

Chemical Modification of Wool in Aprotic Swelling Media

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Synopsis

A limited number of polar, nonhydroxylic organic liquids are suitable swelling media for chemical modification of wool. An effective medium for acylating-type internal modification should have low molecular weight, should lack active hydrogen atoms, be highly polar, swell wool fibers, have a high boiling point, and exert a catalytic effect. Rates of modification by phenyl isocyanate, myristoyl chloride, and dodecenylsuccinic anhydride in different media decrease in the order dimethyl sulfoxide > dimethylformamide > 1-methyl-2-pyrrolidinone > 4-butyrolactone. Nevertheless, equal maximum uptake of a given reagent in these varied media is evidence of internal chemical modification. Further examples of modifying reagents are phenyl isothiocyanate, benzyl chlorides, and α -haloketones. Supercontraction and single-fiber stress-strain data indicate crosslinking by bifunctional isocyanates and acid chlorides.

INTRODUCTION

Wool contains reactive hydrogen atoms on groups such as amino, guanidino, hydroxyl, and carboxyl. These functional groups are potentially able to react with acylating and related reagents, e.g., acid chlorides, acid anhydrides, and isocyanates. This paper deals with such reactions when carried out in certain organic liquids, in particular, dimethylformamide (DMF),^{1,2} dimethyl sulfoxide,³ 1-methyl-2-pyrrolidinone,⁴ and 4-butyrolactone⁵ (Table I). In addition to presenting new data, this report reviews and generalizes past publications⁶⁻¹⁰ and patents.¹¹⁻²¹ Emphasis is given to (1) comparing reaction rates in the above four liquids, (2) criteria for internal chemical modification rather than surface reactions or deposits, and (3) comparing monofunctional with bifunctional reagents and the effects of crosslinking.

The amino acid chains of the wool molecule are held together laterally by electrostatic forces, hydrogen bonds, and disulfide crosslinks. This structure usually prevents easy penetration of all but a few small molecules. Unless penetration occurs, only a very small fraction of the reactive functional groups can be attacked. Chemical modification and internal modification, as the terms are used here, refer to conditions where penetration does occur, i.e., to internal reaction with a substantial fraction of the potentially reactive groups.

Many experiments have shown that (aside from the smallest molecules) undiluted isocyanates, active halides, and acid anhydrides do not chemically modify wool in 1 hr at 105°C. Although these active reagents occasionally form surface

TABLE I
Properties of Some Aprotic Swelling Media

Medium	Structure	Molecular weight	Boiling point, °C	Dipole moment, D	Dielectric constant	Reference
DMF	$\text{HCON}(\text{CH}_3)_2$	73	153	3.8	37	1,2
Dimethyl sulfoxide	$(\text{CH}_3)_2\text{SO}$	78	189	4.3	45	3
1-Methyl-2-pyrrolidinone	$\text{CH}_2\text{N}(\text{CH}_3)_2\text{CO}$	99	202	4.1		4
4-Butyrolactone	$\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}$	86	204	4.1	39	5

deposits such as polymers, they cannot by themselves penetrate into and react with wool's functional groups. Furthermore, internal modification cannot be achieved with hot solutions of these reagents in most organic solvents.

Effective chemical modification of keratinous proteins, including wool, was first achieved in hot pyridine.²²⁻²⁵ In recent years, a few other organic liquids that promote internal modification have been discovered (Table I). These liquids do not have the very offensive odor of pyridine, and are generally cheaper and less toxic. These liquids also have a much lower vapor pressure than pyridine and allow rapid chemical modification above 90°C with less danger of fire or toxic vapors.

EXPERIMENTAL

The fabric was undyed wool flannel, 7-8 oz/yd². It was exhaustively extracted in a Soxhlet apparatus with ethyl ether followed by ethanol, then dried at 105°. Most reagents were Eastman highest-purity chemicals. Hexamethylene diisocyanate was from the Carwin Co. and Ott Chemical Co.; dodecanedioyl chloride was from Trubek Laboratories, redistilled. The aprotic swelling media were high grade, commercial: DMF (du Pont Co.), dimethyl sulfoxide (Crown Zellerbach Corp.), and methylpyrrolidinone and 4-butyrolactone (General Aniline & Film Corp.). For the comparative rate experiments, these media were purified by distillation at reduced pressure.

