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3,5-Dinitroperoxybenzoic Acid. A Crystalline, Storable Substitute for Peroxytrifluoroacetic Acid

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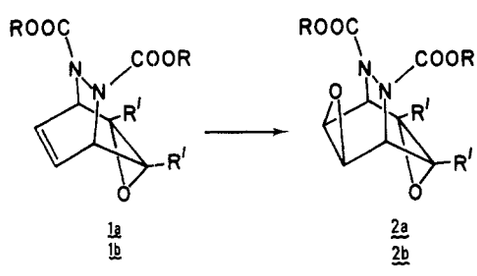
Epoxidations and Baeyer-Villiger oxidations by 3,5-dinitroperoxybenzoic acid (3,5-DNPBA) are described. A preparation of 3,5-DNPBA is also given.

In the course of our syntheses of *sym*-oxepin oxides[1a-d] we were required to effect the difficult epoxidations of olefins **1a** and **1b**. Neither peroxytrifluoroacetic acid epoxidation nor high-temperature epoxidation by *m*-chloroperoxybenzoic acid proved preparatively useful in these systems. Under optimized conditions only low conversions of **1a** and **1b** to the corresponding epoxides could be achieved with peroxytrifluoroacetic acid. Buffered (Na_2CO_3 or Na_2HPO_4) peroxytrifluoroacetic acid reaction mixtures gave, at best, intractable mixtures of starting material, desired epoxide, and unidentified by-products.[2] Treatment of the parent system **1a** with 4,4′-thiobis(6-*tert*-butyl-3-methylphenol) (tbp)[3] stabilized *m*-chloroperoxybenzoic acid at elevated temperatures led to tarry reaction mixtures and low yields of diepoxide **2a**.[1a] Clean, efficient epoxidation of **1a** was achieved using *p*-nitroperoxybenzoic acid, stabilized by tbp,[3] in 1,2-dichloroethane at 90 °C (yield of crystalline **2a**, 65%).[1a] With the substituted derivative **1b**, however, the optimized yield utilizing *p*-nitroperoxybenzoic acid did not exceed 37%.[2] We have found that 3,5-dinitroperoxybenzoic acid (3,5-DNPBA) is an efficient reagent for achieving the conversion **1b** → **2b** (vide infra).[4] Herein we report on the synthetic utility of 3,5-DNPBA for difficult epoxidations and Baeyer-Villiger oxidations.



1a, **1b** **2a**, **2b**

1a and **2a**, R = CH_2CCl_3; R′ = H
1b and **2b**, R = CH_2CCl_3; R′, R′ = $-CH_2CH_2CH_2-$

Results and Discussion

To test the utility of 3,5-DNPBA we have chosen as substrates **1a**, **1b**, and several other olefins or ketones for which literature oxidation procedures exist. Our results and a summary of literature oxidations are presented in Table I. An inspection of the table suggests that 3,5-DNPBA is not as reactive as peroxytrifluoroacetic acid (e.g., compare concentrations and reaction times for ethyl crotonate) but shows that yields for oxidations by these two peroxy acids are comparable.

It should be noted that similar weights of precursor per mole of peroxy acid are needed for 3,5-DNPBA and peroxytrifluoroacetic acid. The procedure for generation of methylene chloride solutions of peroxytrifluoroacetic acid[5] utilizes trifluoroacetic anhydride (mol wt 210.03) and hydrogen peroxide; buffers are routinely utilized to remove the trifluoroacetic acid which is also formed. By our procedure, crystalline samples of 3,5-DNPBA with active oxygen content >90% can be easily made from 3,5-dinitrobenzoic acid (mol wt 212.12).

