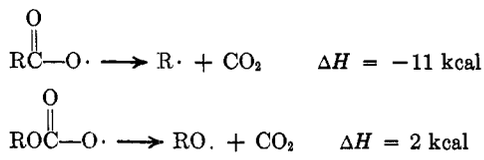
ergy data[21] leads to an exothermicity of 11 kcal/mol. A similar calculation indicates that decarboxylation of the alkoxycarboxyl radical is slightly endothermic.[22]



The calculation is based on heats of formation of the hypothetical ROC(O)OH by group additivity rules[23] and the assumption that the hydrogen–oxygen bond dissociation energy of ROC(O)O–H is 107 kcal/mol, identical with carboxylic acids. That the decarboxylation has a substantial energy of activation is suggested by the low CO_2 yield from decompositions in styrene and α-methylstyrene. If it is assumed, as an upper limit, that *ca.* 10% of the radicals decarboxylate at 110° in α-methylstyrene and that an energy of activation of *ca.* 5 kcal attends the alkoxycarboxyl addition,[24] then the decarboxylation reaction apparently has an activation energy of at least 20 kcal/mol. This is in contrast to the benzoyloxy radical, which was estimated[24] to decarboxylate with an activation energy of 14 kcal/mol. Calculation[23] of the thermochemistry of the decarboxylation of benzoyloxy indicates that it is also slightly endothermic by 1–3 kcal/mol. The decarboxylation of the acetoxy radical requires an estimated[25] 7.5-kcal/mol activation energy.

The high energy of activation associated with the decarboxylation of alkoxycarboxyl radicals and the reverse reaction may have interesting implications for other systems. For example, when di-*t*-butyl peroxyoxylate is decomposed in viscous solvents[26] at 45° and *t*-butoxy radicals are held in a solvent cage with carbon dioxide, addition of the *t*-butoxy to carbon dioxide (at the carbon atom) does not occur and the cage recombination product is di-*t*-butyl peroxide rather than di-*t*-butyl monopercarbonate. The percarbonate would be indefinitely stable at the 45° reaction temperature,[16] and should persist if formed.

Registry No.—I, R = *c*-C_6H_{11}, 1561-49-5; II, R = *t*-C_4H_9, R′ = *c*-C_6H_{11}, 21690-93-7.

(21) S. W. Benson, private communication. The heats of formation and bond dissociation energies necessary for the calculation are the same as listed in ref 18, with the exception that the O–H bond dissociation energy in CH_3COO–H has been revised to 107 kcal/mol.

(22) The author is indebted to Dr. D. M. Golden of Stanford Research Institute for this calculation.

(23) S. W. Benson, "Methods for the Estimation of Thermochemical Data," John Wiley & Sons, Inc., New York, N. Y., 1968, p 23.

(24) J. C. Bevington and J. Toole, *J. Polymer Sci.*, **28**, 413 (1958), choose 7 kcal as the activation energy for benzoyloxy addition to styrene. Their results also indicate a ratio of *A*'s of 10^4 for decarboxylation *vs.* addition to styrene for benzoyloxy radical. This ratio was used in the α-methylstyrene calculation above.

(25) J. C. Martin, private communication.

(26) R. Hiatt and T. G. Traylor, *J. Amer. Chem. Soc.*, **87**, 3766 (1965).

Acylketene Aminals

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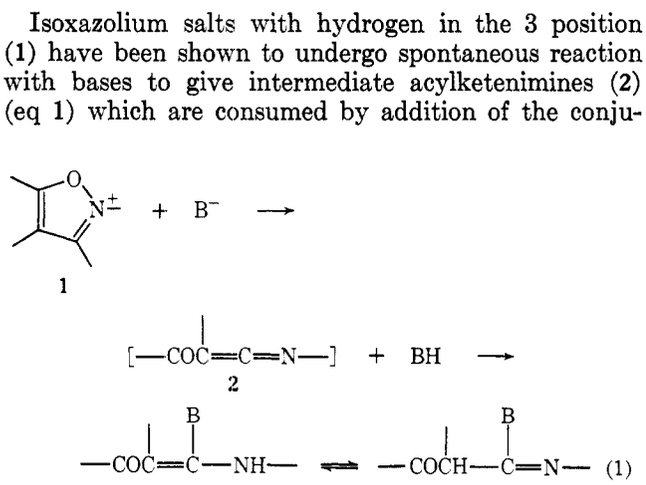
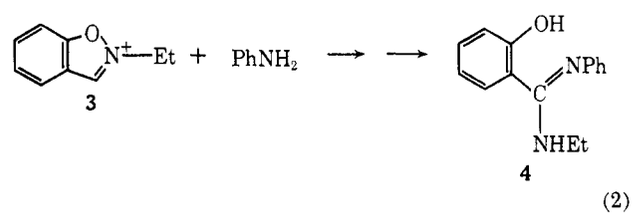
New 3-unsubstituted isoxazolium salts were prepared by SN1 alkylation, and an improved method was found to prepare 4-phenylisoxazole and achieve N-alkylation in one step. New stable acylketenimines were isolated from ring-opening of the isoxazolium salts, including the first stable acylketenimines without bulky, branched substituents on nitrogen. Primary and secondary amines were found to combine efficiently with acylketenimines to give acylketene aminals. The ketoketenimines from 4-methyl-5-phenylisoxazolium salts gave, instead, the tautomeric acylamidines.

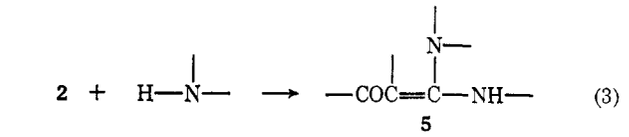
Isoxazolium salts with hydrogen in the 3 position (**1**) have been shown to undergo spontaneous reaction with bases to give intermediate acylketenimines (**2**) (eq 1) which are consumed by addition of the conjugate acid of the starting base.[2,3] The reaction with an amine, aniline, was reported in one case, with the N-ethylbenzisoxazolium cation (**3**) to give "a strongly basic substance," presumably the amidine **4** (eq 2).[3] In the present study it has been found that free primary and secondary amines themselves, in the absence of the conjugate acid ions, combine with acylketenimines in an efficient reaction to give acylketene aminals (**5**).



