




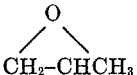


TABLE I

Solvent	$R_f$ , product	$R_f$ , III	Resolution
	0.16, 0.34	0.16	Good
	0.13, 0.40	0.13	Good
Ligroin (bp 60–80°)	0.07, 0.15, 0.21, 0.26, 0.41	0.15	Good
CCl <sub>4</sub>	0.21, 0.25, 0.31, 0.44, 0.59	0.44	Good
CCl <sub>2</sub> F–CClF <sub>2</sub> (Freon 113)	0.20, 0.51	0.20	Good
	0.62–0.79	0.68	Partial
	0.53–0.70	0.58	Partial
	0.45–0.69	0.56	Partial
CHCl <sub>3</sub>	0.70	0.70	Poor
(CH <sub>2</sub> Cl) <sub>2</sub>	0.58–0.68	0.65	Poor
CH <sub>3</sub> CCl <sub>3</sub>	0.64	0.64	Poor
C <sub>6</sub> H <sub>6</sub>	0.57–0.68	0.59	Poor
	0.62–0.78	0.65	Poor

**Attempted Insertion of SO<sub>2</sub>.**—Biphenylene (0.001 mol, 0.151 g) was refluxed under a slow stream of SO<sub>2</sub> for 41 hr. There was a slight gain in weight (0.001 g vs. the theoretical 0.064 g), and the reaction product upon thin layer chromatography showed two new products in very low yield, but neither was the desired sulfone, and the products were not characterized.

**Registry No.**—Biphenylene, 259-79-0; II, 244-95-1; III, 5381-63-5.

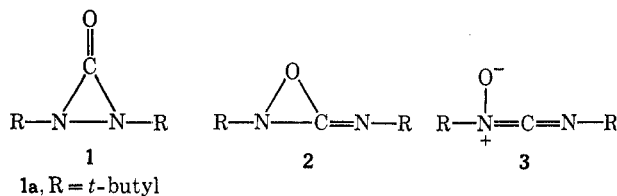
### Diaziridinones. V.<sup>1a</sup> Reduction by Phosphite to Carbodiimide and Peracid Oxidation of Carbodiimide to Diaziridinone<sup>1b</sup>

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Previous papers have described the synthesis and some reactions of diaziridinones (1).<sup>1a,2</sup> Consideration of possible valence isomers 2 and 3 of 1 led to a synthesis of 1 by reaction of RNO with RNC.<sup>1a</sup> We consider here the possibility of preparation of 1 *via*

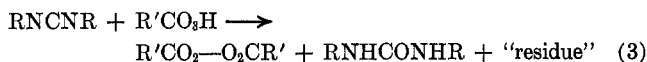
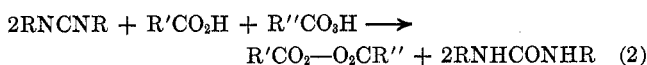
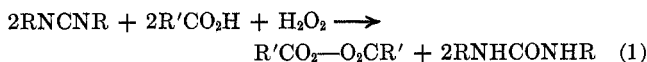


(1) (a) Part IV: F. D. Greene and J. F. Pazos, *J. Org. Chem.*, **34**, 2269 (1969). (b) Financial support from the National Science Foundation (Grant No. GP-5527) is gratefully acknowledged.

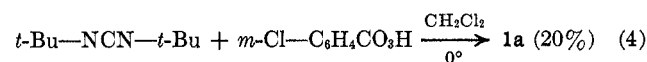
(2) (a) F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, **34**, 2254 (1969); (b) F. D. Greene, W. R. Bergmark, and J. G. Pacifici, *ibid.*, **34**, 2263 (1969).

2 or 3 by the oxidation of a carbodiimide and the reverse problem of removal of oxygen from a diaziridinone, with conversion to a carbodiimide.

