

두 치환체를 가진 비닐시클로프로판의 시클로펜텐으로의 열적자리 옮김반응

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Thermal Rearrangement of 1,1-Disubstituted 2-Vinylcyclopropanes to 4,4-Disubstituted Cyclopentenes

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요 약. 1,1-위치에 두개의 극성치환체를 가진 2-비닐시클로프로판 **1a**, **1b**, **1c**, **1d**를 300°C 이하로 가열한 결과 4,4-위치에 치환된 대응하는 시클로펜텐 **2a**, **2b**, **2c**, **2d** 로의 자리 옮김반응이 용이하게 일어났다. 시아노기가 치환된 **1b**는 용매로 희석시켜서 170°C로 반응시켰을 때 **2b** 로의 자리 옮김이 관찰되었지만, **1c** 와 **1d** 는 200°C 이상의 온도에서 반응이 일어났고, 페닐기가 치환된 **1a** 는 250°C에서 용매 사용없이 열반응으로 **2a** 가 생성되었다. **1a** 의 시클로펜텐으로의 열적 자리 옮김반응은 거의 정량적이었지만 **1b**, **1c**, **1d** 의 경우에는 시클로펜텐외에 상당량의 고분자물질 **3** 이 생성되었다. **1c** 의 경우에는 시클로펜텐외에 시클로프로판 고리가 열린 디엔 **4** 가 관찰되었다. 두 기가 치환된 시클로프로판 **1** 이 용이하게 시클로펜텐 **2** 로 열적 자리 옮김 반응을 하는 이유는 두 극성기가 반응 중간물질인 디라디칼 **5** 를 안정화 시키는 효과로서 설명하였다.

ABSTRACT. The four 1,1-disubstituted 2-vinylcyclopropanes, 1,1-diphenyl-2-vinylcyclopropane (**1a**), 1,1-dicyano-2-vinylcyclopropane (**1b**), ethyl 1-cyano-2-vinylcyclopropanecarboxylate (**1c**), and diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**1d**) rearranged below 300°C to the corresponding 4,4-disubstituted cyclopentenes, 4,4-diphenylcyclopentene (**2a**), 3-cyclopentene-1,1-dicarbonitrile (**2b**), ethyl 1-cyano-3-cyclopentenecarboxylate (**2c**), and diethyl 3-cyclopentene-1,1-dicarboxylate (**2d**). Diphenyl derivative **1a** rearranged almost quantitatively to 4,4-diphenylcyclopentene (**2a**) at the temperature of 250°C. Although dicyano derivative **1b** in solution underwent the thermal rearrangement at rather low temperature of 170°C, the other vinylcyclopropanes, **1c** and **1d**, in solution rearranged thermally above 220°C. In the thermal reaction of **1b**, **1c**, and **1d** considerable amounts of polymers **3** were also produced. Also detected product was the ring-opened

diene, ethyl 2-cyano-2,4-hexadienoate(4), in case of the pyrolysis of **1c**. The observed facile rearrangement of disubstituted vinylcyclopropanes was explained by the radical stabilization effect of substituents on the diradical intermediates **5**.

INTRODUCTION

It is well known that the homodienyl vinylcyclopropane-compounds rearrange thermally to cyclopentenes above 300°C in vapor phase. A vinylcyclopropane derivative has homodienyl vinyl group along with strained cyclopropane ring, and this type of rearrangements occur easily through the breaking of a carbon-carbon bond of the cyclopropane ring¹. Frey² reported the rearrangement of vinylcyclopropane and isopropenylcyclopropane to cyclopentene and to 1-methylcyclopentene above 330°C. The rearrangements were interpreted to be first-order homogeneous unimolecular reactions taking place through a diradical mechanism.

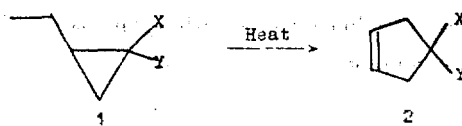
Since the introduction of polar groups on the cyclopropane ring would stabilize the diradicals formed, the thermal rearrangements of those disubstituted vinyl cyclopropanes will be facilitated. *trans*-1-Phenyl-2-vinylcyclopropane³ and 1-cyano-2-isopropenylcyclopropane⁴ exhibited more tendency to rearrange thermally to 4-phenylcyclopentene and to 4-cyano-1-methylcyclopentene respectively. These compounds were the cases of one polar group on the cyclopropane ring. Ketley *et al.*⁵ reported that 1,1-dichloro-2-vinylcyclopropane rearranged in good conversion to 4,4-dichlorocyclopentene when passed the compound through glass wool-packed Vycor tube at 250°C. They suggested that this reaction take place through diradical intermediate and the diradical is stabilized by two chlorine atoms.

