[23] *R. L. Shriner, R. C. Fuson & D. Y. Curtin*, 'The Systematic Identification of Organic Compounds', S. 279, John Wiley & Sons, Inc. New York 1956.
[24] *D'Ans-Lax*, «Taschenbuch für Chemiker und Physiker», 3. Aufl. Band. II, S. 874, Springer-Verlag, Berlin 1964.
[25] vgl. *D. L. Brink, Y. T. Wu, H. P. Naveau, J. G. Bicho & M. M. Merriman*, Tappi *55*, 719 und 1356 (1972); Chem. Abstr. *77*, 50408 z und 166 378 u (1972).
[26] *E. Dyer & R. B. Pinkerton*, J. appl. Polymer Sci. *9*, 1713 (1965); Chem. Abstr. *63*, 6967 h (1965).
[27] *S. Petersen* in *Houben-Weyl*, «Methoden der organischen Chemie», Band VIII, S. 117, G. Thieme-Verlag, Stuttgart 1952.

100. The *Clemmensen* Reduction of α,β-Unsaturated Ketones

by **Charles W. Jefford** and **André F. Boschung**

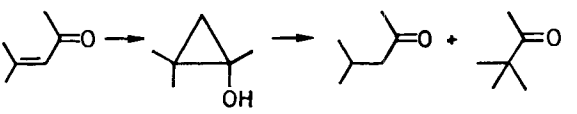
Département de Chimie Organique, Université de Genève
30, quai Ernest Ansermet, 1211 Genève 4

(11. II. 76)

Summary. Eleven structurally different α,β-unsaturated ketones were subjected to the *Clemmensen* reduction under anhydrous conditions using amalgamated zinc, hydrogen chloride in a solution of ethyl ether, and acetic anhydride. In all cases but one the formation of cyclopropyl acetates was observed. 4-Methyl-3-penten-2-one, methyl vinyl ketone, 2-isopropylidene-1-cyclopentanone, and 2-cyclohepten-1-one led to substituted cyclopropyl acetates. Stereospecific reactions were found with 2-ethylidene-1-cyclopentanone, 2-benzylidene-1-cyclohexanone, and methyl 1-cyclohexenyl ketone, whereas 3-penten-2-one, 3-methyl-3-buten-2-one, and 2-methyl-2-cyclohexen-1-one afforded mixtures of the isomeric cyclopropyl acetates.

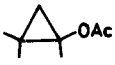
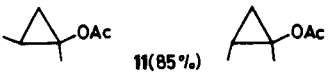
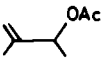
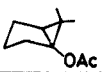
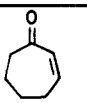
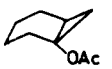
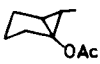
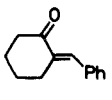
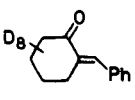
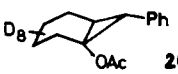
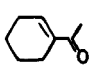
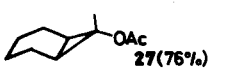
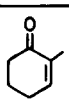
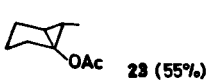
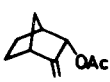
These results are interpreted in terms of the initial formation of an allylic anion which undergoes electrocyclic closure. A stereospecific course is followed when geometric constraints permitted. Exceptions are discussed.

Introduction. – The *Clemmensen* reduction, which uses amalgamated zinc and aqueous hydrochloric acid, is a standard laboratory method for the conversion of aldehydes and ketones to their corresponding hydrocarbons [1]. The reduction usually proceeds in high yield as long as the substrates are not sensitive to acid and provided that certain functional groups are absent. α,β-Unsaturated ketones are also reduced by this method, however reduction occurs only at the double bond accompanied by skeletal rearrangement [2]. The behaviour of 4-methyl-3-penten-2-one (**1**) is typical in that two isomeric ketones are obtained, namely 4-methyl-2-pentanone (**3**) and 3,3-dimethyl-2-butanone (**4**) in a ratio of 28:73 [3]. In order to account for the formation of the rearranged ketone the intermediacy of 1,2,2-trimethylcyclopropanol (**2**) has been postulated. In acidic medium the three-membered ring in **2** could open up in two ways to give the ketones **3** and **4**. In fact the independent synthesis of **2** followed by acidic hydrolysis afforded the ketones **3** and **4** in exactly the same proportions as those observed in the *Clemmensen* reduction itself [4].



