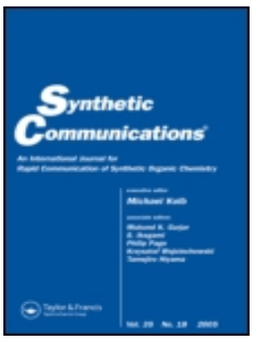

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1,3-DIPOLAR CYCLOADDITION REACTIONS ASSISTED BY MICROWAVE RADIATION AND GAMMA RADIATION

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ABSTRACT

Microwave irradiation and gamma irradiation are shown to be new and most suitable techniques for 1,3-dipolar reactions using unsaturated oximes with conventional dipolarophile.

Earlier we have reported[1] thermal reactions using unsaturated oximes with conventional dipolarophiles which furnished 1,3-dipolar cycloadducts. Use of other techniques may change the course of the reaction. Gamma radiation is a source of energy which is 10^6 times higher than the thermal energy. Reactions carried out using gamma radiation take place at room temperature and thus the products are expected to be purer and in high yields.[2] Various types of reactions induced by gamma radiation have been studied[2] however this method is not used for synthetic purpose.

Recently microwave induced rate acceleration technology has become a powerful tool for synthetic purpose because of the enhanced selectivity, easy reaction condition, rapid reactions and increased yields.[3] Various

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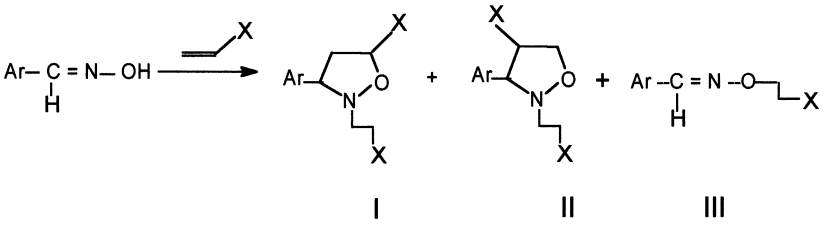
organic reactions like Diels Alder reactions, cyclization and radical reactions are reported[3] using this technique. There is a recent report[4] of 1,3-dipolar reactions carried out using microwave radiation. In the present paper we are reporting the results obtained in the 1,3-dipolar reactions using gamma and microwave radiation.

REACTIONS USING GAMMA RADIATION

Earlier reported thermal reactions of unsaturated oximes with conventional dipolarophiles are shown in Scheme I. In the present work the unsaturated oximes were mixed with acrylonitrile in benzene and irradiated with gamma radiation. Reactions were monitored using tlc. Two products were isolated from these reactions. The major one was shown to be a mixture of isomers of 1,3-dipolar cycloadducts with Michael addition (I & II, Scheme I) and the minor was Michael adduct (III, Scheme I). The presence of Michael adduct indicated that it was the intermediate in the formation of 1,3-dipolar cycloadduct. The probable mechanism might be first Michael addition and then cycloaddition reaction. The role of Michael adduct as an intermediate was confirmed by carrying out further reaction of the isolated Michael adduct, with the dipolarophile which furnished the same mixture of isomers of 1,3-dipolar cycloadducts. The yields and time intervals required for the reactions using gamma



Ar =phenyl X= CN
= 3,4-methylenedioxy phenyl
= 4-nitrophenyl
= 3,4-dimethoxy phenyl
= furyl
= styryl

Scheme I.

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radiation are given in Table I. The substituted isoxazolidines obtained were characterized using PMR and IR spectral data. The products were shown to be mixtures of 4 and 5- cyno substituted isoxazolidines. The differentiation between 4 and 5- cyno substituted cycloadducts was made on the basis of the most down field signal (around 5δ) of C_5H of 5- cyano isomer in the alicyclic region. In a few cases exclusively one isomer was obtained (Table II). It was observed in general that though the time required was much more, the yields of these reactions were almost comparable with that for the thermal reactions (Table I). Dehydration of oximes was not observed during Gamma irradiation except cinnamaldoxime (minor).

Table I.

