157. Acid-Catalysed Dehydration of Tricyclic Unsaturated Alcohols

Kenji Hayakawa and **Hans Schmid**[1])

Organisch-chemisches Institut der Universität Zürich, Rämistrasse 76, CH-8001 Zürich

(28.IV.77)

Summary

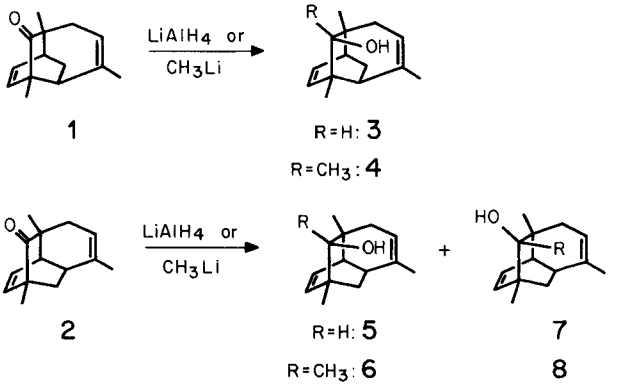
The tricyclic alcohols **3**–**7**, derived from the corresponding ketones **1** and **2** *(Scheme 1)*, by action of acids underwent dehydration with skeletal rearrangements. Dehydration of **3** and **4** with $POCl_3$/pyridine (procedure A) afforded the polycyclic hydrocarbons **9**, **10**, and **12**, **13**, respectively. With TsOH (procedure B), on the other hand, **3** and **4** gave homo-triquinacenes **10** and **14** respectively, as well as the polycyclic ethers **11** or **15** *(Scheme 2)*. Hydrocarbon **9** (or **12**) was converted into **10** (or **14**) by treatment with TsOH *(Scheme 3)*. Ketone **1** isomerized similarly with FSO_3H to the tertiary alcohol **16** *(Scheme 4)*. Plausible mechanisms for these transformations are summarized in *Scheme 8*. Dehydration of the secondary alcohols **5** and **7** was effected only by procedure A. While treatment of alcohol **5** with $POCl_3$/pyridine yielded two isomeric hydrocarbons **17** and **18**, similar dehydration of its epimeric alcohol **7** afforded hydrocarbon **21** as the sole product. The tertiary alcohol **6** was dehydrated by both procedures to yield two isomeric hydrocarbons **19** and **20** *(Scheme 5)*. Hydrocarbon **20** was converted into **19** by procedure B (mechanisms, *Scheme 10*). Reaction of ketone **2** with CF_3COOH gave the addition product **22** converted into vinylsulfonyl fluorides **24** and **25** by treatment with FSO_3H *(Scheme 6)*. *Homo*-triquinacenes **10** and **14** reacted smoothly with 4-phenyl-1,2,4-triazoline-3,5-dione to give the 'ene'-reaction products **26** and **27**, respectively.

1. Introduction. – Recently the facile synthesis of 1,3,6-trimethyl-tricyclo-[5.4.0.$0^{3,9}$]undeca-5,10-dien-2-one (**1**) and 1,3,6-trimethyl-tricyclo[5.3.1.$0^{3,8}$]undeca-5,9-dien-2-one (**2**) was reported [1]. The chemical behaviour of these isomeric ketones was different both in the excited state [2] and in the ground state [1], as a result of different steric interactions in their structures. This prompted us to investigate the reactivity of alcohols **3**–**7**, derived easily from the corresponding ketones **1** and **2**. Reaction of ketone **1** with $LiAlH_4$ or CH_3Li gave only the *syn*-alcohol **3** or **4** respectively, while under the same conditions ketone **2** afforded both *syn*-alcohol **5** or **6** and *anti*-alcohol **7** or **8** [1].

Tricyclic ketones **1** and **2** and alcohols **3**–**8** consist of a propeno-bridge and a bicyclo[2.2.2]octene system which form degenerate carbocations by action of acids

[1]) Deceased December 19, 1976.

