Communications to the Editor

Chem. Pharm. Bull.
31(12)4578—4581(1983)

A NEW OXYGENATING METHOD USING 1-ALKOXYCARBONYL-1,2,4-TRIAZOLES AND HYDROGEN PEROXIDE RELATIVE REACTIVITY OF O-ALKYLPEROXYCARBONIC ACIDS

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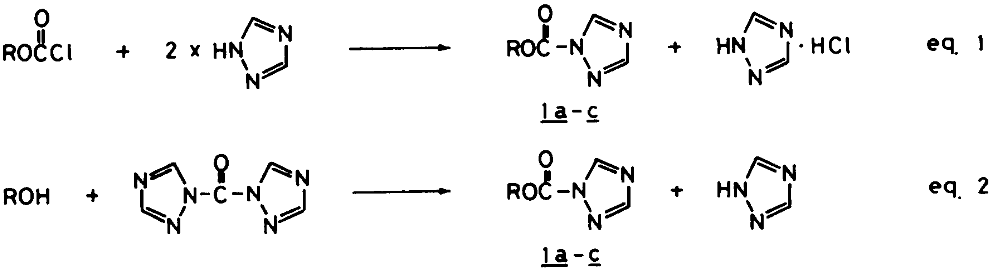
A convenient method is reported for the epoxidation of alkenes and the Baeyer-Villiger oxidation of a variety of carbonyl compounds using the 1-alkoxycarbonyl-1,2,4-triazoles (<u>1a</u>-<u>c</u>)/H_2O_2 system. The reactivities of the resulting peroxycarbonic acids were compared. O-Trichloroethylperoxycarbonic acid prepared in this way was isolated as a chloroform solution and was characterized spectroscopically.

KEYWORDS —— oxygenation with 1-alkoxycarbonyl-1,2,4-triazole/H_2O_2 system; peroxycarbonic acid; epoxidation; Baeyer-Villiger reaction

In a preceding paper we reported an epoxidation method with a variety of O-alkylperoxycarbonic acids generated by the reaction of N-alkoxycarbonylimidazoles and hydrogen peroxide.[2] Although this procedure facilitated convenient epoxidation of a variety of alkenes under mild conditions, the method had the disadvantage of requiring excess reagent (ca. three equivalents) to obtain a good yield. This paper reports an improved method for the preparation of peroxycarbonic acids and their reactivities towards alkenes, aldehydes and ketones.

Since the requirement of excess reagent in the oxidation by the imidazolide/H_2O_2 system was conceived to be due to decomposition of hydrogen peroxide or of peracid catalyzed by imidazole generated in the reaction system, the effect of various amines on the decomposition of hydrogen peroxide was examined as follows: Aq. H_2O_2 (35%) was kept stand at 40°C in the presence of 0.05

Chart 1



1a **1b** **1c**
R: C_2H_5 CCl_3CH_2 $(CF_3)_2CH$

molar equivalent of 1,2,4-triazole, pyridine, imidazole and triethylamine, respectively, in separate incubation tubes. The initial pH values of the solutions were found to be 4.43, 6.93, 7.91 and 8.92 respectively (the pH value of 35% aq. H_2O_2 was 2.28). Iodometric titration of the remaining peroxide after 5-hour incubation revealed that H_2O_2 decomposition in the presence of the respective amine were 5, 30, 58 and 90% and that the decomposition rates apparently followed the order of basicity of the solution. The same kind of catalytic effect by these amines on the decomposition of m-chloroperbenzoic acid (MCPBA) was also observed. These observations suggest that the 1-alkoxycarbonyl-1,2,4-triazole/H_2O_2 system could be a superior alternative to the imidazolide/H_2O_2 system as the oxygenation reagent, since such triazolides were expected to be as reactive as imidazolides towards nucleophiles.[3)]

1-Alkoxycarbonyl-1,2,4-triazoles (1a-c) were prepared according to the Chart 1 as in the case of the preparation of imidazolides.[2)] Such triazolides were stable enough to be stored at room temperature and were also stable to hydrolysis in the neutral aqueous solution, but they were very sensitive to perhydrolysis.

