

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 mono-benzyl 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 repeated 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 C₂₇H₂₃N₃O₃: 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

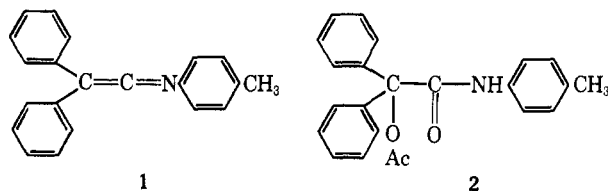
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Received May 18, 1966

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-



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 -benzoxydiphenyl-

acetamide 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 band⁴ as a function of time showed 84% reaction within 4 hr. Conversely, in the reaction of ketenimine with benzoic acid⁵ under the same conditions a consumption

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(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).

of only 19% in 22 hr was found. In the former case, the rapid formation of isonitrile, ketone, and acyloxyamide was apparent from, respectively, the formation of bands at $4.7 \mu^6$ and multiple bands in the region of 6μ , concurrent with the disappearance of the $5\text{-}\mu$ band. Plots of time *vs.* the reciprocal of intensity of the latter band provided good straight-line relationships, indicating first-order consumption of ketenimine. Consumption of peroxybenzoic acid in this reaction was followed iodimetrically⁷ under the same conditions, and good linear plots of time *vs.* the reciprocal of concentration were obtained. Thus first-order reaction of peroxy acid is likewise indicated.

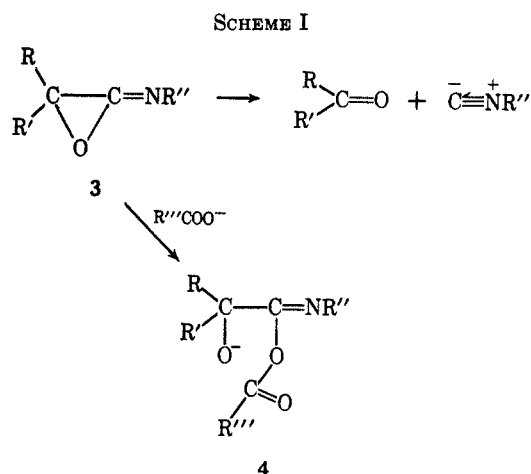
If the reaction of peroxyacetic acid and ketenimine were carried out in solvent ether rather than chloroform, *N*-(*p*-tolyl)diphenylacetamide (75% yield) was obtained as the only amide. Since ether is known to sharply retard the rate of olefinic epoxidation by organic peroxy acids,^{8,9} it is reasonable to assume that this amide arises from the competing, known reaction of acetic acid, present in the reaction mixture, with ketenimine.⁵ When the reaction between ketenimine and peroxybenzoic acid in chloroform was conducted with the addition of a few drops of pyridine, again only *N*-(*p*-tolyl)diphenylacetamide was isolated (28% yield). Both pyridine and ether probably function to depress the activity of peroxybenzoic acid by acting as proton acceptors,¹⁰ making the competitive but slower reaction with carboxylic acid more important.

That the reaction of ketenimine with peroxy acid is much faster than the competing reaction of ketenimine with carboxylic acid is apparent from the preceding data. Substantiation for this observation is further found in the results of an experiment in which diphenylketene-*p*-tolylimine was treated with peroxybenzoic acid in the presence of a 30-fold molar excess of acetic acid. The only amide isolated was the α -acetoxyamide (32% yield); no unsubstituted amide was found. In other cases containing more nearly equal molar ratios of acetic and peroxybenzoic, or benzoic and peroxyacetic, mixtures of both possible α -acyloxyamides were obtained. Since it has been shown that peroxy acid-carboxy acid equilibration proceeds at a negligible or very slow rate,^{11,12} it may be concluded that these results represent interception of a reactive intermediate by the external carboxylic acid reagents. A similar experiment with ketenimine and peroxy acid using solvent methanol as the external reagent produced a mixture of *N*-(*p*-tolyl)- α -methoxydiphenylacetamide and *N*-(*p*-tolyl)diphenylacetamide, each in less than 10% yield. Here the basicity of the solvent depressed the initial activity of the peroxy acid as in other cases.

Inasmuch as ketone and isonitrile are produced in the reaction of ketenimine with peroxy acid, it might at first be conjecture that these products could react

with available carboxylic acid in a Passerini reaction¹³ to form the α -acyloxyamide observed. However, it has been reported¹⁴ that the Passerini reaction fails for the case of aryl ketones and aryl isonitriles.

