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새로운 친전자성 올레핀 양이온 개시제 : Dicyanovinyl Picrates

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New Electrophilic Olefin Initiator for Cationic Polymerization : Dicyanovinyl Picrates

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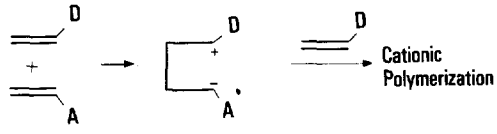
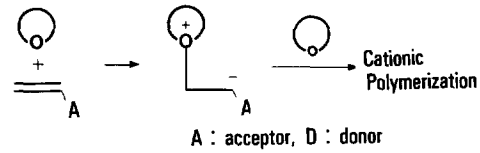
요 약 : Picrate를 가지는 새로운 친전자성 올레핀을 합성하였으며 그들의 양이온 개시능력을 조사하였다. 이들은 각각 2,2-dicyanovinyl picrate와 1-phenyl-2,2-dicyanovinyl picrate이며 picrate anion을 탈리시킬 수 있는 zwitterion 중간체를 생성시켜 carbenium-gegenion pair를 형성한다. 전자가 풍부한 비닐 단량체인 N-vinyl carbazole, p-methoxystyrene, ethyl vinyl ether 및 oxacyclic ether에 대한 효과적인 양이온 개시제로 작용하였다.

Abstract : New electrophilic olefins containing picrate group were synthesized and their ability as a cationic initiator was investigated. These were 2,2-dicyanovinyl picrate and 1-phenyl-2,2-dicyanovinyl picrate. They acted by zwitterionic intermediates which expelled the picrate anion, thus forming a carbenium-gegenion pair. They were active initiators for the cationic polymerization of electron-rich vinyl monomers such as N-vinyl carbazole, p-methoxystyrene and vinyl ether, and oxacyclic ethers.

INTRODUCTION

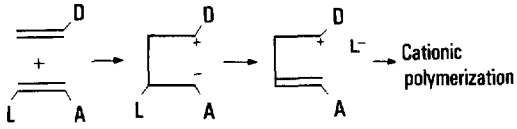
Electron-deficient olefins can initiate cationic vinyl or ring-opening polymerizations by forming reactive zwitterions with electron-rich double bonds or oxacylic monomers.[1]





However, all these zwitterionic intermediates have the disadvantage that the counterion in the propagation reaction is a carbanion, which limits such cationic polymerization to the most electron-rich monomers. The efficiency of such zwit-

terionic initiators is greatly increased if they possess a leaving group in the β-position. Its expulsion leaves a carbenium-gegenion pair, which initiates and propagates more effectively.[2~5]

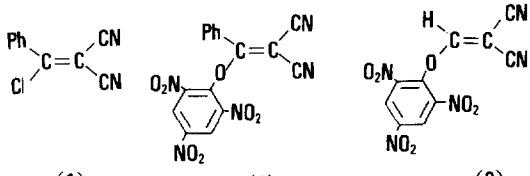


When leaving groups were triflate,[2] sulfonate,[3] trifluoroacetate,[3] iodide,[4] chloride,[2] extensive investigations were carried out for the possible use of the active compound cationic initiator.

Picric acid is a strong acid which has the pKa value of 0.3 and its anion is a good leaving group as a nucleophile, but picrate gegenion has been neglected in the studies of cationic polymerization.

With a protonic acid, the true identity of the resulting gegenion at the propagating center is obscure. Especially, in the media of low dielectric constant, the anion will be solvated by an ill-defined number of acid molecules with hydrogen-bonding. The introduction of picrate at the multisubstituted olefin avoids these problems and render these initiators good solubility in most organic liquids.

In this paper, we report the synthesis of the following type of new electrophilic olefin initiators and their ability to initiate cationic polymerization of electron-rich vinyl and oxacyclic monomers.