During the course of our study⁶ on the 1,5-type isomerization polymerization of 1,1-disubstituted 2-vinylcyclopropanes we have observed

that 1,1-disubstituted 2-vinylcyclopropanes readily rearrange to 4,4-disubstituted cyclopentenes below 300°C as expected. However also observed was that different modes of reactions are operative in these rearrangement reactions, thereby leading to different reaction products depending on the substituent groups. In the present paper we like to report the thermal rearrangement reactions of vinylcyclopropanes with two polar substituent groups on the cyclopropane ring such as phenyl, carbethoxy, and cyano group.

RESULTS

The 1,1-disubstituted 2-vinylcyclopropanes we have studied were 1,1-diphenyl-2-vinylcyclopropane (**1a**), 1,1-dicyano-2-vinylcyclopropane (**1b**), ethyl 1-cyano-2-vinylcyclopropanecarboxylate (**1c**), and diethyl 2-vinylcyclopropane-1,1-dicarboxylate (**1d**). Thermal rearrangement reactions were carried out in the vacuum sealed Pyrex glass ampoules with or without solvents. 1,1-Diphenyl-2-vinylcyclopropane (**1a**) which does not polymerize radically was heated in neat at 250°C. The reaction mixtures were heated in an oven at certain temperature for certain time period. Progress of the reactions and compositions of the reaction products were followed by NMR spectra.



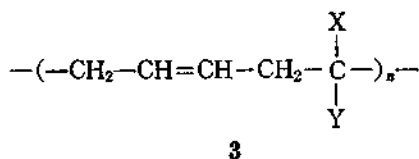
1a, **2a**: X=Y=Ph

1b, **2b**: X=Y=CN

1c, **2c**: X=CN, Y=CO₂Et

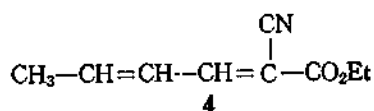
1d, **2d**: X=Y=CO₂Et

Product analysis indicated that **1a** rearranged almost quantitatively to 4,4-diphenylcyclopentene(**2a**). Since the other vinylcyclopropanes readily polymerized under this condition, they were heated with solvents such as toluene or xylene. Even under diluted condition considerable amounts of polymeric materials resulted and the polymers were identified as structure **3** of five-carbon repeating unit in *trans* configuration. This structure was confirmed to be identical with that of the polymers obtained by radical polymerizations⁶.



The reaction of 1,1-dicyano-2-vinylcyclopropane(**1b**) took place at rather low temperature. When the 19% solution (by volume) of **1b** in toluene was subjected to heating at 170°C for 12 hours, the reaction gave 23% of black-brown precipitates, 17% of 3-cyclopentene-1,1-dicarbonitrile(**2b**), and 9% of starting **1b**. On heating at 155°C for 20 hours **1b** (4.3% in toluene) gave **2b** only about 10% and small amounts of polymers, and most of starting **1b** were recovered. Above 200°C most of **1b** changed to polymeric materials(**3**: X=Y=CN).

In the thermal reaction of ethyl 1-cyano-2-vinylcyclopropane-1-carboxylate(**1c**) a linear diene compound, ethyl 2-cyano-2,4-hexadienoate(**4**), was obtained in addition to ethyl 1-cyano-3-cyclopentene-1-carboxylate(**2c**). The 4.5% solution (by volume) of



1c in toluene was heated at 220°C for 7 hours and the reaction was found to have undergone

in 80% conversion. Two thirds of the products were **2c** and the rest were crystalline **4**. Below 200°C the rearrangement of **1c** to **2c** was negligible. However in the reaction above 220°C the ring-opened linear product **4** was not always determined. To see if the product **4** is a further rearranged product of already formed cyclopentene **2c**, a vacuum sealed ampoule containing **2c** was heated to 220°C for 5 hours. The resulting black viscous materials were confirmed to be mostly starting **2c** and no evidence for the formation of **4** was detected by NMR spectra.

Thermal rearrangement of diethyl 2-vinylcyclopropane-1,1-dicarboxylate(**1b**) has been previously reported by Schmid and Wolkoff⁷. They pyrolyzed **1d** at 400~425°C in the vapor phase. In the present work, **1d** (50% by volume in xylene) was heated in liquid phase at 280°C for 11 hours and no more than 10% yield of **2d** was obtained and the residual materials were confirmed to be polymers (**3**: X=Y=CO₂Et).

