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A NEW ROUTE TO THE PHOSPHOLANE RING-SYSTEM

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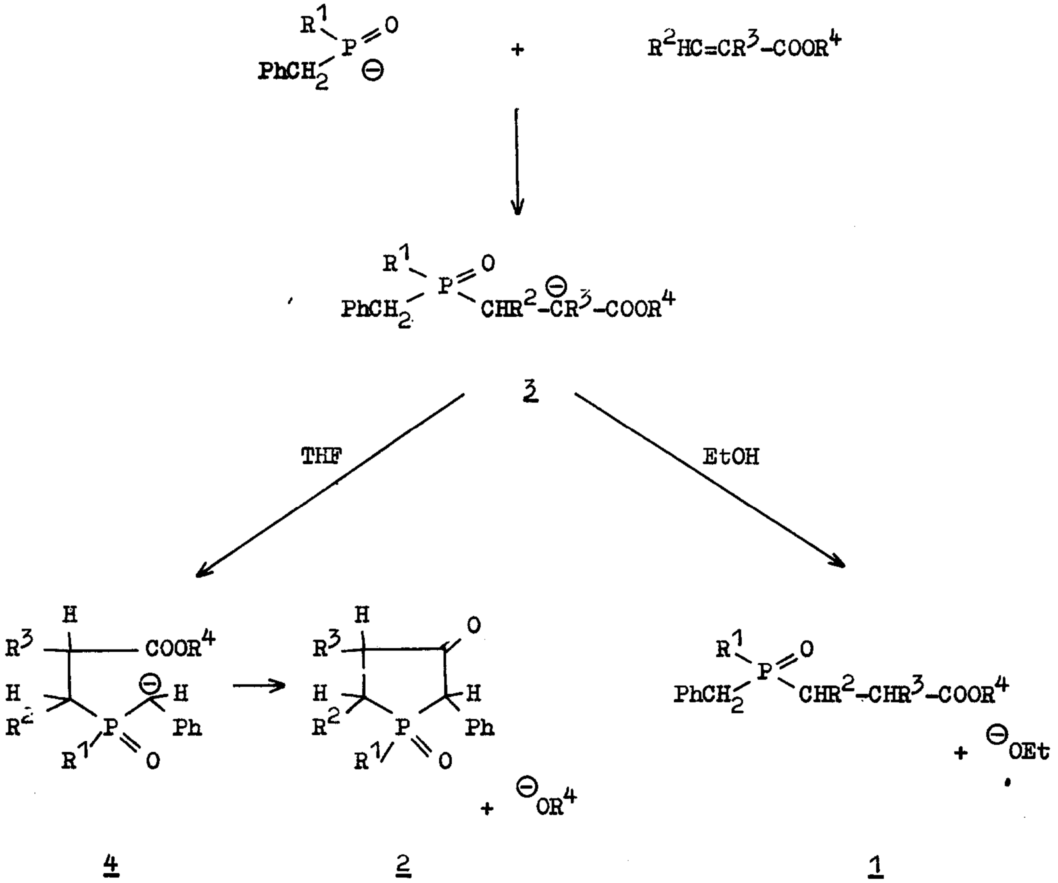
Although five membered heterocycles containing phosphorus atom have received much attention, the synthetic approaches to these compounds are relatively few in number and for the most part of limited applicability [1].

We wish to report the first direct synthesis of phospholan-3-ones; this approach is capable of considerable generalization and should be useful for the preparation of various phospholane, phospholene and phosphole derivatives.[2]

The addition of secondary dibenzylphosphine oxide to α,β-unsaturated esters in the presence of sodium ethoxide in ethanol yields tertiary phosphine oxides 1 [3].

