mL of solvent for lepidine and 11 mL of solvent for quinoxaline at 20 °C. The ratios of reagents, the composition of the solvent, the reaction products, the conversions, and the yields are reported in Table II. The results of Table III were obtained with an identical procedure using the amounts of $Fe_2(SO_4)_3$ reported in the table.

Reaction with *N*-Methylacetamide. Lepidine (4 mmol) 4 mmol of H_2SO_4, 4 mmol of HSA, and 0.12 mmol of $FeSO_4 \cdot 7H_2O$ were dissolved in 5 mL of *N*-methylacetamide and 2 mL of water at 20 °C. The mixture was stirred for 2 h at 20 °C, then diluted with 15 mL of water, basified by a 30% NH_4OH solution, and extracted with CH_2Cl_2 (4 × 10 mL). TLC and GLC analyses revealed the presence of only two products: lepidine (2.76 mmol) and IX (0.73 mmol); conversion 31%; yield based on converted lepidine 59%; the material balance is 87.3%.

Reaction with *N,N*-Dimethylacetamide. The procedure is similar to that used for *N*-methylacetamide starting with 4 mmol of lepidine. TLC and GLC analyses revealed only unreacted lepidine (2.6 mmol) and X (0.93 mmol) and no other product: conversion 35%; yield based on converted lepidine 66%; the material balance is 88.3%.

Reaction with *N,N*-Diethylacetamide. The same procedure used for *N,N*-dimethylacetamide was utilized for *N,N*-diethylacetamide. Unreacted lepidine (91%) was recovered; TLC and GLC analyses did not reveal traces of products of substitution of lepidine; GLC analyses of the solvent revealed the presence of N-ethylacetamide (1.96 mmol) (49% based on HSA).

Acknowledgment. This work was supported by Progetto Finalizzato Chimica Fine e Secondaria, CNR, Rome.

Registry No. Lepidine, 491-35-0; quinoxaline, 91-19-0.

Synthesis, Stability, Structure, Reactivity, and Chemistry of *N*-Alkylbenzoazetinones

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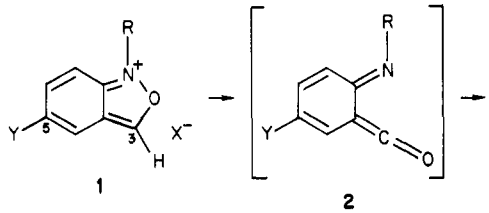
On treatment with triethylamine, 3-unsubstituted anthranilium salts 1 ring open and then recyclize to *N*-alkylbenzoazetinones **3**. When the alkyl group is tertiary, **3** is stable and the X-ray crystal structure of one such derivative, *N*-1′-adamantylbenzoazetinone (**3g**), requires a planar antiaromatic formulation with some bond localization in the benzo moiety. Ring-cleavage products are obtained in the rapid reaction of the β-lactams **3** with nucleophiles such as alcohols (→ **10a–e**), amines (→ **10f,g**), water (→ **11a,c**), benzoate (→ **12**), and azide (→ **14**). When heated, the acyl azides **14** undergo Curtius rearrangement followed by ring closure to benzimidazolones **17**.

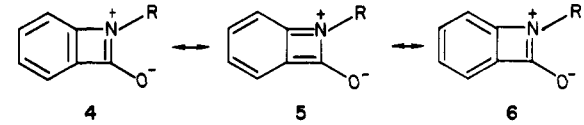
Several years ago, a simple and facile synthesis of *N*-alkylbenzoazetinones **3** was outlined in a preliminary report from this laboratory.[1] The isolation and characterization of the first stable compound **3f** with this ring system also was described.[1] Prior to this report, benzoazetinones had been proposed as short-lived, impossible-to-isolate reaction intermediates in the photolysis of benzotriazinones.[2] Subsequently, other less efficient and practical routes to **3** including isolable derivatives have been published.[3,4]



1 **2** **3**

a, R = methyl; Y = H; X = BF_4
b, R = methyl; Y = H X = CF_3SO_3
c, R = ethyl; Y = H; X = BF_4
d, R = ethyl; Y = H; X = FSO_3
e, R = isopropyl; Y = H; X = BF_4
f, R = *tert*-butyl; Y = H; X = ClO_4
g, R = 1-adamantyl; Y = H; X = ClO_4
h, R = *tert*-butyl; Y = Br; X = ClO_4
i, R = 1-adamantyl; Y = Br; X = ClO_4

Theoretical interest in **3** derives from its relationship to benzocyclobutadiene.[5] In so far as **3** is an amide and canonical structures such as **4–6** contribute to a resonance-stabilized hybrid structure, then **3** is a benzocyclobutadiene analogue and thus a formal violation of Hückel's $4n + 2$ rule. However, **3** is a rare molecule with an option.



4 **5** **6**

(1) Olofson, R. A.; Vander Meer, R. K.; Stournas, S. *J. Am. Chem. Soc.* **1971**, *93*, 1543.

(2) Burgess, E. M.; Milne, G. *Tetrahedron Lett.* **1966**, 93. Ege, G. *Chem. Ber.* **1968**, *101*, 3079. Ege, G.; Pasedach, F. *Ibid.* **1968**, *101*, 3089.

(3) See, for example: Bashir, N.; Gilchrist, T. L. *J. Chem. Soc. Perkin Trans. 1* **1973**, 868 and references therein.

(4) Although discussed in other terms by Kametani, the synthetically useful dehydrative thermolysis of anthranilic acids also must involve **3** as an intermediate: Kametani, T.; Loc, C. V.; Higa, T.; Koizumi, M.; Ihara, M.; Fukumoto, K. *J. Am. Chem. Soc.* **1976**, *98*, 6186; **1977**, *99*, 2306.

(5) Vollhardt, K. P. C. *Top. Curr. Chem.* **1975**, *59*, 113. Gheorghiu, M. D.; Filip, R. *Rev. Roum. Chim.* **1976**, *21*, 1189; **1974**, *19*, 859. Hoffmann, R. *Chem. Commun.* **1969**, 240. Gheorghiu, M. D.; Hoffmann, R. *Rev. Roum. Chim.* **1969**, *14*, 781. Gompper, R.; Seybold, G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 824 and references therein.

