

[CONTRIBUTION No. 241 FROM THE JACKSON LABORATORY, E. I. DU PONT DE NEMOURS & Co., Inc.]

Preparation and Properties of Esters of *N*-Substituted Peroxycarbamic AcidsC. J. PEDERSEN¹

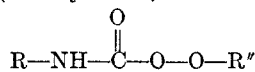
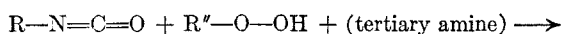
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Nine *tert*-butyl and α -cumyl esters of *N*-substituted peroxycarbamic acids have been prepared by: (a) reacting isocyanates with hydroperoxides in the presence of a solvent and a tertiary amine; or (b) reacting *N*-substituted carbamoyl chlorides with hydroperoxides in the presence of 30% aqueous potassium hydroxide. Various properties of these products are described. They liberate iodine from acidified potassium iodide and initiate the polymerization of vinyl monomers. Polystyrene containing amino groups was prepared by initiating the polymerization with *tert*-butyl *N*-dimethylperoxycarbamate.

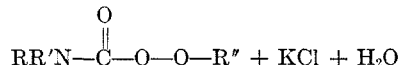
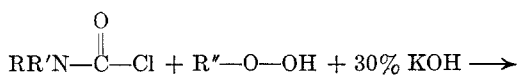
tert-Butyl peroxycarbamate and four of its *N*-monosubstituted derivatives (phenyl, α -naphthyl, *p*-xenyl, and (-)-methyl) were prepared by Davies and Hunter² by three methods: (a) $R-N=C=O + t-C_4H_9-O-OH$ with pyridine as catalyst; (b) $RNHCOC_4H_9 + t-C_4H_9-O-OH$ with pyridine as acid acceptor; and (c) $R-NH_2 + t-C_4H_9-O-O-COCl$. They give little information on the thermal stability of these compounds, and their only reference to polymerization is the statement that *tert*-butyl *N*-phenylperoxycarbamate catalyzes the polymerization of styrene at 85°.

Some other peroxycarbamates were synthesized in order to investigate in greater detail their thermal stability and their ability to initiate polymerization. Two general methods were used for their preparation:

Method I

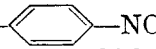


Method II



The first method can be used for the preparation of only peroxycarbamates containing the $-NH-$ group, but the second method is applicable to the synthesis of all types although it is less suitable for the *N*-monosubstituted compounds.

The peroxycarbamates, especially the liquid ones, possess a characteristic odor which is a disagreeable blend of the odors of peroxides and amines. They are colorless unless they contain groups which con-

fer color, such as $-N-$  $-NO_2$. As expected, they are all oxidizing agents which liberate iodine quantitatively from acidified potassium iodide. The preparative conditions and some of the properties are given in Table I.

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(2) A. G. Davies and K. J. Hunter, *J. Chem. Soc.*, **18**, 1808 (1953).

DISCUSSION

tert-Butyl *N*-ethylperoxycarbamate, hexamethylene-*N,N'*-bis(*tert*-butyl peroxycarbamate), and *tert*-butyl *N*-(*p*-nitrophenyl)peroxycarbamate were the most stable compounds prepared, and their half-lives are estimated to lie between 600 and 800 days at 24–28°. At the same temperature the half-life of hexamethylene-*N,N'*-bis(α -cumylperoxycarbamate) is about 250 days; those of *tert*-butyl *N,N*-dimethylperoxycarbamate and *tert*-butyl *N,N*-diethylperoxycarbamate are 57–65 days; and that of α -cumyl *N,N*-dimethylperoxycarbamate is about 32 days. It will be noted that the α -cumyl ester is less stable than the corresponding *tert*-butyl ester. *tert*-Butyl *N,N*-pentamethyleneperoxycarbamate and *tert*-butyl *N*-methyl-*N*-(*p*-nitrophenyl)peroxycarbamate were the least stable compounds synthesized, and their half-lives lie between 2 and 4 days at 30°.

All these compounds begin to decompose rapidly between 80 and 140°, and all decompose violently when dropped on a hot plate at 140–180° except *tert*-butyl *N*-ethylperoxycarbamate which did not explode up to 220°. In no case was the decomposition accompanied by a flame. For possible hazards due to violent reaction see Experimental.