1 **2** **3** **4**

Table 1. *Clemmensen Reduction of α,β-Unsaturated Ketones*

Enones	Products [a], [b]	Yield %
 1	 5	65
 7	 8	32
 9	 11(85%) 12(15%)	40
 10	 11(61%) 12(29%) 13(10%)	28
 14	 16	45
 15	 17	40
 18	 23	45
 19	 25	50
 20	 26	50
 21	 27(76%) (24%)	40
 22	 23 (55%) 24(45%)	40
 28	 29	85

[a] Relative yields are given in brackets.

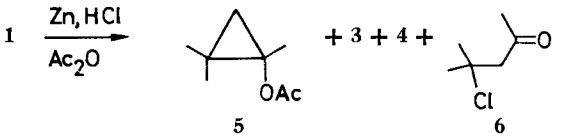
[b] Products present in less than 5% were not determined.

Cyclic alkenones behave similarly, and by using anhydrous conditions it has been possible to trap the intermediate cyclopropyl acetates in the reduction of 2-arylidene-1-cyclopentanones and 2-aryl-2-cyclohexen-1-ones [5].

In view of our interest in the chemistry of three-membered rings [6], we wish to confirm the generality of cyclopropanol formation as an intermediate in the reduction of α,β-unsaturated ketones.

Results. – A series of structurally varied enones was subjected to the *Clemmensen* reduction using anhydrous conditions [7] (Table 1).

4-Methyl-3-penten-2-one (**1**). In a typical procedure, a suspension of **1**, acetic anhydride, and amalgamated zinc in ether was cooled to the desired temperature and the reduction was brought about by the addition of a saturated solution of hydrogen chloride in ether. Four products were obtained, 4-methyl-2-pentanone (**3**), 3,3-dimethyl-2-butanone (**4**), 1,2,2-trimethylcyclopropyl acetate (**5**) and 4-chloro-4-



5 6

methyl-2-pentanone (**6**). The relative distribution of these products was shown to depend strongly on reaction temperature (Table 2). The best yield of the cyclopropyl

Table 2. *Effect of the temperature on the reduction of 4-methyl-3-penten-2-one* (**1**)

Temperature (°C)	Absolute yield of **5** (%)	relative distribution (%) of			
		5	**3**	**4**	**6**
25	23	55	45	< 0.5	0
0	33	68	31	< 0.5	0
−35	67	97	< 1.5	< 0.5	< 1
−78	46	70	< 0.5	< 0.5	29

acetate **5** was obtained at −35°. At lower temperatures more of the hydrogen chloride addition product **6** was obtained, whereas at room temperature the yield of **5** fell off sharply in favour of **3**. These results are in contrast to those obtained in aqueous solution in which the rearranged ketone **4** is obtained at any temperature.

The role of acetic anhydride is to serve as a trap for the intermediate cyclopropanol. 1,2,2-Trimethylcyclopropyl acetate (**5**) is almost exclusively formed if acetic anhydride is added at the end of the reduction. Moreover, omission of the anhydride permits the isolation of 1,2,2-trimethylcyclopropanol (**2**) [4].

The hydrogen chloride addition product **6** is not a precursor of the cyclopropanol: when **6** was independently synthesized and subjected to the *Clemmensen* reduction it was simply recovered unchanged.

Lastly, it was observed that the use of an inert gas atmosphere (nitrogen) or the inclusion of 2,5-di-*t*-butyl-*p*-cresol as a free radical quencher [8] in no way affects the course of the reduction.