0022-3263/84/1949-3367$01.50/0

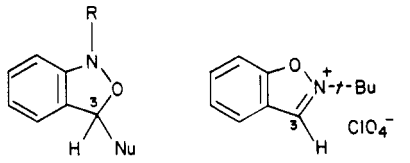
If the instability incurred by violating Hückel's rule overwhelms the stabilizing effect of amide delocalization, **3** can avoid much of the "agony" by bending the R group out of the ring plane—in effect, by rehybridizing the nitrogen from trigonal to tetrahedral and mimicking a simple amino ketone. When molecules such as **3** are encountered, the determination of their exact structures usually advances our understanding of bonding and the relative importance of various bonding mechanisms. Even when such molecules choose to compromise between opposing forces, the result is significant.

A single-crystal, X-ray structure is required to determine whether **3** is best represented as a trigonal amide, a tetrahedral amino ketone, or a flattened pyramidal compromise between these extremes. Since **3f** and the subsequently prepared bromo derivative **3h** were liquids, they were not suitable for such a study. At the suggestion of Gilchrist,[6] the crystalline adamantyl compound **3i** was synthesized, but it proved too light-sensitive to be useful. Advances in X-ray analysis by direct methods have made the simple adamantyl system **3g** a prime candidate for such an investigation. The results of the structure determination are presented here along with details of the synthesis, stability, reactivity, and chemistry of **3**. The following manuscript[7] describes an alternative route to products from **3**. The third paper in this series[8] outlines kinetic and photochemical studies and some complex reactions which afford new insight into the structure of **3**.

Results and Discussion

Anthranils[9] are too weakly nucleophilic to be N-alkylated by classical reagents such as methyl iodide. However, the *N*-methyl and *N*-ethyl salts **1a–d** were readily obtained in high yield by treatment of commercial anthranil with more powerful alkylating agents, $R_3O^+BF_4^-$, CF_3SO_3R, and FSO_3R. The isopropyl salt **1e** was produced by alkylation with $(i\text{-PrO})_2CH^+BF_4^-$,[10] though in mediocre yield because of competitive fragmentation of the reagent to propene. Finally, the *tert*-butyl and 1-adamantyl salts **1f–i** were easily made in high yield by alkylation of the appropriate anthranil with *t*-BuOH or 1-adamantanol in the presence of concentrated $HClO_4$ by using the general *tert*-alkylation method of Woodward and Woodman.[11] That anthranil was not made inert by protonation under these conditions testifies to its low basicity. The C_3H NMR position in **1** is at very low field: δ 9.91–10.06 in CD_3NO_2 (δ 9.3 in the parent anthranils).

Attempts to achieve the desired ring opening and closure, **1** → **3**, by deprotonation with alkoxides, alcohols, and other base classes failed because the base just added to C_3 of **1** to give stable products. This useful reaction, illustrated by the formation of **7** on treatment of **1** with



7, Nu = OMe
8, Nu = $^+NEt_3$
9

NaOMe or Et_3N–MeOH, is explored later.[7] Addition to C_3 of **1** by any base could be unavoidable. However, if the process does not have the thermodynamic advantage of neutralizing the charge in **1**, addition might be reversible.[12] Then a slower proton abstraction could yield **3** cleanly and irreversibly: $[adduct]^+X^- \rightleftharpoons \mathbf{1} + :B \rightarrow \mathbf{3} + HB^+X^-$. Experimentally, this condition was met by $i\text{-Pr}_2NEt$ and later by Et_3N. The reaction was so fast that no direct evidence for formation of **8** could be obtained (but see ref 7).

Treatment of the *N*-ethyl salt **1c** with excess Et_3N in CH_2Cl_2 gave a homogeneous solution whose IR spectrum immediately after mixing contained a strong absorption at 5.54 μm. This peak rapidly decreased in intensity with time and was gone within an hour. The result is in accord with the formation of an unstable benzoazetinone (**3c**) from Et_3N-induced proton abstraction and ring opening of **1c** followed by cyclization of the initially generated imino ketene **2c**. Similar experiments on the *N*-isopropyl (**1e**) and *N*-*tert*-butyl (**1f**) salts yielded solutions with strong absorption at 5.56 μm. However, the IR spectrum of the reaction mixture from **1f** did not change with time and a 14-h period was required before the C=O stretch from reaction of **1e** had completely disappeared. Thus the rate of the decomposition of **3** is governed by steric factors: Et > *i*-Pr > *t*-Bu (reaction of **1a** was ambiguous). In none of the above experiments was an IR absorption seen which could be attributed to the ketene function of **2**.

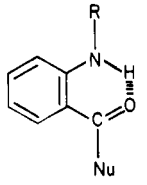
N-*tert*-Butylbenzoazetinone (**3f**) was isolated from solution by precipitation of the byproduct, $Et_3NH^+ClO_4^-$, with ether followed by vacuum distillation of the filtrate. The yield of the yellow liquid (**3f**, bp 83–84 °C at 0.2 mm) was 84% (68% from anthranil). While **3f** rapidly decomposed in the presence of nucleophiles, it was otherwise stable! The assigned structure was supported by a correct combustion analysis and by spectral data including IR (C=O stretch at 5.52 μm in CCl_4), UV (370 [420], 273 [2100], and 222 nm [ϵ 29 400] in cyclohexane), ^1H NMR (*t*-Bu s at δ 1.40 in CCl_4), ^{13}C NMR (C=O at 166.4 ppm in $CDCl_3$), and high- and low-resolution mass spectra. Three other stable *tert*-alkylbenzoazetinones later were isolated: the liquid bromo *tert*-butyl compound **3h** (73% yield) and the crystalline *N*-1′-adamantyl **3g**[6] (97%) and bromo adamantyl **3i** (90%) systems. The spectral data for **3g–i** paralleled the values for **3f**. Finally, a single-crystal X-ray structure of **3g** (see later) guaranteed the assignments.