NMR spectra of thermally rearranged products **2**'s exhibited the characteristic two sharp singlet peaks at 5.5~5.8ppm and at 2.9~3.2 ppm corresponding to olefinic protons (2H) and allylic protons(4H) respectively.

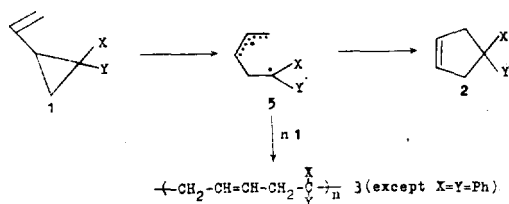
DISCUSSION

The above results indicate that among the disubstituted vinylcyclopropanes presently studied the dicyano derivative **1b** appeared to be most reactive, even though the product was not sole cyclopentene derivative **2b**. Diphenyl derivative **1a** was somewhat less reactive, but the reaction gave cleanly diphenyl cyclopentene **2a**, without forming any polymers even when the reaction was carried out in neat. This result was well predicted from our polymerization studies⁶ on those compounds. We have found that **1b** was most active toward radical poly-

merizations, while **1a** did not homopolymerize under the radical condition. Also interesting to observe is that **1a** did not give any side product diene.

The other disubstituted vinylcyclopropanes, **1c** and **1d** also undergo rearrangement reactions at the temperatures lower than 300°C. However the products were not clean enough to be a useful preparative reaction. Vapor phase pyrolysis^{1,2} may improve in eliminating polymer formation.

Based on the above observations the facile rearrangement tendency of those disubstituted vinylcyclopropanes can be ascribable to the radical stabilization effect of substituents, thereby confirming that the rearrangement reaction of vinylcyclopropane derivatives to cyclopentene and/or to the corresponding diene derivatives indeed took place via diradical intermediates⁹. Also contributing to the reaction is the stability of allylic radicals. Vinylcyclopropane **1** is first activated to form diradical **5** which then either adds to other **1**'s to form polymers **3** or gives cyclopentene **2** by intramolecular coupling of 1-position with 5-position of the radicals.



In case of **1a** no polymer is to form because of its lack of polymerizability. It is well known that 1,1-diphenylethylene does not radically homopolymerize and there are still controversy in its interpretation. Our observation on the polymerizability of **1a** may contribute to this area and is to be published elsewhere.

Richey *et al.*⁹ investigated the kinetics of

thermal rearrangements of 1-dimethylamino-, 1-methoxy-, and 1-phenyl-2-vinylcyclopropane to the corresponding cyclopentenenes, and they suggested that the activation energy of the reaction was considerably lowered by the assistance of substituents by stabilizing the diradical intermediate. Our work seem to confirm this and even less activation energy seems to be required for the rearrangement of disubstituted vinylcyclopropanes.

The formation of dienes, presumably an intramolecular disproportionation product of the diradical intermediates, is rather perplexing. Jones *et al.*¹⁰ reported that they could detect the side product diene in the thermal reaction of 1,1-diphenyl-2-methyl-2-vinylcyclopropane to the corresponding cyclopentene derivative. However we failed to confirm any diene side product formation in the thermal reaction of **1a** and also no corresponding dienes were detected from **1b** and **1d**, while diene formation was significant in the reactions of **1d**¹¹. Our results seem to favor the diradical intermediacy for the thermal rearrangement of vinylcyclopropanes, but leaves yet certain detailed aspects of the reaction which require mechanistic scrutiny.

EXPERIMENTAL

General. Reagent grade chemicals were purified by distillation or recrystallization. Inorganic chemicals were used as received. Butadiene was of polymerization grade taken from Ulsan production line of Korea Oil Corp. and used without further purification. Melting points and boiling points are uncorrected. IR spectra were taken on a Perkin-Elmer Model 267 Spectrophotometer and NMR spectra were obtained on a Varian Model T-60A.

General Procedure of Thermal Rearrangement. Vinylcyclopropane derivatives(**1**) were placed in Pyrex glass ampoules with or without

solvent and degassed completely. After sealing under vacuum the ampoules were heated in an oven at the given temperature. After the reaction was over, the aromatic diluent was evaporated under reduced pressure and the products were obtained by distillation under vacuum. The progress of the reactions and the compositions of the products obtained were determined by the NMR spectra.

