282. *Nafion*-TMS- and TMS-Trifluoroacetate-Induced Rearrangements of Cyclopropyl Ketones - A Procedure for the Regioselective Conversion of Semibullvalenes to Barrelenes[1])

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Summary

Trimethylsilyl trifluoroacetate (TMSTFA) and the polymer-supported sulfonate *Nafion*-TMS exhibit selective reaction modes in the opening of cyclopropyl ketones. The yields are generally high. *Nafion*-TMS rearranges the tricyclooctanones **1a** and **1b** to the bicyclooctenones **4a** and **4b** (while TMSTFA gives ring-opened adducts **6a, b**) with high regioselectivity. Aro-semibullvalenes (**8a**, **14**, **17a, b**) are efficiently rearranged to arobarrelenes (**7a**, **13**, **20a, b**) by both reagents. The latter rearrangements have also been achieved in mixtures of trifluoroacetic acid and tetramethylsilane (TMS), where the acid combines with an unidentified impurity of commercial TMS to form a strong electrophilic agent. The electrophile-assisted rearrangement of the naphtho-semibullvalenes **14a+b** resulted in conversion to the naphthobarrelenes **13a+b** with the opposite regioselectivity to that observed for the thermal equilibration at 220°.

Tricyclo[3.3.0.0^{2,8}]octan-3-ones constitute potential synthons for polycyclopentanoid terpenes [1-3]. We have previously shown [2] [4] that the ring opening of the cyclopropane ring in these compounds can be effected by AcOMs[3]) or methyl and trimethylsilyl trifluoromethanesulfonates. In the case of AcOMs a cooperative action with additional nucleophiles such as Br^- and I^- can be observed. With the first example (**1a**; *Scheme 1*, path *i*), a 1:4 mixture of products **3a** and **5a** was obtained [4], evidently through reactions approximating an S_N2 mode; in contrast, treatment of **1a** with methyl trifluoromethanesulfonate, trimethylsilyl trifluoromethanesulfonate or *Nafion*-TMS[3]) (path *ii*) gave exclusively **4a**. We have suggested an intramolecular elimination to occur from **2**, leading directly to the olefin **4a** [2].

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[1]) Preliminary communications in this series: [2] [4].

[2]) On leave at Mülheim a.d. Ruhr, 1980, from the Indian Institute of Technology, Kanpur.

[3]) Abbreviations: AcOMs, acetyl methanesulfonate; BSTFA, bis-trimethylsilyl trifluoroacetamide; *Nafion*-TMS, polymer-supported analog of trimethylsilyl trifluoromethanesulfonate [5]; TFA, trifluoroacetic acid; TMS, tetramethylsilane; TMSTFA, trimethylsilyl trifluoroacetate.

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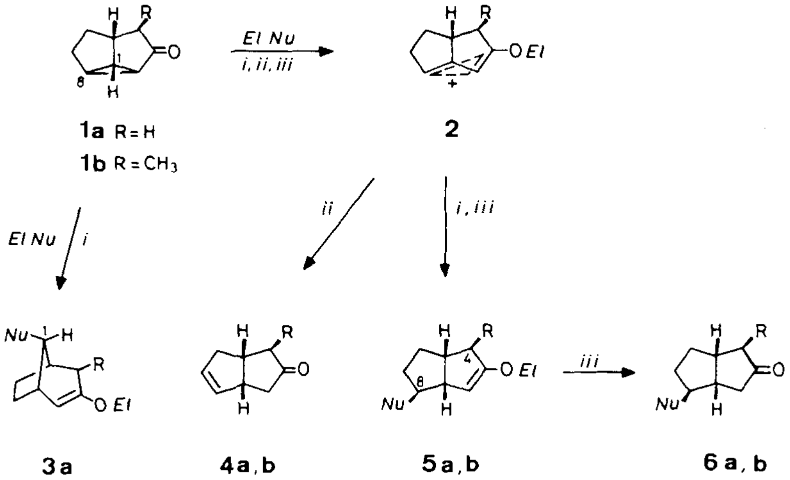
Scheme 1



