

Reactions of *t*-Butyl Peresters, XVIII

Peroxyester Reaction of *t*-Butyl N,N-Dimethylperoxyamidate

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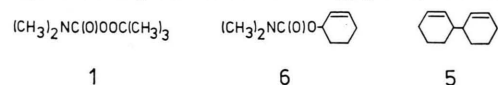
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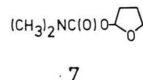
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Copper Ion Catalysis, Photochemistry of Perester, *t*-Butyl N,N-Dimethylperoxyamidate, N,N-Dimethylamidates, 2-Cyclohexen-1-ol

The thermal copper ion catalyzed peroxyester reaction of *t*-butyl N,N-dimethylperoxyamidate (**1**, R=N(CH₃)₂) with cyclohexene results in the formation of the corresponding N,N-dimethylamidate **6** in 20% yield, and 3,3'-dicyclohexenyl (**5**) in 40% yield. Under

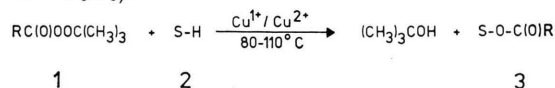


analogous conditions, the reaction of **1**, R=N(CH₃)₂, with tetrahydrofuran gives the corresponding amidate **7** in 6% yield. Only a 2% yield of **6** and no **7** were isolated in the

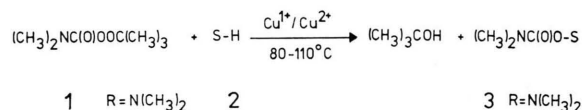


photochemical variant of the peroxyester reaction. Compound **6** is also obtained in a 12% yield from the reaction of 2-cyclohexen-1-ol (**9**) with N,N-dimethyl carbamoyl chloride (**4**) in the presence of pyridine.

Preparative aspects of the peroxyester reaction have been more recently reviewed [1, 2]. In the thermal peroxyester reaction, the interaction of peroxyester **1** with a suitable substrate **2** at 80 to 100 °C with catalysis by the copper ion redox system results, generally, in the formation of *t*-butyl alcohol and a product **3** containing the acyloxy moiety. In the past, reactions of preparative utility involved most often the relatively stable commercially available peroxyesters, *t*-butyl peroxyacetate (**1**, R=CH₃) and *t*-butyl peroxybenzoate (**1**, R=C₆H₅).

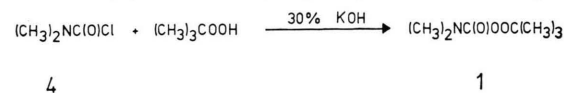


The ready preparation and relative stability of *t*-butyl N,N-dimethylperoxyamidate (**1**, R=N(CH₃)₂) prompted this investigation into the possible usefulness for the introduction of the N,N-dimethyl carbamoyloxy moiety into various organic compounds.



In the past [1-3], most frequently used model substrates for the peroxyester reaction included, among others, hydrocarbons containing activated hydrogen atoms, such as, cyclohexene, and ethers, such as, tetrahydrofuran.

Peroxyamidate **1** (R=N(CH₃)₂) of acceptable purity was prepared in molar quantities by an improvement of the procedure reported by Pedersen [4] utilizing the reaction of N,N-dimethyl carbamoyl chloride (**4**) with *t*-butyl hydroperoxide in the pres-



ence of aqueous potassium hydroxide. On shortening the reaction time from 22 h, as prescribed in literature [4], to 2 h, the yield of peroxyamidate **1** (R=N(CH₃)₂) was increased from 54% [4] to 84%. Unlike previously reported [4], we were unable to purify the peroxyamidate **1** (R=N(CH₃)₂) by distillation at 0.1 torr without a slight decomposition of **1**. However, the peroxyamidate **1** (R=N(CH₃)₂)

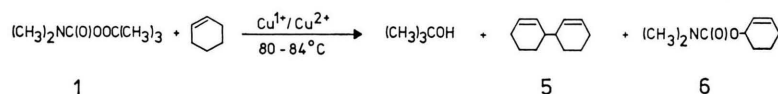
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was obtained in a sufficiently pure form to be used in subsequent reactions without the use of a distillation procedure.

In preliminary experiments, peroxyamidate **1** ($R = N(CH_3)_2$) was allowed to react under the conditions of the peroxyester reaction [1, 3, 5–7] with a number of substrates **2**, *i.e.*, cyclohexene, cumene, tetrahydrofuran, diethyl ether, dimethylformamide, which are known to give preparatively useful results with *t*-butyl peroxyacetate or *t*-butyl peroxybenzoate [1–3]. Attention was focused on the disappearance of the infrared carbonyl absorption of the peroxyamidate **1**, $R = N(CH_3)_2$, at $\nu \simeq 1740\text{ cm}^{-1}$ and the appearance of the infrared carbonyl absorption of the products at $\nu \simeq 1720\text{ cm}^{-1}$, and the extent of gas evolution. The carbon dioxide evolved during the reaction arises from the carbamoyloxy function, which is thus not available for the carbamoyloxylation reaction. No introduction

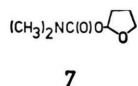
of the carbamoyloxy group was detectable with cumene, diethyl ether, or dimethylformamide. Only in the case of cyclohexene and tetrahydrofuran were we successful in isolating a significant amount of a carbonyl-containing product, and even with these substrates there was considerable evolution of carbon dioxide during the reaction. Furthermore, there was evidence that the carbonyl-containing product was not stable in the reaction mixture, since the carbonyl infrared absorption decreased as a function of time. As a result of these preliminary partly successful results, we decided to study the reaction in greater detail with cyclohexene and tetrahydrofuran.