Epoxidation of alkenes by this method was carried out in the biphasic system in which 10 equivalents of 35% aq. H_2O_2 was added to the CH_2Cl_2 solution of a mixture of 1 equivalent of alkene and 1.2 equivalents of triazolide (1a, 1b or 1c) with stirring at room temperature. The results shown in the Table 1 demonstrate that even inert olefins such as β-methylstyrene and trans-stilbene were epoxidized in quantitative yields with 1b and that these triazolides can be very useful precursors of a variety of peroxycarbonic acids.

Chart 2

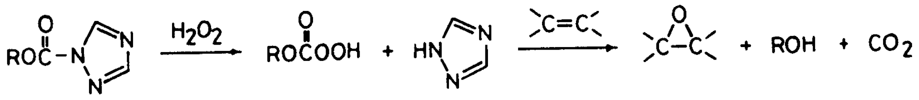


Table 1. Epoxidation of Alkenes with 1a-c/H_2O_2

Reagent	Alkene	Reaction time	Yield (%)
1a/H_2O_2	β-methylstyrene	8	100
	t-stilbene	6	72
1b/H_2O_2	β-methylstyrene	5	100
	t-stilbene	5	98
1c/H_2O_2	cholesteryl acetate	2	100 (64/36)[a)]

a) α-epoxide/β-epoxide ratio.

Since the biphasic oxygenating method using the triazolide/H_2O_2 system (also in imidazolide/H_2O_2 system) should conceivably follow the two step process as shown in the Chart 2, isolation of a peroxycarbonic acid was attempted. Triazolide 1b was thus treated with aq. H_2O_2 in $CHCl_3$ under ice cooling. The $CHCl_3$ layer was separated and was washed successively with cold water, dil. HCl and cold water to remove triazole. The $CHCl_3$ solution containing 2,2,2-trichloroethylperoxycarbonic acid was then dried over sodium sulfate. The IR spectrum of this solution exhibited carbonyl bands at 1920 cm^{-1} (shoulder) and 1807 cm^{-1}. The ^1H-NMR spectrum of this peracid prepared in the same way but in $CDCl_3$ showed two singlets at 4.90 and 4.86 ppm in an intensity ratio of about 3 : 2. In addtion to these signals, weak signals due to small amounts of impurities such as unreacted 1b and trichloroethanol were also observed. The signals at 4.90 and

4.86 ppm were both assigned to the methylene protons of the peracid. Occurrence of two such signals was explained by an equilibrium between two conformers with and without intramolecular hydrogen bonding, since the signal at 4.90 disappeared with the addition of CD_3OD. The peracid solution thus prepared epoxidized equimolar amounts of 1-methylcyclohexene quantitatively.[4)]

The Baeyer-Villiger reaction of a variety of aldehydes with 1b/H_2O_2 was studied. The reaction proceeded very smoothly affording the corresponding carboxylic acid and/or formate in high yields (Table 2). The acid/formate ratios were determined by gas chromatography. Although the yield of p-hydroxyphenol formate, the oxidation product of p-hydroxybenzaldehyde, was determined as p-hydroquinone because of unstableness of the formate, the reaction condition of this method was mild enough for the isolation of other unstable formates. Furthermore, this method was found to be quite useful specifically for the isolation of carboxilic acids, because the by-products, including formate, are neutral or basic compounds and the formed acids can be easily separated.

Table 2. Baeyer-Villiger Oxidation of Aldehydes with 1b/H_2O_2[a)]

RCHO	Yield (%)	RCOOH/ROCHO
n-C_3H_7CHO	100	100/0
C_6H_4CHO	100	100/0
p-$CH_3C_6H_4CHO$	90	26/74
p-$CH_3OC_6H_4CHO$	80	9/91
p-HOC_6H_4CHO	90	0/100
cyclohexyl-CHO	80	21/79

a) Aldehyde (1 eq) and 1b (1.2 eq)in CH_2Cl_2 and H_2O_2 (10 eq), stirring at r. t., overnight.