(1)



(2)



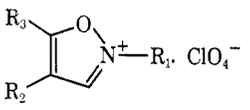
(3)

(1) National Science Foundation Graduate Trainee, 1966–1969.

(2) R. B. Woodward and R. A. Olofson, *J. Amer. Chem. Soc.*, **83**, 1007 (1961); *Tetrahedron Suppl.*, **7**, 415 (1966).

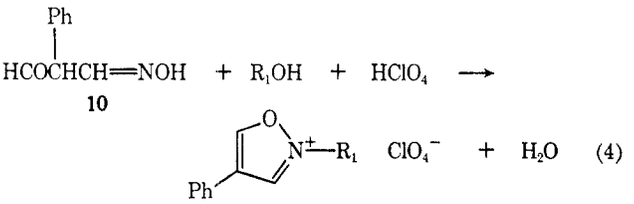
(3) D. S. Kemp and R. B. Woodward, *Tetrahedron*, **21**, 3019 (1965).

The new isoxazolium salts **6–9** used in the investigation were prepared by the recently developed method for SN1 alkylation of isoxazoles.[4] For **7–9** it was possible to achieve both cyclization and N-alkylation by



6, $R_1 = CMe_3$; $R_2 = Me$; $R_3 = Ph$
7, $R_1 = CMe_3$; $R_2 = Ph$; $R_3 = H$
8, $R_1 = CHMePh$; $R_2 = Ph$; $R_3 = H$
9, $R_1 = CHPh_2$; $R_2 = Ph$; $R_3 = H$

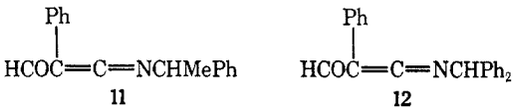
addition of a slight excess of 70% perchloric acid to a nitromethane solution of equivalent amounts of phenylmalonaldehyde monoxime (**10**) and the appropriate alcohol. Near quantitative yields of **7** and **9** were obtained directly by this one-step procedure (eq 4). The



(4)

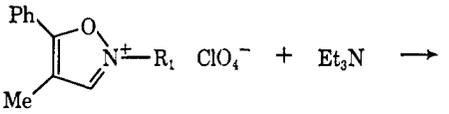
yield of **8** was 70%, despite the possibility of competing elimination with α-methylbenzyl alcohol.[4]

In order to examine the reaction of acylketenimines and amines in the absence of amine salts, it was necessary to use isoxazolium salts which would give intermediates **2** sufficiently stable to be isolated. It had previously been shown that the acylketenimines with bulky N-*t*-butyl substituents are relatively stable, isolable compounds.[5] Similarly, the N-α-methylbenzyl-substituted compound **11**, from **8**, was found to possess enhanced stability. However, the size of the group on the acylketenimine nitrogen is not the sole factor influencing stability since **12**, from **9**, which has a large N-benzhydryl substituent, decomposed completely on attempted isolation. In addition a group

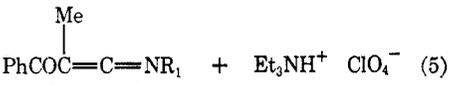


11 **12**

on the cumulene carbon also can have an important effect on acylketenimine stability, as shown by the isolation of **13** and **14** from the salts **15** and **16**, respectively (eq 5). The compounds **13** and **14** are the first



15, $R_1 = CH_2Ph$
16, $R_1 = Ph$



(5)

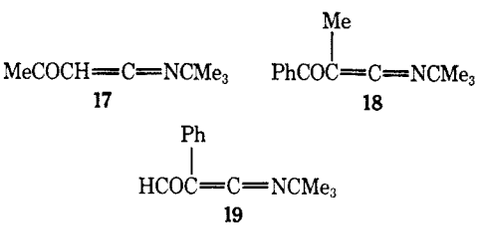
13, $R_1 = CH_2Ph$
14, $R_1 = Ph$

examples of stable acylketenimines which do not have bulky, branched substituents on nitrogen.[6]

The preparation and isolation of the acylketenimines was accomplished by treating dichloromethane solutions of the isoxazolium salts with triethylamine. The reaction mixtures were concentrated by evaporation and added to a large volume of carbon tetrachloride from which the insoluble triethylammonium perchlorate precipitated. Filtration and evaporation of the solutions gave the acylketenimines that were sufficiently pure for nmr spectral studies. The ketenimines were identified by their characteristic infrared absorption bands at 4.9 (C=C=N) and 5.9–6.1 μ (C=O), and their nmr spectra.

The new acylketenimines **11**, **13**, and **19** are yellow oils which are stable with respect to decomposition below 0°, but darken on standing at room temperature. The yellow crystalline **14** possesses similar stability; however, **14** was observed to form a red tar at 25° which was insoluble in carbon tetrachloride. The colorless oil **18** was found to be stable indefinitely at room temperature. The compounds **11**, **13**, **14**, and **18** show no change in their infrared and nmr spectra after prolonged storage at low temperature, with occasional warming to 25° for removal of samples.

