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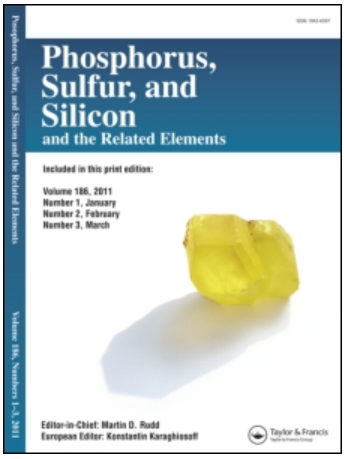

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Mechanism on Iodine Induced Cyclization Reaction of Organophosphorus Compounds

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MECHANISM ON IODINE INDUCED CYCLIZATION REACTION OF ORGANOPHOSPHORUS COMPOUNDS

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Abstract: The iodine induced cyclization reaction of δ,ε- or γ,δ- unsaturated phosphate, phosphonate or phosphoamidate were investigated by P-31 and C-13 NMR spectra. In each case, the diiodo-derivatives were observed and identified. For the δ,ε-unsaturated phosphate and phosphonate the cyclized products formed predominately.

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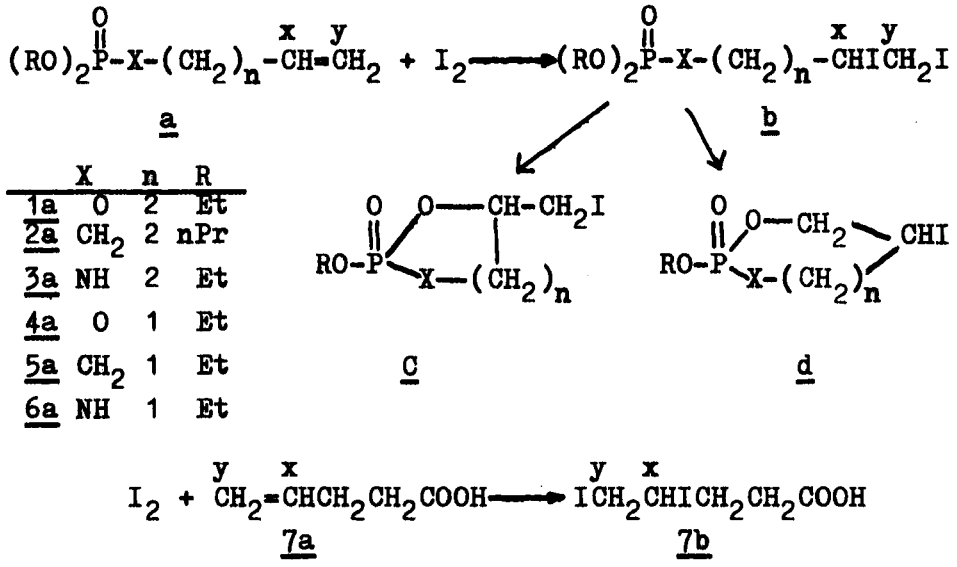
The iodolactonization reaction has been applied to a variety of cyclic and acyclic unsaturated carboxylic acids, esters and ethers for sterocontrol in organic synthesis. But, due to the limitation of the instruments, their intermediates had not been observed yet.[1] We had taken the advantage of P-31 NMR spectra for its simplicity and clearness to study the reaction mixtures of δ,ε-unsaturated phosphonate and iodine.[2] It was discovered that in chloroform, there were two intermediates, the major one being (4,5-diiodopentyl)phosphonate, which had never been proposed before.

In this paper, we wish to report that as each of the δ,ε- or γ,δ-unsaturated phosphate, phosphonate or phosphoamidate 1a-6a was treated with iodine, the diiodo-derivatives were all obserbed by P-31 and C-13 NMR spectra shown in Table I. In addition, as the γ,δ-unsaturated pentanoic acid 7a was treated with one equiv of iodine, we also picked up its diiodo-derivative 7b, which was taken no account as one attempted to evaluate the mechanism of the iodine induced cyclization reaction.[3,4] The Scheme I

SCHEME I: THE REACTION OF IODINE WITH 1a-6a.