Most treatments were done under anhydrous conditions by the "Petri dish technique."⁷ Dried fabric circles, 8-9 cm, were treated with reagent and swelling medium. After treatment and extraction of solvent and excess reagent, the fabric was dried at 105°C. Prior to drying, the final extraction before and after treatment was with ethanol. While it is not possible to remove completely a solvent as large as ethanol by drying at 105°C, procedure controls indicate that the weight increases are accurate with 1-2%. Per cent uptake was calculated as one hundred times increase in dry weight divided by original dry weight.

RESULTS AND DISCUSSION

Characteristics of Modification Media

What are the essential characteristics of a suitable medium (Table I) for chemical modification of wool with acylating type reagents?

1. Since penetration of wool by large molecules is extremely slow,²⁶ the medium should have a relatively low molecular weight.

2. The medium should not contain active hydrogen atoms, since these might react with the acylating agent. Unfortunately, this condition eliminates some

common swelling agents: water, ethanol, and formic acid. Correspondingly, it is generally desirable to use dried wool and anhydrous media.

3. The medium should also be highly polar or have a high dielectric constant. I believe this is important in reducing electrostatic attractive forces within the wool molecule. A high dielectric constant assists the medium in penetrating the keratin structure. The reagent dissolved in the medium is thereby carried to the site of the reactive groups.

4. One of the essential qualities of a suitable medium is its ability to swell wool. The first and third criteria, low molecular weight and high polarity, are such as to promote the swelling of wool. The degree of fiber swelling is very important in controlling the rate of reaction. Any water in the medium and/or wool can cause much more rapid swelling than in a dry system. To some extent, the rate of modification in different media may parallel the rate of swelling in these media. Swelling in such media has been measured on single wool fibers by microscopy.^{27,28} In addition, specific interactions of wool, medium, and reagent may influence the reaction.

5. The medium should have a high boiling point. If the medium is volatile, it is difficult to get a temperature high enough to break the salt linkages, hydrogen bonds, and other noncovalent forces that restrict penetration.

6. Finally, analogous reactions of simpler molecules suggest that an effective medium should have a catalytic effect on some of the reactions.^{2-5,29}

There are probably exceptions to the above criteria. For example, pyridine has a rather low dielectric constant, namely, 12. Moreover, conditions may sometimes be selected to internally modify wool in spite of competing reaction with active hydrogen atoms in the medium. For instance, wool has been chemically modified with acid anhydrides in acetic acid.¹⁶

The descriptive term "aprotic swelling medium" refers to a liquid of Table I or an analogous substance (e.g., pyridine, dimethylacetamide). "Aprotic" specifies absence of reactive protons in these liquids; more precisely, they are "dipolar aprotic."²⁹ The term "swelling" has been tested in some cases.^{27,28} Finally, "medium" rather than "solvent" denotes a heterogeneous rather than a homogeneous reaction.

DMF is often the medium of choice for rapid reaction and to obtain a quality product. Dimethylacetamide (not listed),² mol. wt 87, bp 165°C, dipole moment 3.8 D, dielectric constant 38, is also effective, but is more expensive than DMF and is usually somewhat less active. Dimethyl sulfoxide is usually the most active medium and has low toxicity. However, it can penetrate the skin and may carry dissolved chemicals with it. In addition, it can also supercontract wool.⁶ For the latter reason, and because side reactions are more common, it often gives poorer products than DMF. Moreover, treatments with active halides in dimethyl sulfoxide were avoided because explosions can occur.³⁰

Methylpyrrolidinone is somewhat less active than DMF and also more expensive; on the other hand, it has the advantage of higher boiling point and lower toxicity. The chemically related 4-butyrolactone, although cheaper, is much less active. The five-membered ring makes 4-butyrolactone stable relative to β -propiolactone, which reacts readily with wool.³¹ The effects of these media on the mechanical properties and chemical resistance of wool have been described.³² Ethylene carbonate (not listed), mol. wt 88, bp 248°C, dipole moment 4.6 D, dielectric constant 95, has limited activity.³³

Effect of Medium on Rate

Phenyl Isocyanate. Comparative rates of reaction in different media are illustrated with phenyl isocyanate in Table II. The data at 70°C show that dimethyl sulfoxide is the most active medium, while DMF ranks second. The uptakes at 70°C and 105°C show that methylpyrrolidinone ranks third. Butyrolactone is the least active medium; it requires 1 hr at 105°C for 33% uptake.

