). The acid-catalyzed isomerization of **9** into **4** (via **10**, eq 6) can be viewed as analogous to the isomerization of allylic halides with internal return, as elucidated by the classic studies of Young, Winstein, and Goering.[19] In this view,

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[18] The Al-O bond strength is measured to be 119.5 kcal/mol at 298 K (Hildenbrand, D. L. *Chem. Phys. Lett.* **1973**, *20*, 127), while that of the Al-N bond is 73 kcal/mol (Gaydon, A. G. "Dissociation Energies and Spectra of Diatomic Molecules", 3rd ed., Chapman and Hall: London, 1968.) It should be noted that these measured bond strengths for diatomic molecules may differ considerably from mean bond energies derived from thermochemical data on moleclules. However, these values do reflect the greater bonding between aluminum and a more electronegative atom.

[19] Young, W. G.; Winstein, S.; Goering, H. L. *J. Am. Chem. Soc.* **1951**, *73*, 1958.

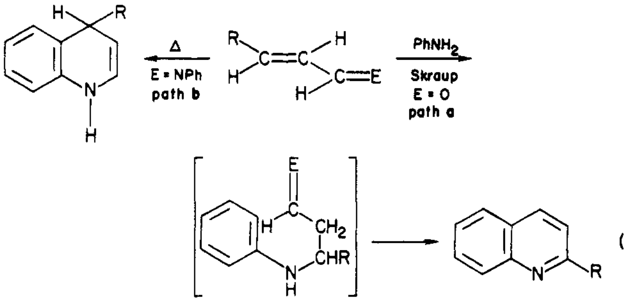
the aniline in **9** could be transferred intramolecularly to the beta position in **10**. Crossover experiments intended to decide between such a pathway and an intermolecular one, involving the elimination and readdition of aniline, are currently underway.

In an attempt to generate chalcone anil (**11**) in the absence of water, benzalaniline (**12**), and acetophenone anil (**13**) were heated with Reddelien's catalyst, $(PhNH_2)_2ZnCl_2$. Aniline was indeed eliminated at 180–190 °C, but only dypnone anil (**2**) could be detected (Scheme IV). If any **11** were formed in this reaction, apparently it added aniline in a conjugate fashion (**14**) and underwent refragmentation to **12** and **13**, just as **4** decomposes into acetophenone and **12**, via **4a** (cf. Scheme III).

In the light of these reactions, the thermodynamic stability of the reactions depicted in Scheme III have been shown to decrease in the order: acetophenone–benzalaniline (**12**) > chalcone–aniline$\sim$amino ketone **4** > water–chalcone anil (**11**) > benzaldehyde–acetophenone anil (**13**). The ordering of the first and last members of this series accords with the finding that formation constants for azomethine derivatives, RR′C=NR″, are greater for aldehydes than for ketones.[20]

The foregoing considerations clarify why chalcone anil would be difficult to synthesize and isolate in the presence of water.

It should be noted that the tendency for the anils of $\alpha,\beta$-unsaturated aldehydes and ketones to rearrange, in the presence of water, to $\beta$-anilino carbonyl derivatives forms the basis for the classic Skraup synthesis of quinolines.[21a] Cinnamaldehyde, for example, condenses with aniline to yield 2-phenylquinoline, rather than 4-phenylquinoline (eq 7, path a, R = Ph). The observed course of the Skraup cyclization requires the intermediacy of 2-anilino-2-phenyl-propanal or its anil (**15**: E = O or NPh). Since the use of the novel reagent **6b** permits us to synthesize anils in the absence of water, we are examining the possibility of cyclizing such anils to the isomeric 4-substituted quinolines.[21b]



(7)

**15**

## Experimental Section

**General Techniques.** All reactions involving organoaluminum compounds or aluminum imides were conducted under an atmosphere of dry, oxygen-free nitrogen gas, which was purified by published procedures.[22a] Reaction solvents, such as hexane, heptane, cyclohexane, toluene, and xylene, were freed of peroxides and protic impurities by known methods.[22b]

The starting carbonyl derivatives, *trans*-cinnamaldehyde, cyclohexanone, acetophenone, benzophenone, fluorenone, and benzoyl chloride, were purchased from commercial sources, and where physical constants and spectral data indicated the presence of impurities, were recrystallized or fractionally distilled just before use. Benzalacetophenone (chalcone) was prepared by a published method.[23] Both neat triethylaluminum and a toluene solution of ethylaluminum dichloride were purchased from Texas Alkyls, Inc., Deer Park, TX and contained 99.9% of the aluminum content in the form of the stated reagent. The aniline employed was >99% pure, as offered by the Aldrich Chemical Co., and was dried and distilled from zinc powder under nitrogen immediately before use.