The reactions of the acylketenimines **11**, **13**, **14**, and **17–19** with amines in carbon tetrachloride, deuteriochloroform, or dimethylformamide solution were monitored by nmr spectroscopy. In most cases consumption of the acylketenimine was complete at ambient temperature within an hour after addition of an equivalent of a primary or secondary aliphatic amine in the 0.5–1.0 *M* concentration range. Uniformly slower reactions were observed with the less nucleophilic aromatic amine aniline. The product spectra from the additions of amines to **11**, **17**, and **19** were in accord with the acylketene aminal structure **5**. The product mixture from **17** and aniline appeared to contain both possible geometrical isomers of **5**, but the spectra of the products from the reactions of **11** with *t*-butylamine and of **19** with benzylamine, α-methylbenzylamine, diethylamine, and aniline were all consistent with a single product isomer.[7]

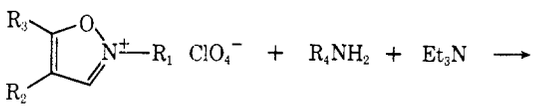


17 **18** **19**

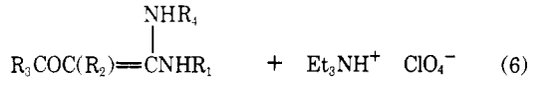
To confirm the product structures several preparative reactions were carried out directly with isoxazolium salts and amines. 3-Anilino-3-*t*-butylaminoacrylophe-

(4) D. J. Woodman, *J. Org. Chem.*, **33**, 2397 (1968).
(5) R. B. Woodward and D. J. Woodman, *J. Amer. Chem. Soc.*, **88**, 3170 (1966).
(6) A kinetic investigation of substituent effects on the reactivity of acylketenimines is in progress.
(7) In most of these cases it is possible that the two acylketene aminal isomers would have nearly superimposable nmr spectra. Only with **19** and aniline can it be concluded that the product actually is a single isomer, since the four possible NH signals should be well separated as with **17** and aniline.

none (**20**) was obtained both from **21** and aniline and from **22** and *t*-butylamine (eq 6). The nmr spectrum



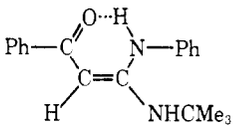
21, $R_1 = CMe_3$; $R_2 = H$; $R_3 = Ph$
22, $R_1 = Ph$; $R_2 = H$; $R_3 = Ph$
25, $R_1 = CMe_3$; $R_2 = H$; $R_3 = Me$



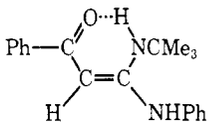
(6)

20, $R_1 = CMe_3$; $R_2 = H$; $R_3 = Ph$; $R_4 = Ph$
23, $R_1 = CMe_3$; $R_2 = H$; $R_3 = Me$; $R_4 = Ph$
24, $R_1 = Ph$; $R_2 = H$; $R_3 = Ph$; $R_4 = H$
26, $R_1 = CMe_3$; $R_2 = Ph$; $R_3 = H$; $R_4 = CH_2Ph$

of the isolated product contained a pair of broad low-field signals corresponding to intramolecularly hydrogen-bonded NH groups, two olefinic CH signals, and two broad NH signals at higher field. Assigning the lower field signal of each pair of NH peaks to the –NHPh groups, integration indicated a mixture of 75% isomer **20a** and 25% isomer **20b**. Similarly, the



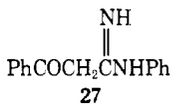
20a



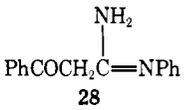
20b

spectra of **23** and **24** from **25** and aniline, and **22** and ammonia, respectively, each showed the presence of two aminal isomers. However, only a single isomer was detected in the spectrum of **26**, isolated from the reaction of **7** and benzylamine.[6]

The compound **24** has been reported previously, but the structure was not formulated correctly. Krishnamurti[8] and Veer[9] both obtained **24** from condensation of aniline with benzoylacetonitrile and considered acylamidine structures. However, neither amidine **27** or **28** would be consistent with the observed nmr spectrum of **24**.



27



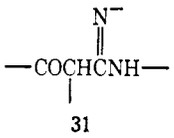
28

Acylamidines, rather than acylketene aminals, are obtained in the reactions of amines with the acylketenimines from the 4,5-disubstituted isoxazolium salts **6**, **15**, and **16**. Tests of the addition of aniline and benzylamine to **13**, **14**, and **18**, *t*-butylamine to **13** and **14**, and β-phenylethylamine and methylamine to **13** all gave product spectra consistent with the acylamidine tautomers. Again structural assignments were confirmed for representative addition products isolated from preparative reactions of amines with isoxazolium salts. Reaction of **16** with *t*-butylamine and diethylamine gave **29** and **30**, respectively. In both cases the

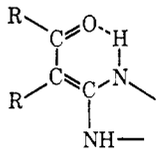
29 **30**

characteristic nmr quartet establishes the presence of hydrogen on the central carbon. The absence of the conjugated aminal system is further confirmed by the uv spectra, which lack the long wavelength absorption found beyond 300 mμ for **20**, **23**, **24**, and **26**.[10]

It is likely that the observed products are the most stable tautomers in each instance, the conjugated acylketene aminal system being the generally preferred form. This assumption is supported in the case of the aminal **20** by the finding that the proton on the central carbon is subject to exchange with deuterium oxide, presumably *via* the amidine **31**. The stability of **31** relative to **5** for the addition products from 4,5-disubstituted isoxazolium salts then may result from an unfavorable steric interaction between the substituents R and R′ in the most stable, hydrogen-bonded conformation (**32**) of **5**, which would be relieved by conversion to **31**.[12]

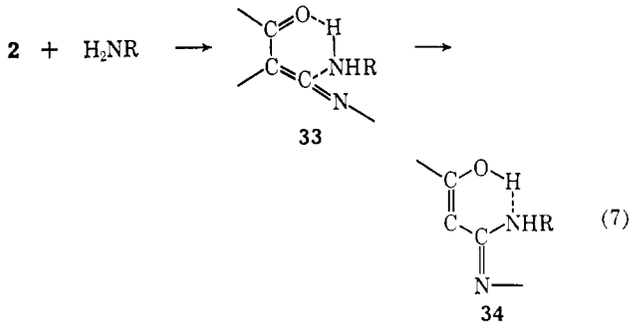


31



32

By analogy with the mechanism proposed[2] for the addition of carboxylic acids to acylketenimines, the formation of acylketene aminals may proceed through a transition state having the geometry **33** to give an intermediate **34** (eq 7). The conversion of **34** to the



(7)

