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Cyclic Acetal-Photosensitized Polymerization

16. Photooligomerization of 2-Substituted 1,3-Diphenylimidazolizine Compounds

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Summary

The photoirradiation onto 1,3-diphenylimidazolize (1,3-DPhI) was carried out in benzene at 40°C without the ordinary initiator to give the oligomer. Furthermore, the effect of substituent on the ring-opening photooligomerization of 1,3-DPhI was discussed.

Introduction

1,3-Dioxolane (1,3-DO) was photoirradiated to give ethyl formate through a radical mechanism, and the ester radical generated as a intermediate could initiate the polymerization of vinyl monomer; 1,3-DO acted as a promoter of the photopolymerization of vinyl monomer (OUCHI et al. 1975). On the contrary, 1,3-dithiolane (1,3-DT) was oligomerized by photoirradiation without the use of ordinary initiator through a biradical mechanism with α,β'-scissions; 1,3-DT acted as a monomer (OUCHI et al. 1979). Alternatively, such a difference of the photosensitive behavior was recognized in five-membered 1,3-heterocyclic compounds having oxgen or sulfur at 1,3-positions.

The present paper deals with the photoirradiation onto 1,3-diphenylimidazolizine (1,3-DPhI); 1,3-DPhI was found to be oligomerized by photoirradiation. Namely, 1,3-DPhI acted as a monomer. The ring-opening polymerization of 1,3-DPhI has not be reported even with ionic catalyst. This article concerns with the

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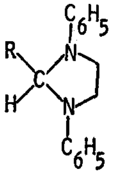
photooligomerization of 1,3-DPhI and the photocopolymerization of 1,3-DPhI with 1,3-DT. Moreover, in order to investigate the effect of the substituent in 1,3-DPhI compound on the photooligomerization, the photooligomerizations of 2-methyl-1,3-diphenylimidazolizine (2-M-1,3-DPhI) and 1,2,3-triphenylimidazolidine (1,2,3-TPhI) were carried out.

Experimental

Materials 1,3-DPhI compounds were prepared by the condensation of corresponding aldehydes with N,N'-diphenylethylenediamine by using Amberlite IR-120B as a catalyst, according to a modification of the method reported (WANZLICK et al. 1953).



R=H(1,3-DPhI),
CH_3(2-M-1,3-DPhI),
C_6H_5(1,2,3-TPhI)

1,3-DPhI; mp 125.5-126.5°C (lit. 126°C), λ_{max} in methanol 255 nm. 2-M-1,3-DPhI; mp 102.5-102.8°C (lit. 102.5°C), λ_{max} in methanol 257 nm. 1,2,3-TPhI; mp 138.0-138.2°C (lit. 137°C), λ_{max} in methanol 255 nm. 1,3-DT was prepared by the method reported in the previous paper. (OUCHI et al. 1979), bp 175-176°C (lit. 175°C), λ_{max} in methanol 243 nm. Benzene was purified by conventional method.

Procedure The photoirradiations onto 1,3-DPhI compounds were carried out at 40°C in quartz or Pyrex tube (10 mm o. d.), using benzene as a solvent. The photoirradiation procedure was the same as that reported previously (OUCHI et al. 1979). After the reaction mixture was poured into a large amount of n-hexane, the oligomer obtained as the precipitate was filtered off, washed with n-hexane, and dried in vacuo. The ESR spectrum was measured at room temperature by using JES-FE-1X spectrometer with 100 $\mathrm{KH_Z}$ field modification.

Characterization of Oligomer The identification of the oligomer obtained was made by measurements of IR and ^{1}H-NMR spectra, and by elemental analysis. The number-average molecular weight ($\overline{M}_n$) of the obtained product was measured by VPO method at 37°C, using chloroform as a solvent.