In the thermal peroxyester reaction of **1** ($R = N(CH_3)_2$) with cyclohexene, the higher boiling products were 3,3'-dicyclohexenyl (**5**) in 40% yield, cyclohex-1-en-3-yl N,N-dimethylamidate (**6**) in 20% yield, as determined by gas chromatography.



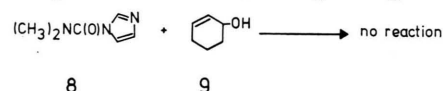
Considerable gas evolution was also evident. The evolved gas can be taken as an indication that, in addition to the desired copper ion catalyzed reaction, the conventional free radical decomposition of peroxyamidate **1**, $R = N(CH_3)_2$, is occurring, and, as a result, appreciable amounts of the dimer **5** are produced. Compounds **5** and **6** were not separable by distillation using a short unpacked column. However, pure amidate **6** was obtained using preparative gas chromatography on a 20% Carbowax column, 20 M on 60/80 chromosorb P. In the photochemical variant [8–10] of the peroxyester reaction, only a 2% yield of amidate **6** was formed.

In the case of tetrahydrofuran as the substrate, the thermal, copper ion catalyzed decomposition of peroxyamidate **1**, $R = N(CH_3)_2$ resulted in only a 6% yield of 2-(N,N-dimethyl carbamoyloxy)-tetrahydrofuran (**7**) after 1 h. No amidate **7** was isolated either on increasing the reaction time or on using the photochemical variant [8–10] of the peroxyester reaction.

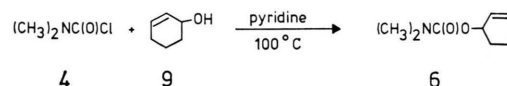


In order to have an authentic sample of **6**, the preparation of cyclohex-1-en-3-yl N,N-dimethyl-

amidate (**6**) by conventional methods was briefly investigated. In our preceding work [11–14], considerable success has been achieved in the phosphorylating of hydroxy compounds *via* imidazolides. Therefore, an attempt was made to apply the imidazole method to the preparation of amidate **6**. However, the reaction of compound **8** with 2-cyclohexen-1-ol (**9**) did not occur even at the elevated temperature of 60 °C, or on prolonged reaction time,



i.e., 3 days, probably because of the deactivating effect of the dialkylamino moiety. Amidate **6** was obtained in 20% yield by the reaction of 2-cyclohexen-1-ol (**9**) with N,N-dimethyl carbamoyl chloride (**4**) in excess of pyridine at 100 °C. Poorer yields of **6** resulted from experiments involving aqueous workup.



2-Cyclohexen-1-ol (**9**) [15] was prepared in 60% yield by the base hydrolysis of cyclohex-1-en-3-yl benzoate (**10**) [3, 5–7], using an aqueous sodium hydroxide solution. This method, utilizing the

rotating evaporator at 20–23 °C/45 torr, and then at 20–23 °C/0.1 torr to give a brown liquid (17.8 g). Quantitative gas chromatographic analysis indicated the presence of 3,3'-dicyclohexenyl (**5**; 6.8 g, 40%) and amidate **6** (6.8 g, 20%), together with other unidentified materials. Distillation at reduced pressure through an unpacked column afforded a fraction (11.8 g, b.p. 44–54 °C/0.15 torr) which contained only dicyclohexenyl (**5**) and amidate **6**. However, a pure sample of amidate **6**, free of dicyclohexenyl **5** could not be obtained by repeated distillation.

In another experiment, the concentration of the reaction mixture at 20–23 °C/0.1 torr resulted in a brown liquid (19.0 g), which on distillation gave a fraction (7.1 g) b.p. 40–50 °C/0.1 torr. Quantitative gas chromatographic analysis indicated that this fraction consisted of three components in a ratio of 1:3:21. Preparative gas chromatography resulted in a homogeneous sample of the major component (n_D^{25} 1.4734) which was identified as cyclohex-1-en-3-yl *N,N*-dimethylamidate (**6**; 6.0 g, 18%).

Analysis for $C_9H_{15}NO_2$

Calcd C 63.88 H 8.93 N 8.28 mol wt 169.22,
Found C 63.93 H 8.86 N 8.08 mol wt 173.

$\nu(C=O)$ 1720 cm^{-1} .

The NMR spectrum of the compound **6** was consistent with the proposed structure.