[Kemp and co-workers[13] have shown that *N*-alkyl-3-unsubstituted benzisoxazolium salts react with bases by concerted proton abstraction and ring cleavage to form keto ketenimine intermediates in a process analogous to **1** → **2**. However, these keto ketenimines have proven too elusive to detect spectroscopically though their existence is certain from product studies and elegant mechanistic

(6) We thank Dr. T. L. Gilchrist for preprints and for sharing valuable insights in his correspondence with us.
(7) Vander Meer, R. K.; Olofson, R. A. *J. Org. Chem.*, second paper in a series in this issue.
(8) Olofson, R. A.; Vander Meer, R. K. *J. Org. Chem.*, third paper in a series in this issue.
(9) Easily made by reducing $o\text{-}O_2NC_6H_4CHO$ or $o\text{-}O_2NC_6H_4CO_2H$, anthranil has been known since 1881, when it was regarded as the dehydration product of anthranilic acid and drawn as the benzo β-lactam (Speroni, G. *Chem. Heterocycl. Cmpds.* **1962**, *17*, 213). Here, ironically we make benzoazetinone from the compound which "stole" its trivial name. Anthranil is preferred over 2,1-benzisoxazole, because the trivial name of 1,2-benzisoxazole is benzisoxazole. This anomaly does not extend to the dihydro series: 1,3-dihydroanthranils are called 2,1-benzisoxazolines.
(10) Borch, R. F. *J. Org. Chem.* **1969**, *34*, 627. Olofson, R. A.; Kendall, R. V. *Ibid.* **1970**, *35*, 2246.
(11) Woodward, R. B.; Woodman, D. J. *J. Org. Chem.* **1966**, *31*, 2039. Woodman, D. J. *Ibid.* **1968**, *33*, 2397.
(12) For more on logic of base choice, see: Olofson, R. A.; Walinsky, S. W.; Marino, J. P.; Jernow, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 6554.
(13) Kemp, D. S.; Woodward, R. B. *Tetrahedron* **1965**, *21*, 3019. Kemp, D. S. *Ibid.* **1967**, *23*, 2001. Kemp, D. S.; Wrobel, S. J.; Wang, S.-W.; Bernstein, Z.; Rebek, J.; *Ibid.* **1974**, *30*, 3969. Kemp, D. S.; Wang, S.-W.; Rebek, J.; Mollan, R. C.; Banquer, C.; Subramanyam, G. *Ibid.* **1974**, *30*, 3955. Kemp, D. S.; Wang, S.-W.; Mollan, R. C.; Hsia, S.-L.; Confalone, P. N. *Ibid.* **1974**, *30*, 3677.

investigations.[13] Extrapolating from the present success,[14] the previously unknown *tert*-butyl salt **9** was made and titrated with Et_3N in CH_2Cl_2. No IR evidence for even a fleeting keto ketenimine or for a ring-closed lactim (analogous to **3**) was found.]

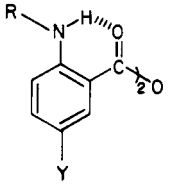
The reactions of benzoazetinones with alcohols and secondary amines seemed uneventful, the products being the ring-opened adducts **10** (but see ref 8). For example,



10a, R = *tert*-butyl; Nu = O-methyl
10b, R = *tert*-butyl; Nu = O-ethyl
10c, R = *tert*-butyl; Nu = O-isopropyl
10d, R = *tert*-butyl; Nu = O-*tert*-butyl
10e, R = ethyl; Nu = O-methyl
10f, R = *tert*-butyl; Nu = N(ethyl)$_2$
10g, R = *tert*-butyl; Nu = N = 1-pyrazolyl

3f reacted with alcohols in CH_2Cl_2 to give the amino esters **10a–d** in 74–95% yields. Similar treatment of the short-lived **3c** generated in situ with MeOH afforded **10e**[15] (61% yield). The amides **10f**, (87% crude) and **10g** (85%) were obtained with Et_2NH and pyrazole.

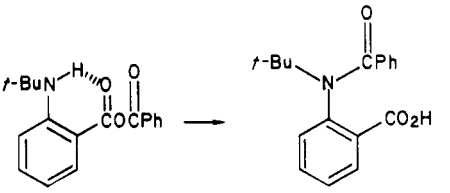
Reaction of **3** with water was more surprising. When water was added to **3f** in CH_3CN, the product was the anhydride **11a** (75% yield). Analogous compounds (**11b,c**)



11a, R = *tert*-butyl; Y = H
11b, R = 1-adamantyl; Y = H
11c, R = *tert*-butyl; Y = Br
11d, R = phenyl; Y = H

were obtained in 81% and 88% yields from reaction of **3g** and **3h**. The high wavelength of the anhydride C=O stretch peaks of **11a–c** (5.74–5.76 and 5.93–5.94 μm) might seem inconsistent with the structural formulation. However, the data agree with the values[2] for *N*-phenylanthranilic anhydride (**11d**, 5.75 and 5.99 μm) and reflect the H bond depicted in **11**.

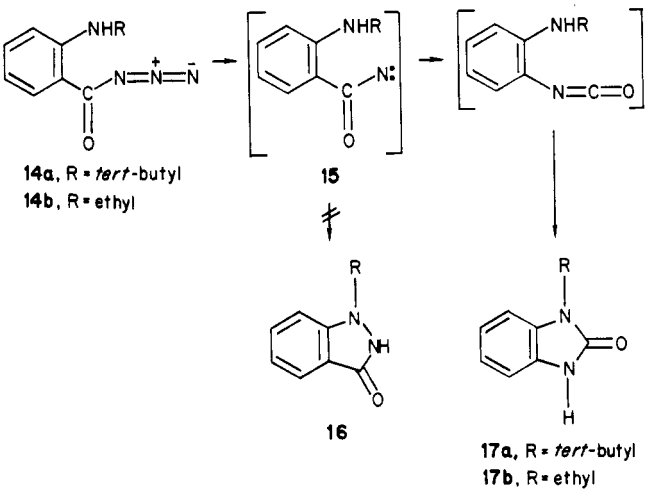
The formation of **11a–c** is readily rationalized by a pathway in which water adds to the benzoazetinone **3**, producing the anthranilic acid which then reacts with another molecule of **3** to yield the isolated anhydride (demonstrating that **3** is more reactive toward water than anhydride **11**). In accord with this explanation, **3f** reacted with benzoic acid to give an unstable oil identified as the mixed anhydride **12**. When **12** was refluxed in acetonitrile, O → N acyl migration to the amide **13** (no NH stretch, strong carboxyl OH, C=O at 5.87 and 6.29 μm in KBr) occurred (78% from **3f**). The C=O stretches for the mixed anhydride **12** (6.63 and 5.89 μm) are positioned between the same peaks in **11a** and benzoic anhydride. Why **11a–c** do not readily undergo the O → N acyl shift exemplified



12 **13**

by **12** → **13** is unclear (H bonds limit accessibility to transition state?). Mixed anhydride **12** could be obtained just by adding **1f** to aqueous sodium benzoate, a practical process also suggesting the generation of **3f** in situ. This approach to benzoazetinone-derived products was extended (see following paper[7]).