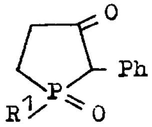
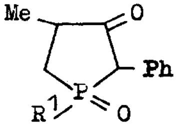
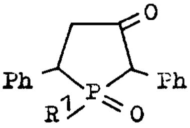
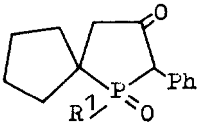
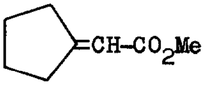
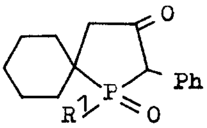
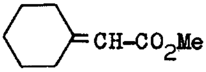
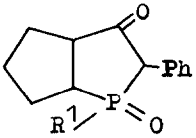
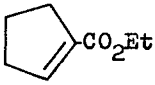
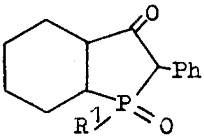
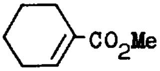
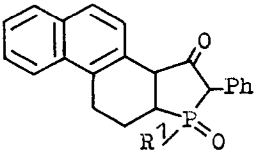
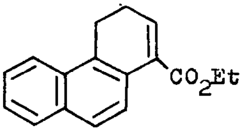
We have now treated secondary phosphine oxides, containing at least one benzyl group, with sodium hydride in tetrahydrofuran at room temperature and then added an equimolar amount of α,β-unsaturated ester at 65°. Under these conditions phospholan-3-ones 2 are formed, usualy in high or moderate yield.

We believe that in the presence of a protic solvent the initial adduct 3 simply picks up a proton to give 1. However in tetrahydrofuran proton transfer in 3 affords the carbanion 4. This anion undergoes subsequent intramolecular condensation as in a Dieckmann reaction to yield the final ketone 2.



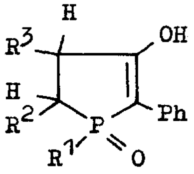
Typical results illustrating the scope and versatility of the method are summarized in Table 1. NMR and IR spectra of all the products are consistent with the structures assigned. The spectral data (strong C=C band at 1610 cm^{-1}, broad OH band at 2330-2700 cm^{-1}) suggest that the phospholan-3-ones 2a - 2m are highly enolized in solid state as well as in such solvents like methanol or pyridine. Phospholan-3-ones 2n and 2o exist mainly in the keto form (strong C=O band at 1725 cm^{-1}).

TABLE 1

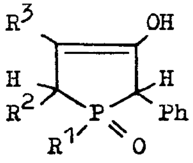
No.	PRODUCTS [4]	R^1	M.p. (°C)	Yields (%)	SUBSTRATES	
					Phosphine Oxides *	α,β-Unsaturated Esters
2a		Ph	239-40	38.0	PhBzPOH	$CH_2=CH-CO_2Et$
2b		Bz *	206-07	41.0	Bz_2POH	
2c		Ph	205-08	45.0	PhBzPOH	$CH_2=CMe-CO_2Et$
2d		Bz	216-18	64.5	Bz_2POH	
2e		Ph	270-72	55.7	PhBzPOH	$PhCH=CH-CO_2Et$
2f		Bz	217	72.2	Bz_2POH	
2g		Ph	287 dec.	57.5	PhBzPOH	
2h		Bz	195	65.0	Bz_2POH	
2i		Ph	312-15	70.0	PhBzPOH	
2j		Bz	228-29	61.0	Bz_2POH	
2k		Ph	251 dec.	43.2	PhBzPOH	
2l		Bz	221	63.3	Bz_2POH	
2m		Ph	214-23	50.1	PhBzPOH	
2n		Bz	200-07	64.0	Bz_2POH	
2o		Bz	270-75	20.0	Bz_2POH	

* Bz = Benzyl

Of the two possible enol forms 5 and 6, only 5 was observed; this is expected as 5 is stabilized by conjugation with phenyl and phosphoryl groups.



5



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The cyclization here described, among other advantages, affords a simple approach to the 2m, 2n and 2o which possess obvious importance for the total synthesis of 17-phosphasteroids.

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REFERENCES

1. F.G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony and Bismuth", Wiley-Interscience, New York, N.Y., 1970.
2. This work was presented in part at The Fifth All-Union Conference on Organophosphorus Compounds, Moscow, June 1972.
3. R.C. Miller, J. Bradley, L.A. Hamilton, J. Am. Chem. Soc., 78, 5301 (1956).
4. Elemental analyses were within the accepted limits.