Epoxidation of the C-C double bond of the ketenimine can lead to an epoxyimine which would be expected to be quite reactive and unstable. This transitory intermediate (3) could decompose, perhaps reversibly, to isonitrile and carbonyl compound or react with carboxylic acid (or its conjugate anion) or other external nucleophile *via* a preliminary attack at C_β ¹⁵ to form intermediate 4 (Scheme I). This in turn could yield α -acyloxyamide by subsequent O-O acyl migration. Direct nucleophilic attack at C_α of 3 to form product is a possible alternative.



It is perhaps noteworthy that such an epoxide is a valence-bond tautomer of the intermediate originally proposed¹⁶ for the first step of the Passerini reaction as a consequence of carbonyl/isonitrile equilibration. Later objection to this mechanism has been made¹⁷ on the basis that this zwitterion $\left(\begin{array}{c} R \\ | \\ R' > C - C \equiv N^+R'' \\ | \\ O^- \end{array} \right)$

would be "unstable" and would not be favored in nonpolar solvents, whereas increases in rate and yields are noted for the Passerini reaction in going from polar to nonpolar solvents. However, formation of neutral intermediate 3 is expected to be favored by decreasingly polar solvents; this may provide a driving force for isonitrile/carbonyl reaction in such solvents. This consideration might vitiate Ugi's objection to the Baker and Stanonis mechanism. Other Passerini-type reactions, *e.g.*, the formation of α -hydroxytetrazoles from isonitriles, carbonyl compounds, and hydrazoic acid,¹⁸ and the reaction of isonitriles, carbonyl compounds, and aqueous mineral acids to form α -hydroxyamides,¹⁹ may be readily accommodated by Scheme I. An epoxyimine intermediate is also very likely involved in the conversion of β -benzoin oxime

(6) I. Ugi and R. Meyer, *Chem. Ber.*, **93**, 239 (1960).

(7) D. Swern, *Org. Reactions*, **7**, 378 (1953).

(8) P. Renalen and J. Ugelstad, *J. Chim. Phys.*, **57**, 634 (1960).

(9) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1965).

(10) Such proton acceptance might well function to retard the formation of the internal zwitterion which has been implicated as the reactive species in peroxy acid attack on double bonds; see H. Kwart and D. M. Hoffman, *J. Org. Chem.*, **31**, 419 (1966).

(11) D. R. Campbell, J. O. Edwards, J. MacLochlen, and K. Polgar, *J. Am. Chem. Soc.*, **80**, 5308 (1958).

(12) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *ibid.*, **80**, 6393 (1958).

(13) M. Passerini, *Gazz. Chim. Ital.*, **51**, 126 (1921).

(14) R. H. Baker and L. E. Linn, *J. Am. Chem. Soc.*, **70**, 3721 (1948).

(15) Tantamount to nucleophilic attack on the carbonyl of an α -lactone.

(16) R. H. Baker and D. Stanonis, *J. Am. Chem. Soc.*, **73**, 699 (1951).

(17) I. Ugi, *Angew. Chem. Intern. Ed Engl.*, **1**, 8 (1962), and preceding papers.

(18) I. Ugi and R. Meyer, *Chem. Ber.*, **41**, 2229 (1961).

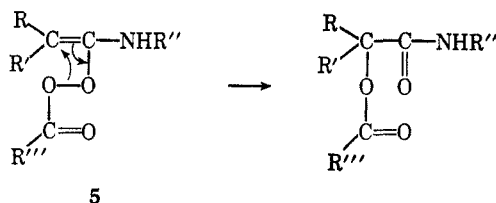
(19) I. Hagedorn and U. Eholzer, *ibid.*, **98**, 936 (1965).

to benzaldehyde and phenylisocyanide by benzenesulfonyl chloride and base.^{16,20,21}

It would thus appear that the present results lead naturally to the concept of a dynamic epoxyimine-isocyanide/carbonyl equilibrium which may be pivotal in a series of reactions whose mechanistic course has been unclear and controversial.

There is no essential conflict in the suggestion that, while benzophenone, *p*-tolylisocyanide, and benzoic acid will not undergo the Passerini reaction, an intermediate which would have to form were that reaction to proceed is indeed responsible for the formation of products in the present instance. Sluggishly reacting ketone may in the first case cause reaction with isocyanide at a negligibly slow rate. On the other hand, epoxide formed in the peroxidation reaction may be caged with carboxylate ion formed from reacting peroxy acid, or its conjugate acid may exist momentarily as an intimate ion pair with carboxylate ion, allowing attack of carboxylate ion to compete with decomposition.