Especially noteworthy, the maximum weight uptake (about 38%) is the same in all four media. The rate of modification varies with the medium, but the uptakes level off at the same maximum. Since the media vary widely in structure, it is very likely that the reaction product involves only wool and phenyl isocyanate. Since phenyl isocyanate is in large excess, it appears to be reacting stoichiometrically with specific wool sites. Some sites have been identified by analysis of enzyme hydrolysates.³⁴

Acid Chlorides and Anhydrides. Media comparisons for myristoyl chloride (Table III) show that dimethylacetamide is about as effective as DMF. The order of decreasing medium effectiveness—DMF>methylpyrrolidinone>4-butyrolactone—is the same for myristoyl chloride as for phenyl isocyanate. Although Table III suggests that the maximum weight uptake of myristoyl

TABLE II
Rate of Phenyl Isocyanate Uptake in Various Media^a

Temperature, °C	Reaction time, hr	% Uptake in indicated medium			
		Dimethyl sulfoxide	DMF	Methylpyrrolidinone	Butyrolactone
70	1.0	36	14		
	2.0	36	29	3	4
	6.0			4	4
80	2.0			6	3
	6.0			23	6
105	.25	35	33	32	
	.50	36	38	34	6
	1.0	37	38	38	33 ^b

^a Dry fabric (1.3 g), 2 ml phenyl isocyanate, 3 ml medium.

^b 38% Uptake in 4.0 hr.

TABLE III
Rate of Myristoyl Chloride Uptake in Various Media^a

Temperature, °C	Reaction time, hr	% Uptake in indicated medium			
		Dimethyl acetamide	DMF	Methylpyrrolidinone	Butyrolactone
70	2.0	20	22	9	3
	6.0	27	26	17	4
105	0.5		27 ^b	30 ^b	
	1.0	27			30 ^c

^a Dry fabric (1.3 g), 2 ml myristoyl chloride, 4 ml medium.

^b Erratic results at 105°C for both DMF and methylpyrrolidinone, maximum about 35% in both media.

^c 33% Uptake in 2.0 hr.

chloride is about 35%, independent of the medium used, the results are less clear-cut than for phenyl isocyanate. The data illustrate that minor competing reactions of a degradative nature occur to a varying degree depending on modifying agent, medium, impurities, and temperature.

The uptake of myristoyl chloride, about 1.67 mmole/g wool, could be from reaction with primary amino groups, 0.21 mmole/g wool, and aliphatic hydroxyl groups, 1.46 mmole/g wool. As expected for stoichiometric reactions, higher maximum weight uptakes are generally obtained as molecular weight increases in a homologous series of acid chlorides.³⁵

A further comparison of media is shown for dodecenylsuccinic anhydride (Table IV). The order of decreasing activity parallels that of phenyl isocyanate and myristoyl chloride: dimethyl sulfoxide > DMF > methylpyrrolidinone > butyrolactone. Unexpectedly, butyrolactone is essentially ineffective.

Internal Modification in DMF

The preceding experiments illustrate a major criterion of chemical modification, namely, a maximum uptake. Accordingly, there is a maximum amount of phenyl isocyanate that will react with a given amount of wool, despite a large

TABLE IV
Rate of Dodecenylsuccinic Anhydride Uptake in Various Media^a

Temperature, °C	Reaction time, hr	% Uptake in indicated medium			
		Dimethyl sulfoxide	DMF	Methylpyrrolidinone	Butyrolactone
70	2.0	27 ^b	14	4	2
	6.0		21	6	4
80	6.0			10	1
	0.5	29	19		
105	1.0	29	23	21	2 ^c

^a Dry fabric (1.3 g), 2 ml dodecenylsuccinic anhydride, 4 ml medium.

^b 22% Uptake in 1 hr.

^c 4% Uptake in 2.0 hr, 105°C; 3% uptake in 2.0 hr, 120°C.