Other acyclic enones. While the reduction of methyl vinyl ketone (**7**) affords 1-methylcyclopropyl acetate (**8**), 3-penten-2-one (**9**) and 3-methyl-3-buten-2-one (**10**) cyclize to a mixture of *trans*- and *cis*-1,2-dimethylcyclopropyl acetates (**11** and **12**)

in a ratio of 85:15 and 61:29, respectively. The reduction of **10** also gives a small amount of 3-methyl-3-buten-2-yl acetate (**13**).

Monocyclic enones. Reduction of 2-isopropylidene-1-cyclopentanone (**14**) and 2-cyclohepten-1-one (**15**) takes place easily to give the expected cyclopropyl acetates **16** and **17**. However, 2-ethylidene-1-cyclopentanone (**18**), 2-benzylidene-1-cyclohexanone (**19**), and its deuteriated derivative **20** are all reduced to give only one of the two theoretically possible cyclopropyl acetates, namely the *exo*-isomers **23**, **25**, and **26**, respectively. On the other hand, the 7-*endo*-methyl compound **27** is obtained from methyl 1-cyclohexenyl ketone (**21**). 2-Methyl-2-cyclohexen-1-one (**22**) cyclizes to give a 55:45 mixture of the *exo*- and *endo*-isomers **23** and **24**.

Bicyclic enones. The reduction of 3-methylidene-2-norbornanone (**28**) is the only case where no trace of cyclopropyl acetate is detected; instead a high yield of *endo*-3-methylidene-2-norbornyl acetate (**29**) is obtained.

Discussion. – The *Clemmensen* reduction of eleven different α,β-unsaturated ketones gave in every case the corresponding cyclopropyl acetate as the major product in an overall yield of 28–65%, with one exception. Polymerization of the enone under the acidic conditions was found to be responsible for diminishing the yields of reduced products. Other reduced compounds are also found in minor quantities (less than 5%), however the isolation of the cyclopropyl acetates could be easily achieved by column or gas-liquid chromatography.

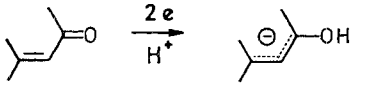
Stereochemical course of the reduction. The configuration of the cyclic products seems to be determined by the constitution and configuration of the starting enone. For example 2-alkylidene- and 2-arylidene-1-cycloalkanones (**18**, **19** and **20**), possessing a fixed (*E*) configuration and a s-*cis* enone moiety, furnish stereospecifically the *exo* compounds whereas methyl 1-cyclohexenyl ketone (**21**) present in the *s-trans* form [9], produces just the *endo* derivative **27**. Similar stereochemical results have already been observed during the reduction of 2-arylidene-1-cyclopentanone [5]. 2-Methyl-2-cyclohexen-1-one (**22**) however, although it exists in the fixed *s-trans* form, leads to a mixture of the isomeric acetates **23** and **24**.

Acyclic enones being free of such steric constraints cyclize in a non-stereospecific manner.

Mechanism. The mechanism of the *Clemmensen* reduction of α,β-unsaturated ketones has been discussed in terms of concerted processes [2] and diradical intermediates [10]. Unfortunately these mechanisms do not explain the stereochemical course of the reaction. It has been suggested that the zinc atom initially attacks the oxygen atom of the carbonyl function thereby engendering ring closure by concerted attack on the double bond [2]. This runs counter to the general view that the metal atom attacks the electropositive end of the carbonyl group [11].

Free radicals or biradicals do not appear to be involved in the reduction or to have an important role as is evidenced by the absence of any effect when radical quencher is present. Furthermore, it has been shown that triplet 1,3-diradicals do not undergo stereospecific cyclization. For example, the thermal decomposition of substituted 1-pyrazoline, which proceeds *via* a 1,3-diradical, leads to a mixture of isomeric cyclopropanes [12]. Similar behaviour is found in the addition of triplet methylene to *cis*- and *trans*-2-butene. Here too, formation of the cyclopropane adduct, which involves a 1,3-diradical, proceeds with loss of the geometry of the starting olefin [13].