In another reaction series, benzoazetinone **3f** was converted to the unstable acyl azide **14a** (NH at 2.99, N_3 at 4.67, and C=O at 6.04 μm, 85% yield) by treatment with ethereal HN_3.[16] A sample of *N*-ethyl azide **14b** also was made.[7] When **14a,b** were heated, they rearranged to



14a, R = *tert*-butyl
14b, R = ethyl

15

16

17a, R = *tert*-butyl
17b, R = ethyl

benzimidazolones **17a,b** in good yield. Samples of the known **17b** were made by ethylation of benzimidazolone[17] and by reduction–phosgenation of *o*-nitro-*N*-ethylaniline.[18] It is surprising that Curtius rearrangement products **17** are obtained from **14** when the intermediate nitrene **15** seems optimally suited to insert into the N–H to give indazolone **16**. Some **16**[19] was made to guarantee identification, but none was found in the thermolysis mixture.

Discussion of Crystal Structure. A crystal of *N*-1′-adamantylbenzoazetinone (**3g**) was subjected to single-crystal X-ray analysis. When all non-hydrogen atoms seemingly were located, *R* was still 0.15, B_{iso} was > 8 for the six basal adamantyl carbons (those furthest removed from the benzoazetinone), and a difference Fourier located peaks midway between each of the three apical adamantyl C's. Refinement of these as C's (0.34 refined occupancy) confirmed the disorder of the adamantyl unit (*R* fell to 0.08). Because the basal C's could not be resolved, the disorder was treated by allowing each anisotropic temperature ellipse to encompass two basal C-positions (a CH and a CH_2 separated along the N–R axis by 0.6 Å). This caused irregular distances and angles within the adamantyl but had minimal influence on benzoazetinone bond distances and angles and as a result anisotropic refinement of all non-H atoms converged at $R = 0.054$. It is amusing,

(14) For illustrations of this stabilizing effect in simple 3-unsubstituted isoxazolium salt systems, compare ref 11 with: Woodward, R. B.; Olofson, R. A. *J. Am. Chem. Soc.* **1961**, *83*, 1007; *Tetrahedron, Suppl.* **1966**, *7*, 415. Olofson, R. A.; Marino, Y. L. *Tetrahedron* **1970**, *26*, 1779.
(15) Vorländer, D. *Chem. Ber.* **1901**, *34*, 1642.
(16) Audrieth, L. F.; Gibbs, C. F. *Inorg. Synth.* **1939**, *1*, 77.
(17) Davoll, J.; Laney, D. H. *J. Chem. Soc.* **1960**, 314.
(18) English, J. P.; Clapp, R. C.; Cole, Q. P.; Krapcho, J. *J. Am. Chem. Soc.* **1945**, *67*, 2263.
(19) Stolle, R. *J. Prakt. Chem.* **1927**, *116*, 192.

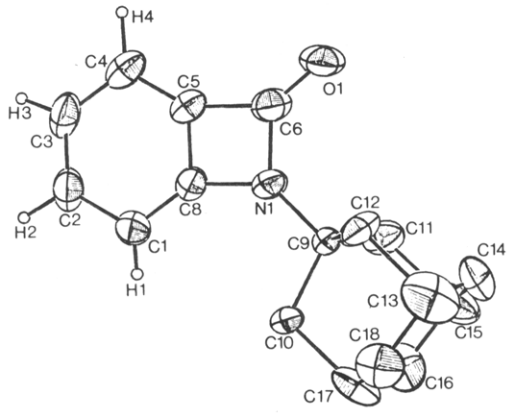


Figure 1. ORTEP representation of *N*-1′-adamantylbenzoazetinone giving the crystallographic numbering system used. Thermal ellipsoids for non-hydrogen atoms represent 35% probability; adamantyl H's and disordered apical adamantyl carbons omitted for clarity (see text).

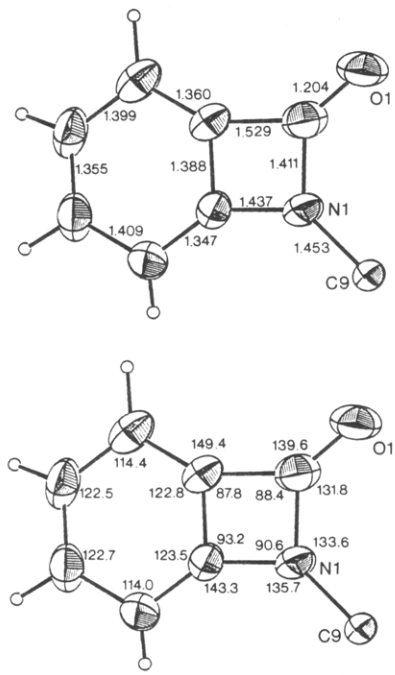


Figure 2. Important bond distances (Å, maximum esd of 0.006 Å) and angles (degrees, maximum esd of 0.4°) in *N*-1′-adamantylbenzoazetinone.

though not surprising, to note that the spherical adamantyl unit—the key to the crystallinity of **3g**—is itself disordered in the crystal.

An ORTEP representation of **3g** giving the crystallographic numbering system is depicted in Figure 1 with important bond distances and angles for the benzoazetinone part of the structure given in Figure 2. The benzoazetinone ring including the 1-adamantyl carbon (C9) is flat within experimental error. Various ring plane definitions (see supplementary material section) place C9 only 0.02, 0.004, and 0.02 Å from these least-squares planes. The 359.97° sum for the three angles around N1 further attests to the planarity of this portion of **3g**. The result could not be a more clear-cut demonstration of trigonal sp^2 hybridization at N1. There is enough space in the crystal to allow bending at N–R and the adamantyl disorder also indicates that deviation from planarity is permissible.

Even many small-ring lactams unconstrained by the "notoriety" of violating Hückel's rule are not planar. The N of an adamantylaziridinone is 0.54 Å from the plane of the C's to which it is bonded.[20] In simple β-lactams the N-substituent often is coplanar,[21] but in fused-ring β-lactam antibiotics, deviations are found: 0.40 Å for penicillin G.[21]

Other unusual features of the benzoazetinone system are revealed in the crystal structure. For example, theory predicts aromatic bond localization when three- and four-membered rings are fused to benzene; i.e., an increase in bond order of the bonds exo to and opposite the small ring and a decrease in the bond order of the other three bonds.[22,23] However, only rarely, despite extensive efforts,[24] has this phenomenon been observed. The best example is biphenylene with variations up to 0.05 Å.[25] Benzoazetinone now joins biphenylene as a clear illustration of this effect although the variations are smaller: C4–C5 1.360 (5) Å, C1–C8 1.347 (5) Å, and C2–C3 1.3555 (6) Å vs. C5–C8 1.388 (5) Å, C3–C4 1.399 (6) Å, and C1–C2 1.409 (5) Å.