TABLE V
Modification by Phenyl Isothiocyanate^a

Phenyl isothiocyanate, ml	DMF, ml	Reaction time, hr	Uptake, %
5	0	2.0	1
4	1	2.0	3
1	4	2.0	5
2	4	1.0	11
4	2	2.0	14
2	4	2.0	17
2	3 ^b	2.0	18
2	3	3.0	20

^a Dry fabric (1.2–1.3 g) treated at 105°C.

^b Samples with an equal volume of butyl acetate, chlorobenzene, or xylene instead of DMF gave 1–2% uptake.

excess of reagent. If phenyl isocyanate were forming an insoluble deposit, for example, by trimerization or by some reaction with the medium, there would not be an invariant upper limit. Further evidence for internal modification is that the maximum uptake is roughly that calculated from the expected reactive groups in wool.²³

Phenyl Isothiocyanate. Phenyl isocyanate was compared with phenyl isothiocyanate, its sulfur analog. Maximum weight uptake with phenyl isothiocyanate in dimethyl sulfoxide was 17% in 2 hr at 105°C. Table V shows a maximum weight uptake (20%) for a 2-to-3 ratio of phenyl isothiocyanate to DMF. Not only is modification by phenyl isothiocyanate slower than by phenyl isocyanate, but the maximum weight uptake is slightly more than one half as high. On a molecular basis, the difference in uptake is even greater, 1.48 mmole/g wool for phenyl isothiocyanate, which is slightly less than one half of 3.18 mmoles/g for phenyl isocyanate. The lower maximum suggests that phenyl isothiocyanate reacts with fewer wool groups than phenyl isocyanate. Correspondingly, isothiocyanates are generally less reactive than isocyanates.

Benzyl Halides and α -Haloketones. If a halomethyl group is attached to an aromatic nucleus, the halogen atom is active. Such compounds, commonly the benzyl halides,¹⁷ will react with labile hydrogen atoms. Table VI shows a high degree of reaction over a wide range in ratio of α -chlorotoluene (benzyl chloride) to DMF, with a maximum weight uptake of 9%. The results suggest

TABLE VI
Modification by α -Chlorotoluene^a

α -Chlorotoluene, ml	DMF, ml	α -Chlorotoluene- to-DMF ratio	Uptake, %
0	6.0	0	1
1.0	5.0	0.2	7
2.0	4.0	0.5	8 ^b
3.0	3.0	1.0	8.5
4.0	2.0	2.0	9
5.0	1.0	5.0	9
6.0	0		1.5

^a Dry fabric (1.2 g) treated 1.5 hr at 105°C.

^b This α -chlorotoluene-DMF ratio gave 5% uptake in seven days, 25°C, and 7% uptake in 4 hr, 60°C.

TABLE VII
Modification by 2,4'-Dibromoacetophenone, BrC₆H₄COCH₂Br^a

Temperature, °C	Reaction time, min	Uptake, %
28	3 days	17
60	30	12
	60	19
	240	20
	105	10
105	20	20
	30	21
	45, 60, 90, 120	22

^a Dry fabric (1.1 g), 1.0 g reagent, 10 ml DMF.

that α -chlorotoluene, which is usually less reactive, reacts with fewer wool groups than phenyl isocyanate. A higher molecular weight compound, *p*-bromo- α -chlorotoluene (1 g) in DMF (6 ml) for 1.0 hr at 105°C, gave a higher weight uptake, 14%. On a molar basis, the corresponding uptake values are much closer, 0.71 mmole/g wool for α -chlorotoluene and 0.68 mmole/g wool for *p*-bromo- α -toluene.

Another class of active halides, with a halomethyl group attached to a carbonyl group, are α -haloacetophenones (phenacyl halides).¹⁴ Modification with 2,4'-dibromoacetophenone (α,p -dibromoacetophenone, *p*-bromophenacyl bromide) in DMF (Table VII) goes slowly but to a high degree (17%) even at 28°C. At 105°C, reaction is rapid and levels off at 22% in 45 min. Since the α -haloketone is in large excess, the overall data indicate stoichiometric reactions with wool.

Dilution of aprotic swelling media with common solvents is usually impractical because modification is too slow. However, 2,4'-dibromoacetophenone (1 g) in 2 ml DMF and 5 ml chlorobenzene for 30 min at 105°C gave 22% uptake. The haloketone and chlorobenzene alone (10 ml) gave only 1.6% uptake.