Scheme 1

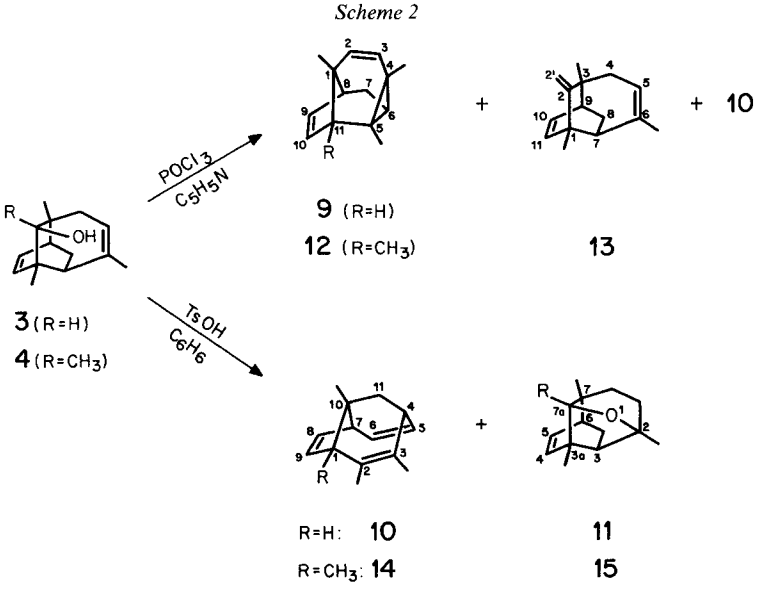


[3–5]. However, the presence of a propeno-bridge is expected to influence the rearrangement of carbocations derived from **3–8**: a) a number of the plausible rearrangement paths are restricted sterically by the propeno-bridge; b) the double bond in the bridge may interact with the resulting carbocations, provided that the bond is held in a suitable environment to interact with the vacant p-orbital of the carbocation; c) migration of the bridge to give other carbon skeletons may also be possible by relief of steric congestion.

We discuss here the structure-reactivity relationship in dehydration of tricyclic alcohols **3–7**, and in the acid-catalysed rearrangements of tricyclic ketones **1** and **2**.

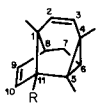
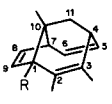
2. Results. – 2.1. *Dehydration of alcohol* **3** (Scheme 2). Treatment of alcohol **3** with phosphorus oxychloride ($POCl_3$) in hot pyridine for 3 h (procedure A) afforded

Scheme 2



1,4,5-trimethyl-tetracyclo[6.3.0.$0^{4,6}$.$0^{5,11}$]undeca-2,9-diene (**9**) and 2,3,10-trimethyl-tricyclo[5.2.1.$1^{4,10}$]undeca-2,5,8-triene (**10**) in 17% and 20% yield respectively. On the other hand, dehydration of **3** with *p*-toluenesulfonic acid (TsOH) in hot benzene (procedure B) gave **10** and 2,3,3a,6,7,7a-hexahydro-2,3a,7-trimethyl-2,7-ethano-3,6-methano-benzofuran (**11**) [6] in 23% and 72.5% yield respectively *(Scheme 2)*.

Table 1. *NMR. spectra of* **9**, **10**, **12**, **14**, *and* **16**[a])

Structure	Compound	Olefinic H	Aliphatic H	Methyl
	**9** R=H	6.40 *d*×*d* H–C(10) (*J*=6, *J*=2.5) 5.77 *d*×*d* H–C(9) (*J*=6, *J*=3) 5.75 *d* H–C(2) 5.54 *d* and H–C(3) (*J*=10)	2.08–1.95 *m* H–C(8) 1.61–1.53 *m* H–C(11) 1.50–1.32 *m* 2H–C(7) 0.35 *d*×*m* H–C(6) (*J*=6)	1.22 *s* 1.18 *s* 0.96 *s*
	12[b]) R=CH_3	6.09 *d* H–C(10) (*J*=6) 5.77 *d*×*d* H–C(9) (*J*=6, *J*=3) 5.78 *d* H–C(2) 5.41 *d* and H–C(3) (*J*=10)	2.16–2.01 *m* H–C(8) 1.48–1.28 *m* 2H–C(7) 0.44–0.30 *m* H–C(6) (*J*=5.5, *J*=3)	1.22 *s* 1.20 *s* 0.93 *s* 0.80 *s*
	10 R=H	6.02 *d*×*d*×*d* H–C(5) (*J*=9.5, *J*=6, *J*=2) 5.84–5.63 *m* H–C(8) (2H) H–C(9) 5.60 *d*×*d* H–C(6) (*J*=9.5, *J*=4)	2.68–2.54 *m* H–C(1) (2H) H–C(7) 2.43 *d*×*t* H–C(4) (*J*=6, *J*=3) 1.84–1.54 *m* 2H–C(11)	1.70 *s* 1.67 *s* 1.17 *s*
	**14**[b]) R=CH_3	6.06 *d*×*d*×*d* H–C(5) (*J*=9.5, *J*=6, *J*=2) 5.63–5.44 *m* H–C(8) (2H) H–C(9) 5.51 *d*×*d* H–C(6) (*J*=9.5, *J*=4)	2.60–2.57 *m* H–C(7) 2.37 *d*×*t* H–C(4) (*J*=6, *J*=3) 1.84–1.46 *m* 2H–C(11)	1.64 *s* 1.59 *s* 1.09 *s* 1.05 *s*
	16[b])[c]) R=OH	6.01 *d*×*d*×*d* H–C(5) (*J*=10, *J*=6, *J*=2) 5.78–5.60 *m* H–C(8) (2H) H–C(9) 5.45 *d*×*d* H–C(6) (*J*=10, *J*=4)	2.84–2.72 *m* H–C(7) 2.47 *d*×*t* H–C(4) (*J*=6, *J*=3) 1.86–1.54 *m* 2H–C(11)	1.75 *s* 1.73 *s* 1.18 *s* 1.61 *s* OH