ElNu in path *i* $= CH_3SO_2OCOCH_3 + Br^-$ or I^- [4]
ElNu in path *ii* $= CF_3SO_2OCH_3$, $CF_3SO_2OSi(CH_3)_3$, *Nafion*-TMS [2]
ElNu in path *iii* $= CF_3CO_2Si(CH_3)_3$

In the present study, we examined the reaction of several cyclopropyl ketones with *Nafion*-TMS[4]) and with TMSTFA[3])[5]). A simple procedure for the regioselective cleavage of the three-membered ring resulted. Furthermore, the conditions were elaborated which direct the reaction path from the assumed carbocation intermediate (*e.g.*, **2** in *Scheme 1*) towards either elimination, addition, or rearrangement.

Treatment of **1a, b** with *Nafion*-TMS in benzene at reflux temperature for 18 h gave **4a, b**[6]) (yields of isolated products >85%; see *Table*). In contrast, the reaction of, *e.g.*, **1a** and **1b** with TMSTFA led to the addition products **6a** and **6b**, respec-

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[4]) A very active form of *Nafion*-TMS was prepared by stirring a mixture of 1 g of the acid form of *Nafion* [6] and 3 ml of BSTFA[3]) at RT. under Ar for 12 h, and removal *in vacuo* of the unchanged BSTFA and trifluoroacetamide formed in the reaction.

[5]) TMSTFA was prepared by the addition of 1.1 mol-equiv. of BSTFA to one mol-equiv. of TFA[3]) and freezing out at −78° the trifluoroacetamide formed. Most recently, TMSTFA has been made commercially available by *Fluka AG* (CH-Buchs).

[6]) *Spectroscopic data.* IR. (film): $\tilde{\nu}$ in cm^{-1}; *s*, *m* and *w* stand for strong, medium and weak. 80-MHz-^1H-NMR. ($CDCl_3$): chemical shifts in δ and coupling constants *J* in Hz; *s*, *d* and *m* stand for singlet, doublet and multiplet. MS.: *m/z* at 70 eV (rel. intensities in parentheses).

Data of **4b**. - IR.: 2980*s*, 1740*s*, 1630*w*, 1450*m*, 1400*w*, 1370*w*, 1160*m*. - ^1H-NMR.: 5.64 (*m*, 2 H); 3.5-1.5 (*m*, 7 H); 1.01 (*d*, $J=7$, 3 H). - MS.: 136 (60, M^+), 121 (18), 107 (10), 93 (37), 79 (100), 66 (18), 53 (15), 39 (31), 27 (21).

Data of **6a**. - IR.: 3010*m*, 1780*s*, 1740*s*, 1445*w*, 1390*w*, 1350*m*, 1225*s*, 1160*s*. - ^1H-NMR.: 5.1 (*m*, 1 H); 3.1-1.4 (*m*, 10 H). - MS.: 236 (7, M^+), 122 (37), 93 (28), 80 (100), 55 (35), 41 (42), 27 (44).

Data of **6b**. - IR.: 3010*s*, 1780*s*, 1740*s*, 1450*w*, 1355*w*, 1225*s*, 1160*s*. - ^1H-NMR.: 5.1 (*m*, 1 H); 3.1-1.4 (*m*, 9 H); 1.04 (*d*, $J=7$, 3 H). - MS.: 250 (23, M^+), 136 (73), 108 (53), 93 (59), 79 (94), 55 (75), 41 (100), 27 (67).

4a, see [11] in [2]. For data of the arobarrelenes see **7a** [8], **13** [7b], **20a, b** [7] in [7b].

