A New Synthesis of Tetra-substituted Ethylenes

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Summary Certain tetra-substituted ethylenes have been synthesised by treating the appropriate carbon acid with thionyl chloride.

In studies of the interaction between thionyl chloride and compounds containing active methylene groups it has been found that compounds with a low enol content generally give a tetra-substituted ethylene, whereas compounds with a high enol content generally give the corresponding sulphide and α-chloro-compound.[1] The only previous example of the reaction was that reported by Michaelis and Phillips in 1890 who prepared di(acetylethoxycarbonylmethyl) sulphide by treating ethyl acetoacetate with thionyl chloride; they did not, however, observe the formation of ethyl α-chloroacetoacetate.[2]

We now report the formation of tetra-substituted ethylenes in the reaction between certain substituted alkyl acetates or similar materials and thionyl chloride. Thus the treatment of ethyl cyanoacetate with a small excess of thionyl chloride followed by heating the reaction mixture under reflux for 3h gave diethyl dicyanofumarate, $EtO_2C(CN)C{=}C(CN)CO_2Et$, (I), 65—70% yield, m.p. 114·5°, τ ($CDCl_3$) 8·55(3H,t) and 5·45(2H,d). The i.r. spectrum of (I) agrees with that obtained by Felton[3] and Kudo[4] who obtained a 10% yield of (I) by the selenium dioxide oxidation of ethyl cyanoacetate. Other results are summarised in the Table.

TABLE

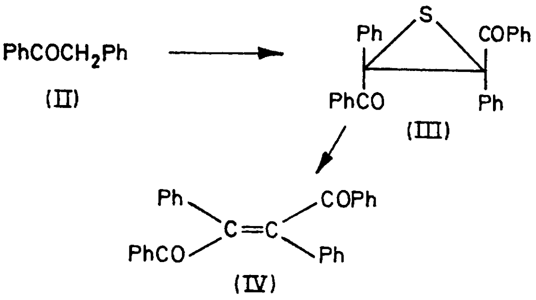
$R^1CH_2R^2 \rightarrow R^1R^2C{=}CR^1R^2$

R^1	R^2	% Yield	Stereo-chemistry	Conditions
CN	CO_2Me	65—70	*trans*	reflux 3h
CN	$CO_2$70	65—70	*trans*	reflux 3h
CN	CO_2Bu^t	—	?	cold 12h
CO_2Et	CO_2Et	85—90	—	reflux 6h
CN	CN	<10	—	cold 6h
Cl	CO_2Et	0	—	reflux 12h
Br	CO_2Et	0	—	reflux 12h
Ph	CO_2Et	4[a]	*cis*	vig. reflux 12h
Ph	COPh	60—65[b]	not known	reflux 3h

[a] The unsaturated anhydride was obtained. [b] The episulphide was obtained.

The formation of a low yield of tetracyanoethylene in the reaction between malononitrile and thionyl chloride suggests that an enolic proton is not a prerequisite for this reaction.

We suggest the formation of an episulphide as an intermediate in this reaction, and this can then lose sulphur to give the alkene. The treatment of deoxybenzoin (II) with thionyl chloride gave 1,2-dibenzoyl-1,2-diphenylthiiran (III), (60—65% yield), m.p. 93—94°, τ ($CDCl_3$) 1·9 (m) and 2·35 (m), ν_{max} 3320, 3070, 1660, and 1600 cm^{-1}. This episulphide[5,6] is known to lose sulphur[5-7] to give the alkene, 1-2-dibenzoylstilbene (IV). The stereochemistry of (III) and (IV) is being further studied.



Results are summarised in the Table. The analytical and spectral data for all new compounds are in agreement with the assigned structures.

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