[a]) See footnote [2]).

[b]) For decoupling experiments, see experimental part.

[c]) NMR. data with $Eu(fod)_3$ are shown in *Table 3*, experimental part.

[2]) NMR. spectra, unless otherwise stated, were measured on a 100 MHz spectrometer in $CDCl_3$. The chemical shifts are expressed as δ values (ppm) with tetramethylsilane as an internal standard ($\delta=0$); *s*=singlet, *d*=doublet, *t*=triplet, *qa*=quartet, *m*=multiplet, br.=broad. The coupling constants are given in Hz.

The nature of **9** and **10** as dehydration products was apparent from IR. and mass spectra (M^+ 186). The ^{1}H-NMR. spectra[2]) which permitted the assignments of the structures are summarized in *Table 1.*

The assignments of the signals of **9** are clearly given in *Table 1.*

The ^{1}H-NMR. spectrum of **10** was very similar to those of **14**, derived from dehydration of **4** *(Scheme 2)*, and **16**, derived from rearrangement of ketone **1** *(Scheme 4)*. The assignments were achieved by comparison with the ^{1}H-NMR. spectra of **14** and **16** (see Table 1 and Sections 2.2 and 2.4). The coupling constant ($J_{5,6}$ = 9.5 Hz) of two olefinic protons (H–C(5) and H–C(6)) indicated the presence of an unsaturated 6-membered ring. Furthermore, two of the three methyl groups (1.70(*s*) and 1.67(*s*)) seemed to be attached to a second double bond.

The skeleton including the double bonds of compound **10** (as well as of **14** and **16**) can be regarded as homo-triquinacene[3]). The pseudo-mirror plane in **10**, **14** and **16**, bisecting C(4), C(10), C(11), and the double bond C(8), C(9), is indicated by the relatively small chemical shift difference of H–C(8) and H–C(9) (*cf. e.g.*, that of H–C(9) and H–C(10) in **9**).

The structure of **11** was similarly determined by IR., NMR. and mass spectra (M^+ 204) (see experimental part), and by comparison with an authentic sample [6].

2.2. *Dehydration of alcohol* **4** (Scheme 2). Dehydration of alcohol **4** by procedure A afforded the tetracyclic hydrocarbon **12** (4.3%) and 1,3,6-trimethyl-2-methylidene-tricyclo[5.4.0.0^{3,9}]undeca-5,10-diene (**13**) (20.4%), and by procedure B the homo-triquinacene **14** (65.4%) and the polycyclic ether **15** (3.6%). The results are similar to those obtained from **3** except for the formation of **13** instead of **14** in the reaction by procedure A.

From the similarities of UV., IR. and NMR. *(Table 1)* spectra of **12** with those of **9**, **12** is a methyl homologue of **9**.

The structure of dehydration product **13** was determined by its IR., mass (M^+ 200) and ^{1}H-NMR. spectra (see experimental part). The latter was very similar to that of **1** [1] except for the appearance of two additional signals of exocyclic olefinic protons (2H–C(2′)) at 4.52(*s*) and 4.44(*s*).

The homo-triquinacene structure of **14** was indicated by the similarities of its IR., UV. and NMR. spectra to those of **10**. In addition the ^{1}H-NMR. spectrum showed that the proton at C(1) of **10** was replaced by a methyl group (Table 1). Compound **15** was shown to have the same skeleton as **11** by IR., UV. and NMR. spectra (experimental part).

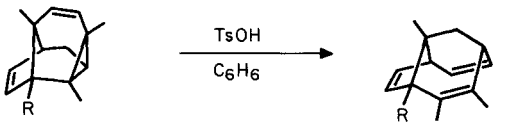
2.3. *Acid-catalysed rearrangements of* **9** *and* **12** (Scheme 3). Compounds **9** and **12** were smoothly converted into **10** and **14**, respectively, in almost quantitative yields by treating with TsOH in hot benzene (procedure B), compounds **10** and **14** being recovered unchanged under these conditions. These results imply that the homo-triquinacenes **10** and **14** are formed *via* dehydration products **9** and **12**.