In **3g** C6–N1 is longer (1.41 Å) and C6–O1 shorter (1.20 Å) than expected for an amide O=C(N<) ↔ $^-$OC(=N$^+$<). The best structure model for an amide conjugated at both termini is *N,N′*-(*p*-phenylene)dibenzamide where the analogous distances are 1.36 and 1.22 Å.[26] In the fused-ring β-lactam ampicillin, the values are 1.37 and 1.20 Å.[21] Although C6–N1 is long in **3g**, it is even longer in tribenzamide: 1.44 Å.[27] Thus, any suggestion that amide resonance is suppressed in benzoazetinones would be premature.

A definitive discussion of benzoazetinone structure awaits sophisticated calculations based on the experimental data reported here. Certainly, this molecule does not choose to bend R out of the ring plane in deference to Hückel. Whether the observed aromatic bond alternation and amide bond lengths are mostly consequences of a compromise with Hückel or an accommodation with Baeyer (angle strain) remain for theoreticians to determine.

Experimental Section[28]

Reagents and solvents were of the best available commercial grade and were dried by standard methods when anhydrous conditions were required.

***N*-Methylanthranilium Fluoroborate (1a).** $Me_3O^+BF_4^-$ (14.8 g, 0.1 mol) in CH_3NO_2 (40 mL) was slowly added to a stirred, cooled solution of commercial anthranil (11.9 g, 0.1 mol) in CH_3NO_2 (10 mL). The mixture was left in a refrigerator overnight and then cooled in dry ice–acetone while **1a** was slowly precipitated with EtOAc. Reprecipitation from CH_2Cl_2 with EtOAc afforded pure **1a**: 18.6 g (84% yield); mp 64–65 °C (slightly hygroscopic, moisture sensitive); ^{1}H NMR (CD_3NO_2) δ 9.91 (s, 1 H), 7.5–8.4 (m, 4 H), 4.77 (s, 3 H).

The triflate salt **1b** similarly was made by alkylation with CF_3SO_3Me: mp 92.5–93.5 °C after precipitation from CH_2Cl_2 with

(20) Angles around N total 314°: Wang, A. H.-J.; Paul, I. C. *J. Chem. Soc., Chem. Commun.* **1972**, 43.
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ether; ^{13}C NMR (CD_3NO_2) 162.0 (C_3), 142.8, 129.7, 124.1, and 110.9 (CH of Ar), 149.0 and 121.5 (quaternary C of Ar), 122.4 (q, J_{CF} = 321 Hz), 39.5 ppm (Me).

N-Ethylanthranilium Fluoroborate (1c). Reaction as above of anthranil with $Et_3O^+BF_4^-$ in CH_2Cl_2 gave **1c**; 84% yield, mp 79.5–80.5 °C (hygroscopic, moisture labile); ^1H NMR (CD_3NO_2) δ 9.97 (s, 1 H), 7.5–8.3 (m, 4 H), 5.05 (q, 2 H, J = 7 Hz), 1.72 (t, 3 H, J = 7 Hz).

Alkylation with FSO_3Et afforded **1d**; mp 62.5–64 °C after precipitation from CH_2Cl_2 with ether; ^{13}C NMR (1:1 $CDCl_3$:CH_2Cl_2) 161.4 (C_3), 141.6, 128.3, 123.4, and 109.3 (CH of Ar), 146.7 and 120.1 (quaternary C of Ar), 48.5 (CH_2), 13.1 ppm (Me).

N-Isopropylanthranilium Fluoroborate (1e). Anthranil (4.16 g, 0.035 mol) in CH_2Cl_2 (6 mL) was added to freshly prepared $(i\text{-PrO})_2CH^+BF_4^-$[10] (6.5 g, 0.035 mol) in CH_2Cl_2 cooled to 0 °C affording a solution from which **1e** was precipitated with ether after 2 h at 25 °C: 3.20 g (37% yield); mp 77–78 °C when reprecipitated from CH_3CN with ether at −80 °C (hygroscopic, moisture sensitive); ^1H NMR (CD_3NO_2) δ 9.96 (s, 1 H), 7.5–8.35 (m, 4 H), 5.63 (septet, 1 H, J = 7 Hz), 1.80 (d, 6 H, J = 7 Hz).

N-tert-Butylanthranilium Perchlorate (1f). $HClO_4$ (71%, 10 g, 0.07 mol) was slowly added to a stirred mixture (0 °C) of anthranil (2.98 g, 0.025 mol) and t-BuOH (1.85 g, 0.025 mol). The mixture was stirred at 25 °C overnight. Enough acetone was added to bring any precipitated solid into solution; then ether was added until precipitation ceased. Filtered product was reprecipitated from acetone with ether and dried at high vacuum: yield 5.48 g (81%); mp 149 °C dec; ^1H NMR (CD_3NO_2) δ 10.00 (s, 1 H), 7.5–8.35 (m, 4 H), 1.98 (s, 9 H).

N-1'-Adamantylanthranilium Perchlorate (1g). Anthranil (1.50 g, 0.013 mol) was added to a stirred slurry of 1-adamantanol (1.90 g, 0.013 mol) and $HClO_4$ (71%, 15 g, 0.1 mol). After reaction at 25 °C overnight, ether was added to precipitate **1g** which was purified by reprecipitation (acetone–ether): 3.68 g (80% yield); mp 195 °C (light sensitive); ^1H NMR (CD_3NO_2) δ 10.06 (s, 1 H), 8.0–8.3 (m, 3 H), 7.5–7.8 (m, 1 H), 2.2–2.8 (m, 9 H), 1.8–2.1 (m, 6 H); ^{13}C NMR (1:1 $CDCl_3$:CH_2Cl_2) 160.7 (C_3), 141.2, 127.7, 124.1, and 110.7 (CH of Ar), 145.2 and 120.8 (quaternary C of Ar), 72.0 (Ad quaternary C), 40.8, 34.9, and 29.4 ppm (Ad).

