372. *Organic Peroxides. Part II.* Esters of the Monopercarbonic Acids.*

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tert.-Butyl chloroperformate (I), di-*tert.*-butyl dipercarbonate (II), *O*•*O*-*tert.*-butyl *O*-ethyl monopercarbonate (IV), and the *tert.*-butyl esters of percarbamic acid and a number of *N*-alkylpercarbamic acids (III) have been prepared as illustrated in the reaction scheme below.

MANY percarboxylic esters have been prepared by the reaction of alkyl hydroperoxides with acid halides (*e.g.*, Milas and Surgenor, *J. Amer. Chem. Soc.*, 1946, **68**, 642) or acid anhydrides (Davies, Foster, and White *) under basic conditions. The preparation of some alkyl monopercarbonates is now reported.

Investigation has been directed to carbonic acid derivatives because (*a*) they are structurally very similar to the known percarboxylic esters, (*b*) H_2CO_3 is a weak acid, and this should enhance the stability of the O–O bond of the resultant peresters towards heterolysis (Criegee and Dietrich, *Annalen*, 1948, **560**, 127), and (*c*) a number of salts of the monopercarbonic acids have been reported (reviewed by Partington and Fathallah, *J.*, 1950, 1934). *tert.*-Butyl hydroperoxide was chosen as the esterifying hydroperoxide because it is stable and readily prepared, and forms stable percarboxylic esters. A number of dialkyl dipercarbonates (RO•CO•O•O•CO•OR), which, however, are not peroxy-esters in the sense discussed here, have been prepared by earlier workers (Wieland, van Hove, and Borner, *Annalen*, 1925, **446**, 46; Strain, Bissinger, Dial, Rudoff, De Witt, Stevens, and Langston, *J. Amer. Chem. Soc.*, 1950, **72**, 1254; Cohen and Sparrow, *ibid.*, p. 611) by the action of sodium peroxide on alkyl chloroformates. *O*•*O*-*tert.*-Butyl *O*-*iso*propyl monopercarbonate ($Pr^iO{\cdot}CO{\cdot}O{\cdot}OBu^t$) and impure di-*tert.*-butyl dipercarbonate [$O{:}C({\cdot}O{\cdot}OBu^t)_2$] have also been isolated (Strain *et al.*, *loc. cit.*) by reaction of *tert.*-butyl hydroperoxide with *iso*propyl chloroformate and with carbonyl chloride respectively.

The reactions outlined in the annexed scheme have now been accomplished. We were unable to isolate pure *tert.*-butyl chloroperformate (I) from the reaction between carbonyl chloride and *tert.*-butyl hydroperoxide in the absence or presence of pyridine because decomposition apparently occurred on distillation, but it was concluded that a fraction of b. p. 30—40°/120 mm. contained a large proportion of (I) because it could be converted into the corresponding *N*-phenyl- and *N*-1-naphthyl-amides (III) in good yield. By reaction of carbonyl chloride with two mols. of the hydroperoxide in the presence of excess of pyridine, di-*tert.*-butyl dipercarbonate (II) was obtained as a stable oil.

O•*O*-*tert.*-Butyl *O*-ethyl monopercarbonate (IV) was isolated as a stable liquid after reaction of ethyl chloroformate and *tert.*-butyl hydroperoxide, and of *tert.*-butyl chloroperformate (I) and ethyl alcohol, both reactions being carried out in the presence of excess of pyridine.

Esters (III) of the unknown percarbamic acids have been prepared by the three following types of reaction. (1) The reaction between phenyl, 1-naphthyl, and *p*-diphenylyl *iso*cyanate and *tert.*-butyl hydroperoxide proceeds readily at room temperature on the addition of a trace of pyridine, and the *tert.*-butyl *N*-arylpercarbamates (III) have been obtained as crystalline solids melting with decomposition and becoming discoloured when kept for some weeks at room temperature. *tert.*-Butyl *N*-(—)-menthylpercarbamate (III; R = menthyl), prepared by a similar reaction, is more stable, melting without decomposition and not decomposing on storage. *tert.*-Butyl percarbamate itself (III; R = H) was obtained by depolymerising cyanuric acid vapour in a red-hot tube and passing the resulting cyanic acid into a mixture of *tert.*-butyl hydroperoxide and pyridine. (2) *tert.*-Butyl *N*-phenyl- and *N*-1-naphthyl-percarbamate were also obtained by the reaction of aniline and 1-naphthylamine respectively on *tert.*-butyl chloroperformate (I). (3) *tert.*-Butyl *N*-phenylpercarbamate was prepared by treatment of *N*-phenylcarbamyl chloride with *tert.*-butyl hydroperoxide in the presence of excess of pyridine.