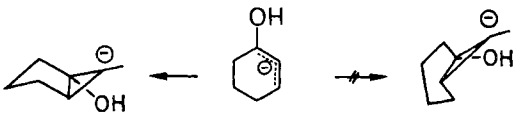
A clue to the possible reaction course is provided by a consideration of the mechanism of the polarographic reduction of conjugated enones [14]. In a two-electron process the formation of an allylic anion **30** has been proposed. In view of the parallel between polarographic and metal reductions, the assumption can be reasonably made that in the *Clemmensen* reduction of α,β-unsaturated ketones an allylic anion of type **30** is initially formed. It follows that formation of the three-membered ring



30

will occur by electrocyclic closure in a conrotatory fashion [15] [16]. Accordingly, only one of the possible pair of isomers should be formed. If this mechanism is correct, enones **18**, **19**, and **20** should all give the *exo* compounds **23**, **25**, and **26**, whereas **21** possessing an *s-trans* configuration, should only afford the *endo* compound **27**. All these expectations were confirmed by experiment. On the other hand, 3-penten-2-one (**9**) and 3-methyl-3-buten-2-one (**10**), which do not have fixed configurations [17], gave mixtures of the two possible isomers **11** and **12**.

Unfortunately, the aforementioned mechanism does not appear to hold in the case of the cycloalkenones **15** and **22**. For reasons of steric constraint, these enones are obliged to cyclize in a disrotatory fashion, otherwise the highly strained *trans* intermediate **31** would form. We therefore conclude that either a different mechanism is operating or that the activation energies of the allowed and forbidden ring closures are not greatly different. Indeed, a recent calculation has shown that this difference in energy is of the order of 9 kcal/mol [18]. Once the cyclopropyl anion **32** is formed, protonation can take place on either side of the molecule leading automatically to a mixture of the isomeric cyclopropanols. Accordingly, the reduction of 2-methyl-2-cyclohexen-1-one (**22**) to give both acetates **23** and **24** is no surprise.



32 **31**

The allylic anion hypothesis also provides an explanation for the formation of most of the minor reduction products. Protonation of the hydroxy allylic anion **30** can occur at either end to afford the allylic acetate or the saturated ketone. Examples of this ambivalent protonation are seen in the reduction of **10**, **21**, **28** and **1**.

The reduction of **1** under anhydrous conditions gives none of the rearranged ketone **4** which is observed in aqueous hydrochloric acid [3]. We therefore conclude that the cyclopropanol **2** is a stable species under our reaction conditions, a fact which we were able to establish by carrying out the reduction in the absence of acetic anhydride. Therefore, 4-methyl-2-pentanone (**3**) must be formed in a step prior to cyclization, namely *via* the protonation of the corresponding allylic anion (*v. supra*).

The absence of a cyclopropyl acetate derivate in the case of 3-methylidene-2-norbornanone (**28**) is probably due to the prohibitive increase in strain in creating a

cyclopropane ring fused *cis* to the norbornane skeletion. Consequently, protonation of the allylic anion occurs from the *exo* side to give the *endo* acetate **29**.

Conclusions. – The formation of cyclopropanol intermediates in the *Clemmensen* reduction of α,β-unsaturated ketones appears to be general. The configuration of the enone determines the stereochemical course of the reaction and we believe that an allylic anion is the key intermediate.

We are indebted to the *Fonds National Suisse de la Recherche Scientifique* (grant No 2.238.0.74) for support of this work. We wish also to record our gratitude to *G. Galeazzi* for his assistance with the experiments.