Advantages of 3,5-DNPBA over peroxytrifluoroacetic acid are (1) no buffers are needed in 3,5-DNPBA oxidations and (2) 3,5-DNPBA can be stored for long periods without significant loss of active oxygen content. We have routinely stored 3,5-DNPBA in a freezer (<−10 °C) for periods up to 1 year without noticeable loss of reactivity. A more quantitative measure of the loss of active oxygen content from samples of 3,5-DNPBA and peroxytrifluoroacetic acid is given in Table II. At least some loss of active oxygen content from peroxytrifluoroacetic acid solutions is due to evaporation of the volatile peroxy acid. At ambient temperature sufficient evaporation occurs from an approximately 0.2 M solution of peroxytrifluoroacetic acid in methylene chloride to give an immediate, positive KI/starch test at the top of an ice–water cooled spiral condenser attached to a flask of the solution. Our studies of loss of active oxygen content from peroxytrifluo-

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Table I. Oxidations by 3,5-DNPBA and Other Peroxy Acids

substrate/ peroxy acid/ additive	product	registry no.	equiv of peroxy acid	g of substrate/ amount of solvent	reaction time/ temp, °C	yield, %/ purification (lit. ref)
1a[e]/3,5-DNPBA[o]/ 1 wt % tbp[a]	**2a**	66511-15-7	3.78	0.237/1.0 mL ($ClCH_2CH_2Cl$)	55 min/75	52/crystallized
1a/*p*-nitroperoxybenzoic acid[p]/ 1 wt % tbp[a]	**2a**		3.97	2.39/7.5 mL ($ClCH_2CH_2Cl$)	2.5 h/90	65/crystallized (ref 1a)
1b[f]/3,5-DNPBA/ 1 wt % tbp[a]	**2b**	66402-64-0	4.06	2.58/12.0 mL ($ClCH_2CH_2Cl$)	1 h/75	59/crystallized
1b/*p*-nitroperoxybenzoic acid/ 1 wt % tbp[a]	**2b**		4.25	0.116/0.45 mL ($ClCH_2CH_2Cl$)	2 h/93	37/crystallized
1-octene[g]/ 3,5-DNPBA	1-octene oxide	2984-50-1	1.14	2.28/40.0 mL (CH_2Cl_2)	2 h/ambient temp	87/vacuum transferred[b]
1-octene/ CF_3CO_3H[h]/Na_2CO_3	1-octene oxide		1.50	22.4/250 mL (CH_2Cl_2)	30 min/reflux	87/distilled (ref 5)
1-decene[i]/ 3,5-DNPBA	1-decene oxide	2404-44-6	1.20	13.9/200 mL (CH_2Cl_2)	1.0 h/ice bath and 2.5 h/ ambient temp	80/distilled[c]
1-decene/ CH_3CO_3H	1-decene oxide		1.20	42/408 g of 0.9 M solution (CH_3COOH)	28 h/ambient temp	56/distilled (ref 6)
methyl methacrylate[j]/ 3,5-DNPBA	methyl α-methyl glycidate	58653-97-7	1.14	2.04/40 mL (CH_2Cl_2)	7.75 h/reflux	80/vacuum transferred[b]
methyl methacrylate/ CF_3CO_3H/ Na_2HPO_4	methyl α-methyl glycidate		1.25	20.0/250 mL (CH_2Cl_2)	30 min/reflux	84/distilled (ref 5)
ethyl crotonate[k]/3,5-DNPBA	ethyl β-methyl glycidate	19780-35-9	1.13	2.36/40 mL (CH_2Cl_2)	9.5 h/reflux	87/vacuum transferred[b]
ethyl crotonate/ CF_3CO_3H/ Na_2HPO_4	ethyl β-methyl glycidate		1.25	22.8/250 mL (CH_2Cl_2)	30 min/reflux	73/distilled (ref 5)
ethyl acrylate[l]/ 3,5-DNPBA	ethyl glycidate	4660-80-4	2.19	10.0/200 mL ($CHCl_3$)	8.0 h/reflux	79/distilled[c]
ethyl acrylate/ CF_3CO_3H Na_2HPO_4	ethyl glycidate		2.25	20.0/300 mL ($ClCH_2CH_2Cl$)	30 min/reflux	54/distilled (ref 5)
methyl cyclopropyl ketone[m]/ 3,5-DNPBA/ 1 wt % tbp[a,d]	cyclopropyl acetate	4606-06-8	2.50	15.4/366 mL ($CHCl_3$)	12.0 h/reflux	59 (GC yield) 53/distilled[c]
methyl cyclopropyl ketone/ CF_3CO_3H/ Na_2HPO_4	cyclopropyl acetate		2.00	16.8/300 mL (CH_2Cl_2)	1.0 h/reflux	53/distilled (ref 7)
BENZOPHENONE[n]/ 3,5-DNPBA/ 1 wt % tbp[a]	phenyl benzoate	93-99-2	2.50	3.72/51 mL ($ClCH_2CH_2Cl$)	3.5 h/reflux	87 (crude yield) 70/recrystallized (mp 68.5–69.5 °C)
benzophenone/ CF_3CO_3H/ Na_2HPO_4	phenyl benzoate		1.50	36.4/200 mL (CH_2Cl_2)	1.0 h/reflux	86 (crude yield, mp 65–67 °C) (ref 7)