A possible alternative to direct epoxidation of the ketenimine C-C double bond is addition of peroxy acid directly across the C-N double bond to form an intermediate **5** which may undergo a rearrangement *via* a four-center intramolecular collapse to α -acyloxyamide.



Prototropic addition across the double bond is a facile reaction,^{5,22} while an analogous four-center rearrangement has been postulated⁵ for the addition of carboxylic acids to ketenimines. Such a path provides a direct route to α -acyloxyamide, and may account for some product; intermediate **5** may also readily rearrange to epoxyimine. However, the observation that the rate of reaction between ketenimine and peroxy acid was markedly faster in chloroform than in ether, and that in the latter solvent a competitive reaction took place which *must* involve addition of acid across the C-N double bond, only emphasizes the difference between the nature of the two reactions.

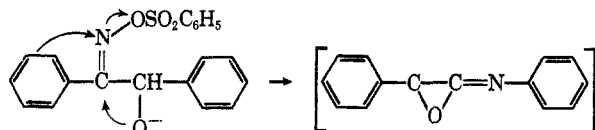
In our opinion, the foregoing arguments lend substantial credence to the plausibility of a common epoxyimine intermediate in the Passerini and the ketenimine-peroxy acid reactions.

Experimental Section

Rate Measurements.—Solutions of diphenylketene-*p*-tolylimine and resublimed peroxybenzoic acid in chloroform were prepared so as to give concentrations of 10^{-2} molarity of each compound upon admixture; a slight excess ($1-8 \times 10^{-3}$ mole) of

(20) A. Werner and T. Detschew, *ibid.*, **38**, 69 (1905).

(21) Formation of oxime benzenesulfonate anion, followed by



(22) I. Lillien, *J. Org. Chem.*, **29**, 1631 (1964).

peroxy acid was used. The solutions were chilled and admixed at ice-bath temperatures. Aliquots were withdrawn at 30-min intervals, placed in chilled infrared liquid microcells, and scanned rapidly from 4 to 7 μ . Plots of the reciprocal of the intensity of the 5- μ -ketenimine band *vs.* time were linear for three runs. These were followed to approximately 85% completion (4 hr). In a separate experiment, the intensities of the 5- μ band for a series of ketenimine solutions of concentrations apropos to the reaction range were recorded and found to be directly proportional to concentration. In a parallel series of runs, consumption of peroxybenzoic acid was determined iodimetrically.⁷ Similar solutions of ketenimine and peroxy acid were prepared and admixed, and aliquots were withdrawn at 30-min intervals and quenched in aqueous potassium iodide-acetic acid. Released iodine was titrated with sodium thiosulfate to a starch end point. Plots of the reciprocal of the concentration of peroxy acid *vs.* time were linear for eight runs. Six of these were followed to almost 90% completion. Added benzoic acid had the effect of depressing the rate of reaction.

Reaction of Diphenylketene-*p*-tolylimine and Peroxybenzoic Acid.—To a solution of 1.4 g (5 mmoles) of diphenylketene-*p*-tolylimine in 35 ml of chloroform at room temperature was added a solution of 1.0 g (7 mmoles) of recrystallized, resublimed peroxybenzoic acid^{7,23} in 10 ml of chloroform. The penetrating, characteristic isocyanide odor was immediately evident, and the yellow ketenimine began to fade rapidly. After 4 hr, the solution was extracted with aqueous sodium bicarbonate, washed with water, dried over sodium sulfate, concentrated to approximately 10 ml, diluted with an equal volume of petroleum ether (bp 30–60°), and allowed to stand in the refrigerator overnight. The crystalline precipitate was filtered: yield 0.42 g (20%) of *N*-(*p*-tolyl)- α -benzoxydiphenylacetamide, mp 160–162°.²⁴ Recrystallization from ethanol raised the melting point to 163–164°, mixture melting point with authentic material (see below) was undepressed, and the infrared spectra were superimposable.

Anal. Calcd for $C_{28}H_{23}NO_3$: C, 79.89; H, 5.49. Found: C, 80.01; H, 5.36.

Addition of 0.01 mole (1.2 g) of benzoic acid to the chloroform solution of peroxybenzoic acid prior to the reaction increased the yield of acyloxyamide to 28.4%. However, doubling the added benzoic acid to 0.02 mole decreased the yield once more to 20.8%.

The solution remaining after the removal of the amide was concentrated *in vacuo*, and the residual oil was poured onto an alumina column (Brockman No. 4). Elution of the column with hexane produced 0.21 g (23.6%) of benzophenone, identified as its 2,4-dinitrophenylphdrazone. Elution of material remaining on the column with chloroform-ether (1:1) produced an oil on evaporation, which after trituration with ether-hexane at Dry-Ice bath temperature deposited 80 mg of crystals. These had at melting point of 141–142° after two crystallizations from benzene-acetone and did not depress the melting point of authentic di-*p*-tolylformamidine.²⁵ Furthermore, their infrared spectra were superimposable.