Although α,p -dibromoacetophenone has two bromine atoms, only the α -bromocarbonyl group is active. 2-Bromoacetophenone (α -bromoacetophenone, phenacyl bromide, Table VIII), with no bromine atom in the benzene ring, gives 14% uptake with 0.3 g haloketone and 15% with 0.5 g. The lower maximum for 2-bromoacetophenone (15%) than for 2,4'-dibromoacetophenone (22%) reflects the difference in molecular weights (199 versus 278). Maximum weight uptake generally increases with molecular weight of modifying agent because stoichiometric reactions are involved. Nevertheless, the maximum molar uptake will probably decrease if the molecule becomes too large to penetrate the wool structure.

TABLE VIII
Modification by 2-Bromoacetophenone, C₆H₅COCH₂Br^a

Reaction time, hr	Uptake, %	
	0.3 g Reagent	0.5 g Reagent
0.5	14	
1.0	14	15
1.5	14	15
2.0		15

^a Dry fabric (1.2 g), reagent, 10 ml DMF, 105°C.

TABLE IX
Modification by 2-Chloro-4'-phenylacetophenone, C₆H₅C₆H₄COCH₂Cl^a

Reaction time, hr	% Uptake for reagent weight shown		
	1.0 g	2.0 g	3.0 g
0.50	10	9	14
0.75	14	14	
1.0	14		16
1.5	15	16	17
2.0	16		

^a Dry fabric (1.1 g), reagent, 10 ml DMF, 105°C.

Modification with 2-chloro-4'-phenylacetophenone (*p*-phenylphenacyl chloride) in DMF is shown in Table IX. There is only a slight increase in uptake (to 17%) with threefold increase of haloketone concentration.

Diisocyanates. The reaction of wool with hexamethylene diisocyanate in DMF is shown in Table X. Up to 14% uptake, there is almost complete utilization of diisocyanate (0.9 fractional weight uptake). At 1.5 hr, uptakes increase to 36% with 0.8 ml diisocyanate, but go no higher than 46% through 2.0 ml. These reactions are primarily chemical modification, since uptake increases very slowly above 0.8 ml diisocyanate. Nevertheless, uptakes at 1.5 hr do not have a sharp upper limit, indicating some other factor, probably polymerization of hexamethylene diisocyanate. Whitish deposits or very stiff sections of fabric at very high uptake are visible evidence of a surface-type side reaction. Polymerization of diisocyanates is well known.

Crosslinking

Certain properties of wool can be markedly affected if the modifying agent introduces additional crosslinks.³⁶ Wool fibers normally supercontract in some environments, e.g., they will contract to less than their original length when boiled in dilute aqueous NaHSO₃, which breaks the disulfide linkages. Addition of new stable crosslinks often prevents supercontraction by stabilizing the molecular structure. Since monofunctional reagents sometimes introduce protective groups that prevent supercontraction, it is desirable to compare the bifunctional reagent with a corresponding monofunctional reagent.

This comparison has been made for isocyanates and acid chlorides (Table XI). In each case, supercontraction of the monofunctional reagents, 22% and 23%,

TABLE X
Hexamethylene Diisocyanate Wool Treatments^a

Hexamethylene diisocyanate, ml	Fractional weight uptake ^b	Reaction time, hr	Uptake, %
0.10	.93	1.5	7.6
0.12	.94	1.5	9.3
0.15	.83	1.5	10.1
0.20	.88	1.5	14.2
0.30	.77	1.5	18.7
0.60	.64	1.5	32
0.80	.54	1.5	36
1.0	.46	1.5	39 ^c
1.0	.54	2.0	45 ^c
1.2	.43	1.5	46 ^c
1.2	.56	3.0	57 ^d
1.5	.35	1.5	45 ^c
1.5	.54	3.0	69 ^d
2.0	.27	1.5	44

^a Dry fabric (1.2–1.3 g), reagent, 5.0 ml DMF, 105°C.

^b Weight gain of sample divided by weight of hexamethylene diisocyanate (density = 1.043) used.

^c Slightly coated fabric.

^d Moderately coated fabric.

is almost as high as that of untreated wool, 24%. The bifunctional reagents, on the other hand, almost stop supercontraction (0.4% and 4%). These data are good evidence for crosslinking by bifunctional reagents.