**Peracid Oxidation of Carbodiimide.**—Reaction of dicyclohexylcarbodiimide with carboxylic acids and hydrogen peroxide (eq 1) or with a carboxylic acid and a percarboxylic acid (eq 2) affords diacyl peroxides in good yield.<sup>3</sup> Reaction of dicyclohexylcarbodiimide with a peracid afforded the urea and diacyl peroxide in moderate yield along with a residue which could not be characterized (eq 3).<sup>3</sup>



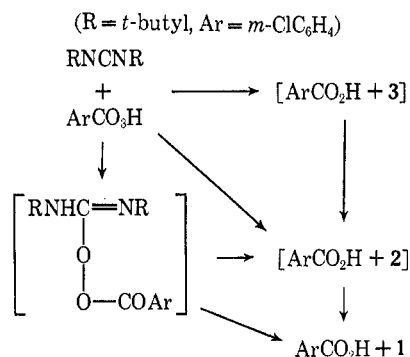
Use of a more hindered carbodiimide, di-*t*-butylcarbodiimide, and *m*-chloroperbenzoic acid in methylene chloride has resulted in the isolation of di-*t*-butyldiaziridinone (1a) in 20% yield. The yield of 1a was ap-



proximately the same when the reaction was carried out in a vigorously stirred two-phase system of methylene chloride and a phosphate buffer. When the reaction was carried out in carbon tetrachloride and monitored continuously by ir, diaziridinone bands (1880 cm<sup>-1</sup>) built up immediately.

The major possibilities for diaziridinone formation are summarized in Scheme I. The generation of car-

SCHEME I



boxylic acid in the reactions of Scheme I and the greater reactivity of RCO<sub>2</sub>H in comparison with RCO<sub>3</sub>H toward carbodiimide<sup>3</sup> provide additional paths for reaction accounting for the complexities in eq 3 (R = cyclohexyl) and for the low yield of 1a in eq 4.

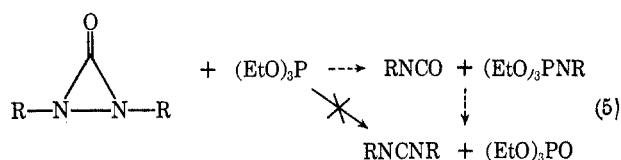
**Phosphite Reduction of Diaziridinone.**—The possibility of formation of 1 *via* 2 or 3, indicated above and in the reaction of RNO with RNC,<sup>1a</sup> raises the question of the reversible formation of 2 or 3 from 1. Phenyl isocyanate, a species which appears to trap an inter-

(3) F. D. Greene and J. Kazan, *ibid.*, **28**, 2168 (1963).

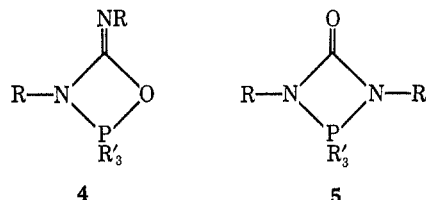
(4) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965.

mediate (considered to be 3) in the RNO + RNC reaction,<sup>1a</sup> does not react with 1 under moderate conditions, suggestive that 1 is not in facile reversible equilibrium with 3. In view of the affinity of phosphorus compounds for oxygen,<sup>4</sup> reaction with 1 was examined.

Trivalent phosphorus compounds effect the deoxygenation of di-*t*-butyldiaziridinone (1a). Triphenylphosphine reacts with 1a to give di-*t*-butylcarbodiimide (44%) and triphenylphosphine oxide. Reaction of 1a with triethyl phosphite affords di-*t*-butylcarbodiimide (90%) and *t*-butyl isocyanate (4%). Analysis after partial reaction showed considerably more isocyanate (20%). The buildup of isocyanate excludes the formation of phosphate and carbodiimide by direct oxygen transfer from 1 or 2 or 3 to the phosphite.



