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PHOTOCYCLOADDITION OF PERFLUOROOXAALKANOIC ACID FLUORIDES TO PERFLUOROALKENES

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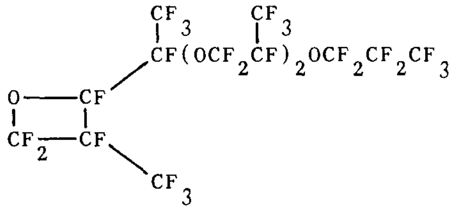
Since perfluoroethers are assuming increasing importance as operative fluids, they are the object of continuous research. New perfluorooxetanes characterized in having one or more ether bonds in the substituents,



(I)

were synthesized through the UV promoted cycloaddition between the proper acid fluorides and alkenes.
The reaction was carried out under atmospheric pressure.
The selectivity of the synthesis was good provided that the olefin is used in an adequate excess.
The thermal stability of the oxetanes is high and in the same range as that of known acyclic perfluoroethers.
The presence of more isomeric structures both geometrical and stereochemical prevents them from crystallization even at very low temperatures : the only thermal phenomenon, below their boiling point, is the glass transition (-109°C for I), whereas analogous oxetanes lacking ether oxygens in the substituent show sharp freezing points.
The complexity of the isomeric mixture is also evident by the examination of NMR spectra.
Details on the synthesis and on the NMR interpretation are given.