Wet single-fiber properties have also been examined for crosslinking. New crosslinks often increase molecular constraints, an effect shown in Table XII. The two monofunctional reagents have essentially the same extension at break, 39% elongation, as untreated wool, 40%. There is a dramatic lowering of extension, to 18%, for fibers treated with bifunctional reagents. Since stress (force to stretch or break) increases with fiber strain (elongation), it is reasonable that fibers treated with bifunctional reagents also have a lower stress at break. The stress drops from 6.4 to 3.1 g/tex for the isocyanates, and from 5.1 to 2.8 g/tex for the acid chlorides. The data strengthen the evidence for crosslinking previously shown by supercontraction.

CONCLUSIONS

A limited number of polar, nonhydroxylic organic liquids are suitable swelling media for anhydrous chemical modification of wool. Rates of modification in these media decrease in the order dimethyl sulfoxide > DMF > methylpyrrolidi-

TABLE XI
Fiber Supercontraction by Monofunctional Versus Bifunctional Reagents

Reagent ^a	Formula	Uptake, %	Super- contraction, ^b %
None (untreated wool)			24
Octyl isocyanate	CH ₃ (CH ₂) ₇ NCO	20	22
Hexamethylene diisocyanate	OCN(CH ₂) ₆ NCO	19	0.4
Lauroyl chloride	CH ₃ (CH ₂) ₁₀ COCl	19	23
Dodecanedioyl chloride	ClOC(CH ₂) ₁₀ COCl	20	4

^a Conditions selected for nearly equal uptake at 105°C: (1) 1 ml octyl isocyanate, 5 ml DMF, 20 min; (2) 0.3 ml hexamethylene diisocyanate, 5 ml DMF, 90 min; (3) 2 ml lauroyl chloride, 4 ml DMF, 10 min; (4) 1 ml dodecanedioyl chloride, 5 ml DMF, 20 min.

^b Fibers removed from fabric and steamed 1 hr in 5% NaHSO₃.

TABLE XII
Wet Single-Fiber Properties for Monofunctional Versus Bifunctional Reagents

Reagent ^a	Uptake, %	Extension at break, ^b %	Stress at break, ^b g/tex
None (untreated wool)		40.4 ± 2.9	7.0 ± 0.6
Octyl isocyanate	20	39.5 ± 5.8	6.4 ± 1.1
Hexamethylene diisocyanate	19	18.3 ± 6.0	3.1 ± 0.7
Lauroyl chloride	19	39.3 ± 3.0	5.1 ± 0.7
Dodecanedioyl chloride	20	18.4 ± 8.1	2.8 ± 0.6

^a Treatment as in Table XI footnote.

^b Fibers removed from fabric, tested under water at 21°C, with constant extension rate of 1/2 in./min using 1-in. gauge length. Values show 95% confidence limits.

none>4-butyrolactone. Although reaction rate varies in these media, the final wool-reaction products are similar and do not include the medium. An effective medium for acylating-type internal modification of wool should have low molecular weight, lack active hydrogen atoms, be highly polar, swell wool fibers, have a high boiling point, and exert a catalytic effect.

From present data and literature references, evidence for internal chemical modification and stoichiometric reactions of acylating-type reagents with wool in aprotic swelling media is (1) fairly sharp upper limits to the weight uptakes of a variety of modifying reagents independent of the amount of reagent, provided the amount is above that required for maximum uptake; (2) equal maximum uptake of a given modifying agent in media of varied chemical structure; (3) reasonable agreement between the maximum experimental uptakes and maxima calculated from known reactions and percentages of reactive wool groups; (4) increase of maximum weight uptake corresponding to increase in molecular weight in a homologous series of modifying agents; (5) expected analytical values for per cent nitrogen and sulfur in modified samples, and a decrease in amino nitrogen values; (6) effect of bifunctional reagents on supercontraction, peracetic acid-ammonia test,¹⁰ and single-fiber mechanical properties in accord with wool crosslinking reactions; (7) marked changes in resistance to chemical attack by acids, bases, and oxidizing reagents; (8) identification of some sites of reaction with phenyl isocyanate by analysis of enzyme hydrolysates;³⁴ (9) supporting unpublished studies by x-ray diffraction and infrared analysis.

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