Aside from establishing the presence of carbon dioxide and basic substances among the decomposition products from peroxycarbamates, the products were not identified except those from *tert*-butyl *N*-(*p*-nitrophenyl)peroxycarbamate and *tert*-butyl *N*-methyl-*N*-(*p*-nitrophenyl)peroxycarbamate. The latter will be discussed in detail in another paper.

Peroxcarbamates initiate the polymerization of vinyl monomers as shown in Table II which compares *tert*-butyl *N,N*-pentamethyleneperoxycarbamate to benzoyl peroxide for the bulk polymerization of styrene at different temperatures. It will be observed that benzoyl peroxide is more effective at 82°, but the peroxycarbamate is the better initiator at lower temperatures. *tert*-Butyl *N*-ethylperoxycarbamate, *tert*-butyl *N*-(*p*-nitrophenyl)peroxycarbamate, *tert*-butyl *N*-methyl-*N*-(*p*-nitrophenyl)peroxycarbamate, hexamethylene-*N,N'*-bis(*tert*-butyl peroxycarbamate), and hexamethylene-*N,N'*-bis(α -cumyl peroxycarbamate) also accelerated the bulk polymerization of styrene at 80°.


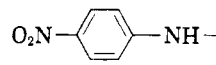
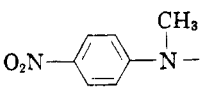
TABLE I

$$\text{O}$$

$$\parallel$$

$$\text{A}-\text{C}-\text{O}-\text{O}-\text{R}$$

PREPARATION AND PROPERTIES OF

| No. | A | R ^a | Method | Solvent | Catalyst | Yield, ^b % | M.P., °C. ^c | Purity by KI, % | Nitrogen Con- tent, % | |
|-----|---|----------------|--------|------------------|--------------------|--------------------------|---------------------------|-----------------------|--------------------------|-------|
| | | | | | | | | | Calcd. | Found |
| 1 | C ₂ H ₅ NH— | R' | I | Benzene | Pyridine | 18 | 39–40 ^d | 99 | 8.7 | 8.7 |
| 2 | (CH ₃) ₂ N— | R' | II | None | — | 54 | Liquid ^e | 100 | 8.7 | 8.7 |
| 3 | (CH ₃) ₂ N— | R'' | II | None | — | 40 | 60 ^d | 100 | 6.3 | 6.3 |
| 4 | (C ₂ H ₅) ₂ N— | R' | II | None | — | 43 | Liquid ^f | 100 | 7.4 | 7.4 |
| 5 |  | R' | II | None | — | 81 | Liquid ^g | 99 | 7.0 | 7.1 |
| 6 |  | R' | I | Benzene | Triethyl- amine | 59 | 93 ^h | 100 | 11.0 | 10.9 |
| 7 |  | R' | II | Petrol. ether | — | 68 | 66 ^h | 100 | 10.5 | 10.4 |
| 8 | R'—O—O—C(=O)—NH—(CH ₂) ₆ —NH— | R' | I | Benzene | Pyridine | 6 | 64–5 ^d | 100 | 8.0 | 8.1 |
| 9 | R''—O—O—C(=O)—NH—(CH ₂) ₆ —NH— | R'' | I | Benzene | Triethyl- amine | 57 | 105 ^d | 98 | 5.9 | 6.3 |

^a R' is tertiary-butyl and R'' is alpha-cumyl. ^b Yields are based on isocyanate or carbamoyl chloride. They are approximate and no effort was made to secure maximum yields. ^c These points were determined on a bronze block and are uncorrected. In general the compounds decomposed on melting. ^d White crystals. ^e Colorless; boiling at 43–45°/0.1–0.2 mm. without decomposition. ^f Undistilled. ^g Undistillable at 0.005 mm. Pale yellow. ^h Yellow crystals.

The peroxy-carbamates initiate the polymerization of other monomers. For example, in the solution polymerization (solvent: benzene) of chloroprene at 49°, 3.32 g. of polymer were obtained by using a given concentration of *N,N'*-azobis(α -isobutyronitrile), and 5.93 g. were obtained by using an equimolar quantity of *tert*-butyl *N*-pentamethylene-peroxy-carbamate.