N-tert-Butyl-5-bromoanthranilium Perchlorate (1h). Reaction of 5-bromoanthranil[29] (3.95 g, 0.025 mol), t-BuOH (1.85 g, 0.025 mol), and $HClO_4$ (71%, 10 g, 0.07 mol) in acetone (10 mL) overnight followed by standard workup gave **1h**: 6.62 g (75% yield); mp 144 °C dec; ^1H NMR (CD_3NO_2) δ 9.93 (s, 1 H), 8.4–8.5 (m, 1 H), 8.1–8.2 (m, 2 H), 2.01 (s, 9 H).

N-1'-Adamantyl-5-bromoanthranilium Perchlorate (1i). Alkylation of 5-bromoanthranil as described for **1g** afforded **1i** in 83% yield: mp 200 °C, very light sensitive; ^1H NMR (CD_3NO_2) δ 9.94 (s, 1 H), 8.35–8.45 (m, 1 H), 8.1–8.2 (m, 2 H), 2.6–2.75 (m, 6 H), 2.25–2.5 (m, 3 H), 1.8–2.1 (m, 6 H).

N-tert-Butylbenzoazetinone (3f). **1f** (2.75 g, 0.01 mol) in CH_2Cl_2 (25 mL) was dripped into a stirred, ice-cooled solution of Et_3N (4.0 g, 0.04 mol) in CH_2Cl_2 (10 mL). After a few minutes, volatiles were evaporated in vacuo and the remaining oil was triturated several times with ether to remove the insoluble $Et_3NH^+ClO_4^-$. Distillation of the ether extract gave pure **3f** as a yellow liquid: 1.40 g (84% yield), bp 83–84 °C (0.2 mm); IR (CCl_4) 3.23 (w), 3.36 (m), 3.4–3.5 (bw), 5.52 (s), 6.25 (s), 6.83 (w), 6.99 (m), 7.19 (m), 7.3 (m), 7.78 (m), 8.07 (m), 8.16 μm (m) (C=O stretch at 5.56 in CH_2Cl_2); UV (cyclohexane) λ_{max} (ε) 370 nm (420), 273 (2100), 222 (29 400); ^1H NMR (CCl_4) δ 6.4–7.15 (m, 4 H), 1.40 (s, 9 H); ^{13}C NMR ($CDCl_3$) 166.4 (C=O), 132.6, 120.7, 119.7, and 105.7 (CH of Ar), 158.1 and 135.8 (quat C of Ar), 54.7 (CMe_3), 27.2 ppm (Me).

N-1'-Adamantylbenzoazetinone (3g). Reaction as above of **1g** gave **3g** (yellow solid): 97% yield, mp 98–100 °C (lit.[3] mp 98–99 °C); IR (CCl_4) 5.48 (s), 5.55 (s), 6.27 μm (s); ^1H NMR (CCl_4) δ 6.3–7.4 (m, 4 H), 2.09 (bs, 9 H), 1.71 (bs, 6 H); ^{13}C NMR ($CDCl_3$) 166.7 (C=O), 132.5, 120.7, 119.9, and 105.9 (CH of Ar), 158.0 and 136.2 (quaternary C of Ar), 55.8 (Ad quaternary C), 40.6, 35.8, and 28.8 ppm (Ad).

N-tert-Butyl-4-bromobenzoazetinone (3h). Similarly, **1h** gave **3h** in 73% yield: bp 100–101 °C (0.4 mm); IR (CCl_4) 5.52 μm (s); ^1H NMR (CCl_4) δ 6.9–7.2 (m, 2 H), 6.41 and 6.28 (2 s, 1 H), 1.39 (s, 9 H).

N-1'-Adamantyl-4-bromobenzoazetinone (3i). Treatment as above of **1i** produced **3i** in 90% yield; mp 130–131 °C after recrystallization from CCl_4 (decomposed by light); IR (CCl_4) 5.48 (s), 5.53 μm (s); ^1H NMR (CCl_4) δ 6.95–7.2 (m, 2 H), 6.2–6.4 (m, 1 H), 2.0–2.3 (m, 9 H), 1.6–1.9 (m, 6 H).

Formation and Stabilities of N-Methyl-, N-Ethyl-, and N-Isopropylbenzoazetinones (3a,c,e). Unlike the *tert*-alkyl compounds, less hindered *N*-alkylbenzoazetinones were too unstable to isolate. Solutions containing **3c** or **3e** could be obtained by rapidly adding excess Et_3N or $i\text{-Pr}_2NEt$ to the precursor **1c,e** in CH_2Cl_2 (reactions over before first IR spectrum could be taken). The C=O stretch of **3c** (5.54 μm) completely disappeared within 1 h at 25 °C and the lifetime of **3e** (5.56 μm) was ca. 14 h. Reaction of **1a** with Et_3N afforded a solution in which two medium peaks at 5.47 and 5.63 μm decreased in intensity somewhat faster than the C=O stretch of **3c**.

N-tert-Butylbenzisoxazolium Perchlorate (9). Standard *tert*-butylation of benzisoxazole gave **9**: 90% yield, mp 165–166 °C; ^1H NMR (CD_3NO_2) δ 9.98 (s, 1 H), 7.6–8.4 (m, 4 H), 2.02 (s, 9 H).

Methyl N-tert-Butylanthranilate (10a). A solution of **3f** (2.63 g, 0.015 mol) and MeOH (0.96 g, 0.03 mol) in CH_2Cl_2 (15 mL) was refluxed overnight. Vacuum evaporation followed by crystallization from MeOH gave **10a** as a white solid: 2.95 g (95% yield), mp 40–40.5 °C; ^1H NMR (CCl_4) δ 7.7–8.2 (m, 2 H), 6.3–7.4 (m, 3 H), 3.78 (s, 3 H), 1.43 (s, 9 H).

Ethyl N-tert-Butylanthranilate (10b). Reaction with 5 equiv of EtOH gave **10b**: 87% yield, bp 95 °C (0.5 mm); ^1H NMR (CCl_4) δ 7.8–8.3 (m, 2 H), 6.3–7.4 (m, 3 H), 4.23 (q, 2 H, J = 7 Hz), 1.4 and 1.28 (s and t, J = 7 Hz, 12 H).

Isopropyl N-tert-Butylanthranilate (10c). This was similarly made in 74% yield: bp 121 °C (0.4 mm); ^1H NMR (CCl_4) δ 7.8–8.2 (m, 2 H), 6.3–7.4 (m, 3 H), 5.16 (septet, 1 H, J = 6 Hz), 1.43 (s, 9 H), 1.30 (d, 6 H, J = 6 Hz).

