A New Alkene Synthesis from Vicinal Dicarboxylic Acids by Decomposition of their Peresters

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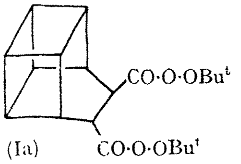
WE report a new method for alkene formation from vicinal dicarboxylic acids. Previously this was achieved with lead tetra-acetate,[1] or by anodic oxidation: improved techniques for the latter reaction have recently been reported.[2] Our method is simple, quick, and gives a moderate yield in neutral non-aqueous solution. Treatment of the acyl chlorides of the dicarboxylic acids with t-butylhydroperoxide[3] gives di-t-butyl peresters (I) which are then decomposed either thermally or photochemically to provide the corresponding alkenes. The photolysis process is applicable to the synthesis of thermally unstable alkenes.

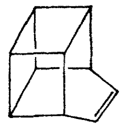
Solutions of the peresters† in t-butylbenzene were deoxygenated by a stream of argon or nitrogen (60 min.) and then heated to give the alkenes (35—50%). In this solvent, saturated hydrocarbons (resulting from hydrogen abstraction) were absent, in contrast to decompositions effected in a solvent containing t-aliphatic hydrogens (*p*-cymene), where saturated hydrocarbon accounted for as much as 20% of the hydrocarbon product.

(I)

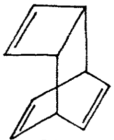
Results of the perester decompositions are shown in the Table. Carbon dioxide evolution was determined by absorption on Ascarite and amounted to 75—85% of the theoretical amount; t-butyl alcohol was isolated by preparative g.l.c. Volatile, low-molecular weight alkenes (cyclohexene and norbornene) were isolated by distillation from the reaction mixture into a cold trap. Product analysis was then carried out by g.l.c., the alkenes being identified by retention volume, against authentic samples. These alkenes were also isolated by preparative g.l.c. and were identified with authentic samples (n.m.r.). Partial isomerization of hydrocarbon (II)[4] to Nenitzescu's hydrocarbon (III)[5] precluded its isolation as pure (II); it was fully isomerised [$t_{\frac{1}{2}}$ (100°), 115 min.] by additional heating and then isolated.



(Ia)



(II)



(III)

Photolytic decompositions were effected at room temperature in deoxygenated benzene solution with a Hanovia medium-pressure lamp and a Vycor filter. Products were identical to those obtained by thermal decomposition and yields were similar; photolysis of (Ia) provided (II) uncontaminated by (III). For alkenes which are more thermally unstable, it is obviously possible to lower the temperature by choosing an appropriate solvent system.

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Olefin formed	Thermal decomp. Temp.	Thermal decomp. Time (min.)	Photochemical decomp. Time (min.)	CO_2 evolved (%)	Yield of olefin (%)
Cyclohexene	110°	120		84	38
Norbornene	135	120		79	34
			90	74	30
(III) [from (II)]	120	12		75	48
(II)			110	68	40

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† All vicinal peresters were *trans*- except the cyclohexene precursor.

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[2] P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, *Tetrahedron Letters*, 1968, 5117; H. H. Westberg and H. J. Dauben, jun., *ibid.*, 1968, 5123.

[3] P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, 1958, **80**, 1398. All peresters were crystalline and were readily purified by chromatography on a short column of Florisil by elution with pentane.

[4] S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Letters*, 1966, 1017.

[5] C. D. Nenitzescu, M. Auram, J. J. Pogany, G. D. Mateescu and M. Farcasin, *Studii Cercetari Chem. Acad. R.P.R.*, 1963, **11**, 7.