It was experimentally established that polystyrene prepared with *tert*-butyl *N,N*-dimethylperoxy-carbamate contained amino groups: 0.9% nitrogen by Dumas' method; and 0.73% nitrogen by titrating the amino groups with perchloric acid in benzene solution. The polymer prepared with benzoyl peroxide contained no nitrogen. It is concluded, therefore, that the nitrogen-containing fragments from the peroxy-carbamates participate in the formation of polymers, and that polymers incorporating amino groups can be produced by means of the esters of peroxy-carbamic acids.

EXPERIMENTAL

Materials used. *tert*-Butyl hydroperoxide and α -cumyl hydroperoxide were commercial products used without purification; the former was 60% pure and the latter 72%. All other materials were either laboratory or commercial products, or were prepared by well known methods.

Quantitative analysis. The peroxy-carbamates were analyzed for purity by adding a weighed quantity to an equimolar mixture of acetone and acetic acid containing potassium iodide, and warming under nitrogen at 45–50° from 10 to 70 min. depending on the stability of the peroxy-carbamates. The equipment was protected from strong light

during this period, and the liberated iodine was titrated with standard thiosulfate solution.

Preparation. The peroxy-carbamates were prepared by two general methods. Method I is useful for the syntheses of compounds containing the —NH— group and Method II for the others.

Method I. *tert*-Butyl *N*-ethylperoxy-carbamate (No. 1). Ethyl isocyanate, 2.57 g. (0.036 mole), dissolved in 10 ml. of benzene, *tert*-butyl hydroperoxide, 3 g. of 60% product (0.02 mole), and 5 drops of pyridine were mixed together at 5° in an Erlenmeyer flask. The flask was kept in an ice bath for 2 hr. and in the dark at room temperature for 5 days. At the end of this time the reaction mass was clear, colorless, and smelled of ethyl isocyanate and *tert*-butyl hydroperoxide. It was shaken with 25 ml. of water and left at room temperature for a day. The water layer was then separated and discarded. Ten ml. of benzene were added to the benzene portion and allowed to stand for 6 hr. in contact with 50 ml. of water containing 2.5 ml. of concentrated ammonium hydroxide. The ammonia layer was removed and replaced with 10 ml. of 10% aqueous sodium hydroxide, and the mixture was left overnight at room temperature. The benzene layer was separated, washed twice with 25 ml. of water, dried with anhydrous sodium sulfate and evaporated to dryness under reduced pressure.

The viscous oil which solidified shortly, 1.17 g., was 88% pure by KI analysis (yield: 18% based on the isocyanate). The product was purified by dissolving it in petroleum ether (30–60°) at 45° and cooling with a mixture of alcohol and solid carbon dioxide. White crystals were obtained melting at 39–40°.

Anal. Calcd. for C₇H₁₅NO₃: C, 52.2; H, 9.3; N, 8.7. Found: C, 52.1; H, 9.3; N, 8.7. Infrared bands in Nujol solution: N—H at 3.01 μ ; C=O at 5.78 μ ; C—O at 8.73 μ ; and probably O—O at 11.80 μ . Other properties of the compound are shown in Table I.

Hexamethylene-*N,N'*-bis(*tert*-butyl peroxy-carbamate) (No. 8). This compound was made by the method used for the previous compound. Data concerning it are given in Table I.

Anal. Calcd. for $C_{16}H_{22}N_2O_6$: C, 55.2; H, 9.2; N, 8.0. Found: C, 55.9; H, 9.2; N, 8.1.

The above preparations were the first two attempted by Method I. Better yields would probably have been obtained if the simplified method used for the next compound had been employed.

