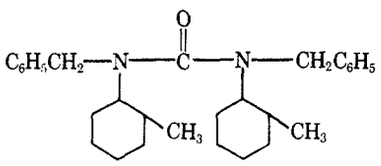
radicals have separate identities. There is a similar though somewhat smaller (~1 cps) splitting for the γ-methyl (a) and the methine (b) signals for the same reason. The isobutyl methylene protons (c) do not appear themselves to be nonequivalent despite their lack of a symmetry element. Still the fact that there is so much multiplicity in the spectrum for the phosphorus substituents suggests that the predominant amide isomer may have the *o*-methylphenyl group *cis* to the phosphoryl group in order to explain the influence of the anisotropic field of the ring over such a distance.

Substituted Urea XXVII.—At a temperature of 40° the spectrum of XXVII shows no multiplicity.



XXVII

However, at −40° (see Figure 1f) the *o*-methyl signal is very broad and the methylene signals apparently are split into two sets. One of these sets is a broad singlet, but the other is an AB pattern ($\langle\nu_a - \nu_b\rangle = 0.62$ ppm, $J_{AB} = 14$ cps). The AB pattern probably arises from slow rotation about the benzene–nitrogen bond, as with the other compounds cited in this report; however the existence of two *sets* of signals could arise either because of (1) *cis–trans*-amide isomerism or (2) the coexistence of epimers. At the moment from experience with other ureas,[8] alternative 2 seems more probable.

Geminal Protons Other Than >NCH₂.—Potentially all pairs of geminal protons in the types of amides described here are nonequivalent. However, in general nonequivalence is not observable for geminal protons α to the carbonyl group. This is true even for carbamylmethylenephosphonates, >POCH₂CON<, and also for the geminal protons of an *o*-ethyl group, although in the latter case the spectrum is skewed enough by the small chemical shift between α and β protons that a small degree of nonequivalence could be masked. For VIII and XVII the introduction of an ether linkage develops a small nonequivalence. Evidently, as a rule, the field gradient is small at these positions in the molecule, and/or internal molecular motions produce a good approximation of symmetry, but the disymmetry supplied by the ether linkage is enough to offset these effects.

Future Work.—Further investigations of molecular asymmetry that arises from slow rotation around the benzene–nitrogen bond are in progress in this laboratory. The pmr spectra are very complex for compounds that have two such centers of slow rotation in close proximity, as in oxalamides for example. This complexity presumably indicates extensive ramifications in the structure of these molecules, ramifications that we have not yet deduced from spectral interpretation. Multiple, unsymmetrical substitution in the benzene ring is also of interest, both for the spectra that are produced and for the effect on the rate of rotation of the benzene ring.

Formation and Alkylation of Di- and Trialkali Salts of 2,2′-Diphenyldiacetamide[1a,b]

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Mono- and dialkylations of 2,2′-diphenyldiacetamide were effected in liquid ammonia through its dilithio- and tripotassio salts, respectively; these salts were prepared by means of 2 and 3 molecular equiv of lithium amide and potassium amide, respectively. A metallic cation effect in the monoalkylation was observed. Further monoalkylation of one of the products was effected through its tripotassio salt.

Recently, certain imides[2,3] were converted to their dialkali salts by means of 2 molecular equiv of alkali amide in liquid ammonia, and the salts were alkylated with alkyl halides in this medium to form C-alkyl derivatives. For example, N-acetylbenzamide was converted to its dipotassio salt **1** which was benzylated to afford terminal derivative **2**.

$C_6H_5CONCOCH_2K$ (K) — **1**

$C_6H_5CONHCOCH_2CH_2C_6H_5$ — **2**

We have now similarly monoalkylated imide **3** at its benzyl group through its dilithio salt **4** to form **5a–c**, and, more significantly, have dialkylated **3** through its tripotassio salt **6** to give **7a–c**, (Scheme I). The results are summarized in Table I.

Structures **5a–c** were supported by analyses (Table I) and by spectral studies. The infrared spectra had bands at 2.9–3.2 and 5.75–6.1 μ for the N–H and imide carbonyl groups,[4] respectively. The nmr spectra (see Table II) were also consistent with the assigned structures. In each spectrum a singlet (two protons) characteristic of the benzyl methylene hydrogens was present, along with the expected absorption for the methinyl hydrogen attached to the carbon bearing the alkyl substituent.

