Rearrangement Products of a Thermally Generated Oxycarbene

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Summary Thermal decomposition of the dry sodium salt (**3**) of 4-hydroxy-4-methylvaleric acid γ-lactone toluene-*p*-sulphonylhydrazone leads to 2,2-dimethylcyclobutanone (**7**) and 2,2-dimethyl-2,3-dihydrofuran (**8**).

SEVERAL investigations in recent years have focussed attention on the photochemical transformation of cyclic ketones (**1**) into products presumably derived from intermediate oxycarbenes (**2**).[1–4] We report here the generation

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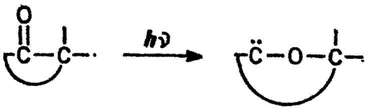
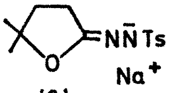
of such an oxycarbene by a non-photochemical, thermal route, together with our observation that a significant reaction of this oxycarbene is rearrangement to the related ketone, *i.e.*, (**2**) to (**1**).

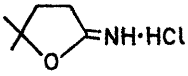


(**1**) (**2**)

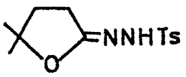
Thermal decomposition of the salts of toluene-*p*-sulphonylhydrazones has provided a convenient source of carbene intermediates in a variety of chemical systems,[5] and we have accordingly prepared and investigated the pyrolysis of the lactone toluene-*p*-sulphonylhydrazone salt (**3**). The iminolactone hydrochloride (**4**),‡ which was synthesized by adaptation of a known procedure,[6] underwent reaction[7] with toluene-*p*-sulphonylhydrazide in ethanol to furnish the lactone hydrazone (**5**).‡ On treatment with sodium hydride in dry diethylene glycol diethyl ether this gave the required salt (**3**),‡ which could be isolated, recrystallized, and stored as a stable compound.



(**3**)

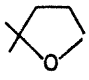


(**4**)

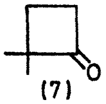


(**5**)

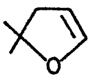
This salt (**3**) was decomposed at 310° and 0·1 Torr in a closed system without solvent. From previous reports,[5] these conditions should particularly favour formation of oxycarbene (**6**) with a minimum of competing alternative processes. The volatile products from this pyrolysis were trapped at –78° and amounted to *ca.* 45% of theory. Two components were separated by preparative g.l.c. and identified by spectroscopic comparisons with authentic samples as 2,2-dimethylcyclobutanone (**7**, 70%),[8] and 2,2-dimethyl-2,3-dihydrofuran (**8**, 30%).[9] The formation of (**8**) is reminiscent of the photochemical production of enol ether (**9**) from camphor (**10**),[4] a reaction believed to involve oxycarbene (**11**). The ring contraction leading to (**7**) is of considerable interest, since the photochemical conversion of ketone (**7**) into oxycarbene (**6**) has been known[2] for several years. Our results indicate that this photochemical transformation, (**7**) → (**6**), may be thermally reversed, (**6**) → (**7**), a process that possibly contributes to the difficulty[3,10] in trapping oxycarbene-derived products from photolysis of cyclic ketones.



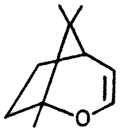
(**6**)



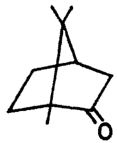
(**7**)



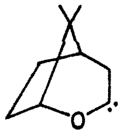
(**8**)



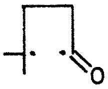
(**9**)



(**10**)



(**11**)



(**12**)

For photochemical conversion of ketones into oxycarbenes both a concerted process and the intermediate formation of a biradical, such as (**12**), have been considered.[11] Clearly, similar mechanistic possibilities (apart from electronic state) exist for the reverse thermal transformation described here.

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‡ The structure of this new compound is supported by i.r. and n.m.r. spectra as well as elemental analysis.

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