***tert*-Butyl N-tert-Butylanthranilate (10d).** Reaction as above (three-day reflux) afforded **10d** (75% yield) first isolated by distillation, bp 110–112 °C (0.4 mm), and then by crystallization from MeOH: mp 49–50 °C; ^1H NMR (CCl_4) δ 7.6–8.3 (m, 2 H), 6.3–7.4 (m, 3 H), 1.56 (s, 9 H), 1.44 (s, 9 H).

Methyl N-Ethylanthranilate (10e). **1c** (2.00 g, 0.0085 mol) in CH_2Cl_2 (15 mL) was rapidly added to stirred, ice-cooled Et_3N (4.0 g, 0.04 mol) in CH_2Cl_2 (20 mL). After 2 min, absolute MeOH (20 mL) was added and the solution was stirred for 5 min. Vacuum evaporation afforded a residue which was extracted twice with ether. Distillation of the ether extract gave **10e**: 0.94 g (61% yield); bp 85–87 °C (0.4 mm) (lit.[15] bp 172–175 °C at 45 mm).

Diethyl-N-tert-butylanthranilamide (10f). A CH_2Cl_2 (20 mL) solution of **3f** (1.00 g, 0.0057 mol) and Et_2NH (1.31 g, 0.013 mol) was refluxed overnight. Vacuum evaporation afforded crude **10f**, 1.20 g (87% yield), which was isolated pure by vacuum distillation: bp 93–93.5 °C (0.4 mm); ^1H NMR (CCl_4) δ 6.35–7.1 (m, 4 H), 4.76 (s, 1 H), 3.30 (q, 4 H, J = 7 Hz), 1.30 (s, 9 H), 1.07 (t, 6 H, J = 7 Hz).

Pyrazolylamide of N-tert-Butylanthranilic Acid (10g). Similarly, **3f** (1.75 g, 0.01 mol) and pyrazole (0.54 g, 0.01 mol) in CCl_4 (25 mL) (refluxed overnight) yielded **10g**: 1.95 g (85% yield), mp 43–44 °C, recrystallized from hexanes, same mp; ^1H NMR (CCl_4) δ 8.1–8.4 (m, 2 H), 7.5–8.0 (m, 2 H), 6.3–7.4 (m, 4 H), 1.45 (s, 9 H).

N-tert-Butylanthranilic Anhydride (11a). A CH_3CN (20 mL) solution of **3f** (1.00 g, 0.0057 mol) and water (1.0 g, 0.056 mol) was left overnight at 25 °C, and the excess water was then removed with anhydrous Na_2SO_4. The oil obtained after solvent evaporation was crystallized from hot CH_3CN: 0.85 g (75% yield), mp 94–96 °C; IR (CCl_4) 2.98 (w), 5.76 (s), 5.94 μm (s); ^1H NMR (CCl_4) δ 7.8–8.2 (m, 4 H), 6.3–7.5 (m, 6 H), 1.48 (s, 18 H); ^{13}C NMR ($CDCl_3$) 165.1 (C=O), 135.3, 132.8, 113.9, and 113.8 (CH of Ar), 151.9 and 108.7 (quaternary C of Ar), 50.9 (CMe_3), 29.5 ppm (Me).

N-1'-Adamantylanthranilic Anhydride (11b). Reaction as above of **3g** gave **11b** in 81% yield: mp 253–254 °C after re-

(29) From $SnCl_2$ in concentrated HCl reduction (Wünsch, K. H.; Boulton, A. J. *Adv. Heterocycl. Chem.* **1967**, *8*, 303) of 2-nitro-5-bromobenzaldehyde. In the published synthesis (Bamberger, E.; Lublin, J. *Chem. Ber.* **1909**, *42*, 1676), anthranil + Br_2 gave the product in poor yield.

crystallization from 1:1 CH_3CN–$CHCl_3$; IR (CCl_4) 3.00 (w), 5.76 (s), 5.95 μm (s); ^1H NMR (CCl_4) δ 7.5–8.3 (m, 4 H), 6.9–7.5 (m, 4 H), 6.3–6.7 (m, 2 H), 2.12 (br s, 18 H), 1.75 (br s, 12 H); ^{13}C NMR ($CDCl_3$) 165.2 (C=O), 135.1, 132.9, 114.7, and 113.9 (CH of Ar), 151.9 and 108.8 (quaternary C of Ar), 52.0 (Ad quaternary C), 42.3, 36.5, and 29.6 ppm (Ad).

***N-tert*-Butyl-4-bromoanthranilic Anhydride (11c).** Similarly, **3h** produced **11c**: 88% yield, recrystallized from CH_2Cl_2–CH_3CN; mp 193–195 °C; IR (CCl_4) 2.98 (w), 5.74 (m), 5.93 μm (m); ^1H NMR (CCl_4) δ 7.9–8.2 (m, 2 H), 7.3–7.5 (m, 2 H), 6.7–6.9 (m, 2 H), 1.47 (s, 18 H).

***N-tert*-Butylanthranilic Benzoic Mixed Anhydride (12).** **3f** (1.20 g, 0.0068 mol) and benzoic acid (0.87 g, 0.007 mol) in CH_2Cl_2 (25 mL) was refluxed 4 h. The yellow oil (1.96 g, 96%) obtained after solvent evaporation consisted of unstable **12** contaminated with some **13**. Most **13** was removed by preferentially extracting **12** into cold CH_3CN. The sample isolated after vacuum evaporation could not be further purified because O → N benzoyl migration was too facile: IR (CCl_4) 2.99 (w), 5.63 (s), 5.89 μm (s); ^1H NMR ($CDCl_3$) δ 8.2–8.7 (broad s, 1 H), 6.3–8.15 (m, 9 H), 1.40 (s, 9 H).

***N*-Benzoyl-*N*-*tert*-butylanthranilic Acid (13).** Slightly impure **12** (1.40 g, 0.0047 mol) was refluxed overnight in CH_3CN (25 mL). Concentration of the solution afforded **13**: 1.09 g (78% yield); mp 174 °C dec; analysis sample treated with Norit and recrystallized from CH_3CN, mp 175 °C dec; IR (KBr) 5.87 (s), 6.29 (s), 6.4 (s), 6.75 μm (m); ^1H NMR (Me_2SO-d_6) δ 7.0–7.8 (m, 9 H), 1.47 (s, 9 H).