---

3) triquinacene

homo-triquinacene

Scheme 3

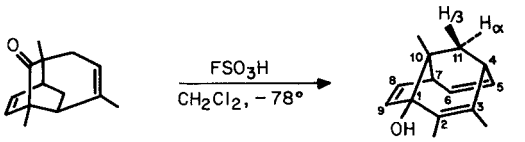


R=H: **9** **10**

$R=CH_3$: **12** **14**

2.4. *Acid-catalysed rearrangement of tricyclic ketone* **1** (Scheme 4). Whereas the tricyclic ketone **1** was recovered unchanged from treatment with trifluoroacetic acid at 50°, it was converted exclusively into 2,3,10-trimethyl-tricyclo[5.2.1.$1^{4,10}$]-undeca-2,5,8-trien-1-ol (**16**) in 46.5% yield by fluorosulfonic acid (FSO_3H) in CH_2Cl_2 at −78°. The IR. and mass spectra (M^+ 202) indicated **16** to be an alcohol, isomeric with **1**. The structural resemblance of **16** to **10** and **14** was apparent from their ^{1}H-NMR. spectra *(Table 1)*. The homo-triquinacene structure of **16** was further confirmed by NMR. spectra, in the presence of Eu(fod)$_3$[4]) (see *Table 3*, experimental part), when the signals of two methyl groups (CH_3–C(2) and CH_3–C(10)), one of the protons (Hβ) at C(11) and an olefinic proton (H–C(9)) were strongly shifted to low field. Thus the signals of H–C(8) and H–C(9) were separated from a *m* into a $d\times d$ ($J=6.0$ and 3.2) and a d($J=6.0$) respectively, indicating that a double bond is present in the 5-membered ring.

Scheme 4



1 **16**

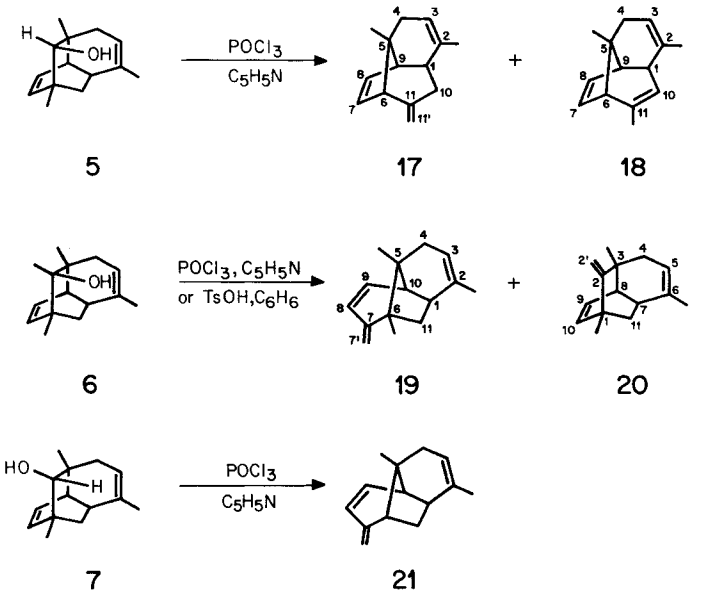
2.5. *Dehydration of alcohol* **5** (Scheme 5). Dehydration of **5** by procedure A gave 2,5-dimethyl-11-methylidene-tricyclo[4.3.2.$0^{5,9}$]undeca-2,7-diene (**17**) and 2,5,11-trimethyl-tricyclo[4.3.2.$0^{5,9}$]undeca-2,7,10-triene (**18**) in 6.6% and 8.7% yield respectively. On the other hand, by procedure B, alcohol **5** was recovered unchanged (>85%).

The IR. and mass spectra (M^+ 186) of **17** and **18** suggested both to be dehydration products. The structures were determined by the ^{1}H-NMR. spectra (see experimental part).

2.6. *Dehydration of alcohol* **6** (Scheme 5). The chemical behaviour of the tertiary alcohol **6** was entirely different from that of the corresponding secondary alcohol **5**. Alcohol **6** was, in pronounced contrast to **5**, dehydrated by both procedures A and B

[4]) Tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)-europium.

