CHAPTER V

Silica-Gel Supported Peracetic Acid Reagent

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Abstract —— The oxidation of carbon-carbon double bond with silica gel-peracetic acid reagent has been investigated. It provides a simple and convenient method for the preparation of epoxides in high yields.

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1. INTRODUCTION

The impetus provided by our earlier work[1] prompted us to investigate the preparation of similar reagent for the purpose of epoxidation. Epoxidation procedures are widely distributed in literature and a selection of a suitable one is often difficult. Here emphasis has been made on the use of better known and readily accessible peracid, i.e. peracetic acid.

The discovery that the oxiranes can be prepared from ethylenic compounds by oxidation with an organic peracid is generally credited to Russian Chemist, Prileschajew,[2] who demonstrated that perbenzoic acid can be used for the conversion of a double bond to the oxirane. Since then peracids have been used most extensively for the selective oxidation of carbon-carbon double bonds. The most useful reagents[3] in this group are performic acid, peracetic acid, trifluoroperacetic acid, perbenzoic acid, monoperphthalic acid, m-chloroperbenzoic acid and p-nitroperbenzoic acid. Due to one reason or another, they have their own advantages and disadvantages.[3] For example, performic acid is an unstable peracid even at low temperature and in concentrated form is a hazardous compound and is rarely isolated. Therefore its use as an oxidizing agent has its own limitations and is evident that performic acid is not usually the epoxidation reagent of choice. Whereas trifluoroperacetic acid is extremely high-speed oxidation reagent and therefore has found wide spread use with negatively substituted unsaturated compounds that undergo epoxidation slowly with usual peracids (perbenzoic acid, peracetic acid and monoperphthalic acid). However, epoxidations with trifluoroperacetic acid need particular care because trifluoroacetic acid, the reaction product of peracid, is a strong acid and the initially formed epoxide is cleaved by this acid to diol monoester.[3] Another reagent that has been employed in the preparation of oxiranes is monoperphthalic acid which offers only minor advantages in most reactions when the epoxidation requires a long period of time for completion, and the greatest stability of monoperphthalic acid[4] compared to perbenzoic acid is an advantage. The most convenient peracids to use are m-chloroperbenzoic acid and p-nitroperbenzoic acid which are commercially available and exceptionally stable at room temperature. p-Nitroperbenzoic acid is five to twenty times more reactive than perbenzoic acid,[5] whereas m-chloroperbenzoic acid is only slightly more reactive[6] and has decided advantages in some cases where isomerization must he avoided.

Peracetic acid is the peracid of choice in chemical industry, however, peracetic acid is not being much used in the laboratory for usual epoxidation procedure chiefly because of its instability. The present work was undertaken to see if peracetic acid can be supported on an inorganic support such as silica gel in such a way that its keeping quality is improved. Such a reagent would also be convenient from the handling point of view. Of course, it was anticipated that such a reagent will possibly leach out from the solid support into the solvent in which the epoxidation reaction will be carried out. Hence, peracetic acid-on-silica gel will be essentially a means for storage and handling of peracetic acid. However, since the solvents normally used for epoxidation are invariably immiscible with water, this reagent would furnish an essentially anhydrous solution of peracetic acid in the solvent used for epoxidation.

In the following pages, the preparation of such a reagent and its use in the epoxidation of olefin is reported, however, the stability of the reagent leaves much to be desired.

2. RESULTS AND DISCUSSIONS

2.1 Peracetic acid-on-silica gel

The reagent was initially prepared by addition of a known volume of peracetic acid to a known weight of silica gel[7] (silica gel/AcO_2H= 5: 1). It was soon found that such a preparation is quite labile and rapidly deteriorates even at 0°C of storage temperature. Thus the need to make this reagent more stable for practical purposes was obvious. It was envisaged that inorganic salts originally present in the silica gel as impurities might be the cause of deterioration of peracetic acid and it was thought reasonable to give water washings to silica gel to improve keeping quality. This, however, only slightly improved the keeping quality of the reagent. Next we considered chemical treatment such as exposure of silica gel to phosphoric acid[8] (aq. 5% v/v), sulphuric acid (aq. 5% v/v) or sodium hydroxide (aq. 5%, w/v). However, this also did not prove much helpful. Further investigations revealed that sodium tripolyphosphate[8] treatment or ethylene diaminetetraacetic acid treatment of silica gel considerrably improved the storage life of the reagent (Table 1).