(1) (2) (3)

EXPERIMENTAL

Chemicals and Instruments

p-Methoxystyrene, styrene, ethyl vinyl ether, 1, 3-dioxolane, tetrahydrofuran were vacuum distilled over calcium hydride. N-vinyl carbazole was recrystallized from n-hexane at −50℃. Trioxane was dried in molten state at 65℃ over calcium hydride and vacuum distilled. Methylene chloride was purified by distillation from sodium metal and calcium hydride. Acetonitrile was dried by distillation from phosphorus pentoxide. Silver carbonate, picric acid, benzonyl chloride, ethyl formate and malononitrile(Aldrich Chem. Co.) were used without further purification.

NMR spectra were recorded with a T-60A Varian nuclear magnetic resonance spectrometer. The infrared spectra were obtained by a Perkin-Elmer Model 1310 Spectrophotometer.

Preparation of Silver Picrate

3g(13.1mmole) of picric acid was dissolved in 100ml of dry ethyl ether and 4.3g(15.6mmole) of silver carbonate was added. The mixture was stirred at room temperature in the dark for 12hrs.

The solvent was filtered off and washed with ethyl ether. The solid was dissolved in hot dry acetonitrile and the remaining solid was filtered off and recrystallized at room temperature.

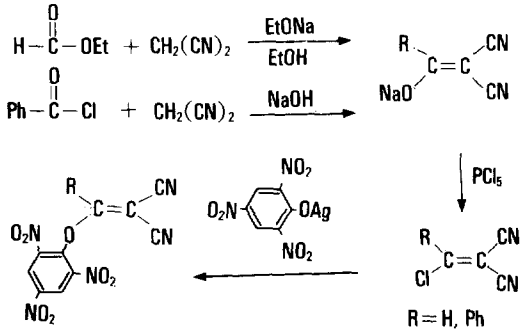
Yield : 86%, mp : 333℃, ^{1}H-NMR(60MHz, CD_3CN) : δ=8.8(s, picrate, 2H)

Preparation of 1-chloro-2,2-dicyanoethylene

A solution of potassium ethoxide was prepared by dissolving 20g(0.5g atoms) of potassium metal in 400ml of absolute ethanol. To this warm solution, 33g(0.5mole) of malononitrile, 75g(1.01mole) of ethyl formate and 75ml of absolute ethanol were added successively.

The mixture was stirred with reflux for 1.5 hrs and cooled. The precipitated potassium salt of hydroxymethylene-malononitrile was collected by filtration and washed throughly with ether and dried. Yield was 50.5g(70%).

A slurry of 25g(0.19mole) of the dry potassium salt in 100ml of methylene chloride was treated with 39.5g(0.19mole) of phosphorus pentachloride in one portion. The mixture was stirred under reflux for 4hrs and filtered. The solid was washed with fresh methylene chloride and the combined filtrate was concentrated by distillation at reduced pressure. The dark residue was distilled through



a 20cm vigreux column to provide 51g(62%) of 1-chloro-2,2-dicyanoethylene, bp. 73℃(10mm).

Yield : 62%, ^{1}H-NMR(60MHz, CD_3CN) : δ=7.8(s, vinyl, 1H), IR(KBr, cm^{-1}) : 3060(=CH), 2260(C≡N), 1600(C=C), 1550(NO_2), 1350(NO_2).

Preparation of 1-chloro-1-phenyl-2,2-dicyanoethylene

To a stirred solution of malononitrile and benzoyl chloride in methylene chloride at 0℃, was added dropwise 0.1 eq. of benzyltriethylammonium chloride in excess 6N-NaOH. The precipitated sodium salt was collected by filtration, washed with methylene chloride and recrystallized from methanol/water(80/20) to give a 65% yield of product. 10g of the dry sodium enolate was treated with 80 ml of phosphorus oxychloride in one portion. The mixture was stirred under reflux for 12hrs at 120 ℃. After reaction, excess phosphorus oxychloride was distilled off under reduced pressure. The remained dark residue was extracted by 100ml of methylene chloride, the extraction was repeated two times, then filtered and evaporated.