	X	n	R
1a	O	2	Et
2a	CH_2	2	nPr
3a	NH	2	Et
4a	O	1	Et
5a	CH_2	1	Et
6a	NH	1	Et

TABLE I:[a,b] C-13 NMR of $(RO)_2P(O)-X-(CH_2)_n-CH=CH_2$

entry	X (ppm)	y (ppm)
1a	132.7	116.8
1b	26.8	13.1
2a	137.6	115.4
2b	31.4	13.2
3a	134.6	116.2
3b	28.9	13.5
4a	132.2(5.8)	117.2
4b	25.3(8.8)	8.2
5a	136.3(17.6)	113.8
5b	31.4(19.1)	12.7
6a	135.9(5.9)	114.9
6b	32.8(5.9)	9.5
7a	136.2	115.5
7b	34.1	12.8

a. Coupling constants in parenthesis given in hertz.
b. A 1.7 M solution of 1a-6a in chloroform was treated with one equiv of iodine at 21°, after few min the C-13 NMR spectra was taken with 2000 pulses and TMS as the reference.

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and Table II show that for the 1a and 2a, the six member ring products 1c and 2c were formed predominately. While for 3a, the cyclization was not completed, after equilibrium, there was still 14% diiodo compound 3b and only 35% six member ring 3c formed. For the case of compound 4a, there was no significant cyclized product at all; the iodine addition compound 4b was the final product. For 5a the cyclization occurred but it was not regioselective, both five and six member rings 5c and 5d were isolated.

From these results it is obvious that the extent of iodine induced cyclization is dependent on the molecular structures. Thus, for each of the 4a-6a, which is one carbon shorter than 1a-3a respectively, did not give good cyclization product. It suggested that the carbon chain, which separates the double bond from the polarizable atom and group, is an important structural factor. Hence, we proposed that the stability of the bridged ion is the key to the cyclization. The examples in eq 1-3 are the evidence for this proposal.[2,5]

TABLE II[§] : The percentage of the equilibrated reaction mixtures of the organophosphorus compounds 1a-6a, with two equiv of iodine.

entry	a		b		c		d		§§
	ppm	(%)	ppm	(%)	ppm	(%)	ppm	(%)	(%)
1						(84)			
2	32.3	(0)	31.4	(0)	24.7	(77)			§§§(13)
3	9.1	(0)	8.8	(14)	-13.4	(35)			§§§§(50)
4	-0.8	(30)	-1.8	(70)					
5	31.3	(0)	29.9	(22)	48.2	(27)	25.2	(31)	(20)
6	9.2	(0)	7.7	(36)	-1.4	(46)			(18)

§. A 1.7 M solution of 1a-6a and iodine in chloroform was stood at 21° for a specified time, its P-31 NMR was taken on a FT-80A spectrometer at 32.2 MHz by broad band decoupled technique with 85% H_3PO_4 as external reference.
§§. The % of the side products.
§§§. There were quite a few side products.
§§§§. At 5.25; 4.76 ppm (26%). At -1.76; -2.31 ppm (23%).

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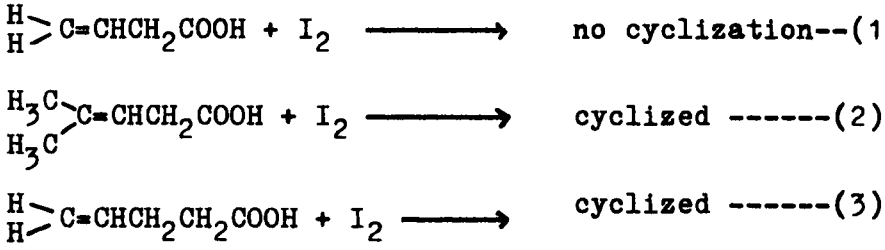
Also, the nucleophilicity of the phosphoryl oxygen plays a crucial role in the cyclization reaction. In conclusion, the two principles—stability of the bridged ion and the nucleophilicity of the phosphoryl oxygen will lead to the extent of cyclization.



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