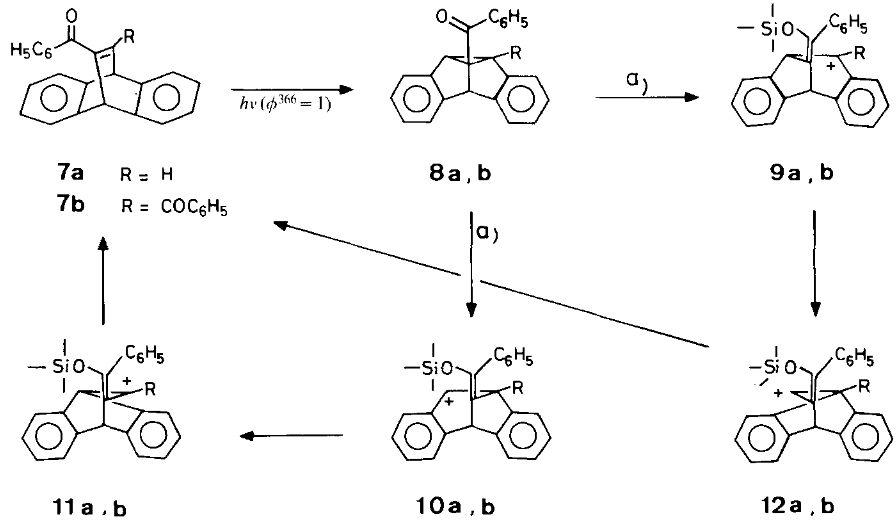
tively[6]) (path *iii* in *Scheme 1*). The isolation of **5a** and **5b** was not possible, since traces of moisture during the handling were sufficient to hydrolyze these products to **6a** and **6b**, respectively[6]).

The most remarkable degree of regioselectivity in nucleophile addition was achieved by the transformation of **1a** into **6a** with *ElNu*$=CF_3CO_2Si(CH_3)_3$. This result contrasts with our earlier finding [4] that the reaction of **1a** with, *e.g.*, *ElNu* =AcOMs afforded a 1:4 regioisomeric mixture of **3a** and **5a** only. The example thus shows that regioselectivity is enhanced with reagents in which increased electrophilic power is coupled with lowered nucleophilic strength.

As partial structures of aro-semibullvalenes, the cyclopropyl ketones in general react similarly with *Nafion*-TMS and TMSTFA[7]). Treatment of the semibullvalene **8a** (formed by photoisomerization of the barrelene **7a** [8]) with either of the two reagents in benzene at RT. afforded in nearly quantitative yields the barrelene **7a** (see *Table*). This reaction can be understood in terms of the pathways shown in *Scheme 2*. Initial cleavage of the cyclopropane ring in **8a** could lead either to **10a** or **9a**, which in turn could rearrange to the corresponding cationic intermediates, **11a** and **12a**. Adopting the same scheme, one would anticipate no reaction for the dibenzoyl derivative **8b**, since the corresponding cations **9b** and **11b** would be very unstable. And indeed, **8b** does not afford any barrelene **7b** with either reagent, *Nafion*-TMS and TMSTFA, under conditions similar to those leading to the smooth rearrangement of **8a** to **7a**.

In this connection a surprising observation deserves special mention. The same rearrangement (**8a**→**7a**) was observed in equally good yield when a catalytic

Scheme 2



a) *Nafion*-TMS or TMSTFA at RT.

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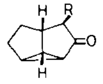
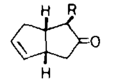
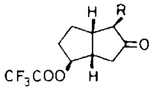
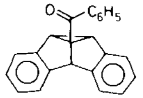
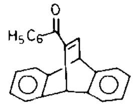
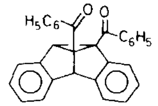
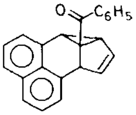
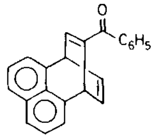
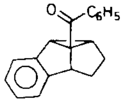
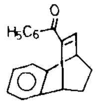
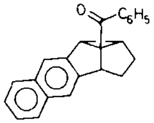
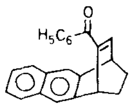
[7]) We have reported earlier on one particular case (see [7] and *Scheme 3*).