[a] tbp is an abbreviation for 4,4′-thiobis(6-*tert*-butyl-3-methylphenol); see ref 3. [b] Product vacuum transferred with residual solvent at ambient temperature/P < 0.1 mmHg; ^1H NMR shows only the indicated product and residual solvent; yield determined by ^1H NMR. [c] Product >95% pure by GC and ^1H NMR. [d] This oxidation done prior to the peroxy acid stability study summarized in Table II; addition of tbp may not be necessary. [e] Registry no. 66511-146. [f] Registry no. 66358-47-2. [g] Registry no. 111-66-0. [h] Registry no. 359-48-8. [i] Registry no. 872-05-9. [j] Registry no. 80-62-6. [k] Registry no. 10544-63-5. [l] Registry no. 140-88-5. [m] Registry no. 765-43-5. [n] Registry no. 119-61-9. [o] Registry no. 66358-48-3. [p] Registry no. 943-39-5.

roacetic acid/methylene chloride solutions contradict Emmons' original finding[8] that "such a solution [concentration not given] lost essentially no active oxygen during a reflux period of 24 h."

Caution: All peroxy acids are potentially explosive. Oxidations using 3,5-DNPBA or the preparation of the peroxy acid should be conducted with adequate shielding and reaction temperatures should be carefully monitored. We have not been able to detonate 3,5-DNPBA by impact, nor have we experienced any problems during 3,5-DNPBA oxidations. We

Table II. Loss of Active Oxygen from Samples of 3,5-DNPBA and Peroxytrifluoroacetic Acid

3,5-DNPBA[d]			peroxytrifluoroacetic acid[c]		
storage or treatment	physical state	remaining fraction of active oxygen[a]	storage or treatment	physical state	remaining fraction of active oxygen[a]
114 days, <−10 °C	crystalline	93.5/93.5	2 h, reflux; straight bore condenser	0.210 M in CH_2Cl_2	0.189/0.210
16 days, ambient temp	crystalline	92.8/93.5	2 h, reflux; ice–water cooled spiral condenser	0.205 M in CH_2Cl_2	0.196/0.205
80 days, ambient temp	crystalline	84.0/93.5		0.205 M in CH_2Cl_2	0.193/0.205
2 h, reflux	1 M in $CHCl_3$	79.0/93.5	2 h, reflux; straight bore condenser	0.703 M in CH_2Cl_2	0.560/0.703
2 h, reflux	1 M in $CHCl_3$, 1.5 wt % tbp[b]	79.0/93.5		0.750 M in CH_2Cl_2	0.583/0.750
2 h, reflux	1 M in $ClCH_2CH_2Cl$	7.5/93.5		0.698 M in CH_2Cl_2	0.535/0.698
2 h, reflux	1 M in $ClCH_2CH_2Cl$, 1.5 wt % tbp[b]	32.5/93.5	24 h, ambient temp; sealed vessel	2.87 M in CH_2Cl_2	1.82/2.87
				2.95 M in $CHCl_3$	2.60/2.95
				2.94 M in $ClCH_2CH_2Cl$	2.31/2.94
			24 h, refrigerator (+5 °C); sealed vessel	1.50 M in CH_2Cl_2	1.32/1.50

[a] Percentage of active oxygen determined by iodometric titration. [b] tbp is an abbreviation for 4,4′-thiobis(6-*tert*-butyl-3-methylphenol); see ref 3. [c] Solutions of peroxytrifluoroacetic acid prepared by the method in ref 5. [d] Initial sample 93.5% active oxygen.

have deliberately detonated a 200-mg sample by heating the peroxy acid to just above its melting point (mp ~112 °C) (see also the caution outlined in ref 9).