Cyclohexenyl H: δ 1.6–2.2 (m, 6H),
N(CH₃)₂: δ 2.82 (s, 6H),
allylic H: δ 5.08 (m, 1H),
vinylic H: δ 5.75 (m, 2H).

Photochemical peroxyester reaction of **1**, $R=N(CH_3)_2$, with cyclohexene

A mixture of peroxyamidate **1** ($R=N(CH_3)_2$; 32.2 g, 0.2 mol), copper(I) bromide (0.29 g, 0.002 mol), and dry cyclohexene (227.5 g, 2.77 mol) was irradiated under nitrogen for 4.5 d at room temperature until the peroxyamidate infrared carbonyl absorption (1740 cm^{-1}) could no longer be detected. Quantitative gas chromatographic analysis at this stage indicated the presence of 3,3'-dicyclohexenyl (**5**; 6.8 g, 42%) and cyclohex-1-en-3-yl *N,N*-dimethylamidate (**6**; 0.7 g, 2%).

In a blank experiment in which the copper salt was omitted, irradiation for 6 d was required before the peroxyamidate infrared carbonyl absorption (1740 cm^{-1}) could no longer be detected. Extensive tar formation occurred, necessitating frequent cleaning of the photochemical reactor. Quantitative gas chromatographic analysis at this stage indicated only the presence of 3,3'-dicyclohexenyl (**5**; 6.2 g, 38%). No amidate **6** was detected.

Hydrolysis of cyclohex-1-en-3-yl benzoate (**10**) [3, 5–7]

A vigorously stirred mixture of cyclohex-1-en-3-yl benzoate (**10**; 50 g, 0.25 mol) and aqueous sodium hydroxide (120 ml of a 30% w/v solution) was boiled for 24 h. On cooling, the reaction mixture solidified

to an ether-insoluble rubbery mass. Hot water (300 ml) was added to dissolve the mass. The cooled mixture was extracted with ether (4 × 100 ml). The combined ether layers were dried (CaSO₄) and filtered. The filtrate was concentrated on a rotating evaporator at 20–23 °C/10–15 torr to give the crude **9** (n_D^{25} 1.4869). The oil was distilled to give 2-cyclohexen-1-ol (**9**; 14.7 g, 60%), b.p. 34–36 °C/0.2 torr, n_D^{25} 1.4790; lit. [15] b.p. 85 °C/35 torr, n_D^{25} 1.4820. The material was homogeneous on gas chromatographic analysis, with satisfactory infrared and NMR spectra.

Reaction of 2-cyclohexen-1-ol (**9**) with *N,N*-dimethylcarbamoyl chloride (**4**) in the presence of pyridine

A mixture of 2-cyclohexen-1-ol (**9**; 10.8 g, 0.11 mol), *N,N*-dimethylcarbamoyl chloride (**4**; 10.8 g, 0.1 mol) and anhydrous pyridine (39.5 g, 0.5 mol) was heated for 6 h at 100 °C. After cooling to room temperature, the dark reaction mixture was shaken with ether (3 × 50 ml), each time separating the ether layer from the dense, black, ether-insoluble tar. The combined ether layers were passed through a 1.5 cm packing of alumina. The eluate was concentrated on a rotating evaporator at 20–23 °C/14 torr. The residue was distilled twice to give cyclohex-1-en-3-yl *N,N*-dimethylamidate (**6**; 2.1 g, 12%), b.p. 44.5 to 45.5 °C/0.05 torr n_D^{25} 1.4739. The NMR, infrared, and gas chromatographic data were identical to those of the material obtained from the peroxyester reaction.

Preparation of *N,N*-dimethyl-1'-imidazolyl carbamide (**8**)

A solution of *N,N*-dimethylcarbamoyl chloride (**4**; 2.16 g, 0.02 mol) in benzene (20 ml) was added dropwise at 20–23 °C to a suspension of imidazole (0.68 g, 0.002 mol) and triethylamine (2.20 g, 0.02 mol) in benzene (30 ml). Following the addition, the reaction mixture was stirred at room temperature for 20 h, then filtered. The filtrate was concentrated on a rotating evaporator at 20–23 °C/10–15 torr to give the pure **8** (2.6 g, 96%), the white solid melting at 36–37 °C (dec.).

Analysis for $C_6H_9N_3O$

Calcd C 51.79 H 6.52 N 30.20 mol wt 139.2,
Found C 51.88 H 6.50 N 29.91 mol wt 136.

Attempted reaction of *N,N*-dimethyl-1'-imidazolyl carbamide (**8**) with 2-cyclohexen-1-ol (**9**)

Carbamide **8** (5.56 g, 0.04 mol) and 2-cyclohexen-1-ol (**9**, 3.92 g, 0.04 mol) were allowed to react either a) in dioxan (30 ml) at 20–23 °C for 3 d, b) in dioxan (30 ml) at 60 °C for 20 h, or c) in nitromethane (20 ml) at 60 °C for 20 h. The reaction mixture was then analyzed by gas chromatography. At no time could any amidate **6** be detected.

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