		Thermal		Gamma Irradiation		Microwave Irradiation	
Entry	Oxime	Time (hr.)	Yield (%)	Time (hr.)	Yield (%)	Time (min.)	Yield (%)
1.	Benzaldoxime	48	90	96	81	09	92
2.	Pipernaloxime	120	71	160	69	22	85
3.	p.Nitrobenzaldoxime	36	98	72	71	08	85
4.	Veratraldoxime	48	72	168	70	30	83
5.	Furfuraldoxime	12	76	96	66	05	93
6.	Cinnamaldoxime	18	72	–*		07	73

*Dehydration product and Michael adduct was obtained.

Table II.

	Oxime	Thermal		Gamma Irradiation		Microwave Irradiation	
		4-Cyano	5-cyano	4-Cyano	5-cyano	4-Cyano	5-cyano
1.	Benzaldoxime	–	*cis*	–	*cis*	trans	–
2.	Pipernal oxime	mixture		mixture		–	*cis*
3.	p.Nitrobenzaldoxime	–	*cis:trans* 3:2	–	*cis*:*trans*1:2	–	trans
4.	Veratraldoxime	mixture		mixture		mixture	
5.	Furfuraldoxime	minor	*cis* major	2 : 1[+]		2 : 1[+]	
6.	Cinnamaldoxime	mixture		nil*		exclusively	–

[+]Ratio is of 4-isomer and *cis* 5-cyano isomer.
*Dehydration product and Michael adduct was obtained.

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REACTIONS USING MICROWAVE RADIATION

Unsaturated oximes were mixed with acrylonitrile in an Erlenmeyer flask and exposed to microwave radiation in a domestic microwave oven. In all the reactions substituted isoxazolidines were obtained along with minor amounts of dehydrated products. These results were described in Table I. In the reaction of cinnamaldehyde oxime after five minutes irradiation, Michael adduct was formed. It was converted to 1,3-dipolar adduct by exposing it to microwave radiation for further two minutes. This indicated that Michael adduct was the intermediate in this reaction. A similar observation was obtained during gamma radiation reactions as mentioned above. A remarkable decrease in the time required for the reaction was observed for all oximes (Table I). Yields were also much more as compared to that in the thermal reactions and reactions using gamma radiation. In most of the cases the reactions were regioselective (Table II). It was also observed that when nitro group was present on the benzene ring the reactions were fast as compared to the reactions of oximes having electron donating methoxyl group on the benzene ring (entry 3,2 & 4 respectively in Table I).

CONCLUSION

Gamma radiation are used for the first time for synthetic purpose for 1,3-dipolar reactions. These reactions were clean and yields obtained were similar to that of thermal reactions. No dehydration was observed in general during these reactions. Microwave radiation reactions were very clean and rapid. Moreover the yields were high. Thus this method is shown to be most suitable for 1,3-dipolar reactions. These results introduced two new techniques for 1,3-dipolar reactions.

EXPERIMENTAL

General Remarks

IR spectra were recorded on Perkin-Elmer FTIR 1600 spectrophotometer. ^{1}H NMR were recorded on Jeol FX90Q (90 MHz). The reactions were carried out using ^{60}Co Gamma rays source with Dose rate 2000 Gy(gray)/min. Microwave reactions were carried out in a domestic microwave Oven (Daewoo, KOR-616T 1200 W). Oximes were prepared by the reported procedures.

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General Procedure for Gamma Irradiation

Oxime (0.002 mole) was mixed with acrylonitrile (2.5 ml) in dry benzene (10 ml) in a conical flask and was exposed to Gamma radiation. The reaction was monitored using tlc. Solvent was removed and the reaction mixture was chromatographed using silica gel with hexane-ethyl acetate (2.5%) as an eluent to furnish the products.

General Procedure for Microwave Irradiation

Oxime (0.002 mol) was dissolved in excess of acrylonitrile (5 ml) and exposed to Microwave radiation. The reactions were monitored by tlc after every two minutes. Acrylonitrile was evaporated and the reaction mixture was chromatographed using silica gel with hexane-ethyl acetate (2.5%) as an eluent to furnish the products.

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