(1) (a) Supported at Virginia Polytechnic Institute by the Petroleum Research Fund of the American Chemical Society, and at Duke University by the National Science Foundation. (b) Presented at the Southeast-Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec. 3, 1965. (c) To whom inquiries regarding this paper should be addressed at Virginia Polytechnic Institute.

(2) S. D. Work, D. R. Bryant, and C. R. Hauser, *J. Am. Chem. Soc.*, **86**, 872 (1964).

(3) D. R. Bryant and C. R. Hauser, *ibid.*, **83**, 3469 (1961).

(4) See L. J. Bellamy, "The Infrared Spectra of Complex Molecules." 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p 221.

TABLE I

MONO- AND DIALKYLATION PRODUCTS OF 2,2'-DIPHENYLDIACETAMIDE

Di- or trialkali salt	Alkyl halide	Mono- or dialkyl derivative	Mp, °C	Yield, %	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
4	$C_6H_5CH_2Cl$	2,3-Diphenyl-N-(phenylacetyl)-propionamide (**5a**)	157–158[a]	58	$C_{23}H_{21}NO_2$	80.44	6.16	4.08	80.28	6.36	4.08
4	CH_3I	N-(Phenylacetyl)hydratropamide (**5b**)	145.5–146.5[b]	36	$C_{17}H_{17}NO_2$	76.38	6.41	5.24	76.60	6.34	5.32
4	CH_3CH_2Br	2-Phenyl-N-(phenylacetyl)-butyramide (**5c**)	120–122[c,d]	63	$C_{18}H_{19}NO_2$	76.84	6.84	4.98	76.78	6.67	4.89
6	$C_6H_5CH_2Cl$	2,2',3,3'-Tetraphenyldipropionamide (**7a**)	150–151[e]	65	$C_{30}H_{27}NO_2$	83.15	6.24	3.24	83.06	6.17	3.29
6	CH_3CH_2Br	2,2'-Diphenyldibutyramide (**7b**)	110–114[f]	66	$C_{20}H_{23}NO_2$	77.64	7.49	4.53	77.41	7.44	4.46
6	n-C_4H_9Br	2,2'-Diphenyldihexanamide (**7c**)	114–117[b]	70	$C_{24}H_{31}NO_2$	78.86	8.55	3.83	79.08	8.79	3.80

[a] Recrystallized from isopropyl alcohol. [b] Recrystallized from 95% ethanol. [c] Recrystallized from absolute ethanol. [d] In one experiment another crystalline modification of **5c**, mp 107–109°, was isolated. [e] Recrystallized from absolute ethanol–hexane. [f] Recrystallized from aqueous ethanol.

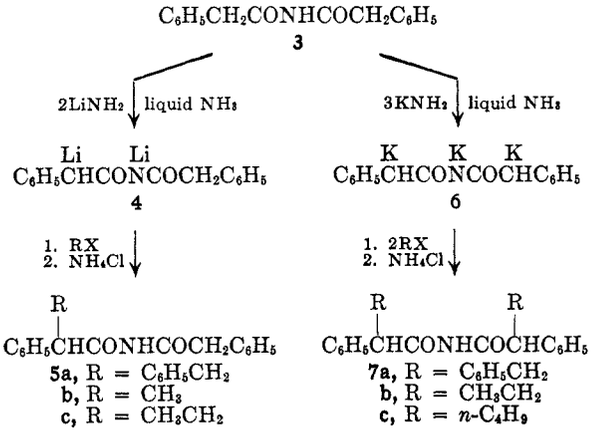
TABLE II

NMR DATA FOR MONO- AND DIALKYLATION PRODUCTS[a,b]