33

34

aminal **5** must be rapid since no intermediate was detected in any of the reactions monitored by nmr spectroscopy which gave **5**. On the other hand, in three reactions which gave the tautomeric amidines, transient nmr signals attributable to intermediates could be seen. Presumably in these cases the observed intermediate is **5** which undergoes relatively slow conversion to the more stable amidine **31**, although the possibility that

(8) P. Krishnamurti, *J. Chem. Soc.*, 415 (1928).
(9) W. L. C. Veer, *Rec. Trav. Chim.*, **69**, 1118 (1950).
(10) The structure **29** is assumed, rather than the alternative amidine tautomer by analogy with other N-phenylamidines.[11]
(11) P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. I, W. A. Benjamin, Inc., New York, N. Y., 1965, p 178.
(12) A similar steric interaction has been proposed to account for the shift of the equilibrium between *trans* and intramolecularly hydrogen-bonded *cis* isomers of acylenamines.[13]
(13) G. O. Dudek and G. P. Volpp, *J. Amer. Chem. Soc.*, **85**, 2701 (1963).

34, rather than **5**, is observed cannot be ruled out on the basis of the nmr evidence.

Experimental Section[14]

2-*t*-Butyl-4-methyl-5-phenylisoxazolium Perchlorate (6).[15]—A mixture of 1.0 g (6.3 mmol) of 4-methyl-5-phenylisoxazole[17] and 0.47 g (6.4 mmol) of *t*-C_4H_9OH was stirred at 0° while 1.55 ml (18 mmol) of 70% $HClO_4$ was added at a slow drop rate. The reaction mixture solidified during the addition of the acid and was allowed to stand 22 hr. The solid material was stirred in 5 ml of water, filtered, washed with water, and dried, giving 1.85 g (93.5%) of white crystals. Precipitation of the product from MeCN with ether gave snow white crystals: mp ~ 178° (turns brown); uv max (CH_2Cl_2); 296 mμ (ε 21,000); nmr (DMSO-d_6) δ 1.79 (s, 9), 2.45 (s, 3), 7.67–8.15 (unresolved, 5), 9.89 (s, 1).

Anal. Calcd for $C_{14}H_{18}ClNO_5$: C, 53.25; H, 5.74; Cl, 11.23; N, 4.44; O, 25.33. Found: C, 53.29; H, 5.86; Cl, 11.13; N, 4.49; O, 25.17.

Phenylmalonaldehyde Monoxime (10).—A mixture of 5 g (28.6 mmol) of 3-dimethylamino-2-phenylacrolein[18] and 2 g (29 mmol) of hydroxylamine hydrochloride in 150 ml of HOAc was stirred for 24 hr, until solution of the hydrochloride salt was complete. The solution was evaporated to 20 ml and added to 100 ml of water. The mixture was cooled in ice and a brown precipitate, 3.8 g (81.5%), was filtered. Recrystallization of the product from CCl_4 gave tan crystals: mp 128–130°; uv max (95% EtOH) 240–270 mμ (ε ~200); nmr (Me_2CO) δ 4.2 (t, 1, J = 1.5 Hz), 5.6 (d, 1, J = 1.5 Hz), 7.0–7.55 (unresolved, 6).

Anal. Calcd for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.15; H, 5.48; N, 8.40.

2-*t*-Butyl-4-phenylisoxazolium Perchlorate (7).[15]—A solution of 0.9 g (5.5 mmol) of phenylmalonaldehyde monoxime (**10**) and 1.2 g (16 mmol) of *t*-C_4H_9OH in 10 ml of $MeNO_2$ was stirred while 1.4 ml (16.2 mmol) of 70% $HClO_4$ was added. The reaction mixture was allowed to stand overnight and was then added to 125 ml of anhydrous ether, giving 1.6 g (100%) of crystalline product. Precipitation from 30 ml of $MeNO_2$ with 125 ml of ether gave white crystals: dec above 130°; uv max (CH_2Cl_2) 235 mμ (ε 17,200); nmr (98% H_2SO_4, positions upfield relative to solvent) δ 2.02 (s, 1), 2.24 (s, 1), 3.65 (s, 5), 7.65 (s, 9).

Anal. Calcd for $C_{13}H_{16}ClNO_5$: C, 51.75; H, 5.35; Cl, 11.75; N, 4.64; O, 26.51. Found: C, 51.59; H, 5.45; Cl, 11.62; N, 4.64; O, 26.72.

2-(α-Methylbenzyl)-4-phenylisoxazolium Perchlorate (8).[15]—A solution of 1.0 g (6.14 mmol) of **10** and 0.76 (6.2 mmol) of *dl*,α-methylbenzyl alcohol in 20 ml of $MeNO_2$ was stirred while 0.6 ml (7 mmol) of 70% $HClO_4$ was added dropwise. The reaction mixture was allowed to stand overnight and poured into 125 ml of anhydrous ether giving 1.5 g (70%) of crystals. Precipitation of the product from 15 ml of MeCN with 100 ml of ether gave white crystals: mp 95–96°; uv max (CH_2Cl_2) 234 mμ (ε 19,000); nmr (98% H_2SO_4, positions upfield relative to solvent) δ 2.12 (s, 1), 2.27 (s, 1), 3.0–4.07 (unresolved, 10), 5.48 (q, 1, J = 7 Hz), 9.03 (d, 3, J = 3 Hz).

Anal. Calcd for $C_{17}H_{16}ClNO_5$: C, 58.38; H, 4.61; Cl, 10.14; N, 4.00. Found: C, 58.56; H, 4.72; Cl, 10.02; N, 4.11.

2-Benzhydryl-4-phenylisoxazolium Perchlorate (9).[15]—A solution of 0.4 g (2.5 mmol) of **10** and 0.5 g (2.7 mmol) of benzhydrol in 15 ml of $MeNO_2$ was stirred while 0.24 ml (2.8 mmol) of 70% $HClO_4$ was added slowly. The mixture was allowed to stand overnight and poured into 125 ml of anhydrous ether giving 1.0 g (99%) of white crystals: dec above 130°; uv max (CH_2Cl_2) 230 mμ (ε 14,800); nmr (MeCN) δ 7.4 (s, 1), 7.39–7.5 (unresolved, 15), 9.45 (s, 1), 9.52 (s, 1).