Scheme 5



5 17 18

6 19 20

7 21

to give the same products, 2,5,6-trimethyl-7-methylidene-tricyclo[4.4.1.$0^{5,10}$]undeca-2,8-diene (**19**) and 1,3,6-trimethyl-2-methylidene-tricyclo[5.3.1.$0^{3,8}$]undeca-5,9-diene (**20**), but in different ratios (procedure A: **19** (20%) and **20** (54%); procedure B: **19** (76.5%) and **20** (7%)) *(Scheme 5)*. Hydrocarbon **20** was found to be efficiently converted into **19** by brief treatment with TsOH in hot benzene.

The structural assignments were achieved on the basis of IR., UV., NMR. and mass spectra (**19** and **20**, M^+ 200) (see experimental part). The presence of an exocyclic double bond in both isomers was deduced from the IR. (wagging vibrations at 880 cm^{-1} (**19**) and 885 cm^{-1} (**20**)) and ^{1}H-NMR. spectra. A strong absorption at 242 nm ($\varepsilon = 16\,700$) in the UV. spectrum of **19** is due to a conjugated diene system.

2.7. *Dehydration of* **7** (Scheme 5). Alcohol **7** was dehydrated in a different way from its epimer **5**, procedure A giving exclusively (67% yield) 2,5-dimethyl-7-methylidene-tricyclo[4.4.1.$0^{5,10}$]undeca-2,8-diene (**21**), not observed in the analogous reaction of **5**. Application of procedure B to **7** gave 86% of a complex mixture of five alcoholic products, one of which (38%) was identical (GC.) with the starting material.

The structural similarity of **21** and **19** was apparent from their IR. (wagging vibration at 875 cm^{-1}), UV. (conjugated diene system) and NMR. spectra, the signal of a methyl group at the methine position at C(6) being replaced by the signal of a bridgehead proton (see experimental part).

2.8. *Acid-catalysed reaction of tricyclic ketone* **2** (Scheme 6). Treatment of the tricyclic ketone **2** with FSO_3H in CH_2Cl_2 at $-78°$ resulted in nearly complete decomposition. On the other hand, treatment of **2** in neat CF_3COOH at RT. gave 61% of a crystalline addition product **22** (IR.: 1780 and 1710 cm^{-1}), which, with

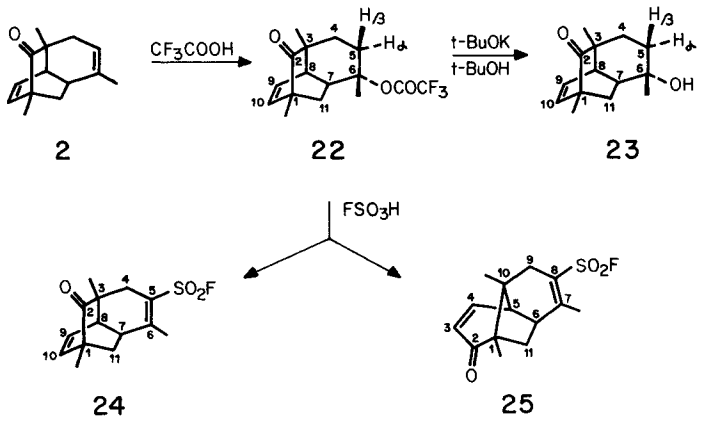
potassium *t*-butoxide in *t*-butyl alcohol, yielded quantitatively the corresponding alcohol **23** (IR.: 3380 and 1715 cm^{-1}).

While in the spectrum of **22** two aliphatic protons Hα–C(5) and H–C(7) appeared at relatively low field (2.56 and 2.19), indicating a *cis* relationship to the ester group, in the spectrum of **23** the methine proton H–C(8) (1,3-diaxial relationship with the OH group) was strongly shifted to low field (2.97, $d \times d \times d$) (see experimental part).

These phenomena are only consistent with an *anti*-configuration at C(6)[5]. Thus, the differing chemical behaviour of ketones **1** and **2** in the presence of acids [1] is easily understood by considering their structural differences. Whereas the double bond in the propeno-bridge of **1** is sterically strongly shielded against electrophilic attack, the corresponding double bond of **2** is 'opened' from *anti*-side and the reagent may attack from this side to lead to **22**.

Furthermore, treatment of **22** with FSO_3H in CH_2Cl_2 gave 5-fluorosulfonyl-1,3,6-trimethyl-tricyclo[5.3.1.$0^{3,8}$]undeca-5,9-dien-2-one (**24**) and 8-fluorosulfonyl-1,7,10-trimethyl-tricyclo[4.4.1.$0^{5,10}$]undeca-3,7-dien-2-one (**25**) in 22% and 25% yield, respectively *(Scheme 6)*.