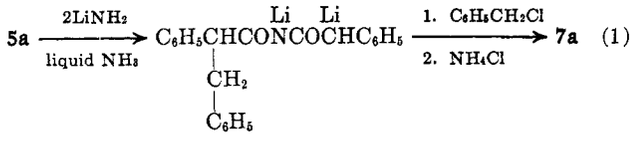
Compd	Types of hydrogen and chemical shifts, τ: NH	Phenyl	PhCHCO	$PhCH_2CO$	$PhCH_2$	$MeCH_2$	CH_3	$Me(CH_2)_3$
5a	0.80[c]	2.78[d]	5.76[e,f]	6.10[c]	6.80[g]	...	...	...
5b	1.00[c]	2.74[c]	6.05[d]	6.02[h]	...	...	8.58[h]	...
5c	0.70[c]	2.75[e]	6.30[d]	6.05[c]	...	8.10[d]	9.20[e]	...
7a	0.90[c]	2.90[d]	5.60[e,f]	...	6.87[g]	...	...	...
7b	1.00[c]	2.74[h]	6.00[e,f]	...	...	8.18[d]	9.18[i]	...
7c	1.00[e]	2.75[d]	5.90[e,f]	...	...	...	9.12[d,i]	8.30[d]

[a] The nmr spectra were obtained on a Varian Associates A-60 spectrometer using deuteriochloroform as the solvent and tetramethylsilane as internal standard. [b] Chemical shifts are measured to the center of a singlet or multiplet. In each spectrum the peak areas were consistent with the assignments given in the above table. [c] Singlet. [d] Multiplet. [e] Triplet. [f] Each peak of this triplet appeared with some fine splitting. [g] Octet. [h] Doublet. [i] Quartet. [j] This multiplet appeared as a major singlet with shoulders.

SCHEME I



The identity of **5a** was further supported by its conversion to **7a** by means of lithium amide (eq 1).



Structures **7a–c** were supported by analytical (Table I) and spectral data. The infrared spectrum of each imide had N–H absorption at 2.9–3.0 μ and carbonyl absorption in the 5.75–6.0-μ region. The nmr spectra presented in Table II were also consistent with the proposed structures. In all cases the benzyl methinyl protons and the adjacent α-methylene protons of the alkyl substituent give rise to absorption characteristic of an ABX system in which J_{AX} and J_{BX} are identical.[5] For example, the spectrum of **7a** had a triplet at τ 5.6 ascribable to two methinyl hydrogens, and an octet centered at 6.87 for four benzyl methylene hydrogens. The spectra of **7b** and **7c** had similar triplets for the methinyl hydrogens, but the α-methylene hydrogens of the alkyl substituents gave rise to multiplets more complex than the octet observed for **7a**.

That structures **7a–c** were correctly assigned was further substantiated by their hydrolysis to the related α-substituted phenylacetic acids **9a–c** (eq 2). The yields and physical constants for these acids are presented in Table III.

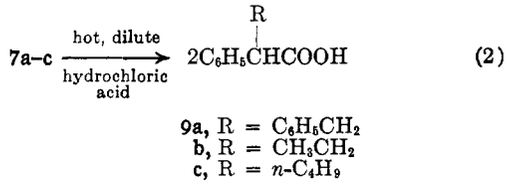


Table I shows that, with the exception of the monomethylation product **5b**, the mono- and dialkylation products **5a–c** and **7a–c** were obtained in good yields (58–70%). Apparently only one of the two possible diastereoisomers of **7a–c** was isolated in each case. Thus, not only were unsuccessful attempts made to isolate a second isomer by fractional crystallization of the crude products, but thin layer chromatograms of each of the crude products showed the presence of but one component.

(5) See L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry" Pergammon Press Inc., New York, N. Y., 1959, p 91.

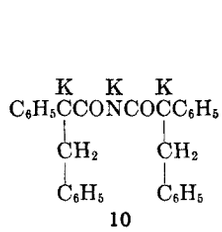
TABLE III
HYDROLYSIS OF DIALKYLATION PRODUCTS 7a–c TO FORM ACIDS 9a–c

Dialkylation product 7	Acid Form	Yield, %	Mp or bp (mm), °C	Lit. mp or bp (mm), °C
7a	9a	85	95–95.5[a]	95.5–96.5[b]
7b	9b	74	41–42[c]	41–42[d]
7c	9c	84	195–197 (27)	182–183 (20)[e]

[a] Recrystallized from hexane. [b] See C. R. Hauser and W. J. Chambers, *J. Am. Chem. Soc.*, **78**, 4942 (1956). [c] Recrystallized from ether. [d] See M. Rising, *ibid.*, **42**, 128 (1920). [e] See R. Dolique, *Ann. Chim.*, **15**, 425 (1931).