Anal. Calcd for $C_{22}H_{18}ClNO_5$: C, 64.17; H, 4.40; Cl, 8.61; N, 3.40; O, 19.43. Found: C, 64.10; H, 4.48; Cl, 8.65; N, 3.35; O, 19.55.

General Method for the Preparation and Isolation of α-Acylketenimines.—The appropriate isoxazolium salt was dissolved in a small volume of CH_2Cl_2 at 0° and an excess (*ca.* 10%) of Et_3N was added. The reaction mixture was allowed to stand 15 min and CCl_4 (five times the volume of CH_2Cl_2) was added. The solution was concentrated to 25 ml and filtered to remove the $Et_3NH^+ClO_4^-$ which had precipitated. The remainder of the solvent was evaporated giving the desired ketenimine, usually in quantitative yield.

N-(α-Methylbenzyl)formylphenylketenimine (11).—The ketenimine was prepared from the perchlorate **8** and isolated as a pale yellow oil: nmr ($CDCl_3$) δ 1.77 (d, 3, J = 7 Hz), 5.2 (q, 1, J = 7 Hz), 7.0–7.58 (unresolved, 10), 9.65 (s, 1). The nmr spectrum contained two additional signals, δ 8.53 and 8.64, probably due to 4-phenylisoxazole from competing attack by Et_3N on an α-methyl proton of the isoxazolium salt.

Spectral Test for the Formation of N-Benzhydrylformylphenylketenimine (12).—An attempt to isolate **12** as above gave a residue which did not have the expected simple nmr spectrum or any absorbance in the cumulene region of the ir spectrum. The following spectral test was carried out to confirm that **12** was actually formed but underwent rapid decomposition.

To 1 ml of a 0.1 *M* solution of the isoxazolium salt **9** was added three drops of Et_3N. The ir spectrum of the solution showed strong bands at 4.9 (C=C=N) and 6.08 μ (C=O). The band at 4.9 μ decreased from 10% transmittance to 70% transmittance within 30 min.

N-Benzylbenzoylmethylketenimine (13).—The ketenimine was prepared from 2-benzyl-4-methyl-5-phenylisoxazolium perchlorate (**15**)[19] and isolated as a pale yellow oil; nmr (CCl_4) δ 1.74 (s, 3), 4.52 (s, 2), 6.9–7.52 (m, 10).

N-Phenylbenzoylmethylketenimine (14).—The ketenimine was prepared from 2,5-diphenyl-4-methylisoxazolium perchlorate (**16**)[19] and isolated as yellow crystals; nmr (CCl_4) δ 1.97 (s, 3), 6.95–7.77 (unresolved, 10).

N-*t*-Butylacetylketenimine (17).—The ketenimine[5] was prepared from 2-*t*-butyl-5-methylisoxazolium perchlorate (**25**)[5] and isolated as a pale yellow oil.

N-*t*-Butylbenzoylmethylketenimine (18).—The ketenimine was prepared from the perchlorate **6** and isolated as a colorless oil; nmr (CCl_4) δ 1.1 (s, 9), 1.82 (s, 3), 7.25–7.7 (m, 5).

N-*t* Butylformylphenylketenimine (19).—The ketenimine was prepared from the isoxazolium salt **7** and isolated as a pale yellow oil; nmr (CCl_4) δ 1.47 (s, 9), 7.0–7.62 (m, 5), 9.55 (s, 1).

General Method of Monitoring the Addition of Amines to Acylketenimines by Nmr Spectroscopy.—A 0.5–1.0 *m* solution of an acylketenimine in the appropriate solvent was prepared, and 0.5 ml of the solution was placed in an nmr tube. An initial nmr spectrum was obtained and an area of the spectrum, usually an aliphatic methyl or *t*-butyl signal, was selected for monitoring during the amine addition reaction. One equivalent of the desired amine was added to the nmr tube from a microliter syringe and the resulting solution was mixed vigorously. The preselected area of the spectrum was scanned repeatedly and the change in the spectrum was recorded. The time intervals for the successive scans ranged from a few seconds to several hours, depending on the rate of reaction. A final product spectrum was obtained at the end of the reaction. Signal positions for spectra taken in DMF are reported in hertz upfield (+) or downfield (−) relative to the median position of the methyl signals of DMF.

Reaction of Ketenimine 11 with *t*-Butylamine.—The reaction of **11** with *t*-butylamine in $CDCl_3$ was complete by the time of the first monitoring scan, giving the product spectrum consistent with an acylketene aminal structure: δ 1.28 (d, J = 7 Hz, CH_3); 1.33 [s, $C(CH_3)_3$]; 4.27 (m, CH); 5.17 (broad, NH); 6.92–7.43 (unresolved, aromatic H); 8.78 (s, CHO); 10.6 (broad, hydrogen bonded NH).

Reaction of Ketenimine 13 with Aniline.—Addition of aniline to **13** in DMF gave slowly the spectrum of an acylamidine: +76 (d, J = 7 Hz, CH_3); −101 (s, CH_2); −103 (q, J = 7 Hz, CH); −250 to −300 Hz (unresolved, aromatic H).

(14) Melting points were determined with a Mel-Temp capillary apparatus and are uncorrected. The nmr spectra were run on a Varian A-60 spectrometer, and chemical shifts are reported in δ values relative to tetramethylsilane (δ, 0.00) as an internal standard. The uv spectra were recorded on a Cary 14 spectrophotometer and the ir spectra on a Perkin-Elmer 137 spectrophotometer with 0.2-mm cells. Elemental analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Bonn, West Germany.

(15) In view of the explosion hazard associated with the use of perchloric acid, preparations of isoxazolium salts were carried out behind a sturdy safety shield. Although no detonations were encountered in the present work, it should be noted that some isoxazolium perchlorates have been found to be impact-sensitive explosives.[16]

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Reaction of 13 with Benzylamine.—The reaction of **13** with benzylamine in CCl_4 was complete within 30 min giving an amidine product spectrum: δ 1.33 (d, J = 7 Hz, CH_3); 4.42 (broad, CH_2); 4.45 (q, J = 7 Hz, CH); 4.47 (s, CH_2); 6.97–7.75 (unresolved, aromatic H).