The melting points were measured in a Thomas-Hoover capillary melting point apparatus and are uncorrected. Spectral data were obtained with the following instruments: $^1H$ NMR, Varian EM-360; IR, Perkin-Elmer 457; UV, Carey 14; MS, Hewlett-Packard, 5993. Aluminum analyses were performed by titration with ethylene–diaminetetraacetic acid according to a literature description.[24]

**Preparation of Aluminum Imides. (a) Bis(diethylaluminum) Phenylimide (6a).** A 500-mL, two-necked, round-bottomed flask was provided with 200 mL of dry xylene and a magnetic stirrer and then equipped with a pressure-equalizing funnel and a reflux condenser. The condenser was cooled by circulating cooled silicone oil through the cooling jacket, and the reaction flask was flushed with and maintained under an atmosphere of dry nitrogen. Then 7.67 g (70 mmol) of triethylaluminum (*CAUTION*: pyrophoric liquid) in 25 mL of dry xylene was introduced into the reaction vessel. Thereafter 3.12 g (30 mmol) of pure aniline in 25 mL of xylene were added at 25 °C over a 45-min period. Upon heating the resultant mixture in an oil-bath at 120–130 °C for 20 h, gas was steadily evolved. After cooling the reaction mixture was subjected to reduced pressure and the xylene was distilled off. The viscous brown residue remaining after solvent removal was the desired bis(diethylaluminum) phenylimide (**6a**). An aliquot of this product was weighed in a gastight syringe and then cautiously hydrolyzed in 100 mL of 0.5 N aqueous $H_2SO_4$ (gas evolution). A 10-mL aliquot of the solution was treated with 40 mL of a 0.02M aqueous EDTA solution, which was buffered to a pH of 4.5–5.4. The mixture was heated to boiling, cooled, and then admixed with 75 mL of an aqueous solution of 2-propanol and $NH_4Cl$. The dithezone indicator was added and the solution back-titrated with 0.02 M aqueous $ZnSO_4$. Analysis indicated that a 93% conversion to **6a** had been achieved. Anal. Calcd. for $C_{14}H_{25}NAl_2$: Al, 20.65. Found: Al 19.1.

**(b) Bis(dichloroaluminum) Phenylimide (6b).** An apparatus similar to that described for the preparation of **6a** was employed, except that a 2-L flask was used. Into such a nitrogen-flushed apparatus were transferred 804 g of a solution of ethylaluminum dichloride in toluene. Based upon an aluminum analysis (cf. supra), this solution contained 185.4 g (1.46 mol) of $EtAlCl_2$. (*CAUTION*: the handling and transfer of large amounts of the pyrophoric $EtAlCl_2$ in toluene solution must be done with great care. The chemist should study published techniques for these transfers with greater attention.[25])

Then 67.8 g (730 mmol) of freshly distilled aniline was introduced dropwise over a 45-min period. Subsequent heating and stirring of the resultant mixture at reflux for 20 h caused the evolution of gas. Withdrawal of an aliquot, removal of most of the toluene under nitrogen in vacuo, and recording the $^1H$ NMR spectrum (cyclohexane) showed the presence of a singlet that was about 10 Hz wide at half-height and the absence of the N–H and $CH_3CH_2$–Al signals. Hence, it could be concluded that all the aniline had reacted from **6b**. Therefore, a simple aluminum analysis could be used to determine the concentration of **6b** in the toluene solution.

**General Procedure for Anil Formation. (a) Bis(dichloroaluminum) Phenylimide.** Under a nitrogen atmosphere a two–necked, round–bottomed flask, which was equipped as described in the preparation of **6b**, was charged with the desired mmol of **6b** in toluene. A solution of the carbonyl substrate

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(20) Conant, J. B.; Bartlett, P. D. *J. Am. Chem. Soc.* **1932**, *54*, 2881.

(21) (a) Elderfield, R. C. In "Heterocyclic Compounds"; Elderfield, R. C., Ed.; Wiley: New York, 1952, Vol. 4, p 17 ff. (b) Eisch, J. J.; Dluzniewski, T., studies in progress, 1985. Indeed, the formation of 4-phenylquinoline by passing air and *trans*-cinnamaldehyde anil over $Al_2O_3$ at 400–450 °C has been observed: Ardaschev, B. I.; Tertov, B. A. *J. Gen. Chem. USSR, Eng. Ed.* **1956**, *26*, 233–235; *Chem. Abstr.* **1956**, *50* 13926i.

(22) (a) Eisch, J. J. "Organometallic Syntheses"; Academic Press: New York, 1981; Vol. 2, pp 7–20. (b) Reference 22, pp 20–26.