The concentrated solution was eluted with a 20 cm-length of the silica gel column. After the solution was evaporated, the solid product was recrystallized from ethyl acetate/hexane(50/50) to give a light yellow product.

Yield : 65%, ^{1}H-NMR(60MHz, CD_3CN) : δ=7.5(m, arom, 5H). IR(KBr, cm^{-1}) : 3080(arom, CH), 2260(C≡N), 1600(C=C).

Preparation of 2,2-dicyanovinylpicrate

To a solution of silver picrate 2.54g(7.56mmole) in 70ml of dry acetonitrile, 1.27g(9.07mmole) of 2,2-dicyanovinylchloride was added at room temperature under nitrogen in the drak. After 2hrs, silver chloride was filtered off and the solvent was evaporated. The remaining solid was recystallized from 1,2-dichloroethane.

Yield : 60%, mp : 109℃, ANAL. Calc'd for : C, 46.7%, H, 1.2%, N, 27.2%, Found : C, 45.0%, H, 1.1%, N, 27.8%, ^{1}H-NMR(60MHz, CD_3CN) : δ=8.8(s, picrate, 2H), 7.8(s, vinyl, 1H). IR(KBr, cm^{-1}) : 3080(arom, CH), 2240(C≡N), 1600(C=C), 1550(NO_2), 1350(NO_2).

Representative Cationic Polymerization of p-methoxystyrene with 2,2-dicyanovinyl Picrate

0.2g of p-methoxystyrene in 1ml of 1,2-dichloroethane and 0.0136g(3mole%) of 3 in 1ml of 1,2-dichloroethane were placed in septum-capped Y-typed polymerization tube under nitrogen. Two solutions were mixed at once and placed for 20hrs at room temperature. The mixture was reprecipitated into petroleum ether and the white powdery solid was filtered, and dried in vacuo at 50℃.

Similar polymerization procedures were applied to the cationic polymerization of other monomers with initiator 2 or 3.

RESULTS AND DISCUSSION

Reaction of silver picrate with 2,2-dicyanovinyl chloride in acetonitrile formed immediately 2,2-dicyanovinyl picrate(3). In contrast, 1-chloro-1-phenyl-2,2-dicyanoethylene was less reactive to nucleophiles such as picrate, sulfonate and phosphate. The reaction is rather slow even at 60℃ for 48hrs. The corresponding picrates 2 and 3 were obtained as yellow crystals in moderate yields. Their NMR and IR spectra matched well with reactants from which 2 and 3 had been synthesized. They showed a good stability to water, thus excluding the possibility of polymerization by picric acid resulting from hydrolysis.

Various electron-rich vinyl and cyclic monomers such as N-vinyl carbazole, p-methoxystyrene, ethyl vinyl ether, styrene, 1,3,5-trioxane, 1,3-dioxolane and tetrahydrofuran were polymerized with 1-phe-

Table 1. Cationic Polymerization of Electron-rich Monomers with 2 and 3

Monomer (g)	Initiator (mol%)	Solvent (ml)	Temp. (℃)	Time (hr)	Yield (%)	MW*
N-vinyl carbazole	2(3)	$(CH_2Cl)_2$(2)	25	5	80	58,000
(0.2)	3(3)	$(CH_2Cl)_2$(2)	25	5	~100	47,000
p-MeO-styrene	1(3)	$(CH_2Cl)_2$(1)	60	20	15	3,044
(0.5)	2(3)	$(CH_2Cl)_2$(1)	25	20	< 5	12,600
	2(3)	$(CH_2Cl)_2$(1)	60	20	55	12,600
	3(3)	$(CH_2Cl)_2$(1)	25	20	75	27,000
	3(3)	CH_3CN(1/2)	25	20	90	3,300
	3(3)	$(CH_2Cl)_2$(1)	60	20	95	21,000
Ethyl vinyl ether	3(3)	$(CH_2Cl)_2$(1)	25	20	65	–
(0.5)	3(3)	CH_3CN (1)	25	20	85	–
	3(3)	$(CH_2Cl)_2$(1)	60	20	>90	–
Styrene	3(3)	$(CH_2Cl)_2$(1)	60	48	trace	–
(0.5)	3(3)	CH_3CN (1)	60	20	<20	–

* Gel permeation chromatography was carried out with two columns(Waters μ-styragel 10^3Å and 10^4Å) calibrated with polystyrene standards, chloroform as eluent at 254nm.