As a result of the above work, we came to the following conclusions:

TABLE 1. Silica gel supported Peracetic acid

Effect of concentration of sodium tripolyphosphate soln. and temp. on the stability of AcO_2H-on-SiO_2

No.	SiO_2	Sodium tripoly-phosphate (%,soln.)	SiO_2/ AcO_2H ratio	Storage temp. °C	Estimation of AcO_2H (%) on silica gel										
					0.25h	24h	48h	72h	96h	120h	144h	168h	240h	360h	480h
1.	-80,+200 mesh	1	5:1	10	54	29	18	12.5	11	6.5	5	3.5	1	-	-
				0		34	26	21	19	17	14	13	8.5	2.0	-
2.	"	2	5:1	10	54	28	23	18	11	8	5.5	5	3	-	-
				0		37	34	32	31	28.5	26	25	20	9	-
3.	"	3	5:1	10	54	29	19	12.5	10.5	6.5	5	4	3	-	-
				0		37	33	30	28.5	28	25	23	18	11	-
4.	"	5	5:1	10	54	37	30	26	21	17	15	14	9	2.7	-
				0		49.5	45.5	43	41	39	37	35	30	24	20
5.	EDTA treated	5	5:1	0	54	50	47	44	41	39	37	35	28	19.5	14

(i) It was necessary to give hot water wash to silica gel and

(ii) soaking of silica gel over sodium tripolyphosphate solution (aq. 5% w/v) prior to the adsorption of peracetic acid on silica gel.

Therefore, finally water washed and sodium tripolyphosphate (aq. 5% w/v) treated silica gel was chosen as a support and used throughout this work. The reagent was prepared by addition of peracetic acid on silica gel as described above (for details see Experimental). It was also observed from iodometric titration[9] of peracetic acid supported silica gel that there was no substantial loss of peracetic acid during the adsorption procedure. This preparation (see Experimental) was fairly stable for about a fort-night at 0°C. This was used for epoxidation of a variety of olefins. Table 2 lists compounds that have been epoxidized with silica gel supported peracetic acid reagent. The reaction is carried out by simply stirring the olefin with the reagent (in equimolar proportions in terms of peracid) in chloroform at 20-25° for 4 hr. Work-up of the reaction is simple and is outlined under Experimental. It was found that consumption of peracetic acid is substantially complete in 4 hr when only 1.0-1.1 mole of peracetic acid/mole of double bond is employed, 90-95% of the theoretical quantity

TABLE 2. Epoxidation of olefins[a] with peracetic acid-on-SiO_2

No.	Olefin	Moles	Reaction conditions		Yield[b] (%)	Purity of epoxide (%,GLC)
		AcO_2H/olefin	Temp. °C	Time (hr)		
1.	3-Carene	5.3:5	20-25°	4	92	98
2.	Limonene	"	20-25	4	88	98
3.	3-Menthene	"	20-25	4	92	97
4.	4(8)-Menthene	"	20-25	3.5	90	98
5.	Dihydromyrcene	"	20-25	4	82	95
6.	Pulegone	"	20-25	4	88	97
7.	Styrene	"	20-25	4	90	98
8.	Camphene	"	0-5	24	87	92
9.	Longifolene	"	0	1.5	34	37

[a] Reaction was done on a 5 mmole scale.

[b] Represents isolated product, after distillation.

of peracetic acid being consumed.[10] The product isolated consisted of oxirane compounds containing only small amount of unreacted olefin. The reaction was shown to be general and afforded a simple and convenient method for the preparation of a number of epoxides. For most of the epoxides prepared, the yields were very good except in the case of longifolene where steric compression at C_3 in the epoxide is relieved by its isomerization to aldehyde[10] and is the cause of poor yield.

In the course of our systematic study, we had occasion to perform epoxidation of different types of olefins. The greatest problem in the oxidation with aqueous peracetic acid is not to effect the oxidation but to isolate the reaction products in a sufficiently pure state, since further reaction frequently occurs between the epoxide and acetic acid[11,12]. Sometimes buffer is used to suppress this reaction. Surprisingly, no such reaction products or rearranged products with our silica gel supported reagent were isolated, though rearrangement of epoxides over silica gel is well known.[13]

3. EXPERIMENTAL

For general remarks see Chapter II under Experimental.