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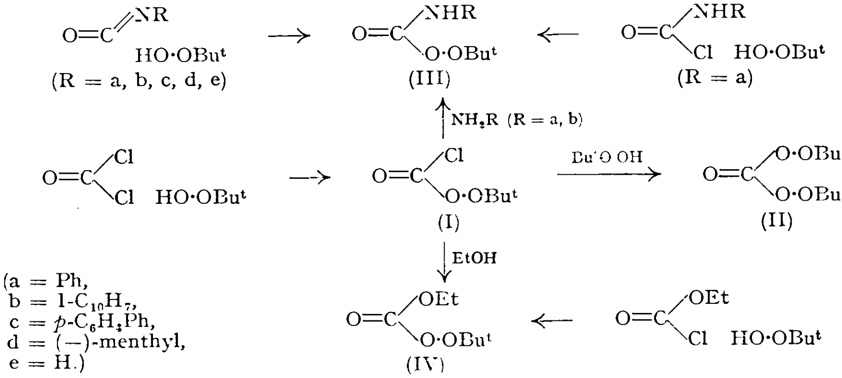
It has been shown that *tert.*-butyl *N*-phenylpercarbamate catalyses the polymerisation of styrene at 85°, confirming that it contains a peroxide linkage which can undergo homolysis under the conditions of this experiment. Although the structures of the derivatives of percarbamic acid are written above in the lactam form (III) the possibility of these molecules existing in prototropic equilibrium with the lactim form (III*a*) is not excluded:



(a = Ph,
b = 1-$C_{10}H_7$,
c = *p*-C_6H_4Ph,
d = (−)-menthyl,
e = H.)

(III)  (III*a*)

$$O{:}C(NHR)(O{\cdot}OBu^t) \rightleftharpoons HO{\cdot}C(=NR)(O{\cdot}OBu^t)$$

The proportion of the lactim form would be expected to be largest in the case of the *N*-arylamides where stabilisation of this form will result from conjugation between the C=N double bond and the aromatic ring. The infra-red absorption spectra of *tert.*-butyl *N*-phenyl- and *N*-1-naphthyl-percarbamate demonstrate the presence of the lactam form, but the evidence for the existence of a proportion of the lactim form is inconclusive.

EXPERIMENTAL

tert.-Butyl hydroperoxide (b. p. 43—45°/28 mm.) was prepared by Criegee and Dietrich's method (*Annalen*, 1948, **560**, 135) on half the scale there described, precautions being taken against explosion.

tert.-*Butyl Chloroperformate* (I).—Carbonyl chloride (1·7 g.) was passed into *tert.*-butyl hydroperoxide (1·35 g.) at −10°, and the mixture then allowed to warm to room temperature during 90 min. Distillation, apparently accompanied by decomposition, yielded impure *tert.*-butyl chloroperformate (0·8 g.), b. p. 30—40°/120 mm. This was the material used in the preparation of *tert.*-butyl *N*-phenyl- and *N*-1-naphthyl-percarbamate. No advantage was gained by addition of pyridine to the reaction mixture, or by short-path distillation of the product at room temperature.

Di-tert.-*butyl Dipercarbonate* (II).—A toluene solution of carbonyl chloride (85 g. of 12½% solution) was added at 0° during 30 min. to a stirred solution of *tert.*-butyl hydroperoxide (16·2 g.) in pyridine (35 g.). After 60 min., water was added and the toluene layer separated and thoroughly washed with 5% hydrochloric acid and water. From the toluene solution *di*-tert.-*butyl dipercarbonate* (15 g.) was recovered, having b. p. 54—55°/0·5 mm., n_D^{25} 1·4139, d_4^{25} 0·975 (Found: C, 53·0; H, 8·6. $C_9H_{18}O_5$ requires C, 52·4; H, 8·8%).