Experimental Part

General. Gas liquid chromatography (GLC.) was carried out on *Perkin-Elmer* models F11 and 990 instruments. IR. spectra were recorded on a *Perkin-Elmer* model 402 spectrophotometer. NMR. spectra were determined at 60 MHz on *Perkin-Elmer* model R12 or *Varian* model T60A instruments. Determinations at 100 MHz were performed on a *Varian* model XL-100 spectrometer. In all cases CCl_4 and $CDCl_3$ were used as solvents, chemical shifts are expressed as ppm with reference to tetramethylsilane taken as zero. Signal intensities are reported in proton units (1H, 2H, etc.). Signal multiplicity is noted as singlet (*s*), doublet (*d*), triplet (*t*), quartet (*q*) and multiplet (*m*); the coupling constants J are given in Hz. MS. were recorded on *Varian* model SM1 or EM 600 spectrometers.

α,β-Unsaturated ketones. 4-Methyl-3-penten-2-one (**1**), methyl vinyl ketone (**7**), 3-penten-2-one (**9**), 3-methyl-3-buten-2-one (**10**), 2-cyclohepten-1-one (**15**), methyl 1-cyclohexenyl ketone (**21**), and 3-methylidene-2-norbornanone (**28**) are commercially available compounds (purchased from *Fluka* or *Aldrich*).

2-Isopropylidene-1-cyclopentanone (**14**), 2-ethylidene-1-cyclopentanone (**18**) and 2-benzylidene-1-cyclohexanone (**19**) were obtained by condensation of the appropriate enamine with the aldehyde or ketone according to the procedure of *Hünig* [19] and *Birkhofer* [20]. 2-Methyl-2-cyclohexen-1-one (**22**) was prepared according to *Johnson* [21].

2-Benzylidene-octadeuterio-1-cyclohexanone (**20**). Oxidation [22] of 2,2,3,3,4,4,5,5,6,6-decadeuteriocyclohexanol, furnished by *Ciba-Geigy AG*, gave the corresponding ketone which was converted to its 2-benzylidene derivative as above. Further treatment with deuterium oxide and base gave 2-benzylidene-octadeuterio-1-cyclohexanone **20** [23].

Amalgamated zinc [24]. 50 g of zinc powder (*Merck*) were shaken for 10 min with a solution of 6 g of mercuric chloride, 4 ml of conc. hydrochloric acid and 100 ml of water. The solution was decanted and the amalgamated zinc washed thoroughly with water, acetone, and ether, and finally dried in a dessicator for 24 h.

General reduction procedure. A stirred suspension of 1 g of enone, 1 ml of acetic anhydride and 5 g of amalgamated zinc in 10 ml of dry ether was cooled to $-35°$ and 5 ml of a saturated solution of hydrogen chloride in ether was added during 5 min. Stirring was continued at $-35°$ for 15 min, then the solution was decanted and poured into 50 ml of a saturated solution of sodium hydrogencarbonate. The mixture was extracted with ether. The organic layer was washed, dried over $MgSO_4$ and evaporated. The residue was directly analyzed by GLC. or distilled (bulb to bulb) prior to preparative GLC. Yields were always based on distilled products. In addition to the main analysed components, there were always small quantities of several unidentified compounds present.

Reduction of 4-Methyl-3-penten-2-one (**1**). **1** gave 1,2,2-trimethylcyclopropyl acetate (**5**) in 65% yield [25]. – NMR. ($CDCl_3$): 0.39 and 0.62 (*AB*, J = 6.0, 2H); 1.08 (*s*, 3H); 1.12 (*s*, 3H); 1.49 (*s*, 3H); 1.99 (*s*, 3H).

Reduction of Methyl vinyl ketone (**7**). **7** gave 32% of 1-methylcyclopropyl acetate (**8**) [25]. – NMR. ($CDCl_3$): 0.55–0.95 (*m*, 4H); 1.53 (*s*, 3H); **1**.98 (*s*, 3H).