Alternatively, the oily reaction mixture (after removal of the amide and solvent) was either directly treated with 2,4-dinitrophenylhydrazine reagent to form benzophenone-DNP or treated in succession with 2 *N* hydrochloric acid for 24 hr, then sodium carbonate to alkalinity. The solution was extracted with ether, the ether was evaporated, and the residual tar was dissolved in pyridine and treated with acetic anhydride to yield *p*-acetamidotoluene. A mixture melting point with authentic material showed no depression. Repeated attempts to trap *p*-tolylisocyanide as its 2,4-dinitrosulfonyl derivative²⁶ failed.

The reaction of ketenimine (0.50 g, 1.76 mmoles) and peroxy acid (0.75 g, 5.0 mmoles) was carried out as above with the prior addition of 20 drops of pyridine to the ketenimine solution. The only amide isolated was *N*-(*p*-tolyl)diphenylacetamide²⁷ (0.15 g, 28%). Likewise, the addition of ketenimine to peroxy acid in glacial acetic acid as a solvent in place of chloroform gave only *N*-(*p*-tolyl)diphenylacetamide in 76% yield.

Reaction of Diphenylketene-*p*-tolylimine and Peroxybenzoic Acid in the Presence of Acetic Acid.—Under the same conditions

(23) Active oxygen titer was 92%. The dry, crystalline material was found to be quite stable to refrigerator storage for periods as long as several months.

(24) All melting points are uncorrected.

(25) A. Senier, *Ber.*, **18**, 2296 (1885).

(26) J. Havlils and M. M. Weld, *J. Am. Chem. Soc.*, **77**, 5172 (1955).

(27) C. L. Stevens and J. C. French, *ibid.*, **75**, 657 (1953).

outlined above, 0.50 g (1.76 mmoles) of diphenylketene-*p*-tolylimine in chloroform solution was treated with a chloroform solution of 0.84 g (5.6 mmoles) of peroxybenzoic acid and 10.5 g (0.175 mmole) of glacial acetic acid. *N*-(*p*-Tolyl)- α -acetoxydiphenylacetamide, 0.20 g (32%), had a melting point of 195–196° after two crystallizations from acetone-petroleum ether, the mixture melting point with authentic material (see below) was not depressed, and the infrared spectra were superimposable.

Anal. Calcd for $C_{23}H_{21}NO_3$: C, 76.86; H, 5.89. Found: C, 77.10; H, 6.12.

Reaction of Diphenylketene-*p*-tolylimine and Peroxyacetic Acid.—To 0.50 g (1.76 mmoles) of diphenylketene-*p*-tolylimine in 25 ml of chloroform was added 4 ml of commercial (Becco "40%") peroxyacetic acid, containing approximately 1.5 g (21 mmoles) of peroxy acid. The reaction mixture was treated in the same manner as in the reaction with peroxybenzoic acid, resulting in the isolation of a 24% yield of *N*-(*p*-tolyl)- α -acetoxydiphenylacetamide.

If the reaction were carried out in ether as a solvent in place of chloroform, *N*-(*p*-tolyl)diphenylacetamide (0.39 g, 74%) was the only amide isolated.

Chromatography of the residual oil remaining after removal of α -acetoxyamide and evaporation of the solvent, as above, again yielded benzophenone and di-*p*-tolylformamidine. An intermediate benzene eluate, however, also produced *N*-(*p*-tolyl)diphenylacetamide in 33% yield. This was presumably due to the action of the large amount of acetic acid contained in the Becco reagent.

***N*-(*p*-Tolyl)- α -benzoxydiphenylacetamide.**—To a solution of 3.3 g (0.01 mole) of *N*-(*p*-tolyl)- α -chlorodiphenylacetamide²⁷ and 2.4 g (0.02 mole) of benzoic acid in 50 ml of dry benzene was added 2.8 g (0.01 mole) of silver carbonate. The flask was protected from the light; the contents were vigorously stirred for 24 hr at room temperature. The benzene was filtered several times, extracted with dilute aqueous sodium carbonate, washed with water, dried over sodium sulfate, and concentrated to a

few milliliters. Addition of petroleum ether precipitated crystals of *N*-(*p*-tolyl)- α -benzoxydiphenylacetamide, 3.6 g (86%), mp 163–164°, after one crystallization from ethanol.