Hexamethylene-N,N'-bis(α -cumyl peroxy carbamate) (No. 9). Hexamethylenediisocyanate, 1.25 g. (0.0074 mole), dissolved in 24 ml. of benzene, α -cumyl hydroperoxide, 3.2 g. of 72% product (0.015 mole), and 6 drops of triethylamine were mixed together at 5° in an Erlenmeyer flask. The charge was kept cool for 2 hr. and at room temperature for 22 hr. Fifty ml. of petroleum ether (30–60°) was added to the yellowish viscous reaction mixture, shaken vigorously, and allowed to settle. The precipitated paste, isolated by decantation, was dissolved in 30 ml. of benzene, filtered, and the filter washed with 20 ml. of benzene. The combined benzene solution was poured into 100 ml. of petroleum ether and mixed thoroughly. The solid which separated was collected, washed with petroleum ether, and dried on several layers of filter paper. The properties of the product, 2.01 g. (yield: 57% based on the diisocyanate), are shown in Table I.

tert-Butyl N-(p-nitrophenyl) peroxy carbamate (No. 6). This compound was prepared by the previous method using the appropriate intermediates. Its properties are given in Table I. It has an absorption maximum at 292 $m\mu$ ($\epsilon = 13,000$ in isooctane).

Method II. tert-Butyl N,N-dimethylperoxy carbamate (No. 2). *N,N*-Dimethylcarbamoyl chloride, 21 g. (0.234 mole), and 30% aqueous potassium hydroxide, 43.4 ml. (0.3 mole) were separately but simultaneously added dropwise in the course of 45 min. with stirring to 35 g. of 60% *tert*-butyl hydroperoxide. The temperature was maintained throughout at 10–15° by external cooling. After complete addition the charge was permitted to come up to room temperature and stirred for 22 hr. The upper organic layer was separated and taken up in 300 ml. of petroleum ether and washed three times with 25 ml. of 30% aqueous sodium hydroxide to remove the unreacted hydroperoxide. The petroleum ether solution was filtered through a plug of glass wool and dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure at room temperature. The clear, nearly colorless oil, 34.6 g., was 73% pure by KI analysis (yield at this stage: 70% based on the carbamoyl chloride).

A colorless liquid product (20.3 g., 54%) was obtained by distillation under high vacuum, b.p. 43–45°/0.1–0.2 mm. (without decomposition), n_D^{20} 1.4303, d_4^{25} 0.935. Infrared bands without diluent: N—H band absent; C=O at 5.73 μ ; C—O at 8.75 μ ; and probably O—O at 12.08 μ . Other properties of the compound are shown in Table I.

Safety tests. *tert*-Butyl *N,N*-dimethylperoxy carbamate, No. 2, was submitted to safety tests. Although it decomposes vigorously at elevated temperatures, it does not detonate like a true explosive. It must be emphasized, however, that peroxy carbamates should be handled with care, especially in large quantities, and stored in a cool place. It is also possible that some of them may be much more sensitive to disruptive influences than *tert*-butyl *N,N*-dimethylperoxy carbamate.

No decomposition was noted in 13 attempts to decompose this compound through impact by dropping a 5-kg. weight 55 in. Thermal decomposition tests were run with 7.5-ml. samples in a 75-ml. stainless steel cylinder in the absence of air, the temperature being raised 2.65°/min. It was found that the decomposition temperature was in the range of 60–63°, the maximum pressure was 1100 lb./sq. in. accompanied by a rapid rise in temperature to about 165°, and the maximum pressure development was 6140 lb./sq. in./sec. On the basis of this limited experience, it has been concluded that the compound can be handled safely as far as impact alone is concerned. but that elevated temperatures

should be carefully avoided especially when it is under confinement.

Although neither the pure compound nor 60% *tert*-butyl hydroperoxide ignited when dropped in the open on a bronze block heated to 158–160°, a mixture of the two products instantly burst into flame.

Alpha-cumyl N,N-dimethylperoxy carbamate (No. 3), *tert*-butyl *N,N*-diethylperoxy carbamate (No. 4), *tert*-butyl *N,N*-pentamethyleneperoxy carbamate (No. 5). These compounds were prepared by the same method as was used for the previous compound, and pertinent data are given in Table I. Unfortunately, *tert*-butyl *N,N*-diethylperoxy carbamate and *tert*-butyl *N,N*-pentamethyleneperoxy carbamate could not be purified by distillation even at 0.005 mm. because of thermal instability. They did not crystallize on cooling but formed glasses.