Reduction of 3-Penten-2-one (**9**). An 85:15 mixture of *cis*- and *trans*-1,2-dimethylcyclopropyl acetate (**11** and **12**) was obtained in 40% yield. Separation of the isomers was achieved by GLC. (column: Apiezon L 20%). Shift reagent was used to clarify the NMR. spectrum. – *cis*-Isomer **11**: NMR. ($CDCl_3$): 0.20 (*m*, 1H); 1.05 (*m*, 3H); 1.50 (*s*, 3H); 2.02 (*s*, 3H). – *trans*-Isomer **12**: NMR. ($CDCl_3$): 0.11 (*m*, 1H); 1.07 (*m*, 3H); 1.46 (*s*, 3H); 1.96 (*s*, 3H).

Reduction of 3-Methyl-3-buten-2-one (**10**). **10** afforded a 61:29:10 mixture of *cis*- and *trans*-1,2-dimethylcyclopropyl acetates (**11** and **12**) and 3-methyl-3-buten-2-yl acetate (**13**). GLC. separation of the three compounds was not possible, however after catalytic hydrogenation, the two isomeric acetates were easily separated from the saturated acyclic acetate. – **13**: NMR. ($CDCl_3$): 1.29 (*d*, J = 5.5, 3H); 1.73 (*s*, 3H); 2.03 (*s*, 3H); 4.7–5.1 (*m*, 2H); 5.1–5.5 (*m*, 1H).

Reduction of 2-Isopropylidene-1-cyclopentanone (**14**). A 45% yield of 1-acetoxy-6,6-dimethylbicyclo[3.1.0]hexane (**16**) was obtained. – NMR. ($CDCl_3$): 1.04 (*s*, 3H); 1.05 (*s*, 3H); 2.02 (*s*, 3H); 1.1–2.4 (*m*, 7H).

Reduction of 2-Cyclohepten-1-one (**15**). 1-Acetoxybicyclo[4.1.0]heptane (**17**) was formed in 40% yield. – NMR. ($CDCl_3$): 0.5–2.2 (*m*, 11H); 1.95 (*s*, 3H).

Reduction of 2-Ethylidene-1-cyclopentanone (**18**). *exo*-1-Acetoxy-6-methylbicyclo[3.1.0]hexane (**23**) was obtained in 45% yield. – NMR. ($CDCl_3$): 1.02 (*m*, 3H); 2.03 (*s*, 3H); 1.00–2.4 (*m*, 8H).

Reduction of 2-Benzylidene-1-cyclohexanone (**19**). A 50% yield of *exo*-1-acetoxy-7-phenylbicyclo[4.1.0]heptane (**25**) was obtained. Purification was carried out by column chromatography (aluminium oxide, activity III using pentane as eluant). – NMR. ($CDCl_3$): 1.62 (*s*, 3H); 7.09 (*s*, 5H); 1.0–2.4 (*m*, 10H).

Reduction of 2-Benzylidene-octadeuterio-1-cyclohexanone (**20**). A 50% yield of *exo*-1-acetoxy-7-phenyl-2,2,3,3,4,4,5,5-octadeuterio-bicyclo[4.1.0]heptane (**26**) was obtained. The NMR. spectrum was clarified by shift reagent. – NMR. ($CDCl_3$): 1.46 (*s*, 3H); 7.22 (*s*, 5H); 1.64 and 1.88 (*ABq* J_{AB} = 7.0, 2H).

Reduction of methyl 1-cyclohexenyl ketone (**21**). A 76:24 mixture of 7-acetoxy-7-*endo*-methylbicyclo[4.1.0]heptane (**27**) and methyl cyclohexyl ketone was obtained. The *exo* isomer of **27** was independently synthesized and shown to be different from **27** [26]. – *endo*-Isomer **27**: NMR. ($CDCl_3$): 0.8–1.0 (*m*, 2H); 1.0–1.8 (*m*, 8H); 1.46 (*s*, 3H); 2.07 (*s*, 3H).