Table 2. Cationic Polymerization of Oxacyclic Ethers with Initiator 2 and 3

Monomer (g)	Initiator (mol%)	Solvent (ml)	Temp. (℃)	Time (hr)	Yield (%)
Trioxane	2(3)	neat	65	20	<14
(0.5)	3(3)	neat	65	20	31
1,3-Dio-	2(3)	neat	60	20	<15
xolane	3(3)	neat	60	20	35
(0.5)	3(3)	CH_3CN(1)	60	20	65
Tetrahy-	2(2)	neat	60	48	trace
drofuran	3(2)	neat	60	48	trace

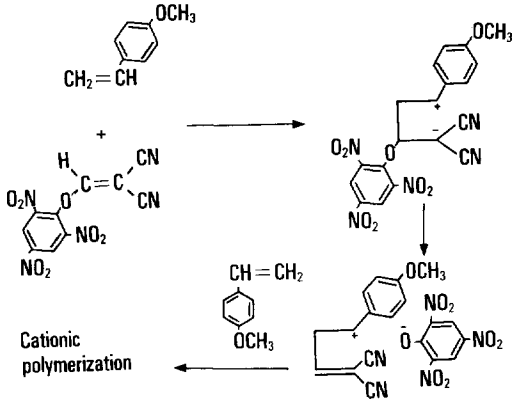
nyl-2,2-dicyanovinyl picrate(2) or 2,2-dicyanovinyl picrate(3). The amount of catalyst used was 3mol-% and the polymerization temperature was 25℃ or 60℃~65℃ if necessary. The results of polymerizations are summarized in Table 1 and 2.

Initiator 3 polymerized N-vinyl carbazole in quantitative yield in 1,2-dichloroethane at 25℃, while 2 was less reactive.

In the case of p-methoxy styrene, initiator 2 gave less than 5% of polymer in 1,2-dichloroethane at 25℃, but at 60℃ higher yield was obtained. As in the most case of cationic polymerization, the more polar solvent such as acetonitrile gave a higher yield of polymer at 25℃. At 25℃, the relative reactivity of the different initiators could be determined from the polymer yields as 1<2<3. Similary, initiator 3 polymerized ethyl vinyl ether in 65% and 85% yield in 1,2-dichloroethane and acetonitrile, respectively. The initiator 3 is more effective than 2 in the polymerization of electron-rich vinyl monomers. Styrene gave only traces amount of polymer even after 48hrs at 60℃.

As to the oxacyclic monomers, 1,3-dioxolane gave only low yield in bulk but acetonitrile gave 65% yield of polymer with initiator 3 at 60℃. Cationic ring-opening polymerization of molten trioxane proceeded well. Initiator 3 gave 31% yield of polymer, while the initiator 2 gave only 14% yield of polymer in 24hrs. The initiators 2 and 3 were not effective initiators for the cationic polymerization of tetrahydrofuran. The tendency of picrate, which depart as a leaving group and generate a cation, determines the mechanism of polymerization as follows :

The ability of 2 and 3 to initiate polymerization is superior to that of 1 containing chloride to act as a leaving group. Initiator 3 gave moderately



better yield than 2 in most of the electron-rich vinyl and oxacyclic monomers. Phenyl substituted initiator 2 was inactive at room temperature, but showed an appreciable reactivity at higher temperature.

It was conceivable that the displacement of the phenyl group in 2 might make less reactive toward monomers because of increasing the electron density of double bond and steric hindrance.

Finally, it is also of interest to compare these results with the ealier results.[4] It can be offered on the basis of present and earier results[4] that the reactivity of 3 is between 2,2-dicyanovinyl tosylate and 2,2-dicyanovinyl iodide.

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