Results and Discussion

The photoirradiations onto 1,3-DPhI compounds were carried out in benzene at 40°C. The results obtained are shown in Table I. With reaction, the color of system changed from colorless to yellow. However, the evolution of gas was not observed when the tube was

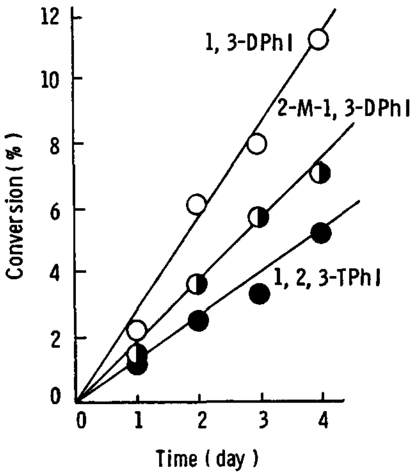


Fig. 1. Time-conversion curves for photooligomerizations of 1,3-DPhI compounds at 40°C: 1,3-DPhI compounds 0.2 g, benzene 5 cm^3. (○) 1,3-DPhI, (◑) 2-M-1,3-DPhI, (●) 1,2,3-TPhI

TABLE I

Photooligomerizations of 2-Substituted-1,3-DPhI[a] Compounds

No.	2-Substitited- 1,3-DPhI	Time (h)	Conversion (%)	Oligomer				
				C(%)	H(%)	N(%)	$\overline{M}_n$	dp(°C)
1	1,3-DPhI	24	6.50	81.45	7.29	11.26	1310	>400
2	"	36	7.56	81.61	7.53	10.86	1370	>400
3	"	48	8.37	81.74	7.69	10.57	1400	>400[c]
4	"	48[b]	0	—	—	—	—	—
5	"	135	12.15	82.67	8.40	8.92	—	>400
6	2-M-1,3-DPhI	1	1.19	81.76	8.05	10.19	1090	>400[c]
7	"	2	2.45	81.75	8.16	10.19	1180	>400
8	"	3	3.30	82.30	7.94	9.76	1320	>400
9	"	4	5.12	82.43	7.84	9.73	1650	>400
10	1,2,3-TPhI	1	1.36	84.68	6.80	8.52	1190	>400
11	"	2	3.60	84.70	6.74	8.56	1300	>400
12	"	3	5.58	84.40	6.60	8.90	1640	>400
13	"	4	7.00	84.25	6.93	8.82	1840	>400

[a] 2-Substituted-1,3-DPhI 0.2 g, benzene 5 cm^3; 40°C.

[b] in dark.

[c] Decomposition point was measured as about 450°C in air by DTA method.

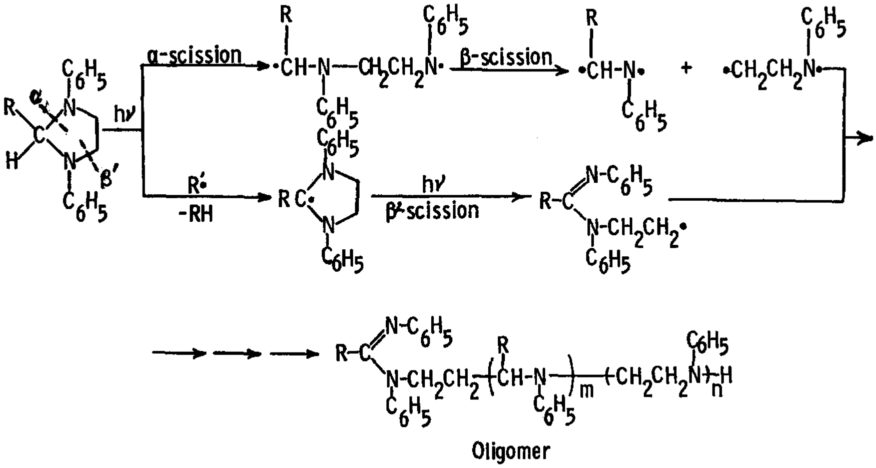
sealed off. Since the molecular weights of the precipitates obtained by pouring the reaction mixture into n-hexane were 1090-1840, they could be called as the oligomers; 1,3-DPhI compounds could act as monomers. Thus, these oligomers may be produced through the ring-opening polymerization. The time-conversion curves for the photooligomerizations of 1,3-DPhI compounds are shown in Fig. 1. There were the linear relationships. The rate of oligomerization increased in the order of 1,3-DPhI > 1,2,3-TPhI > 2-M-1,3-DPhI. These oligomers obtained were easily soluble in chloroform and N,N-dimethylformamide, and their decomposition points were measured as above 400°C. The IR and ^{1}H-NMR spectra of monomers and oligomers were almostly resemble each other. Nevertheless, the latter absorptions were more broad than the former absorptions, and the peak at 1650 cm^{-1} assigned to C=N was recognized in latter IR spectra.