Although alkylation of dilithio salt **4** afforded the essentially pure monoalkyl derivatives, that of the corresponding disodio or dipotassio salt with benzyl chloride produced apparently a mixture of the mono- and dibenzyl derivatives, **5a** and **7a**, respectively. The pure monobenzyl derivative **5a** was isolated from the product of the disodio salt but the yield was only 20%, which is much lower than that (58%) obtained from the dilithio salt **4**.

Finally, 2,2′,3,3′-tetraphenyldipropionamide (**7a**) was converted to tripotassio salt **10** by means of potassium amide in liquid ammonia. Treatment of **10** with excess benzyl chloride afforded a single product, evidently **11**, in 75% yield.



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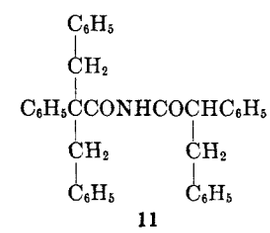
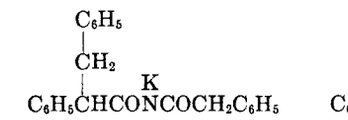


11

That the product was the monobenzyl derivative **11**, and not the possible dibenzyl derivative, was supported by elemental analysis and spectra. The nmr spectrum had a triplet at τ 5.14 characteristic of a single methinyl proton; this signal should have been absent from the spectrum if dibenzylation had occurred. In addition, there was absorption for 25 aromatic hydrogens centered at τ 3.0, and a multiplet centered at 6.85 for six benzyl methylene hydrogens. The N–H absorption appeared at τ 2.15. The infrared spectrum of **11** had the expected N–H band at 3.0 and carbonyl absorptions at 5.8 and 6.0 μ.

Discussion

The fact that the monobenzyl derivative **5a** was obtained satisfactorily with the dilithio salt **4** but not with the corresponding disodio or dipotassio salt illustrates the importance of the metallic cation in such alkylations. Recently,[6] a similar metallic cation effect was observed in alkylations of dialkaliacetylacetones, where the disodio salt, but not the dipotassio salt of the acetylacetone, was satisfactory for monoalkylation. Such effects appear ascribable to the relative ease of proton–metal exchange between the monoalkali salt of the alkylation product such as **12** and the original dialkali salt. The observation that, although the disodio salt of the acetylacetone is satisfactory whereas the dilithio salt of the dibenzyl imide **4** appears to be required, is not surprising since a methyl hydrogen is involved in the case of the β-diketone and a more acidic benzyl hydrogen in that of the imide. The dialkylations of tri-



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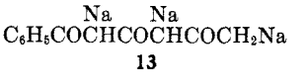

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potassio salt **6** (see Scheme I) are of particular interest, since they apparently represent the first examples of a dialkylation of a 1,3,5 trianion. Another trianion, that of trisodio salt **13**, has recently been alkylated, but only monoalkylation was observed; this occurred at the terminal position.[7]

Also the further monoalkylation of the dibenzyl derivative **7a** through its tripotassio salt **10** to form **11** is of interest since, in contrast to the dialkylation of tripotassio salt **6**, no dialkylation was observed. This appears to have been due to a steric factor.

Experimental Section[8]

2,2′-Diphenyldiacetamide (3).—A mixture of 68.1 g (0.50 mole) of phenylacetic acid and 58.5 g (0.50 mole) of phenylacetonitrile was heated at 170° for 20 hr under a nitrogen atmosphere. The reaction mixture was cooled to produce a light yellow solid which was collected by filtration, washed with ether, and recrystallized from 95% ethanol to give 45.1 g (36%) of **3**: mp 200–201° [lit.[9] mp 189–191°]; infrared absorption at 2.9 (NH), 5.85, and 6.1 μ (imide C=O).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 76.01; H, 5.98; N, 5.54. Found: C, 76.06; H, 6.00; N, 5.42.

Mono- and Dialkylation of 2,2′-Diphenyldiacetamide (3) (Scheme I).—In Table I are summarized the results obtained from mono- and dialkylations of **3** to form the C derivatives **5a–c** and **7a–c**, respectively. General procedures are described below.

A. Monoalkylations.—To a stirred suspension of 0.0474 mole of lithium amide in 300 ml of commercial, anhydrous liquid ammonia contained in a three-necked flask was added 6.00 g (0.0237 mole) of finely powdered **3**. After 45 min, the green-yellow suspension was assumed to contain 0.0237 mole of dilithio-2,2′-diphenyldiacetamide (**4**).