Table. *Rearrangement and addition products formed upon* Nafion-*TMS and TMS-trifluoroacetate treatment of various cyclopropyl ketones*

Starting cyclopropyl ketones a)		Reagent	Product 6)		Yield b) [%]	Reaction time [h]
1a	 R = H	*Nafion*-TMS c)	**4a**		90	18
1a		TMSTFA d)	**6a**		85	96
1b	R = CH_3	*Nafion*-TMS c)	**4b**		84	18
1b		TMSTFA d)	**6b**		80	96
8a		*Nafion*-TMS e)	**7a**		96	6
8a		TMSTFA h)	**7a**		95 f)	4
8b		*Nafion*-TMS e)	no reaction			
8b		TMSTFA h)	no reaction			
14		*Nafion*-TMS e)	**13**		99	2
14		TMSTFA h)	**13**		95	4
17a		*Nafion*-TMS e)	**20a**		86	17
17a		TMSTFA h)	**20a**		77 g)	20
17b		*Nafion*-TMS e)	**20b**		81 g)	20
17b		TMSTFA h)	**20b**		58 g)	24

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a) The starting ketones **1a,b** [2], **8a** [8], **14a–c** [7b] and **17a,b** [8b] were prepared according to the literature, and **8b** was prepared in analogy to **8a**.

b) Yields determined, after isolation of crude product, by GC. on OV 101 glass capillary columns of 23 or 35 m length.

c) The *Nafion*-TMS used in these experiments was prepared according to [5]. The reaction mixtures were refluxed with 20% (*w/w*) of *Nafion*-TMS in dry benzene under Ar. In the work-up, *Nafion*-

TMS was simply filtered off and carefully washed with benzene. The combined filtrates were passed through a short column of silica (*Merck*, 70-230 mesh) to remove residual traces of polymer. The recovered *Nafion*-TMS, if stored under Ar, can be used a second time.

[d] For the preparation see footnote 5. The reactions were run in neat TMSTFA at 60° under Ar. Work-up involved either evaporation of the volatile components at 1 Torr or addition of water, separation of the organic layer, and drying of the residue at reduced pressure after evaporation of the solvent. Both procedures gave the same results.

[e] The reagent was prepared according to footnote 4. The reaction mixtures were stirred with a 30% *w/w* of *Nafion*-TMS in dry benzene under Ar. For the isolation of the products see [c].

[f] The yield of **7a** decreased to about 64% on keeping the mixture for 9 days at RT.; other products were formed under these conditions (GC.).

[g] Side products were formed (GC.).

[h] Treatment of the substrates with 2 mol-equiv. of TMSTFA (footnote 5) in dry benzene at RT. under Ar. For the work-up see [d].

amount of TFA was added to **8a** and TMS³) *(Merck)* in either benzene or $CDCl_3$. The reaction proceeded smoothly at RT., at a rate proportional to the concentration of TFA. Searching for the reasons of this catalysis, solutions of **8a** in benzene or $CDCl_3$ were independently treated with TMS and TFA alone, but no reaction occurred. Similarly, when TMS was carefully purified⁸) prior to mixing with solutions of **8a** and TFA in the two solvents, no rearrangement was detected⁹). We have to conclude, therefore, that a hitherto unknown impurity¹⁰) is present in the commercial TMS and forms a powerful electrophilic reagent with TFA, similar in reaction properties to *Nafion*-TMS and TMSTFA.

Experiments with **8a** and **14** in 0.2-0.5% solutions of TMSTFA in benzene confirmed that catalytic amounts of silyl reagents, *i.e.* quantities comparable to those of the reactive impurities in TMS, suffice to effect the semibullvalene → barrelene rearrangement. The initially slow reactions to **7a** and **13**⁶), respectively, showed corresponding rate enhancements when TFA was added portionwise.