Reaction of 1f with Aqueous Sodium Benzoate. **1f** (2.75 g, 0.01 mol) in 30 mL of CH_2Cl_2 was rapidly added to sodium benzoate (7.2 g, 0.05 mol) in 50 mL of water and the mixture shaken vigorously for a few minutes. The separated aqueous layer was extracted with 2 × 30 mL of CH_2Cl_2. The combined CH_2Cl_2 solutions were evaporated in vacuo, yielding an unstable orange oil spectrally (IR, NMR) identical with **12**. Rearranged **13** was obtained by refluxing the oil in CH_3CN; 1.76 g (60% yield); mp 174 °C dec.

***N-tert*-Butylanthraniloyl Azide (14a).** An anhydrous ether (10 mL) solution of **3f** (1.75 g, 0.01 mol) was slowly added with stirring to ethereal hydrazoic acid[16] (23 mL, ca. 0.025 mol of HN_3) and the mixture was refluxed overnight. After vacuum evaporation, the thermally unstable **14a** (oil) remained: 1.86 g (85% yield); IR (CCl_4) 2.99 (w), 4.67 (s), 6.04 (s), 6.2 (m), 6.3 μm (s); ^1H NMR (CCl_4) δ 6.3–7.9 (m, 5 H), 1.43 (s, 9 H).

***N*-Ethylanthraniloyl azide (14b)** was made as described in ref 7: IR (CCl_4) 2.98 (w), 4.7 (s), 6.06 (s), 6.35 μm (m); ^1H NMR (CCl_4) δ 6.3–8.0 (m, 5 H), 3.14 (q, 2 H, J = 7 Hz), 1.23 (t, 3 H, J = 7 Hz).

***N-tert*-Butylbenzimidazolone (17a).** The residue from refluxing **14a** (1.5 g, 0.007 mol) in 20 mL of CCl_4 overnight followed by solvent removal was washed with hexanes to give essentially pure **17a**: 0.68 g (52% yield), mp 144–146 °C; analysis sample recrystallized from 1:1 benzene–pentane, mp 145–146 °C; IR (CCl_4) 2.87 (w), 3.08–3.7 (m), 5.90 (s), 6.75 μm (m); ^1H NMR (CCl_4) δ 11.58 (s, 1 H), 6.7–7.4 (m, 4 H) 1.82 (s, 9 H).

***N*-Ethylbenzimidazolone (17b).** Thermolysis of **14b** as above gave **17b** in 74% yield: mp 119–120 °C (lit.[17] mp 118–120 °C); IR (CCl_4) 2.89 (w), 3.06–3.52 (m), 5.90 (s), 6.16 (w), 6.7 μm (m); ^1H NMR (CCl_4) δ 11.09 (s, 1 H), 6.9–7.2 (m, 4 H), 3.95 (q, 2 H, J = 7 Hz), 1.35 (t, 3 H, J = 7 Hz).

Comparison samples of **17b** were made by ethylation of benzimidazolone[17] and from *N*-ethyl-*o*-nitroaniline[18] (spectra, mmp okay). The reaction mixture also was examined (IR, TLC) for the presence of *N*-ethylindazolone (**16**) but none was found in any fraction. **16** was prepared by heating *N*-ethyl-*N*-phenylcarbamoyl azide,[19] mp 133–134 °C (lit.[19] mp 134 °C).

X-ray Crystallographic Analysis. Data were collected on an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation, λ = 0.709267 Å) and programs were part of the ENRAF-NONIUS SDP as revised in 1977 and implemented on a PDP 11/34 computer. Crystals of **3g** were grown as large rhombic platelets (cut to 0.25 × 0.27 × 0.33 mm) by slow evaporation from heptanes.

***N*-1′-Adamantylbenzoazetinone (3g):** $C_{17}H_{19}NO$, M_r 253.35; triclinic, a = 10.594 (5) Å, b = 11.392 (4) Å, c = 6.555 (3) Å, α = 95.28 (4)°, β = 102.82 (3)°, γ = 116.43 (3)°, V = 673.9 (7) Å^3; d_0 = 1.2 g/cm^3, d_c = 1.248 g/cm^3 for Z = 2 molecules/unit cell, space group $P\bar{1}$ (no. 2). Of the 2011 reflections collected up to 2θ = 60°, 1072 had $I > 3\sigma(I)$ and were used for the subsequent structure analysis (data corrected for Lorentz and polarization factors but not for absorption). Starting positions for the benzoazetinone ring were obtained from MULTAN E-map synthesis. The subsequent structure analysis was complicated by the presence of two rotomers in the adamantyl unit (see supplementary material for methods used in treating this problem). Anisotropic refinement of all non-hydrogen atoms (H's fixed at B_{iso} = 3) then converged with R = 0.054 and R_w = 0.073 with an esd of 1.69. The final difference map was featureless with maxima and minima of ±0.27 e/Å^3. Tables of atomic positional parameters, bond distances and angles, thermal parameters, and a stereoview of the unit cell are available as supplementary material. Structure factors are given in the thesis of Hoskin.[30]

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Registry No. **1a**, 31767-66-5; **1b**, 91201-88-6; **1c**, 31767-67-6; **1d**, 91201-89-7; **1e**, 33032-36-9; **1f**, 31562-01-3; **1g**, 63609-49-4; **1h**, 91201-91-1; **1i**, 91201-93-3; **3c**, 91201-94-4; **3e**, 91201-95-5; **3f**, 31562-07-9; **3g**, 41225-84-7; **3h**, 91201-96-6; **3i**, 91201-97-7; **9**, 91201-98-8; **10a**, 61752-06-5; **10b**, 91202-00-5; **10c**, 91202-01-6; **10d**, 91202-02-7; **10e**, 17318-49-9; **10f**, 91202-03-8; **10g**, 91202-04-9; **11a**, 61752-04-3; **11b**, 41225-86-9; **11c**, 91202-05-0; **12**, 91202-06-1; **13**, 91202-07-2; **14a**, 31562-05-7; **14b**, 91202-08-3; **17a**, 31562-06-8; **17b**, 10045-45-1; MeOH, 67-56-1; EtOH, 64-17-5; Et_2NH, 109-89-7; $PhCO_2H$, 65-85-0; $PhCO_2Na$, 532-32-1; isopropyl alcohol, 67-63-0; *tert*-butyl alcohol, 75-65-0; pyrazole, 288-13-1.

Supplementary Material Available: A unit cell stereoview, tables of atomic positional and thermal parameters, and bond distances and angles for **3g**; also additional spectral and analytical data for new compounds (10 pages). Ordering information is given on any current masthead page.

(30) Hoskin, D. H., Ph.D. Dissertation, The Pennsylvania State University, 1981.