To a stirred suspension of dilithio salt **4** (0.02–0.0474 mole) was added 0.02–0.0474 mole of the appropriate halide in 75–100 ml of anhydrous ether. The resulting gray suspension was stirred for 1–1.25 hr and neutralized with excess solid ammonium chloride. The ammonia was evaporated (steam bath) as an equal volume of ether was added. A mixture of 20 ml of 12 *N* hydrochloric acid and 150 g of crushed ice was added to dissolve inorganic salts. The two layers were separated and the aqueous layer was extracted with three 100-ml portions of ether. The ethereal extracts and the original ethereal layer were combined, washed with 5% sodium bicarbonate solution, dried ($MgSO_4$), and concentrated. The residues were recrystallized from appropriate solvents. Analytical data and yields are presented in Table I.

Similarly the disodio and dipotassio salts of **3** were prepared by means of 2 molecular equiv of the corresponding alkali

(6) K. G. Hampton, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **30**, 61 (1965).

(7) K. G. Hampton, T. M. Harris, C. M. Harris, and C. R. Hauser, *ibid.*, **30**, 4263 (1965).

(8) Melting points were taken on a Thomas–Hoover melting point apparatus in open capillary tubes and are corrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Thomas D. Greenwood using an F & M Model 185 C, H, and N analyzer. Infrared spectra were taken on a Beckman IR-5 infrared spectrophotometer and a Perkin-Elmer Model 137 Infracord using potassium bromide pellets for solids and neat samples between sodium chloride plates for liquids. Thin layer chromatograms were carried out with an Eastman chromagram apparatus using Chromagram Sheets Type K301R (silica gel) with fluorescent indicator and benzene as the developing solvent. Spots were detected with ultraviolet light.

(9) See R. H. Wiley and W. B. Guerrant, *J. Am. Chem. Soc.*, **71**, 981 (1949).

amide in liquid ammonia and treated with benzyl chloride. The disodio salt afforded a white solid (mp 148–153°) which was recrystallized three times from isopropyl alcohol to give the monobenzyl derivative **5a** (mp 155–157°) in 20% yield. The dipotassio salt afforded a mixture (mp 118–126°) which failed to yield a pure product after repated recrystallizations.

B. Dialkylations.—To a stirred solution of 0.0474 mole of potassium amide in 300 ml of liquid ammonia was added 4.00 g (0.0158 mole) of finely powdered **3** to produce a clear, orange solution for about 2 min, and then a bright yellow suspension. After 30 min, the suspension was assumed to contain 0.0158 mole of tripotassio-2,2′-diphenyldiacetamide (**6**).

To a stirred suspension of tripotassio salt **6** (0.01–0.04 mole) was added 0.02–0.08 mole of the appropriate halide in 100–150 ml of anhydrous ether. The bright yellow color of **6** was discharged almost immediately. After 0.5–1.0 hr the reaction mixture was processed in the same manner as the monoalkylation reactions above. The crude products were recrystallized from appropriate solvents. Analytical data and yields are summarized in Table I.

Benzylation of 5a to form 7a.—A 3.43-g (0.01 mole) sample of finely divided **5a** was added to 0.02 mole of lithium amide in 300 ml of liquid ammonia. The resulting greenish yellow suspension was stirred for 45 min and a solution of 2.54 g (0.02 mole) of benzyl chloride in 20 ml of anhydrous ether was added. After 1 hr the reaction mixture was processed in the usual manner to give 2.12 g (49%) of **7a**, mp 142–145°, and 149–150° after several recrystallizations from absolute ethanol. A mixture melting point with a sample of **7a** prepared from tripotassio salt **6** (see above) was not depressed. The infrared spectra of the two samples were identical.