Thermal Rearrangement of 1,1-Diphenyl-2-vinylcyclopropane(1a). 1a was prepared as follows; 19.4 g (0.10 mole) of diphenyldiazomethane¹² and 19.0 g (0.35mole) of butadiene in 40ml of diethyl ether were introduced into a pressure bottle and the mixture was heated at 85°C for 13hr. Solvent and excess butadiene were then evaporated and the residual liquid was distilled giving 1a, 19.2g (86% yield based on diphenyldiazomethane), b. p 80~90°C (0.15 mmHg). NMR and IR spectra were identical with those of the compound reported recently by Shimizu *et al.*¹³

The 1a(0.5g) in an ampoule was heated at 250°C for 8 hr. The resulting yellowish liquid was almost pure 4,4-diphenylcyclopentene(2a), b. p 50°C (0.14 mmHg): IR (neat) 3060, 3030, 2930, 2850, 1600, 1495, 1445, 1040, 950, 750, 675 cm⁻¹; NMR(CCl₄) δ 7.10(10H, singlet), 5.75(2H, singlet), 3.10(4H, singlet).

Thermal Rearrangement of 1,1-Dicyano-2-vinylcyclopropane(1b). 1b was prepared in the yield of 50% by the reaction of 1,4-dibromo-2-butene (or 1,4-dichloro-2-butene) with malonitrile in the presence of silver oxide according to the procedure of Ciganek.¹⁴

The 1b(1.4g) in 6ml toluene (19% by volume) was introduced into an ampoule and was heated at 170°C for 12hr. The pyrolyzed products were 0.32 g (23%) of black-brown precipitates, starting 1b 0.12 g(9%), and 3-cyclopentene-1,1-dicarbonitrile¹⁵ (2b) 0.23 g(17%). 2b: b. p

36°C (0.16 mmHg); IR(neat) 3070, 2920, 2860, 2250, 1620, 1445, 1335, 1305, 1260, 950, 890, 750, 660 cm⁻¹; NMR (CDCl₃) δ 5.80 (singlet, 2H), 3.20(singlet, 4H). The residue of distillation was black viscous material. The precipitates were identified as polymer 3 (X=Y=CN).

Thermal Rearrangement of Ethyl 1-Cyano-2-vinylcyclopropanecarboxylate (1c). 1c was prepared by the condensation of 1,4-dichloro-2-butene with ethyl cyanoacetate by the procedure similar to that of Kiersted *et al.*¹⁶ in the yield of 38.6%¹⁷. NMR spectrum of the product indicated the contamination by ethyl 1-cyano-3-cyclopentenecarboxylate (2c). The isomeric mixture(1.4g) and 30 ml of toluene in an ampoule was heated at 220°C for 7 hr. By vacuum distillation was obtained the product (b. p 50°C, 0.11 mmHg) 1.12 g(80%). The product was a mixture of 2c and ethyl 2-cyano-2,4-hexadienoate(or ethyl 2-cyanosorbate, 4) in the ratio of 2 to 1 according to NMR analysis. On standing at room temperature from the distillate crystallized white crystals 4, m. p 55~56.5°C (lit.¹⁸ m. p 57~58°C). 2c: IR (neat) 3060, 2980, 2930, 2245, 1735, 1440, 1370, 1270, 1220, 1070, 1005, 955, 855 cm⁻¹; NMR (CCl₄) δ 5.66(singlet, 2H), 4.26(quarter, 2H), 3.00(singlet, 4H), 1.33(triplet, 3H). 4: IR (neat) 3030, 2985, 2215, 1720, 1625, 1580, 1290, 1240, 1080, 1015, 995, 950, 765 cm⁻¹; (NMR) δ 7.83~7.60(multiplet, 1H), 6.77~6.47 (multiplet, 2H), 4.27(quarter, 2H), 2.05 (broad doublet, 3H), 1.33(triplet, 3H). The residue of distillation was confirmed as polymer 3(X=CN, Y=CO₂Et).

Thermal Rearrangement of Diethyl 2-Vinylcyclopropane-1,1-dicarboxylate (1d). Solution of 1d(2.0g) and 2 ml of xylene in an ampoule was heated at 280°C for 11 hr and the resulting viscous black oil was distilled under

vacuum giving diethyl 3-cyclopentene-1,1-dicarboxylate (**2d**) in less than 10% yield. The residue was polymer **3** ($X=Y=CO_2Et$). **2d**: NMR(CCl_4) δ 5.54(singlet, 2H), 4.13(quartet, 4H), 2.92(singlet, 4H), 1.24(triplet, 6H).

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