Scheme 6



2 **22** **23**

24 **25**

High-resolution mass spectra (**24**, M^+ 284.0889; **25**, M^+ 284.0877) and elemental analyses showed that both compounds had a molecular formula of $C_{14}H_{17}FO_3S$. The unchanged tricyclic carbon skeleton of **24** with respect to **2**, **22**, and **23** was recognized by comparison of its NMR. spectrum with those of **2** [1], **22** and **23** (see experimental part).

The IR. and UV. spectra of **25** suggested the partial structure of an α,β-unsaturated ketone. The chemical shifts and coupling constants of H–C(3) and H–C(4) in the ^{1}H-NMR. spectrum were reasonable for a six-membered α,β-unsaturated ketone. The downfield shift of a methyl signal (2.27 CH_3–C(7)) was attributable to the deshielding effect of the neighbouring SO_2F group.

---

[5]) *Anti* and *syn* are defined by the position of the trifluoroacetoxy or hydroxy group with respect to the carbonyl group (see *Scheme 6*).

2.9. *Reactions of the homo-triquinacenes* **10** *and* **14** *with 4-phenyl-1,2,4-triazoline-3,5-dione* (Scheme 7). All three double bonds of the title hydrocarbons **10** and **14** are homo-conjugated. Therefore, the reaction of these compounds with the strong azo-dienophile 4-phenyl-1,2,4-triazoline-3,5-dione was investigated with the hope of getting homo-*Diels-Alder* adducts which might serve as precursors for new heterocyclic cage compounds. Indeed, hydrocarbons **10** and **14** reacted smoothly with the azo-dienophile in benzene at RT. to give crystalline products **26** and **27** in 97% and 66% yield, respectively.

Scheme 7

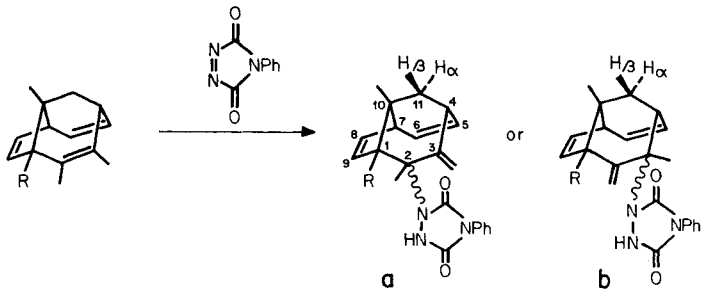


Table 2. *NMR. spectra of adducts* **26** *and* **27**[a])[b])

	26	**27**
H–C(1)	3.67 $d \times d$ ($J = 3, J = 1$)	–
2H–C(2′)	5.24 *s*	5.26 *s*
or C(3′)	5.17 *d* ($J = 1.5$)	5.24 *s*
H–C(4)	3.22–3.04 *m*	3.75–3.59 *m*
H–C(5)	5.92 $d \times d \times d$	5.88–5.57 *m* (4H)
	($J = 9, J = 7.5, J = 1.5$)	
H–C(6)	5.65 $d \times d$ ($J = 9, J = 4$)	
H–C(8)	5.88–5.58 *m* (2H)	
H–C(9)		
H–C(7)	2.80–2.68 *m*	2.84–2.70 *m*
Hα–C(11)	1.65 $d \times d$ ($J = 13, J = 3.5$)	1.70 $d \times d$ ($J = 14, J = 4$)
Hβ–C(11)	2.21 $d \times d$ ($J = 13, J = 4$)	2.40 $d \times d$ ($J = 14, J = 2$)
CH_3	1.66 *s*	1.51 *s*
	1.22 *s*	1.33 *s*
	–	1.03 *s*
Aromatic	7.65–7.35 *m* (5H)	7.64–7.32 *m* (5H)
NH	8.12 *s*	7.28 *s*

[a]) See footnote [2]).
[b]) For decoupling experiments, see experimental part.

The nature of these products as 1:1 adducts was apparent from elemental analyses and mass spectra (**26**, M^+ 361; **27**, M^+ 375), the IR. spectra suggesting the presence of a NH-group (**26**, 3200 cm^{-1}; **27**, 3250 cm^{-1}) and a triazolidinedione moiety (**26**, 1765 and 1695 cm^{-1}; **27**, 1770 and 1700 cm^{-1}). The NMR. spectra *(Table 2)* supported the structures as being derived from 'ene'-reactions of **10** and **14** with the azo-dienophile, *i.e.* no skeletal rearrangements had occurred. Although it was impossible to assign the position of the triazolinedione-substituent (C(2) or C(3)) from these data, the large difference of chemical shifts between Hα and Hβ at C(11), and the apparent downfield shift of H–C(4) in comparison with that of **10** and **14** are in agreement with the *exo*-position of the triazolinedione moiety.