Hydrolysis of Dialkylation Products 7a–c.—A mixture consisting of a 1.00–2.00-g sample of each imide, 50–75 ml of 12 *N* hydrochloric acid, and 50 ml of water was refluxed for 12 hr. The solution was then extracted with ether. The ethereal solution was extracted with 5% sodium bicarbonate. The bicarbonate extracts were washed once with ether and acidified with 12 *N* hydrochloric acid. The crude acids were dissolved in ether. The ethereal solutions were dried and concentrated. The carboxylic acids were distilled or recrystallized from appropriate solvents. The results are summarized in Table III. The infrared spectra of acids **9a–c** were identical with those of authentic samples obtained from the hydrolysis of appropriate α-substituted phenylacetic esters.[10]

Benzylation of Tripotassio Salt 10.—A 2.0-g (0.0046 mole) sample of **7a** was added to 0.0138 mole of potassium amide in 300 ml of liquid ammonia. After 30 min, the reaction mixture presumably contained 0.0046 mole of bright yellow tripotassio salt **10**. A solution of 1.27 g (0.01 mole) of benzyl chloride in 30 ml of dry ether was added and stirring was continued for 1 hr during which time the yellow color was discharged. The reaction mixture was processed in the usual manner. The crude ethereal solution was dried and concentrated to afford 2.29 g of crude product, mp 140–150°. Two recrystallizations from isopropyl alcohol afforded 1.74 g (75%) of 2-benzyl-2,2′,3,3′-tetraphenyldipropionamide (**11**), mp 155–156°.

Anal. Calcd for $C_{37}H_{33}NO_2$: C, 84.86; H, 6.35; N, 2.68. Found: C, 85.16; H, 6.33; N, 2.90.

(10) See C. R. Hauser, W. G. Kenyon, and R. B. Meyer, *J. Org. Chem.*, **28**, 3108 (1963).

The Reaction of Ketenimines with Organic Peroxy Acids. An Inverse Passerini Reaction

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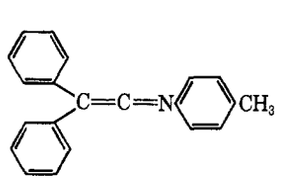
Model ketenimines have been found to react rapidly with organic peroxy acids with cleavage to ketone and isonitrile and concurrent formation of α-acyloxyamide. Data support the concept that products may arise *via* intramolecular collapse of a common intermediate, and possible mechanisms bearing on that for the Passerini reaction are discussed.

Diphenylketene-*p*-tolylimine (**1**) has been found to react with peroxybenzoic or peroxyacetic acid with the formation of benzophenone, *p*-tolylisonitrile, and N-(*p*-tolyl)-α-acyloxyamide (**2**). In a typical case, ad-



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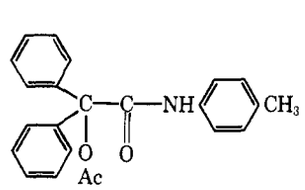

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mixture of chloroform solutions of diphenylketene-*p*-tolylimine and peroxybenzoic acid produced immediate reaction, as evidenced by the penetrating, characteristic odor of isonitrile and the prompt disappearance of the yellow ketenimine. Benzophenone, characterized as its 2,4-dinitrophenylhydrazone, could be isolated in 20–24% yield from the reaction mixture after several hours. N-(*p*-Tolyl)-α-benzoxydiphenylacetamide could be obtained as a crystalline precipitate in yields of 10–20%. *p*-Tolylisonitrile was identified as *p*-acetamidotoluene, by treatment of the residual reaction mixture successively with hydrochloric acid and acetic anhydride, or it could be isolated directly as its derivative di-*p*-tolylformamidine. The use of carefully purified, resublimed peroxybenzoic acid did not affect the outcome of the reaction. However, addition of a fourfold molar excess of benzoic acid to the initial reactants increased the yield of α-benzoxyamide, a trend which was reversed when the excess of benzoic acid was again doubled. An entirely analogous reaction occurred with peroxyacetic acid, producing ketone, isonitrile, and α-acetoxyamide in similar yields.

Ketenimines possess a distinctive absorption in the infrared at close to 5 μ. In the reaction of diphenylketene-*p*-tolylimine with peroxybenzoic acid at ice-bath temperatures, the disappearance of this band[4] as a function of time showed 84% reaction within 4 hr. Conversely, in the reaction of ketenimine with benzoic acid[5] under the same conditions a consumption

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(2) To whom requests for reprints should be sent.

(3) Portions of this work were done at Wayne State University, Detroit, Mich., the Detroit Institute of Technology, and the University of Miami.

(4) A linear relationship between appropriate concentrations of ketenimine and intensity for the 5-μ band was shown to exist.

(5) C. L. Stevens and M. E. Munk, *J. Am. Chem. Soc.*, **80**, 4065 (1958).