Reaction of 13 with *t*-Butylamine.—The initial spectrum of the reaction of **13** with *t*-butylamine in DMF showed two singlets of medium intensity at +87 and +93 Hz. The signal at +87 Hz, attributed to an intermediate *t*-butyl peak, disappeared within 20 min, while the signal at +93 Hz increased. During this change the formation of the product methyl doublet centered at +85 Hz was observed. The intermediate methyl signal corresponding to the *t*-butyl peak at +87 Hz was not seen in the spectrum, presumably due to its low intensity or masking by other peaks. The reaction was complete within 1 hr giving an amidine spectrum: +85 (d, J = 7 Hz, CH_3); +93 [s, $C(CH_3)_3$]; −106 (d, J = 3 Hz, CH_2) −113 (q, J = 7 Hz, CH); −250 to −300 Hz (unresolved, aromatic H).

Reaction of 13 with β-Phenylethylamine.—Addition of β-phenylethylamine in CCl_4 rapidly produced the spectrum of an amidine characterized by a methyl doublet at δ 1.22 (J = 7 Hz). The usual aromatic proton signals were observed while the methine proton quartet was buried in the low-field CH_2 signals.

Reaction of 13 with Methylamine.—The reaction of **13** with methylamine (40% in H_2O) in DMF immediately gave an amidine product spectrum: +63 (s, CH_3); +87 (d, J = 7 Hz, CH_3); −62 (broad, H_2O + NH); −110 (q, J = 7 Hz, CH); −256 to −290 Hz (unresolved, aromatic H).

Reaction of Ketenimine 14 with Aniline.—The reaction of aniline with **14** in DMF produced, after several hours, an amidine spectrum: +71 (d, J = 7 Hz, CH_3); −111 (q, J = 7 Hz, CH_3); −225 to −310 Hz (unresolved, aromatic H).

Reaction of 14 with Benzylamine.—The initial spectrum of the reaction of **14** with benzylamine showed no starting ketenimine methyl signal at +50 Hz. A singlet of medium intensity, attributed to an intermediate methyl, was observed at +59 Hz along with an amidine product methyl doublet centered at +77 Hz. Within 15 min the peak at +59 Hz was gone and the product spectrum was obtained: +77 (d, J = 7 Hz, CH_3); −100 (broad s, CH_2); −100 (q, J = 7 Hz, CH); −250 to −300 Hz (unresolved, aromatic H).

Reaction of 14 with *t*-Butylamine.—The addition of *t*-butylamine to **14** was monitored in DMF and the following evidence for an intermediate aminal was observed. The initial spectrum of the reaction mixture showed a decrease in the starting ketenimine methyl signal at +50 Hz, a peak of high intensity at +84 Hz (intermediate $C(CH_3)_3$), and peaks of low intensity at +78 Hz (intermediate CH_3 plus one-half the amidine product CH_3 doublet) and +84 Hz (amidine product $C(CH_3)_3$). As the reaction progressed the starting ketenimine methyl peak at +50 Hz disappeared completely. The intermediate *t*-butyl and methyl signals also disappeared within 15 min giving a final spectrum as observed for the isolated amidine **29**.

Reaction of Ketenimine 17 with Aniline.—The addition of aniline to **17** led to the formation of the spectrum of the isolated aminal **23** within 15 min.

Reaction of Ketenimine 18 with Benzylamine.—The reaction of **18** with benzylamine in DMF was extremely slow. Although the reaction was not followed to completion, the methyl doublet at +80 Hz, characteristic of an amidine structure, was observed after several hours.

Reaction of 18 with Aniline.—Addition of aniline to **18** was complete after 1.5 days giving the spectrum of the isolated amidine **29**.

Reaction of Ketenimine 19 with Aniline.—The reaction of **19** with aniline in $CDCl_3$ led to slow formation, during several hours, of an aminal spectrum: δ 1.37 [s, $C(CH_3)_3$]; 4.0 (broad, NH); 6.5–7.67 (unresolved, aromatic H); 8.98 (s, CHO); 10.1 (broad, hydrogen-bonded NH).

Reaction of 19 with Benzylamine.—Within 20 min the reaction of **19** with benzylamine in $CDCl_3$ gave the spectrum of the isolated aminal **26**.

Reaction of 19 with Diethylamine.—Addition of diethylamine to **19** in $CDCl_3$ immediately produced an aminal spectrum: δ 1.02 (t, J = 7 Hz, CH_3); 1.33 [s, $C(CH_3)_3$]; 3.18 (q, J = 7 Hz, CH_2); 5.77 (broad, NH); 7.1–7.43 (unresolved, aromatic H); 8.96 (s, CHO).

Reaction of 19 with *dl*,α-Methylbenzylamine.—Within 15 min the reaction of *dl*,α-methylbenzylamine with **19** in $CDCl_3$ produced the same acylketene aminal spectrum as obtained from the reaction of **11** with *t*-butylamine.

3-Anilino-3-*t*-butylaminoacrylophenone (20). Reaction of 2-*t*-Butyl-5-phenylisoxazolium Perchlorate (21) with Aniline and Triethylamine.—To a solution of 1.0 g (3.3 mmol) of **21**[20] in 25 ml of MeCN was added 0.33 g (3.3 mmol) of Et_3N followed by 0.31 g (3.3 mmol) of aniline. The reaction mixture was allowed to stand overnight and was then poured into 125 ml of water. The aqueous mixture was extracted four times with 75-ml portions of ether and the combined organic phases were dried (K_2CO_3). Evaporation of the solvent gave 0.89 g (92%) of crude product. Recrystallization from 95% EtOH gave cream colored crystals: mp 140–141°; uv max (95% EtOH) 237 (ε 14,000), 334 mμ (ε 21,800). The nmr spectrum ($CDCl_3$) was consistent with a mixture of 75% of the isomer **20a** with the anilino group hydrogen-bonded to the carbonyl [δ 1.37 (s, 9), 4.77 (broad, 1), 5.57 (s, 1), 13.33 (broad, 1)] and 25% of the isomer **20b** with the *t*-butylamino group *cis* to the carbonyl [δ 1.52 (s, 9), 5.35 (broad, 1), 6.35 (broad, 1), 11.8 (broad, 1)]. The unresolved aromatic protons for the mixture of isomers gave signals at δ 7.03–8.0.