The *tert*-butyl esters of *N,N*-hexamethyleneperoxy carbamic and *N,N*-(3-oxapentamethylene)peroxy carbamic acids, and α -cumyl *N,N*-pentamethyleneperoxy carbamate were also prepared by this method. The products were liquids which could not be purified by distillation. Although the compounds were obtained their properties are not reported because of their low purity. The crude products decomposed vigorously at about 160°.

tert-Butyl *N,N*-pentamethyleneperoxy carbamate (No. 5). The pure product and equal volume mixtures with piperidine and glacial acetic acid, respectively, were stored at room temperature in the dark, and samples were analyzed at intervals. After 70 hr. of storage the pure compound had decomposed 37%, the acetic acid mixture 58%, and the piperidine mixture 78%.

The liberation of carbon dioxide during decomposition was established by passing the off-gases through protected aqueous barium hydroxide, and identifying the white precipitate as barium carbonate by x-ray diffraction. The gases coming off this peroxy carbamate contained a substance which was strongly alkaline to Brilliant Yellow test paper.

tert-Butyl *N*-methyl-*N*-(*p*-nitrophenyl)peroxy carbamate (No. 7). *N*-Methyl-*N*-(*p*-nitrophenyl)carbamoyl chloride, 6.32 g. (0.029 mole), dissolved in 650 ml. of petroleum ether was cooled in an ice bath to 5°, and 4.84 g. (0.032 mole) of 60% *tert*-butyl hydroperoxide was added. With vigorous agitation, 7.07 g. (0.037 mole) of 30% aqueous potassium hydroxide was added dropwise during 15 min., and stirring was continued for 2 hr. in the cold. Light yellow crystals, 3.5 g., were obtained by filtering the solids, washing four times with water, and drying in a vacuum desiccator containing anhydrous calcium chloride. By concentrating the petroleum ether solution 1.79 g. more of the product were recovered. Total quantity: 5.29 g. (yield: 68% based on the carbamoyl chloride). The compound was purified by recrystallizing from 600 ml. of petroleum ether warmed to 45° for a very short time. Data on this product are given in Table I. In order to maintain high purity, crystals of this compound must be kept cool at all times, around 0–5°. This compound has an absorption maximum at 295 $m\mu$ ($\epsilon = 12,000$ in isooctane).

Polymerization. Polymerization tests were made with freshly distilled styrene containing no inhibitor and freshly distilled chloroprene containing 2 parts per million of phenothiazine. Styrene was polymerized in 30 ml. screw-capped glass vials under conditions given in the text and in Table II. The polymers were isolated by precipitating and washing with methanol, and drying overnight in a vacuum oven at 50°.

Polystyrene containing substituted amino groups was prepared in the following way: 41.6 g. (0.4 mole) of styrene, 100 ml. of benzene, and 8.05 g. (0.05 mole) of *tert*-butyl *N,N*-dimethylperoxy carbamate were refluxed (90–91° max. temp.) under nitrogen for 6 hr. The charge was steam-distilled until 900 ml. of water had come over, and the polymer was washed with water and dried to constant weight at 80°. The water condensate was titrated with standard

TABLE II
BULK POLYMERIZATION OF STYRENE^a

| Temp., °C. | Catalyst Concn., Molar | Polymer Obtained, Grams | |
|---------------|------------------------------|-------------------------|----------------------------|
| | | Benzoyl peroxide | Com- pound ^b |
| 41 | 0 | 0.011 | 0.011 |
| | 2×10^{-4} | 0.023 | 0.070 |
| | 2×10^{-3} | 0.069 | 0.195 |
| 61 | 2×10^{-2} | 0.214 | 0.493 |
| | 0 | 0.058 | 0.058 |
| | 2×10^{-4} | 0.180 | 0.384 |
| 82 | 2×10^{-3} | 0.486 | 1.067 |
| | 2×10^{-2} | 1.574 | 2.820 |
| | 0 | 0.522 | 0.522 |
| | 2×10^{-4} | 1.385 | 1.216 |
| | 2×10^{-3} | 2.581 | 2.263 |
| | 2×10^{-2} | Solid | 3.900 |

^a Nine g. of freshly distilled styrene heated in the dark under nitrogen for 6 hr. ^b The compound is *tert*-butyl *N,N*-pentamethyleneperoxycarbamate.

hydrochloric acid to a phenolphthalein end point and found to contain 0.01 equivalent of base. The polymer, 32 g., was brittle and possessed the following properties: molecular weight by boiling point elevation of benzene, 2360; nitrogen by Dumas' method, 0.9%; nitrogen by titrating the amino groups with perchloric acid in benzene, 0.73%. The former value for the nitrogen content calculates to 1.5 amino groups per molecule, assuming that 2360 is the molecular weight of the polymer.