The combination of the photoisomerization **7a** → **8a** with its reversion **8a** → **7a** at RT. in homogeneous phase with TMSTFA has been presented previously as a model of a potential chemical low-energy storage cycle [7]. The introduction of the polymeric catalyst *Nafion*-TMS in the dark process is now a significant further improvement. After five cycles, material losses were <5% by GC., and 90-92% of **7a** could be recovered in pure crystalline form. Judged by the limiting criteria for such recycling systems [9], the cycle **7a** → **8a** thus appears to be superior in all respects to the published examples [10]¹¹), although still insufficient for any practical purposes.

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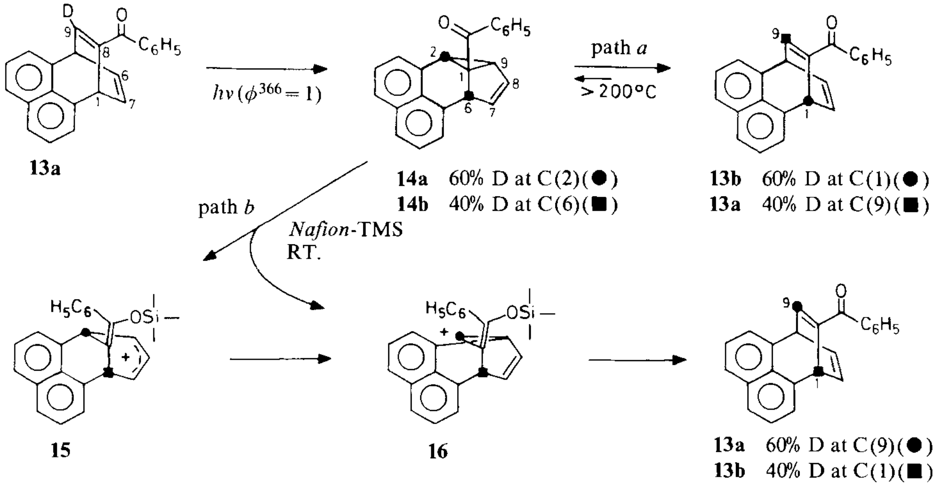
8) Preparative GC. on a 4 × 600 cm column with 20% *Apiezon* M on *Chromosorb* P (60-80 mesh).

9) Analysis was performed on a GC. glass capillary column OV 101, length 23 m.

10) Careful GC. analyses on an OV 1 glass capillary column revealed at least five components in concentrations below 0.2%, but coinjection with commonly known silyl derivatives did not allow conclusive structural assignments.

11) The materials **7a** and **8a** are crystalline, stable below 200°, and readily soluble in most organic solvents. The isomerizations proceed to full conversion and in essentially quantitative yields. The photochemistry of **7a** can be effected by direct irradiation at relatively long wave-lengths (*e.g.*, at 366 nm), and modification of the light-absorbing chromophore (benzoyl in the present case) with the aim to red-shift the absorption spectrum even further, appears feasible. The full cycle can be carried out at RT. and in a closed system without work-up, as a heterogeneous catalyst can be used for the dark process.

Scheme 3



Some insight into the mechanism of the electrophile-assisted rearrangement of the semibullvalenes was gained in a study of the deuterium isotopomers **14a** and **14b**, a mixture of which was obtained photochemically from **13a** [7b] [11][12]. The thermal reversion **14a, b**→**13a, b** initially proceeds with high regioselectivity (*Scheme 3*, path *a*) and the deuterium positions are progressively scrambled with increasing conversion [7b] [11]. It was proposed that the regioselective reaction is due to either a thermally allowed concerted or a stepwise process. The former would involve a ${}_{\pi}2 + {}_{\pi}2 + {}_{\sigma}2 + {}_{\pi}10$ or 16-electron *Möbius* cyclic array with one non-trivial sign inversion, and the latter (*E*)- and (*Z*)-enoxyl radical intermediates which react regioselectively.