Reduction of 2-Methyl-2-cyclohexen-1-one (**22**). A 55:45 mixture of *exo*- and *endo*-1-acetoxy-6-methylbicyclo[3.1.0]hexane (**23** and **24**) was obtained in 40% yield. Separation was effected by preparative GLC. (column: Apiezon L 20%). Shift reagent was used to clarify the NMR. spectrum. – *endo*-Isomer **24**: NMR. ($CDCl_3$): 1.07 (*m*, 3H); 1.96 (*s*, 3H); 1.0–2.4 (*m*, 8H).

Reduction of 3-Methylidene-2-norbornanone (**28**). An 85% yield of *endo*-3-methylidene-2-norbornyl acetate **29** was found. – NMR. (CCl_4): 1.2–1.9 (*m*, 6H); 2.03 (*s*, 3H); 2.4–2.8 (*m*, 2H); 4.75 (*m*, 1H); 4.9 (*m*, 1H); 5.2 (*m*, 1H).

IR. and MS. of cyclopropyl acetates. IR.: all cyclopropyl acetates showed strong absorptions at 1740–1745 cm^{-1} (carbonyl) and 1240 cm^{-1} (acetate). MS.: cyclopropyl acetates, in addition to the parent peak M^+, showed peaks at $M-15$, $M-42$ and $M-57$.

REFERENCES

[1] *E. Clemmensen*, Chem. Ber. *46*, 1837 (1913); *47*, 681 (1914); *E. L. Martin*, Org. Reactions *1*, 155 (1942).
[2] *J. G. St. C. Buchanan & P. D. Woodgate*, Quart. Rev. *23*, 522 (1969).
[3] *B. R. Davis & P. D. Woodgate*, J. chem. Soc. (C) *1966*, 2006.
[4] *C. H. DePuy, W. C. Arney, Jr. & D. H. Gibson*, J. Amer. chem. Soc. *90*, 1830 (1968).
[5] *I. Elphimoff-Felkin & P. Sarda*, Tetrahedron *31*, 2781 (1975).
[6] *C. W. Jefford*, Chimia *24*, 357 (1970).
[7] *E. Vedejs*, Org. Reactions *22*, 401 (1975).
[8] *P. D. Bartlett & M. S. Ho*, J. Amer. chem. Soc. *96*, 627 (1974).
[9] *J. K. Groves & N. Jones*, Tetrahedron *25*, 223 (1969); *F. H. Cottee, B. P. Straughan, C. J. Timmons, W. F. Forbes & R. Shilton*, J. chem. Soc. (B) *1967*, 1146.
[10] *I. Elphimoff-Felkin & P. Sarda*, Tetrahedron Letters *1969*, 3045.
[11] *T. Nakabayashi*, J. Amer. chem. Soc. *82*, 3900 (1960).
[12] *T. V. Van Auken & K. L. Rinehardt, Jr.*, J. Amer. chem. Soc. *84*, 3736 (1962).
[13] *J. A. Bell*, J. Amer. chem. Soc. *87*, 4966 (1965).
[14] *P. Zuman & J. Michl*, Nature *192*, 655 (1961).
[15] *L. Farnell & W. G. Richards*, Chem. Commun. *1973*, 334; *M. J. S. Dewar & S. Kirschner*, J. Amer. chem. Soc. *93*, 4290 (1971).
[16] *R. B. Woodward & R. Hoffmann*, 'The Conservation of Orbital Symmetry', Verlag Chemie 1970.