The results suggest the formation of isocyanate and phosphinimide by reaction of 1 (or a valence isomer of 1) with phosphite, ultimately followed by the recombination of isocyanate and phosphinimide and formation of phosphate and carbodiimide (*e.g.*, *via* 4).<sup>5</sup> The prep-



aration of a compound assigned structure 5 (R = CH<sub>3</sub>, R' = Cl) by reaction of PCl<sub>5</sub> with RNHCONHR and its thermal decomposition to RNCO and RNPCl<sub>3</sub> with further conversion, in part, to RNCNR and POCl<sub>3</sub> has been described.<sup>6</sup>

#### Experimental Section

**Reaction of *m*-Chloroperbenzoic Acid with Di-*t*-butylcarbodiimide.**—The *m*-chloroperbenzoic acid was prepared by washing the commercial product with a phosphate buffer<sup>7</sup> until it was 99% pure by titration. To a solution of di-*t*-butylcarbodiimide<sup>5b,8</sup> (2.02 g, 0.013 mol) in 40 ml of CH<sub>2</sub>Cl<sub>2</sub> at -15° was added a solution of *m*-chloroperbenzoic acid (2.26 g, 0.013 mol) in 30 ml of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred overnight and allowed to come to 25°. The filtrate was evaporated and the residue was trap-to-trap distilled. Glpc<sup>2</sup> and ir analysis indicated a mixture of unchanged carbodiimide (2.2 mmol) and di-*t*-butyldiaziridinone 1a (20% based on carbodiimide consumed).

**Reaction of Di-*t*-butylcarbodiimide with *m*-Chloroperbenzoic Acid in the Presence of a Buffered Solution.**—A solution of 1.242 g (7.2 mmol) of *m*-chloroperbenzoic acid (98.4%) in 30 ml of CH<sub>2</sub>Cl<sub>2</sub> was vigorously stirred with 25 ml of a phosphate buffer (1.28 M in K<sub>2</sub>HPO<sub>4</sub>, 0.7 M in KH<sub>2</sub>PO<sub>4</sub>) by means of a vibrator.

In this way, the mixture was thoroughly emulsified. The mixture was cooled to 0° and di-*t*-butylcarbodiimide (1.06 g, 6.85 mmol) in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> was added over a period of 15 min. The reaction mixture was then stirred without the ice bath for another 25 min. The CH<sub>2</sub>Cl<sub>2</sub> layer was separated, dried (K<sub>2</sub>CO<sub>3</sub>), and evaporated. The residue was trap-to-trap distilled affording 0.539 g. Analysis by glpc showed 2.27 mmol of carbodiimide and 1.09 mmol of diaziridinone 1a (24% yield calculated from carbodiimide consumed).

**Reaction of 1a with Triphenylphosphine.**—A solution of triphenylphosphine (4.62 g, 17.6 mmol) and 1a (3.0 g, 17.6 mmol) in 20 ml of benzene was heated at reflux for 37 hr. Filtration afforded 0.82 g of triphenylphosphine oxide, mp 156–158° (lit.<sup>9</sup> mp 153.3°), identical with an authentic sample.<sup>9</sup> Analysis of the filtrate by ir and glpc indicated di-*t*-butylcarbodiimide (6.0 mmol, 45%) and unchanged 1a (3.7 mmol, 20%). Column chromatography of the filtrate afforded additional triphenylphosphine oxide [2.2 g, total (see above) 3.02 g, 10.6 mmol, 75%] and 0.66 g of unchanged triphenylphosphine (0.66 g, 2.5 mmol, 14%). A third component, eluted in low yield, could not be obtained in pure form.