Anal. Calcd for $C_{19}H_{22}N_2O$: C, 77.51; H, 7.53; N, 9.52; O, 5.44. Found: C, 77.52; H, 7.52; N, 9.39; O, 5.57.

3-Anilino-3-*t*-butylaminoacrylophenone (20). Reaction of 2,5-Diphenylisoxazolium Perchlorate (22) with *t*-Butylamine.—A solution of 4.0 g (12.4 mmol) of **22**[20] in 150 ml of MeCN was added at a slow drop rate to a stirred solution of 3.0 g (41 mmol) of *t*-butylamine in 200 ml of MeCN at 0°. The reaction mixture was allowed to stand overnight at room temperature, and the solvent was evaporated, giving 3.4 g (93%) of yellow crystals. Recrystallization of the product from 95% EtOH gave crystals identical with the product obtained from the reaction of aniline with **21**.

1-Anilino-1-*t*-butylamino-1-buten-3-one (23).—To a stirred solution of 3.0 g (12.5 mmol) of the perchlorate **25**[5] and 1.2 g (12.5 mmol) of aniline in 100 ml of MeCN was added 1.26 g (12.5 mmol) of Et_3N. The reaction was allowed to stand overnight, and the solvent was evaporated, giving a yellow oil. The oil was added to 75 ml of water, and the resulting slurry was extracted twice with 50-ml portions of ether. The combined organic phases were dried (K_2CO_3) and filtered, and the solvent was evaporated, giving 2.32 g (80%) of pale yellow crystals. Several recrystallizations of the product from EtOH–water (4:1) gave white crystals: mp 118–119°; uv max (95% EtOH) 232 (ε 8750), 248 (shoulder), 302 mμ (ε 20,600). The nmr spectrum ($CDCl_3$) was consistent with a mixture of 68% of the isomer with the anilino group *cis* to the carbonyl [δ 1.82 (s, 9), 2.03 (s, 3), 4.58 (broad, 1), 4.87 (s, 1), 12.87 (broad, 1)] and 32% of the isomer with the *t*-butylamino group *trans* to the carbonyl [δ 1.48 (s, 9), 1.85 (s, 3), 4.87 (s, 1), 6.25 (broad, 1), 11.33 (broad, 1)]. The unresolved aromatic protons had positions δ 6.92–7.57.

Anal. Calcd for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.69; N, 12.05; O, 6.88. Found: C, 72.58; H, 8.67; N, 11.90; O, 6.86.

3-Amino-3-anilinoacrylophenone (24). Reaction of 2,5-Diphenylisoxazolium Perchlorate (22) with Ammonia.—Anhydrous NH_3 was bubbled through a stirred solution of 3.0 g (9.35 mmol) of **22** in 200 ml of MeCN at 0° for 25 min. The reaction flask was then closed and allowed to stand at room temperature for 3 hr. The solvent was evaporated leaving a yellow solid, which was partitioned between 50 ml of water and 100 ml of ether. The aqueous layer was extracted with 50 ml of ether. The combined organic phases were dried (Na_2SO_4), filtered, and evaporated, giving 1.6 g (51%) of solid product. Recrystallization from $CHCl_3$ gave yellow crystals: mp 164–168° (lit. 163°,[8] 164°)[9]; uv max (95% EtOH) 237 (ε 11,500), 333 mμ (ε 24,000); nmr (DMSO-d_6) δ 5.58 (s, 1), 6.8–8.03 (unresolved, 12), 9.05 (broad, 0.7), 13.5 (broad, 0.3).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.62; H, 5.92; N, 11.75. Found: C, 75.52; H, 5.70; N, 11.65.

3-Benzylamino-3-*t*-butylamino-2-phenylacrolein (26).—To a solution of 1.0 g (3.3 mmol) of the perchlorate **7** in 40 ml of CH_2Cl_2 was added 0.34 g (3.4 mmol) of Et_3N. The mixture was stirred until the salt had dissolved, and 70 ml of CCl_4 was added. The solution was concentrated to 25 ml by evaporation and filtered to remove the triethylammonium perchlorate which had precipitated. The remainder of the solvent was evaporated, giving a pale yellow oil, 0.65 g (100%). The oil was dissolved in

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3 ml of CCl_4 and a solution of 0.35 g (3.3 mmol) of benzylamine in 2 ml of CCl_4 was added. After several minutes a yellow precipitate, 0.9 g (88%), was filtered. Recrystallization of the product from EtOAc gave white crystals: mp 145–147°; uv max (95% EtOH) 280 (shoulder), 314 mμ (ε 10,300); nmr ($CDCl_3$) δ 1.33 (s, 9), 3.82 (d, 2, J = 5 Hz), 4.97 (broad, 1), 7.05–7.4 (unresolved, 10), 8.8 (s, 1), 10.7 (broad, 1).

Anal. Calcd for $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.09. Found: C, 78.06; H, 7.99; N, 9.13.

N-*t*-Butyl-N′-phenyl-2-benzoylpropionamidine (29).—A solution of 1.0 g (3 mmol) of the salt **16**[19] in 100 ml of MeCN was added slowly to a stirred solution of 0.73 g (10 mmol) of *t*-butylamine in 150 ml of MeCN. The reaction was allowed to stand overnight, and the solvent was evaporated. The solid residue was partitioned between 50 ml of water and 75 ml of ether. The organic phase was dried ($MgSO_4$) and filtered, and the solvent was evaporated, giving 0.9 g (97%) of yellow solid. Recrystallization from 95% EtOH gave white crystals: mp 100–101°; uv max (95% EtOH) 242 mμ (ε 21,000); nmr ($CDCl_3$) δ 1.3 (s, 9), 1.42 (d, 3, J = 7 Hz, CH_3–), 4.52 (q, 1, J = 7 Hz, CH–), 4.63 (broad, 1), 6.7–7.84 (unresolved, 10).