These results suggested that the through-space interaction of the homo-conjugated double bonds[6]) in the *homo*-triquinacenes **10** and **14** is not sufficient to allow homo-*Diels-Alder* reaction, known to occur with bicyclo[2.2.1]hepta-diene [7].

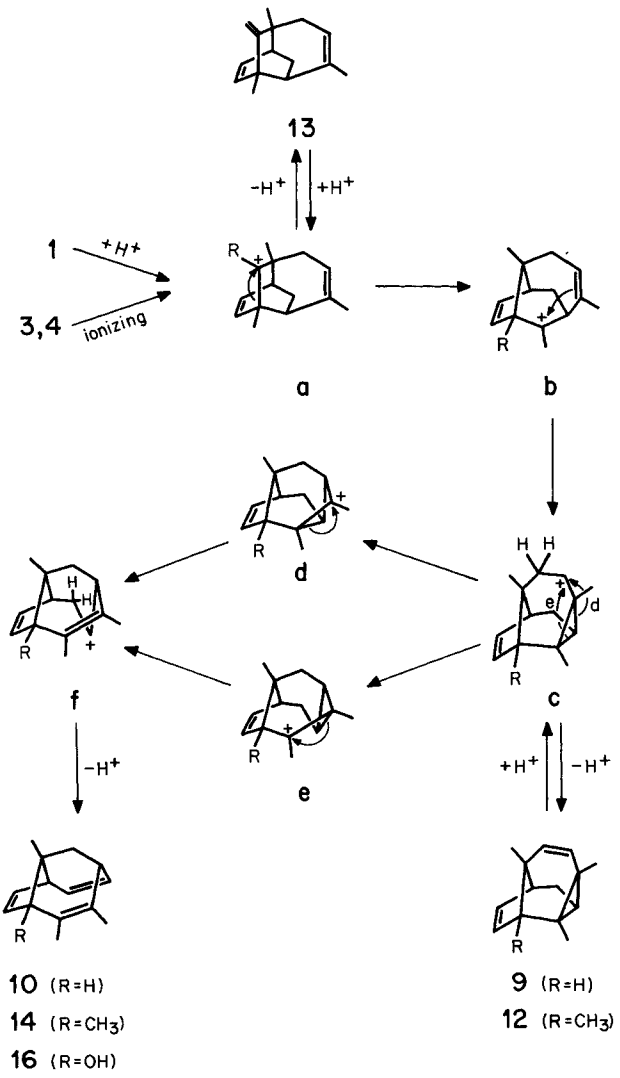
3. Discussion. – The results obtained can be understood by considering the rearrangement of carbocations formed initially from the alcohols, although they ionize in different ways depending on the procedures employed. While TsOH (procedure B) converts the hydroxyl function by protonation into a better leaving group, subsequent decomposition involving a carbocation intermediate, $POCl_3$ (procedure A) may form the ester as an adequate intermediate, thereby increasing the ionizing ability of the C–O bond [9].

The mechanism of dehydration rearrangement of alcohols **3** and **4** is shown in *Scheme 8* (for the sake of clarity and from lack of any mechanistic information, the ions are drawn with localized charges). The alcohols **3** and **4** initially form the carbocation **a**, in which the less substituted vinyl bond (C(11), C(1), originally in a *trans* position to the leaving group) shifts to carbocation centre (1,2-vinyl shift) to yield a tertiary homoallylic cation **b**. A similar skeletal rearrangement is known in bicyclo[2.2.2]octadienyl cation systems [5] [9]. Deprotonation of the tertiary carbocation **a** (R=CH_3) gives **13** which was obtained from **4** only in procedure A. In the presence of TsOH (procedure B), **13** can be again protonated to form **a** (R=CH_3). This was supported by the complete conversion of **13** into **14** by treatment with TsOH. Rearrangement of **b** to the cyclopropylcarbinyl cation **c** can occur by participation of the homo-conjugated π-bond. From intermediate **c**, stabilized by cyclopropane conjugation [10], arise the tetracyclic olefins **9** and **12** by loss of a proton. However, these compounds were only obtained using $POCl_3$ (procedure A). Thus, strong acid such as TsOH may protonate **9** and **12** to give again the stabilized cation **c**, confirmed by the conversion of **9** and **12** into **10** and **14**, respectively.