***N*-(*p*-Tolyl)- α -acetoxydiphenylacetamide.**—To a solution of 3.3 g (0.01 mole) of *N*-(*p*-tolyl)- α -chlorodiphenylacetamide in 50 ml of dry benzene was added 3.34 g (0.02 mole) of silver acetate. The flask was protected from the light; the contents were vigorously stirred for 24 hr at room temperature. The benzene was filtered several times, washed repeatedly with dilute ammonium hydroxide and water, and dried over sodium sulfate. Concentration and dilution with petroleum ether caused crystallization of *N*-(*p*-tolyl)- α -acetoxydiphenylacetamide, 3.2 g (90%), mp 195–196°, after one crystallization from ethanol.

Reaction of Diphenylketene-*p*-tolylimine and Peroxybenzoic Acid in Methanol.—To a solution of 0.5 g (1.76 mmoles) of diphenylketene-*p*-tolylimine in 50 ml of methanol was added 0.42 g (2.8 mmoles) of peroxybenzoic acid. The mixture was swirled until solution was complete and allowed to stand at room temperature for 24 hr. Methanol was removed under reduced pressure, and the residue was taken up in a minimum of chloroform. This was extracted with dilute sodium bicarbonate, washed with water, dried, diluted with petroleum ether, and chilled. Crystals were obtained which could be separated into two fractions on fractional crystallization from ethanol to yield *N*-(*p*-tolyl)- α -methoxydiphenylacetamide²² (55 mg, 9.5%) and *N*-(*p*-tolyl)diphenylacetamide (42 mg, 8.0%).

Acknowledgment.—The authors are indebted to the Chemistry Department of Wayne State University for facilities and materials used in a portion of this work. In particular, we are grateful to Professor Calvin L. Stevens of that department for the use of his resources and for the informative discussions relating to this project in which he was kind enough to engage with us.

Reactions of 2,2-Dicyano-3,3-bis(trifluoromethyl)oxirane with Thiocarbonyl Compounds¹

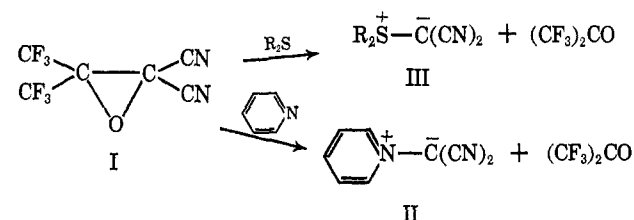
W. J. MIDDLETON

Contribution No. 1219 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware

Received June 8, 1966

2,2-Dicyano-3,3-bis(trifluoromethyl)oxirane reacts with thioureas by transferring a dicyanomethylene group to the sulfur atom to give stable methylenesulfonium ylides. The oxirane reacts with other thioamides to give either thiazoles or dicyanoethylenes.

1,1-Dicyano-2,2-bis(trifluoromethyl)ethylene undergoes many reactions similar to those of tetracyanoethylene.² One example is epoxidation, for 2,2-dicyano-3,3-bis(trifluoromethyl)oxirane (I) can be prepared by oxidation of the ethylene with peracetic acid. This epoxide, like the epoxide of tetracyanoethylene,³ reacts with pyridine to transfer a dicyanomethylene group to the nitrogen atom to give the dicyanomethylide II. Dicyanomethylene groups can also be transferred



(1) Portions of this paper were presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill, Sept 1964.

(2) W. J. Middleton, *J. Org. Chem.*, **30**, 1402 (1965).

(3) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2032 (1963); **87**, 3651 (1965).

from both tetracyanoethylene oxide and I to the sulfur atom in alkyl sulfides to give stable sulfur ylides (III).⁴

We have now extended this investigation of dicyanomethylene transfer to the reaction of dicyanoethylene epoxides with certain thiocarbonyl compounds, including thioureas, thioamides, and a trithiocarbonate. For these studies, we have used the epoxide I instead of tetracyanoethylene oxide, for we found that reactions of I with thiocarbonyl compounds were much cleaner than reactions of tetracyanoethylene oxide with the same compounds. This is probably because carbonyl cyanide, the by-product from reactions of tetracyanoethylene oxide, undergoes secondary reactions causing tar formation, whereas hexafluoroacetone, the by-product from I, is much less reactive than carbonyl cyanide.

Three general types of reactions between I and thiocarbonyl compounds have been observed. They are (1) direct transfer of the dicyanomethylene group to

(4) W. J. Middleton, E. L. Buhle, J. G. McNally, Jr., and M. Zanger, *J. Org. Chem.*, **30**, 2384 (1965).