Anal. Calcd $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.09; O, 5.19. Found: C, 77.75; H, 7.90; N, 9.15; O, 5.05.

N,N-Diethyl-N′-phenyl-2-benzoylpropionamidine (30).—A solution of 2.0 g (6 mmol) of **16** in 150 ml of MeCN was added to a solution of 0.88 g (12 mmol) of diethylamine in 100 ml of MeCN. The reaction mixture was allowed to stand overnight and the solvent was evaporated giving a solid residue. The solid was dissolved in 75 ml of ether and washed with 25 ml of 5% $NaHCO_3$. The aqueous phase was extracted with 25 ml of ether. The organic phase was dried (K_2CO_3) and filtered, and the solvent was evaporated, giving 1.8 g (99%) of solid. Recrystallization from 95% EtOH gave white crystals: mp 77–78°; uv max (95% EtOH) 245 mμ (ε 23,000); nmr (CCl_4) δ 0.87 (t, 6, J = 7 Hz, CH_3–), 1.45 (d, 3, J = 7 Hz, CH_3–), 3.12 (q, 4, J = 7 Hz, CH_2–), 4.15 (q, 1, J = 7 Hz, CH–), 6.5–7.7 (unresolved, 10).

Anal. Calcd for $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.09. Found: C, 77.75; H, 7.63; N, 9.19.

Registry No.—**6**, 21554-99-4; **7**, 21555-00-0; **8**, 21555-01-1; **9**, 21555-02-2; **10**, 21555-03-3; **11**, 21555-04-4; **13**, 21555-05-5; **14**, 21555-06-6; **18**, 21555-07-7; **19**, 21555-08-8; **20a**, 21543-43-1; **20b**, 21543-44-2; **23** (*cis*), 21543-45-3; **24**, 21555-09-9; **26**, 21555-10-2; **29**, 21620-41-7; **30**, 21555-11-3; **23** (*trans*), 21543-46-4.

The Oxidation of Amines with Peroxy Radicals. N-Phenyl-2-naphthylamine[1]

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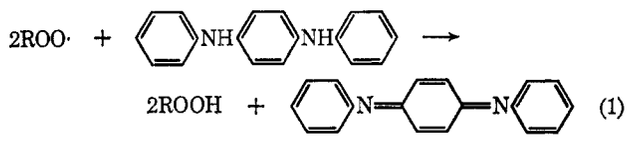
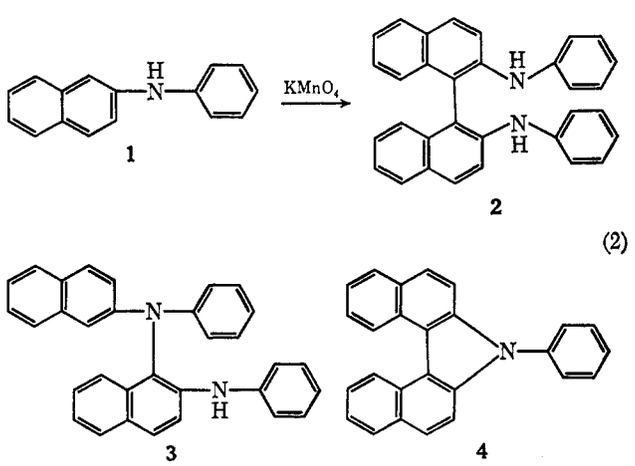
Six products have been identified in the oxidation of N-phenyl-2-naphthylamine by peroxy radicals. Three of the products, 1,1-bis(N-phenyl-2-naphthylamine) (**2**), N,N′-diphenyl-N-(2-naphthyl)-1,2-naphthylenediamine (**3**), and 7-phenyl-dibenzo[*c*,*g*]carbazole (**4**), are formed by the coupling of amino radicals. The remaining products, 2-anilino-1,4-naphthoquinone (**5**), 2-anilino-1,4-naphthoquinone-4-anil (**6**), and 4-(N-phenyl-2-naphthylamino)-1,2-naphthoquinone (**7**), are believed to be formed by the attack of various nucleophiles on 1,2-naphthoquinone-2-anil (**10**). This *o*-quinone imine was not identified among the products, but it is probably formed in the reaction of amino radicals with peroxy radicals.

Aromatic amines are widely used to inhibit the autoxidation of organic materials. Our own work on amine antioxidants has so far been entirely kinetic in nature.[4–7] However, a proper understanding of inhibition requires a knowledge of the products formed in the reactions of the antioxidants with peroxy radicals. Surprisingly little information on this subject is available for amines. Boozer, *et al.*,[8] have shown that N,N′-diphenyl-*p*-phenylenediamine reacts with peroxy radicals to give N,N′-diphenyl-*p*-quinone diimine in high yield (eq 1).



(1)

Bickel and Kooyman[9] have reported that N-phenyl-2-naphthylamine (**1**) reacts with peroxy radicals to give a small amount of a colorless substance, mp 167–167.5°, $C_{16}H_{13}NO$. The oxidation of **1** with potassium permanganate yields a mixture of 1,1′-bis(N-phenyl-2-naphthylamine) (**2**, 63%), N,N′-diphenyl-N-(2-naphthyl)-1,2-naphthylenediamine (**3**, 32%), and 7-phenyldibenzo[*c*,*g*]carbazole (**4**, 0.5%) (eq 2).[10]



(2)

A compound assumed to be **3** (but which is more probably **2**)[10] has been reported to be formed during the atmospheric aging of **1** containing rubber vulcanisates.[11,12] Since 1957, Thomas and coworkers have

(1) Issued as NRCC No. 11,031.
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