Since it was possible that amino-containing impurities had been occluded in the polystyrene, 12 g. of the polymer was dissolved in benzene and reprecipitated with methanol and this process was repeated three times in all. The final dry polymer weighed 5.6 g. and contained 0.85% nitrogen by Dumas method, indicating that the polymer molecules contained amino groups as substituents.

The polystyrene prepared under the same conditions without the initiator did not contain nitrogen.

Vigorous reactions. The following mixtures gave violent reactions: 1.8 g. ethyl isocyanate, 2.78 g. perbenzoic acid, 50 ml. benzene, and 4 drops triethylamine when most of the solvent had been removed under reduced pressure; 3.15 g. toluene-2,4-diisocyanate, 3.0 g. 60% *tert*-butyl hydroperoxide and 10 ml. benzene after standing at room temperature for 2 hr. Isolated products which spontaneously decomposed very rapidly at room temperature were obtained from the following reactions: 0.7 g. *p*-nitrophenyl isocyanate, 0.6 g. perbenzoic acid, 15 ml. benzene, and 1 drop triethylamine; 3.2 g. *p*-nitrophenyl isocyanate, 4.2 g. 72% α -cumyl hydroperoxide, 500 ml. petroleum ether, and 3 drops triethylamine. These mishaps did not cause any bodily harm because adequate protective measures had been taken ahead of time.

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WILMINGTON, DEL.

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND COMPANY, INC. ORGANIC CHEMICALS AND ELASTOMER CHEMICALS DEPARTMENTS, RESEARCH DIVISIONS]

Thermal Decomposition of Crystalline *tert*-Butyl *N*-Methyl-*N*-(*p*-nitrophenyl)peroxycarbamate

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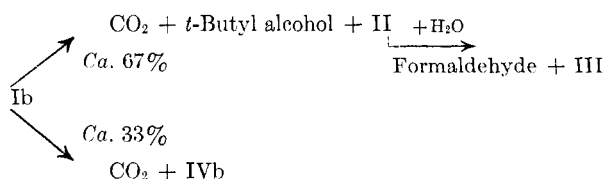
The decomposition of crystalline *tert*-butyl *N*-methyl-*N*-(*p*-nitrophenyl)peroxycarbamate at 30° proceeds by two different mechanisms: about 67% by an intramolecular concerted reaction giving carbon dioxide, *N*-methylene-*p*-nitroaniline, and *tert*-butyl alcohol; and the remainder by a homolytic scission followed by partial recombination of free radicals to give carbon dioxide and *O*-(*tert*-butyl) *N*-(*p*-nitrophenyl)hydroxylamine. The *N*-methylene-*p*-nitroaniline is rapidly converted to formaldehyde and *N,N'*-methylenebis(*p*-nitroaniline) by the moisture in the atmosphere.

This behavior is contrasted to that of crystalline *tert*-butyl *N*-(*p*-nitrophenyl)peroxycarbamate. The action of these compounds in aromatic solvents and styrene is briefly discussed.

During an investigation of the properties of the esters of *N*-substituted peroxycarbamic acids,¹ *tert*-butyl *N*-(*p*-nitrophenyl)peroxycarbamate, Figure 1, (Ia), and *tert*-butyl *N*-methyl-*N*-(*p*-nitrophenyl)peroxycarbamate, (Ib), were synthesized. Stability tests on the crystalline compounds stored in the open air at room temperature showed that Ia is rather stable, but Ib decomposes quietly and nearly completely to a yellow crystalline residue in about four days.

Identification of the products indicates that the

decomposition of crystalline Ib at 30° may be represented as follows:



Every product was definitely identified except II, but its transient existence was suggested by the infrared spectrum (C=N band present) of the residue obtained by decomposing Ib in the absence of

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