Moreover, when the ESR spectrum of the photoirradiated system of 1,3-DPhI was measured at room temperature, three sets of sharp symmetric signals consisting of singlet were observed at g=1.963, 2.003 and 2.036, independently; three kinds of radical species were suggested to be generated. However, we can not assign them at the present time. At all events, it may safely be said that the photooligomerization proceeds through a radical mechanism.

Moreover, the values of elemental analyses of the oligomers obtained differed from those of the corresponding monomeric 1,3-DPhI compounds; the elimination of something was suggested to occur during photoirradiation.

On the basis of the above views, the ring-opening photooligomerization mechanism of 1,3-DPhI compounds may be expressed for convenience as Scheme 1.

The values of C, H, N, m, n, and $\overline{M}_n$ calculated by assuming the formula of oligomer as Scheme 1 are



Scheme 1. The mechanism of photooligomerization of 1,3-DPhI compounds.

TABLE II

The Values Calculated from the Formula of Oligomer Shown in Scheme 1

No.	m	n	C	H	N	$\overline{M}_n$
			(%)			
1	0	9.2	81.23	6.80	11.79	1320
2	0	9.7	81.18	6.86	11.96	1380
3	0	9.9	80.82	7.28	11.90	1400
6	3.6[a]		80.63	7.61	11.76	1100
7	4.0[a]		"	"	"	1190
8	4.5[a]		"	"	"	1310
9	5.9[a]		"	"	"	1640
10	3.4	2.3	84.38	6.56	9.06	1190
11	3.8	2.6	84.26	6.69	9.05	1300
12	5.0	3.7	84.66	6.20	9.14	1650
13	5.4	4.7	84.08	6.71	9.21	1850

[a] (m + n).

summarized in Table II. They were rather close to the experimental values listed in Table I.

Furthermore, the photopolymerization of 1,3-DPhI in the presence of 1,3-DT were carried out to give the results shown in Fig. 2. As can be expected, the cooligomers were found to be obtained in all feeds. The photopolymerizability of 1,3-DPhI became apparent to be smaller than that of 1,3-DT.

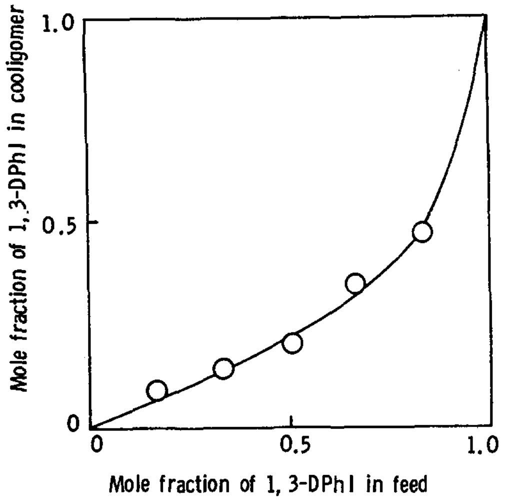


Fig. 2. Composition curve for the photooligomerization of 1,3-DPhI with 1,3-DT at 40°C for 70 h. The compositions of cooligomers were estimated by assuming apparently their formulae as $-(C_{15}H_{16}N_2)_x-(C_3H_6S_2)_{1-x}$

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