Experimental Section

General. Melting points were determined in a capillary apparatus (Mel-Temp) and are uncorrected. Gas chromatographic analyses of reaction products were done on a ⅛ in. × 8 ft aluminum column packed with 4.1% SE-30 on Chromosorb G. ^1H NMR spectra (60 MHz) were determined in $CDCl_3$ or $CDCl_3/CD_3OD$ solution (Me_4Si internal standard) on an Hitachi Perkin-Elmer R-24B or on a Varian T-60 spectrometer; IR spectra were determined on a Perkin-Elmer 567 grating infrared spectrophotometer.

For the preparation of 3,5-DNPBA, Aldrich (99%) 3,5-dinitrobenzoic acid was used without further purification; methanesulfonic acid was obtained from Aldrich (98%) or from Eastman (White Label); hydrogen peroxide (90%) was obtained from FMC Corp. Chlorinated solvents were purified by passage through basic alumina immediately prior to use. Iodometric titrations were done by the method of Silbert et al.[10] For solid 3,5-DNPBA samples, the peroxy acid was directly dissolved in acetic acid, omitting dissolution in benzene as indicated in ref 10.

Preparation of 3,5-Dinitroperoxybenzoic Acid (3,5-DNPBA). Our procedure is adapted from the method of Silbert, Siegel, and Swern[11] for the preparation of aliphatic and aromatic peroxy acids. 3,5-Dinitrobenzoic acid (81.90 g, 0.386 mol) and methanesulfonic acid (177 g) were mixed in a three-neck round-bottom flask[12] equipped with a thermometer, a mechanical stirrer, and a nitrogen inlet. Hydrogen peroxide (90% by weight) (40 mL; approximately 1.5 mol) was added in one portion with stirring under nitrogen. The reaction was maintained at 50 °C[13] for 2 h and 50 min and then cooled to 0 °C with an ice/salt bath. With external cooling still applied, crushed ice (120 g) was slowly added (temperature rose to 25 °C). The reaction mixture was cooled to 0 °C and the nearly white crystals of 3,5-DNPBA were collected by suction filtration through sintered glass. The peroxy acid was dried in a vacuum desiccator (yield, 79.8 g, 91%; active oxygen content 93.5%, determined by iodometric titration; ^1H NMR ($CDCl_3/CD_3OD$) δ (Me_4Si) 4.83 (br s, exchangeable proton), 8.82 (m, 2 H), 8.98 (m, 1 H); IR (Nujol mull) 1758, 1738, 1540, 1342 cm^{-1}). A small sample heated in a capillary apparatus melts at 113–115 °C with gas evolution, resolidifies, then remelts at 195–200 °C. A sample prepared by the above method without further purification and containing 95.0% active oxygen (by iodometric titration) was analyzed by combustion analysis: calculated for 95% $C_7H_4N_2O_7$ + 5% $C_7H_4N_2O_6$: C, 37.00; H, 1.78; N, 12.33. Found: C, 37.00; H, 1.93; N, 11.70.

Oxidations with 3,5-DNPBA. Two representative procedures are given.

Epoxidation of 1b by tbp[3]-Stabilized 3,5-DNPBA. Crystalline **1b** (3.001 g containing 14 wt % benzene, 5.01 mmol), 3,5-DNPBA (5.014 g, 92.5% active oxygen, 20.33 mmol active oxygen), and tbp[3] (54.3 mg) were thoroughly mixed and dried in high vacuum overnight. A thick-walled glass tube was charged with the mixture and with 1,2-dichloroethane (12.0 mL). The tube was flushed with nitrogen, sealed, and heated at 75 °C for 1 h. The reaction mixture was cooled to 0 °C and filtered through sintered glass with a $CHCl_3$ wash (40 mL). The resulting solution was washed with 20% aqueous $NaHSO_3$ (2 × 25 mL), saturated aqueous $NaHCO_3$ (3 × 25 mL), and saturated aqueous NaCl (3 × 25 mL). The organic layer was dried ($MgSO_4$), rotary evaporated to a yellow oil, and re-evaporated from benzene (twice) and from Et_2O, giving an off-white foam. Trituration with Et_2O (3.0 mL) and refrigeration overnight induced crystallization. Collection and drying of the white crystals (mp 137–139 °C) and similar crystallization of the mother liquors yielded 1.66 g of diepoxide **2b**. ^1H NMR of crystalline **2b** shows 94% diepoxide and 6% incorporated benzene; yield of **2b**, 59%.