The results with *Nafion*-TMS and TMSTFA in benzene at RT. were strikingly different. The treatment of **14a**+**b** with either of the two reagents resulted again in a quantitative and regioselective conversion to **13a**+**13b** (*Scheme 3*, path *b*), but the regioselectivity was now inverse to that observed in the initial phase of the thermal equilibration **14a, b**⇄**13a, b** at 220°. Also, the 3:2 ratio of **13a** and **13b** (determined by 55.28-MHz-^{2}H-NMR. in FT-mode) remained invariant even after extended reaction times with either catalyst, and no back reaction (**13**→**14**) was observed. The net result of the electrophile-assisted rearrangement, **14a** (60%) + **14b** (40%)→**13a** (60%) + **13b** (40%), can be adapted to a stepwise reaction path, but finds no alternative explanation in a thermally allowed concerted mechanism. The stepwise reaction (path *b*) requires either that the 1,2-naphthyl shift in **15** is regioselective, or that **15** is circumvented and ring opening and naphthyl shift proceed concertedly without relaxation to the intermediate allylic cation.

The overall sequence of **13a**+$h\nu$→**14a, b** and **14a, b**+*ElNu*→**13a, b** provides a convenient procedure to prepare in quantitative yields labelled barrelenes otherwise difficult to obtain.

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[12] A third, C(9)-deuteriated isomer (< 10%) has been neglected in this study for analytical reasons (limited ^{2}H-NMR. sensitivity), and the total of the percentages of **14a** and **14b** is taken as 100%.

In order to determine the scope of the aro-semibullvalene → arobarrelene isomerization, the dihydrosemibullvalenes **17a** and **17b** were also treated with *Nafion*-TMS and TMSTFA (see *Table 1*). Again, the dihydrobarrelenes **20a** and **20b** were the major products^6), although the reactions were much slower than in the previous cases and, especially with TMSTFA, various minor products could be observed. These are probably due to side reactions of the cationic intermediates, such as proton elimination and nucleophilic addition which have been encountered also with **1a, b**.

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REFERENCES

[1] *M. Demuth, P.R. Raghavan, C. Carter, K. Nakano & K. Schaffner*, Helv. Chim. Acta *63*, 2434 (1980).

[2] *M. Demuth, S. Chandrasekhar, K. Nakano, P.R. Raghavan & K. Schaffner*, Helv. Chim. Acta *63*, 2440 (1980).

[3] *K. Schaffner & M. Demuth*, Chimia *35*, in press (1981).

[4] *M. Demuth & P.R. Raghavan*, Helv. Chim. Acta *62*, 2338 (1979).

[5] *S. Murata & R. Noyori*, Tetrahedron Lett. *21*, 767 (1980).

[6] *J. Kaspi & G.A. Olah*, J. Org. Chem. *43*, 3142 (1978).

[7] a) *M. Demuth, U. Burger, H.W. Mueller & K. Schaffner*, J. Am. Chem. Soc. *101*, 6763 (1979); b) *M. Demuth, W. Amrein, C.O. Bender, S.E. Braslavsky, U. Burger, M.V. George, D. Lemmer & K. Schaffner*, Tetrahedron *37*, 3245 (1981).

[8] a) *N.K. Saxena, (Mrs) Maya & P.S. Venkataramani*, Indian J. Chem. *13*, 1075 (1975); b) *W. Amrein*, Ph. D. Thesis No. 5390, ETH Zürich 1974.

[9] *H.-D. Scharf, J. Fleischhauer, H. Leismann, I. Ressler, W. Schleker & R. Weitz*, Angew. Chem. *91*, 696 (1979); Angew. Chem., Int. Ed. *18*, 652 (1979).

[10] For a review on energy storage in organic photoisomers, see *G. Jones, II, S.-H. Chiang & P.T. Xuan*, J. Photochem. *10*, 1 (1979).

[11] *M. Demuth, C.O. Bender, S.E. Braslavsky, H. Görner, U. Burger, W. Amrein & K. Schaffner*, Helv. Chim. Acta *62*, 847 (1979).