O•O-tert.-*Butyl* O-*Ethyl Monopercarbonate* (IV).—(a) *From ethyl chloroformate.* To a mixture of ethyl chloroformate (5·0 g.) and *tert.*-butyl hydroperoxide (4·1 g.) at 0°, pyridine (7 g.) was added dropwise, a vigorous reaction taking place and pyridine hydrochloride being precipitated. Ether was added and the solution washed with water and sodium hydrogen carbonate solution, and dried (Na_2SO_4). Distillation of the ethereal solution yielded three fractions of 1·8 g. each, *viz.*, b. p. (i) 28—30°, (ii) 30°, (iii) 30—32°, all at 0·8 mm. The middle fraction was redistilled giving OO-tert.-*butyl* O-*ethyl monopercarbonate*, b. p. 30°/0·8 mm., n_D^{20} 1·4052, d_4^{20} 0·984 (Found: C, 51·8; H, 8·5. $C_7H_{14}O_4$ requires C, 51·8; H, 8·7%).

(b) *From* tert.-*butyl chloroperformate.* Carbonyl chloride (2 g.) and *tert.*-butyl hydroperoxide (1·4 g.) were allowed to react together at 0° for 1 hr. and then nitrogen was passed through the solution at room temperature to sweep out hydrogen chloride gas and any unchanged carbonyl chloride. Absolute ethyl alcohol (0·7 g.) was then added, followed by excess of pyridine (2 g.) dropwise at 3—5°. After 30 min., iced water was added and the solution extracted twice with ether. The combined ethereal extracts were washed with dilute aqueous sodium hydrogen carbonate and with water, dried (Na_2SO_4), and distilled, yielding *OO*-*tert.*-butyl *O*-ethyl monopercarbonate (1·0 g.), b. p. 64°/15 mm., n_D^{20} 1·4057 (Found: C, 51·9; H, 9·0%).

tert.-*Butyl* N-*Phenylpercarbamate* (III; R = Ph).—(a) *From phenyl* iso*cyanate.* To a mixture of *tert.*-butyl hydroperoxide (2·7 g.) and phenyl *iso*cyanate (3·6 g.), pyridine (0·05 g.) was added, the temperature of the mixture being kept below 40°. After about 15 min. the mixture solidified to an orange-white solid which was extracted with cold benzene (60 c.c.), leaving a residue of *s*-diphenylurea (0·2 g.; m. p. 242°). The benzene was evaporated off at room temperature, leaving a solid (2·3 g.) which was recrystallised twice from ether–light petroleum. tert.-*Butyl* N-*phenylpercarbamate* (1·7 g.) was obtained as colourless crystals, m. p. 83° (decomp.) (Found: C, 63·6; H, 7·25; N, 6·45. $C_{11}H_{15}O_3N$ requires C, 63·1; H, 7·2; N, 6·7%). Although this was stable at 0° for some months, after 2—3 weeks at room temperature a brown colour developed and a smell resembling that of phenyl *iso*cyanide became apparent. When the reaction was carried out in benzene solution no *s*-diphenylurea was obtained, and a better yield of colourless (III; R = Ph) separated from the mixture.

(b) *From* tert.-*butyl chloroperformate.* After 12 hr., the precipitate obtained by adding excess (0·5 g.) of aniline to *tert.*-butyl chloroperformate (0·3 g.) was filtered off, washed with dilute hydrochloric acid and water, and dried. Recrystallisation from ether–light petroleum yielded (III; R = Ph) (0·2 g.), m. p. 82° (decomp.), undepressed on admixture with the product obtained from phenyl *iso*cyanate.

(c) *From* N-*phenylcarbamyl chloride.* Phenylcarbamyl chloride was prepared by passing hydrogen chloride gas into phenyl *iso*cyanate (3·3 g.) initially at 20° and later at 55°, till the mass solidified (Lengfeld and Stieglitz, *Amer. Chem. J.*, 1894, **16**, 71; Hentschel, *Ber.*, 1885, **18**, 1178). The product was dried in a vacuum-desiccator; it (3·25 g.) then showed m. p. 57—58°. Phenylcarbamyl chloride (0·5 g.) was dissolved in *tert.*-butyl hydroperoxide (0·9 g.), and pyridine (1·9 g.) added; after 15 min. at 0° the mixture was poured on iced water, and the precipitated solid (0·47 g.) recrystallised from ether–light petroleum, yielding *tert.*-butyl *N*-phenylpercarbamate, m. p. 83° (decomp.), undepressed on admixture with the product obtained from phenyl *iso*cyanate.