Epoxidation of Ethyl Acrylate by 3,5-DNPBA. Ethyl acrylate (10.0 g, 0.10 mol) was added to $CHCl_3$ (200 mL) followed by a single portion of 3,5-DNPBA (52.0 g, 96.2% active oxygen, 0.22 mol active oxygen). The mixture was mechanically stirred and brought to reflux for 8 h. The reaction mixture was cooled with an ice bath, diluted with CH_2Cl_2 (100 mL), and filtered through sintered glass with CH_2Cl_2 wash (4 × 50 mL). The resulting solution was washed with 20% aqueous $NaHSO_3$ (1 × 100 mL) and the separated organic layer was drawn off. The aqueous phase (a suspension containing some organic layer) was diluted with an equal volume of saturated aqueous $NaHCO_3$, cautiously mixed, and the remainder of the organic layer was withdrawn. The combined organic layers were washed with saturated aqueous $NaHCO_3$ (3 × 100 mL, solid NaCl added to last wash), dried ($MgSO_4$), filtered, and distilled (105–108 °C (87 mmHg)) yielding 9.20 g (79%) of colorless ethyl glycidate.

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Registry No.—tbp, 96-69-5.

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(13) The temperature of the reaction mixture should be carefully monitored. If the mixture is heated above 53 °C a steady rise in the internal reaction temperature may be seen. The exotherm may lead to frothing, spillage, and peroxy acid batches with low active oxygen content.

Cyanohydrin Synthesis of 2,3-Dihydroxy-2,3-dimethylbutanoic Acid

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From 3-hydroxy-3-methyl-2-butanone (**1**) via cyanohydrin synthesis and subsequent hydrolysis, the intermediates 2,3-dihydroxy-2,3-dimethylbutanonitrile (**2**), 3-chloro-1,2-dihydroxy-2,3-dimethylbutanimine hydrochloride (**3**), 3-chloro-1,2-dihydroxy-2,3-dimethylbutanamide (**4**), and 2,3-dihydroxy-2,3-dimethylbutanamide (**5**) have been isolated en route to 2,3-dihydroxy-2,3-dimethylbutanoic acid (**6**). Compound **2** reverted to **1** in the presence of base. In aqueous NaOH or NaOMe in Et_2O, compounds **3** and **4** gave (by HCl abstraction) 2,3-epoxy-1-hydroxy-2,3-dimethylbutanimine (**7**), tautomeric with 2,3-epoxy-2,3-dimethylbutanamide (**8**). Acid hydrolysis of **2** (at 40–50 °C) led principally to **5**, but at higher temperatures to 3-methyl-2-butanone (**9**) via a pinacol–pinacolone type rearrangement involving the intermediates 2,2-dimethyl-3-oxobutanamide (**10**) and 2,2-dimethyl-3-oxobutanoic acid (**11**), which decarboxylates spontaneously to **9**. In the acid hydrolysis of **2** to obtain **5** and **6** directly, substantial amounts of the byproduct 2-hydroxy-2,3-dimethyl-3-butenoic acid (**12**) were encountered; better yields of the desired products were obtained when the dihydroxynitrile (**2**) was first treated with 2 mol of acetic anhydride per mole to form its diacetate and somewhat diluted hydrochloric acid was used in lieu of saturated aqueous HCl.