(23) Kohler, E. P.; Chadwell, H. M. "Organic Syntheses"; Gilman, H., Blatt, A. H. Ed.; Wiley: New York, 1941; Collect. Vol. I p 78.

(24) Martin, A. J. *Anal. Chem.* **1958**, *30*, 233.

(25) Reference 22, pp 33–37.

dissolved in the same hydrocarbon was added dropwise to the solution of 1.5 equiv of **6b**, which was held at 60–65 °C. Then the reaction mixture was cooled to 25 °C and stirred for 12 h. Thereafter, the reaction mixture was slowly introduced into a 10 N aqueous KOH solution, which was maintained and stirred at 5 °C. Ethyl ether was added to dissolve the liberated anil, and the slurry was then filtered to separate the solid alumina. The organic layer layer was separated, dried over anhydrous $MgSO_4$, and evaporated in vacuo. The residual anil was often obtained quite pure at this stage. Recrystallization or distillation gave the analytically pure anils in yields of 70–95%.

**(b) Benzophenone Anil.** Admixture of reagents over 4.5 h gave 92%, mp 110–110 °C, without recrystallization, lit.[6] 113 °C: $^1$H NMR ($CDCl_3$) 7.3 (m); IR (mineral oil) 1640 $cm^{-1}$ (C=N).

**(c) Benzalacetophenone Anil.** Admixture of reagents over 4.5 h gave 80%, mp 99–101 °C without recrystallization. From 95% ethanol, the anil yielded a pale yellow solid, mp 99–101 °C: $^1$H NMR ($CDCl_3$) 7.2 (m); IR (mineral oil) 1625 $cm^{-1}$; MS, *m/e* 283 (P); lit.[14] 109 °C.

**(d) Fluorenone Anil.** Admixture of reagents over 1 h at 70 °C gave 93%, mp 79–81 °C, without recrystallization, lit.[6] 88 °C; $^1$H NMR ($CDCl_3$) 6.2–7.9 (m); IR (mineral oil) 1650 $cm^{-1}$ (C=N).

**(e) Cyclohexanone Anil.** Admixture of reagents over 3 h at 60 °C gave, by distillation, a 60% yield. However, the yield of the crude anil before distillation was 95% and its $^1$H NMR spectrum was essentially identical with that of the distilled product: $^1$H NMR (neat) 6.8 (m, 5 H), 2.2 (m, 10 H); IR (mineral oil) 1650 $cm^{-1}$ (C=N); MS, *m/e* 173.[26]

**(f) Acetophenone Anil.** Admixture of reagents over 3.5 h at 45–50 °C gave 38% after distillation, bp 175 °C at 13 mmHg: $^1$H NMR (neat) 7.35 (m, 10 H), 2.0 (s, 3H), IR (mineral oil) 1640 $cm^{-1}$ (C=N). In addition, 18% of acetophenone was recovered and 10% of dypnone anil (mp 97–98 °C) was obtained by recrystallization of residue.[27]

**(g) Cinnamaldehyde Anil.** Admixture of reagents over 1 h at 45–50 °C gave 75% of crude anil and 65% after recrystallization from 95% ethanol, mp 105–106 °C (lit.[28] 107 °C).

**(h) Benzoyl Chloride.** Admixture of a 1:1 ratio of reagents at 25 °C and workup after 30 min gave 60% of benzanilide, mp 159–161 °C: $^1$H NMR($CDCl_3$) 7.95 (s, H), 6.0 (m, 10 H).

**Reactions of Bis(diethylaluminum) Phenylimide.** The reagent was allowed to react with benzophenone in a 1:1 ratio and on a 4.0 mmolar size for 2 h at 65 °C and 12 h at 25 °C. The usual workup gave 52% of the anil, mp 113–114 °C. Examination of the ethanolic mother liquor by evaporating the volatiles and measuring the $^1$H NMR spectrum showed the presence of 1,1-diphenyl-1-propanol.

In a similar run with benzalacetophenone, only 15% of the pure anil was isolated, mp 96–98 °C.