[17] *J. Ronayne, M. V. Sargent & D. H. Williams,* J. Amer. chem. Soc. *88,* 5288 (1966).
[18] *M. J. S. Dewar,* Chemistry in Britain *11,* 97 (1975).
[19] *S. Hünig, E. Benzing & E. Lücke,* Chem. Ber. *90,* 2833 (1957).
[20] *L. Birkofer, S. M. Kim & H. D. Engels,* Chem. Ber. *95,* 1495 (1962).
[21] *E. W. Warnhoff, D. G. Martin & W. S. Johnson,* Org. Synth. Coll. Vol. IV, 162.
[22] *K. Bowden, I. M. Heilbron, E. R. H. Jones & B. C. L. Weedon,* J. chem. Soc. *1946,* 39; *P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch & G. W. Wood,* ibid. *1951,* 2402; *A. Bowers, T. G. Halsall, E. R. H. Jones & A. J. Lemin,* ibid. *1953,* 2555.
[23] *A. F. Thomas,* 'Deuterium Labeling in Organic Chemistry', Appleton-Century-Crofts, New York 1971, 167.
[24] *S. Yamamura & Y. Hirata,* J. chem. Soc. (C), *1968,* 2887.
[25] *J. P. Freeman,* J. org. Chemistry *29,* 1379 (1964).
[26] *J. T. Groves & K. W. Ma,* Tetrahedron Letters *1974,* 909.

101. Synthèses de produits organofluorés VI[1])
Solvolyse de chlorofluorocyclopropanes

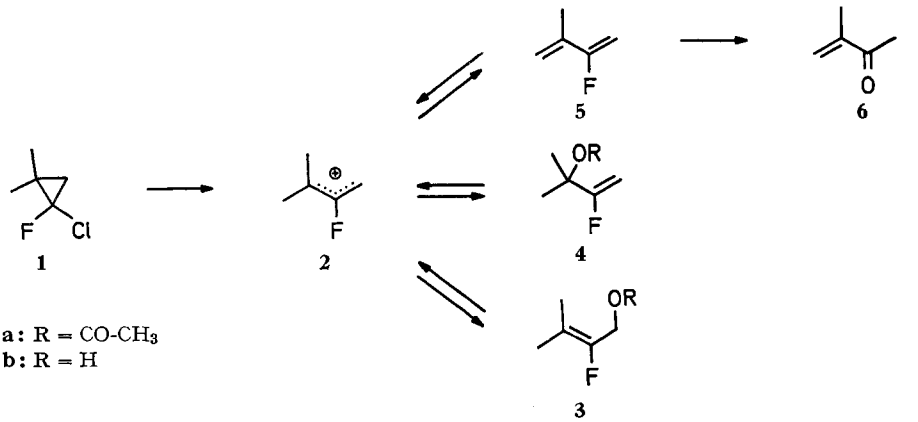
par **Yvonne Bessière** et **Manfred Schlosser**
Institut de chimie organique de l'Université, rue de la Barre 2, 1005 Lausanne

(6. II. 76)

Fluoro-organic Syntheses VI: The Solvolysis of Chlorofluoro-cyclopropanes. – *Summary.* 2-Fluoro-allylic carbocations, generated from 1-chloro-1-fluoro-cyclopropanes or 2-fluoro-allyl *p*-toluene-sulfonates in water or acetic acid, undergo either proton loss or addition of hydroxyl or acetoxyl. In the latter case, an alkyl-substituted 2-fluoro-allyl ion leads predominantly to the more branched product (*e.g.* 3-fluoro-2-methyl-3-buten-2-ol) which may be converted into the less branched one (*e.g.* 2-fluoro-3-methyl-2-buten-2-ol) through reversible reactions.

Par acétolyse en présence de sels d'argent, les *gem*-chlorofluorocyclopropanes (*e.g.* **1**) sont transformés, dans des conditions précédemment décrites [1], principalement en acétates fluoro-2-allyliques primaires (*e.g.* **3**, R = $COCH_3$); des cétones α,β-insaturées (*e.g.* **6**) sont identifiées comme produits secondaires.

En principe, le carbocation fluoro-2-allylique (*e.g.* **2**) formé dans une première étape, peut fixer un anion en conduisant aux dérivés **3** et **4**, ou bien éliminer un



[1]) Fluororganische Synthesen V, voir [1].