All reaction products described in this Chapter are known compounds. These compounds were distilled, purity checked by GLC and their identification established by IR and PMR.

3.1 Materials

Silica gel: See preceding Chapters.

Sodium tripolyphosphate, EDTA, Sodium hydroxide, were all reagent grade.

Peracetic acid was prepared in this laboratory.

All solvents were distilled prior to use.

All olefins were available from this laboratory only.

3.2 Water washed silica gel

Commercial silica gel (-80, + 200 mesh) was repeatedly washed with boiling water (100 ml x 5 for every 100 g of silica gel) till washings were sulfate free (barium chloride test). The product was filtered, washed with distilled water and then with alcohol. It was dried in air and activated at 120-130^{0}/6 hr.

3.3 Ethylenediaminetetraacetic acid(EDTA) treated silica gel

Water washed silica gel was kept covered with EDTA solution (1%, 50 ml for 25 g of silica gel), with occasional shaking (24 hr). The silica gel was filtered, washed with water (25 ml x 3), dried and activated as above.

3.4 Sodium tripolyphosphate treated silica gel

Water washed silica gel (50.0 g) was soaked with 5% aqueous solution of sodium tripolyphosphate (100 ml) and left aside for 24 hr at room temperature (30 ± 2^{0}). At the end of this period, silica gel was filtered and dried in oven at $90^{0}/2$-3 hr which yielded 52 g of the material.

3.5 Sodium hydroxide supported silica gel

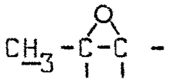
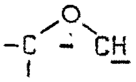
Silica gel (45.0 g) was added to a solution of NaOH (5.0 g; 0.125 mole in 50 ml water) and the mixture shaken mechanically for 1 hr at room temperature. After this the excess water was removed on rotary evaporator ($90^{0}/80$ mm, ½ hr) to get 51.0 g of white free-flowing powder. One gram of this preparation ≡ 0.098 g of NaOH (≡ 2.45 mmole of NaOH).

3.6 Preparation of reagent

3.6.1 Peracetic acid on silica gel: Sodium tripolyphosphate treated silica gel (50.0 g) was taken in a 250 ml three-necked round bottomed flask equipped with a mechanical stirrer and thermometer and cooled to 0°C. Cold peracetic acid (0°C, 10 ml, w% = 54.0) was added to silica gel with stirring in such a way that the temperature of pot maintained at 0°C (3-5 minutes). After stirring for another ten minutes at 0°, the whole thing was transferred into a brown bottle (yield; 60.0 g) and stored at 0°C. The colour of this free-flowing reagent was faint yellow. One gram of this reagent is equivalent to 0.09 g of peracetic acid (≅ 1.1842 mmole of peracetic acid).

3.7 Epoxidation of 3-carene

A typical example

To an ice cold ($\sim 10^{\circ}$), stirred solution of 3-carene (0.68 g; 5 mmole) in chloroform (10 ml), silica gel supported peracetic acid reagent (4.5 g; 5.32 mmole of peracetic acid) was added. There was slight rise in temperature. The mixture was allowed to attain to room temperature ($20\text{-}25^{\circ}$) and stirring was continued for 4 hr at the same temperature. The solids were removed by suction filtration and washed well with hexane (5 ml x 2). The filtrate and washings were mixed and stirred with sodium hydroxide supported silica gel (2.0 g) at 20-25°. This was again filtered and the filtrate gave negative test with starch-iodine. The solvent was removed from filtrate by distillation through a Vigreux column and the residue was purified by distillation; b.p. 100°(bath)/10 mm; n_D^{30} 1.4612, yield 0.7075 g(glc purity, 98%) (Lit.[14], b.p. 92-93°/23 mm; n_D^{20} 1.4664). IR; 840, 1000, 1070, 1210, 1380 and 2910 cm^{-1}. PMR: gem-dimethyl (3H, singlets at 0.7 and 1.0 ppm);  $\mathrm{C\underline{H}_3{-}\overset{O}{\widehat{C{-}C}}{-}}$ (3H, singlet, 1.17 ppm);  $\mathrm{-\overset{O}{\widehat{C - C\underline{H}}}}$ (1H, broad singlet, 2.62 ppm). (Lit.[15]: PMR).

4. REFERENCES AND NOTES

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