It was reported previously that the reaction of cyclohexanone with O-ethylperoxycarbonic acid prepared in situ from ethyl chloroformate and aq. H_2O_2 did not give a detectable amount of caprolactone.[5)] The reaction of cyclohexanone with 1b/H_2O_2, however, afforded caprolactone in quantitative yield. These facts suggeste a large effect of alkyl groups on the reactivity of peroxycarbonic acids. Chemoselectivity of O-ethyl and O-trichloroethylperoxycarbonic acid toward olefin and ketone was, therefore, compared with that of MCPBA using bicyclo[3,2,0]hept-5-en-2-one (2) as the substrate. This compound has both olefinic and ketonic moieties and the latter (cyclobutanone group) is known to be very susceptible to Baeyer-Villiger oxidation by peracids .

The result shown in the Table 3 demonstrated that MCPBA, did indeed, preferentially oxidize the carbonyl group. The peroxycarbonic acids prepared by the triazolide/H_2O_2 method, however, showed significant structural effect. In spite of the higher reactivity of 2,2,2-trichloroethylperoxycarbonic acid to cyclohexanone compared with ethylperoxycarbonic acid, the former reacted with olfinic linkage in a higher ratio than the latter and MCPBA, affording the epoxides 4 and 5 as the major products. Such a structural effect could provide further possibility for the chemoselectivity of these peroxyacids by variation of the alkyl group of the triazolides (1).

It should be noted that the triazolide/H_2O_2 method can self-oxidize in a polyfunctional compound possessing a hydroxy group and other functional groups in the same molecule. To demonstrate such a reaction 1-cytronelloxycarbonyl-1,2,4-triazole (7) prepared from citronellol (6) and N,N'-carbonyl-di-1,2,4-triazole in CH_2Cl_2 was treated with aq. H_2O_2 (Chart 4).

Chart 3

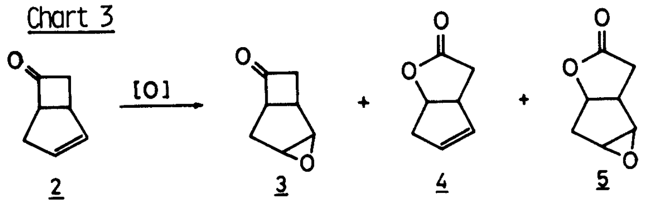


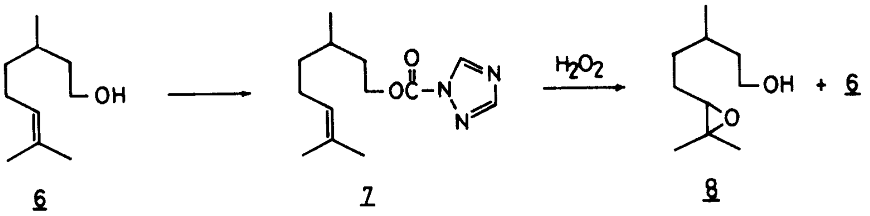
Table 3. Reaction with Compound 2

Chemoselectivity towards Alkene and Ketone

Reagent	Product ratio		
	3	4	5
MCPBA	1.4	95.3	2.8
1a/H_2O_2	9.4	69.3	21.3
1b/H_2O_2	31.3	28.0	40.7

Substrate-reagent ratio was 1 : 1.

Chart 4



Triazolide 7 was rather inert to perhydrolysis and reacted slowly. After 30-hour of stirring the reaction solution containing 100 mg of 7 in 2 ml of CH_2Cl_2 and 0.5 ml of 35% aq. H_2O_2, the compound 7 was converted completely yielding the epoxide 8 (82%), citronellol (6) (12%) and unidentified products. The epoxide 8 could have been formed by either intra- or inter-molecular pathways but the process has not been clarified yet.

REFERENCES AND NOTES

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(Received July 12, 1983)