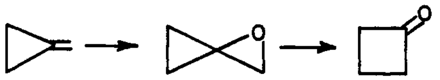
Oxaspiropentane. A Rapid Route to Cyclobutanone

By J. R. SALAÜN and J. M. CONIA*

(*Laboratoire des Carbocycles, Université de Paris-Sud, 91 Orsay, France*)

Summary Methylenecyclopropane, on treatment with an organic peracid, undergoes quantitative oxidation into oxaspiropentane; this so far unknown epoxide is converted into cyclobutanone by a catalytic amount of lithium iodide.

ALKYL- or alkylidene-substituted oxaspiropentanes are known and their rearrangements studied.[1] Until now, the parent compound (**2**) was unknown. We report that (**2**) can be easily prepared from the readily available methylenecyclopropane (**1**)[2] and can be easily converted into cyclobutanone.



(1) (2) (3)

We have prepared (**1**) directly from methylallyl chloride and base, $NaNH_2$–Bu^tONa (yield 60%).[2b]

The addition of *p*-nitroperbenzoic acid[3] (1 mol) to a methylene chloride solution of (**1**) (1 mol) at −10° gives the epoxide (**2**) quantitatively (from the n.m.r. spectrum of the crude solution). After removal of the acid and solvent, pure liquid oxaspiropentane (**2**) is isolated without decomposition by vacuum distillation (20 mm) at room temperature

The n m r spectrum of a pure sample of (**2**) shows a symmetric octet at δ 0 85 p p m (4H, AA′BB′) and a sharp singlet at 3 00 p p m (2H) The mass spectrum of (**2**) (12 or 70 eV) is clearly different from the spectra of its thermal rearrangement products, in particular cyclobutanone (**3**) (*vide infra*), and shows a strong molecular-ion peak at *m/e* 70 The i r spectrum has epoxide bands at 10 9 and 11·7 μm

On heating (liquid phase or g l p c) at 100°, (**2**) undergoes isomerization into $CH_2=C(Me)CHO$ (**4**) (30%), $MeCOCH=CH_2$ (**5**) (30%), and cyclobutanone (**3**) (40%) Flow pyrolysis in the injector (230°) of a gas chromatograph (column 100°) increases the yield of (**3**) to 80%

The effect of Lewis acids on epoxide rearrangements is well known in the field of small-ring chemistry, see refs 1 and 4 We observed that the addition of a catalytic amount of lithium iodide (commercial LiI, 1 5 H_2O) produces the exothermic conversion of oxaspiropentane (**2**) into cyclobutanone (**3**) (yield $> 95\%$) together with traces of compounds (**4**) and (**5**), readily separated by distillation In methylene chloride solution the direct reaction (**1**) → (**2**) → (**3**) is convenient, smooth, and rapid, providing, in high yield, cyclobutanone from commercially available cheap reagents

Mechanistic studies in connection with our interest in the chemistry of small-ring compounds[5] are under investigation

(*Received, October 25th*, 1971, *Com* 1847)

---

[1] J K. Crandall and D R Paulson, *J Org Chem* , 1968, **33**, 991 For references in this field see C R. Johnson G F Katekar, R F Huxol, and E R Janiga, *J Amer Chem Soc* , 1971, **93**, 3771

[2] (a) R Koster, S Arora, and P Binger, *Synthesis*, 1971, **6**, 322, (b) P Caubere and G Coudert, *Bull Soc chim France*, 1971 2234.

[3] M Vilkas, *Bull Soc chim France*, 1959, 1401.

[4] D L Garin, *J Org Chem* , 1971, **36**, 1697

[5] J M Conia and J Salaun, *Accounts Chem Res* , 1971, in the press