**Reaction of Di-*t*-butyldiaziridinone (1a) with Triethyl Phosphite.**—A solution of 1.78 g (10.7 mmol) of triethyl phosphite and 1.05 g (6.20 mmol) of 1a<sup>2</sup> was sealed in a glass tube and heated at 100° for 50 hr. The resulting solution was homogeneous, clear, and colorless. Analysis by ir showed no diaziridinone but *t*-butyl isocyanate (2250 cm<sup>-1</sup>) and carbodiimide (2095, 2115 cm<sup>-1</sup>). Glpc analysis showed four components: *t*-butyl isocyanate, triethyl phosphite, di-*t*-butylcarbodiimide, and triethyl phosphate<sup>10</sup> with yields of 0.27 mmol (4.4%), 5.11 mmol, 5.64 mmol (91%), and 6.4 mmol (100%), respectively. The yields were determined by internal standardization using two independent standard solutions as checks. When 4.38 g (26.4 mmol) of triethyl phosphite and 3.00 g (17.6 mmol) of 1a were sealed in a tube and heated at 100° for 16 hr, 76% of the diaziridinone was consumed (by ir). The yields of the other products (glpc) were *t*-butyl isocyanate, 3.00 mmol (22.4%); di-*t*-butylcarbodiimide, 7.55 mmol (56.5%); triethyl phosphate, 8.15 mmol (60.8%); triethyl phosphite, 7.70 mmol (yields are based on the diaziridinone consumed).

In another experiment a solution of 2.92 g (17.6 mmol) of triethyl phosphite and 3.00 g (17.6 mmol) of 1a was heated at 60–100°. At an early stage of the reaction the carbodiimide and isocyanate bands were of about equal intensity; in the later stages the intensity ratio heavily favored the carbodiimide.

**Attempted Reaction of Sodium Diethyl *t*-Butylamidophosphate with Di-*t*-butyldiaziridinone (1a).**—To a solution of 8.80 mequiv of sodium diethyl *t*-butylamidophosphate in 28 ml of 1,2-dimethoxyethane (distilled from sodium and benzophenone ketyl), prepared<sup>10</sup> from diethyl *t*-butylamidophosphate (Aldrich Chemical Co.) and sodium hydride as base, under dry nitrogen, was added 1.72 ml (1.50 g, 8.80 mmol) of 1a in 10 ml of dimethoxyethane. No change (ir) was observed after 1 hr at room temperature and 6.5 hr at 75°. To ascertain the activity of the amidophosphate anion after this treatment, 0.20 ml (174 mg, 1.75 mmol) of *t*-butyl isocyanate was added and the solution was heated at 75° for 15 min.<sup>5b</sup> Complete conversion to di-*t*-butylcarbodiimide was clearly indicated by the complete disappearance of the 2250-cm<sup>-1</sup> isocyanate band and the appearance of the characteristic 2100-cm<sup>-1</sup> doublet of di-*t*-butylcarbodiimide of appropriate intensity. This resulting mixture was heated an additional 40 hr at reflux with no change detected.

**Attempted Reaction of Phenyl Isocyanate with Di-*t*-butyldiaziridinone (1a).**—Phenyl isocyanate (0.381 g, 3.204 mmol) and di-*t*-butyldiaziridinone (0.422 g, 2.484 mmol) were mixed and an aliquot was sealed in a capillary tube. The tube was heated to 100° for 5.5 hr. Comparison of ir before and after heating indicated no reaction had taken place.

**Registry No.**—1a, 19656-74-7; *m*-chloroperbenzoic acid, 937-14-4; di-*t*-butylcarbodiimide, 691-24-7; triethyl phosphite, 122-52-1.

(5) (a) J. J. Monagle, T. W. Campbell, and H. F. McShane, Jr., *J. Amer. Chem. Soc.*, **84**, 4288 (1962); (b) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Org. Chem.*, **29**, 2816 (1964).

(6) H. Ulrich and A. A. R. Sayigh, *ibid.*, **30**, 2779 (1965).

(7) N. N. Schwartz and J. H. Blumbers, *ibid.*, **29**, 1976 (1964).

(8) E. Schmidt and M. Seefelder, *Justus Liebigs Ann. Chem.*, **671**, 83 (1951).

(9) F. Challenger and V. K. Wilson, *J. Chem. Soc.*, 209 (1927).

(10) Prepared by the method of A. J. Burn and J. I. G. Cadogan, *Chem. Ind. (London)*, 736 (1963), bp 114–119° (25 mm) [D. P. Evans, W. C. Davies, and W. J. Jones, *J. Chem. Soc.*, 1310 (1930), give bp 215° (760 mm)].