Interest in the effects of adding a second methyl group to the β-carbon atom of 2,3-dihydroxy-2-methylbutanoic acid on the acid ionization constant and the chelating properties of the ligand moiety prompted an attempt to synthesize 2,3-dihydroxy-2,3-dimethylbutanoic acid from 3-hydroxy-3-methyl-2-butanone (via a route used in preparing 2,3-dihydroxy-2-methylpropanoic acid and 2,3-dihydroxy-2-methylbutanoic acid from acetol and acetoin precursors, respectively[1,2]). After several failures to obtain the expected amide and acid from unisolated cyanohydrin, using standard procedures, it was decided to perform a step-by-step isolation (by ion-exclusion chromatography and anion exchange when appropriate) of the various intermediates, in order to ascertain at what point the process failed.

While no one (to date) has reported the synthesis of either 2,3-dihydroxy-2,3-dimethylbutanamide (DHDMB amide) or DHDMB acid, Cantacuzène and Ricard[3] prepared the corresponding DHDMB nitrile by acid hydrolysis (dilute H_2SO_4) of 2,3-epoxy-2,3-dimethylbutanonitrile and reported its ^1H NMR spectra in $CDCl_3$, benzene, and DMF and its IR spectrum in CCl_4. Since they failed to obtain the nitrile in crystalline form, only its boiling point [130 °C (15 Torr)] was given.

It was immediately ascertained that DHDMB nitrile could be prepared in good yield from the KCN-catalyzed combination of 3-hydroxy-3-methyl-2-butanone and excess liquid HCN (the reaction temperature being controlled at ~30 °C by refluxing of the HCN). The cyanohydrin (DHDMB nitrile) was readily obtained as a white crystalline solid (mp 67–69 °C) from ethyl acetate, whose ^1H NMR spectrum in $CDCl_3$ coincided with the liquid prepared by Cantacuzène and Ricard[3] from 2,3-epoxy-2,3-dimethylbutanonitrile. Typical of cyanohydrins, our DHDMB nitrile yielded the original ketone and NaCN (instantaneously and quantitatively) when treated with excess aqueous NaOH.

Acid hydrolysis of the DHDMB nitrile posed a problem in that undesired dark byproducts were obtained copiously at elevated temperatures, and conversion of the nitrile was inordinately slow in concentrated hydrochloric acid or dilute acid at room temperature. When the nitrile was dissolved in hydrochloric acid and saturated with HCl gas below 35 °C (a standard procedure), the tertiary 3-hydroxyl was replaced by chloride, and 3-chloro-1,2-dihydroxy-2,3-dimethylbutanimine hydrochloride (rather than the expected DHDMB amide) resulted. This hydrochloride (upon recovery and washing with ether) decomposed spontaneously at room temperature (over a 24-h period) to the corresponding 3-chloro-2-hydroxy-2,3-dimethylbutanamide by evolving HCl.

Dilute (~1 M) aqueous solutions of 3-chloro-2-hydroxy-2,3-dimethylbutanamide (CHDMB amide) slowly generate H_3O^+ via hydrolysis (replacement of the tertiary –Cl by –OH). The resulting DHDMB amide then presumably undergoes very slow hydrolytic conversion to DHDMB acid. At temperatures as low as 80 °C, when either CHDMB amide or DHDMB amide is hydrolyzed in dilute HCl, CO_2 is evolved at an appreciable rate and the major product isolated (and positively identified by its ^1H NMR spectrum) is 3-methyl-2-butanone. The characteristic odor of this ketone could be detected after a day even in conversions carried out at 45 °C. Isolation of 2,2-dimethyl-3-oxobutanamide (mp 120–122 °C),[4] whose oxime melts at 162–164 °C,[5] in the acid hydrolysis of both CHDMB amide and DHDMB amide indicates that DHDMB amide readily undergoes a pinacol–pinacolone type of rearrangement. As the resulting 2,2-dimethyl-3-oxobutanamide hydrolyzes to 2,2-dimethyl-3-oxobutanoic acid, decarboxylation of this unstable substance occurs. The chief product obtained is 3-methyl-2-butanone.

If 3-chloro-2-hydroxy-2,3-dimethylbutanamide in aqueous solution is treated with excess base, abstraction of HCl, rather than replacement of –Cl by –OH, occurs. An epoxyhydroxy-

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