**Reaction of Aniline with Benzalacetophenone (3).** A procedure involving the interaction of these components at 175–180°C in the presence of anhydrous sodium acetate is said to produce the Schiff base, benzalacetophenone anil (**11**), colorless cubes, mp 167–168 °C.[29] However, not only did this product lack the yellow color of the expected anil, but when its spectra were examined in this laboratory, it was concluded to be actually the Michael adduct of aniline with benzalacetophenone, 1,3-diphenyl-1-(phenylamino)-1-propanone (**4**): $^1$H NMR ($CF_3CO_2H$) 3.6 (d of d, 2 H), 4.65 (m, H), 6.5–7.1 (m, 14), 7.5 (d of d, 2 H); IR (mineral oil) 3395 (s, NH), 1675 (s, C=O).[8]

Even when a known procedure for converting alkyl aryl ketones into anils was employed (Reddelien's technique of using an aniline–zinc chloride complex[6]), only the same Michael adduct was isolated. Thus, a mixture of benzalacetophenone (20.1 g, 97 mmol), freshly distilled aniline (17.6 g, 190 mmol), and 2.0 g of the aniline–zinc chloride (2/1) complex was slowly brought to 175–180 °C by stirring the reactants in an oil bath under a nitrogen atmosphere. During the 90-min heating period the refluxing aniline was observed to contain water. Thereafter, the aniline was distilled off under reduced pressure (about 12 mL); the aniline distillate was also found to contain water and acetophenone. The residual reaction mixture was dissolved in 150 mL of chloroform, the undissolved zinc salts filtered off and the chloroform removed in vacuo. The TLC analysis showed the presence of **4** (major), dypnone anil (**2**), and benzalaniline (**12**). Dissolution of the residue in hot 95% ethanol and cooling deposited 12 g (41%) of **4**, mp 165–167 °C.

**Decomposition of 1,3-Diphenyl-3-(phenylamino)-1-propanone (4).** A solution of 350 mg of **4** in 30 mL of benzene was allowed to reflux over a pellet of KOH for 90 min. Removal of the solvent left a mixture of **4**, benzalacetophenone, and aniline (TLC, IR, and $^1$H NMR).

Likewise, a solution of 0.50 g of **4** in 50 mL of benzene was allowed to reflux in the presence of 10 mg of *p*-toluenesulfonic acid for 12 h. Removal of the solvent left a mixture of **4**, benzalacetophenone, and aniline.

A 3.0-g samples of **4** was heated at 175–195 °C for 90 min, during which time a 2.1-g mixture of aniline and acetophenone volatilized from the melt. At the end of the reaction the residue was found to contain benzalacetophenone and benzalaniline (**12**).

**Condensation of Acetophenone Anil (13) and Benzaldehyde.** In attempts to prepare benzalacetophenone anil (**11**) by a cross-aldol condensation, freshly distilled acetophenone anil (1.27 g, 6.50 mmol), and benzaldehyde (630 mg, 5.9 mmol) were heated at 165–175 °C with 100 mg of the 2:1 complex of aniline and $ZnCl_2$ for 40 min. There was no steam evolution observable. Cooling and dilution of the mixture with 10 mL of benzene eventually deposited 0.70 g (40%) of 1,3-diphenyl-3-(phenylamino)-1-propanone (**4**), mp 166–168 °C (mixture melting point).

**Attempted Condensation of Acetophenone Anil (13) and Benzalaniline (12).** A mixture of 5.0 g (25.6 mmol) of freshly distilled acetophenone anil and 4.30 g (23.8 mmol) of recrystallized benzalaniline (mp 50–51 °C) was heated with 100 mg of $(PhNH_2)_2ZnCl_2$ at 180–190 °C for 90 min. The aniline generated was distilled off, and the residue was examined by $^1$H NMR spectroscopy. Besides the starting materials, only dypnone anil (**2**) could be detected. Slow crystallization of this oil from 95% ethanol gave dypnone anil, mp 96–98 °C.

**Treatment of Chalcone Anil (11) with Deuterium Oxide.** A partial solution of 236 mg (0.83 mmol) of **11** in 5 mL of anhydrous THF containing 16 mg (0.83 mmol) of $D_2O$ (99.8%) and a trace of *p*-toluenesulfonic acid was stirred at 25–30 °C for 80 h. Removal of solvent and TLC analysis showed the presence of traces of aniline and chalcone; the dominant product was 1,3-diphenyl-3-(phenylamino)-1-propanone (**4**). Dissolution of the organic residue in hot 95% ethanol and cooling gave 220 mg (87%) of **4**, mp 164–166 °C. Its IR spectrum displayed the characteristic C=O band at 1675 $cm^{-1}$, but the NH was weak, showing partial N–D formation. The mass spectrum at 70 eV had peaks at 303 (4.6), 302 (7.6), 301 (<0.1), 183 (40), 182 (100), 181 (18), 121 (1.5), 120 (3.7), 105 (60), 94 (4.3), and 93 (7.7). The peaks at 303 and 302 revealed the presence of di- and monodeuterated **4**; those at 183 and 182, mono- and undeuterated $(PhCH{=}NHPh)^+$; those at 121 and 120, mono- and undeuterated $(PhCOCH_3)^+$; and those at 94 and 93, mono- and undeuterated $(PhNH_2)^+$.

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