tert.-*Butyl* N-1-*Naphthylpercarbamate* (III; R = 1-naphthyl).—(a) *From* 1-*naphthyl* iso*cyanate.* After 12 hr., from a mixture of *tert.*-butyl hydroperoxide (0·9 g.), 1-naphthyl *iso*cyanate (1·7 g.), and pyridine (0·05 g.) in benzene (3 c.c.) the solid (1·4 g.) which had been precipitated was filtered off and recrystallised from ether–light petroleum. tert.-*Butyl* N-1-*naphthylpercarbamate* was obtained as pale buff crystals, m. p. 80° (decomp.) (Found: C, 69·7; H, 6·7; N, 5·3. $C_{15}H_{17}O_3N$ requires C, 69·5; H, 6·6; N, 5·4%).

(b) *From* tert.-*butyl chloroperformate.* 1-Naphthylamine (0·60 g.) was added to *tert.*-butyl chloroperformate (0·30 g.) in ether at <20°. After 20 min. the precipitated 1-naphthylamine hydrochloride was filtered off and washed with ether. The combined ethereal layers were washed with dilute hydrochloric acid and water, and dried (Na_2SO_4), and the solvent evaporated off, yielding *tert.*-butyl *N*-1-naphthylpercarbamate, which, recrystallised from ether–light petroleum, showed m. p. 79° (decomp.) alone and when mixed with the specimen obtained from 1-naphthyl *iso*cyanate.

tert.-*Butyl* N-p-*Diphenylylpercarbamate* (III; R = *p*-diphenylyl).—To a mixture of *tert.*-butyl hydroperoxide (0·72 g.) and *p*-diphenylyl *iso*cyanate (1·55 g.) in benzene (20 c.c.) at 0°, pyridine (0·05 g.) was added; after 20 min. an orange colour slowly developed. Next morning the solution was filtered from a small amount of *s*-di-*p*-diphenylylurea and evaporated to dryness. The crude tert.-*butyl* N-p-*diphenylylpercarbamate* (0·85 g.) obtained was recrystallised from ether–light petroleum, forming pale buff needles, m. p. 85° (decomp.) (Found: C, 71·6; H, 6·8; N, 5·1. $C_{17}H_{19}O_3N$ requires C, 71·5; H, 6·7: N 4·9%).

tert.-*Butyl* N-(−)-*Menthylpercarbamate* [III; R = (−)-menthyl].—A solution of *tert.*-butyl hydroperoxide (0·23 g.), (−)-menthyl *iso*cyanate (0·47 g.; $[\alpha]_D^{22}$ −64·2°), and pyridine (0·06 g.) in dry benzene (5 c.c.) was kept at room temperature for 12 hr. The solvent was evaporated off under vacuum and the colourless solid obtained (0·7 g.) was recrystallised twice from light petroleum, yielding tert.-*butyl* N-*menthylpercarbamate*, m. p. 101°, $[\alpha]_D^{18}$ $-59° \pm 2°$ ($l = 1$, $c = 0·761$ in $CHCl_3$) (Found: C, 66·3; H, 10·5; N, 5·65. $C_{15}H_{29}O_3N$ requires C, 66·4; H, 10·8; N, 5·2%).

tert.-*Butyl Percarbamate* (III; R = H).—Sublimed cyanuric acid (0·4 g.) was led in a current of dry air through a 6-inch length of red-hot Pyrex tubing, and the resulting cyanic acid condensed into a mixture of *tert.*-butyl hydroperoxide (0·85 g.) and pyridine (0·10 g.) cooled in ice–ammonium chloride. After 12 hr. at room temperature the mixture was extracted with ether, to yield a white crystalline solid (0·15 g.), m. p. 47—48°. Recrystallisation from ether–light petroleum gave tert.-*butyl percarbamate* (0·10 g.), m. p. 51° (Found : C, 44·6; H, 8·0; N, 10·2. $C_5H_{11}O_3N$ requires C, 45·1; H, 8·3; N, 10·5%).

We are indebted to Dr. G. J. Minkoff for recording and interpreting the infra-red absorption spectra of *tert.*-butyl *N*-phenyl- and *N*-1-naphthyl-percarbamate.

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