The homoallylic cation **f** may arise from **c** through cyclobutyl cation or cyclopropylcarbinyl cation rearrangement (indicated by arrow d and e) yielding the cations **d** or **e**. Deprotonation of cation **f** yields the homo-triquinacenes **10** and **14**. The formation of **16** is similarly understood by considering the initial protonation of carbonyl group in **1** to give **a** (R=OH). Compounds **10**, **14** and **16** are stable under the reaction conditions and recovered unchanged from treatment with TsOH in boiling benzene. Conversions of hydrocarbons **9**, **12** and **13** into the homo-

[6]) Compounds **10** and **14** (as well as **16**) show the longest UV. absorption band in the region of 216 nm which is indicative of homo-conjugative effects in these homo-trienes (*cf.* [8]).

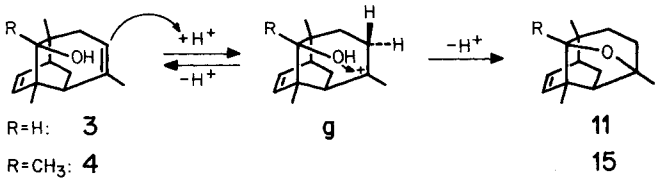
Scheme 8



triquinacenes **10** and **14** by treatment with TsOH, and the formation of **16** as the sole product from ketone **1** by treatment with FSO_3H suggest that carbocation **f** is the lowest energy intermediate.

Formation of tetracyclic ethers **11** and **15** is probably effected by protonation of the double bond in the propeno-bridge (yielding **g**) followed by nucleophilic attack of the hydroxyl function *(Scheme 9)*. However, ether formation is stereochemically restricted to the *syn*-alcohols **3** and **4**. Ether **11** was reported to be also obtained together with two other isomers from **3** by reaction with mercuric acetate followed by reduction with sodium borohydride [6].

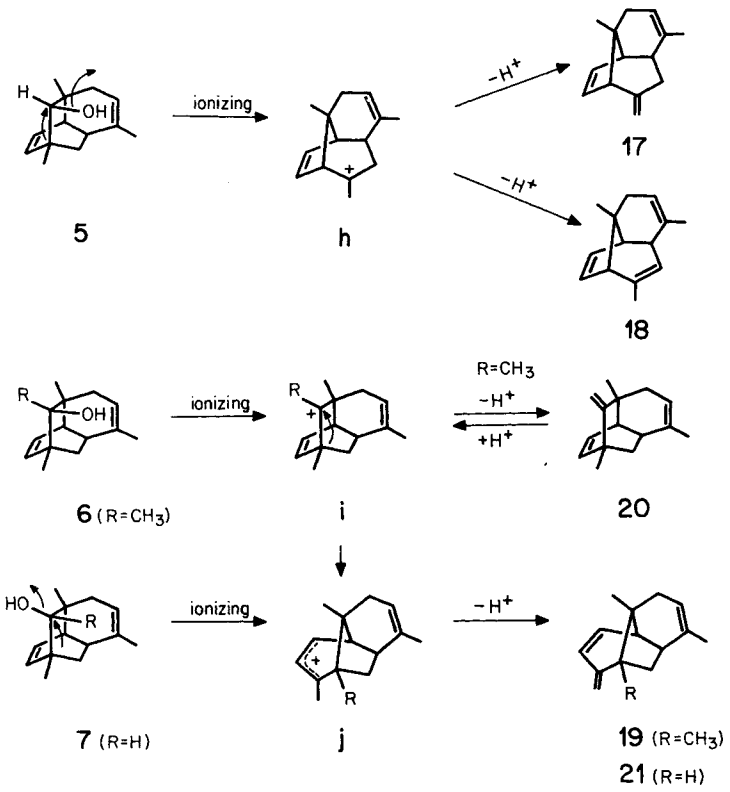
Scheme 9



Dehydration of the secondary alcohols **5** and **7** was effected only by procedure A. The poorer efficiency of procedure B may be attributed to the instability of the initially formed secondary carbocations, since the related tertiary alcohol **6** was easily dehydrated by both procedures A and B. The rearrangements are depicted in *Scheme 10* as stepwise, although they may partially be concerted.

Removal of the hydroxyl function of **5** through ester formation with $POCl_3$ followed by a 1,2-vinyl shift (note the *trans* relationship of the vinyl moiety and the leaving group) yields the tertiary carbocation **h** *(Scheme 10),* deprotonation of which affords **17** and **18**. On the other hand, the epimeric alcohol **7** undergoes a 1,2-shift of the methylene group (C(11), *trans*-situated to the leaving group) to give the allylic cation **j** (R=H) precursor of **21**. In contrast to the secondary alcohols **5** and **7**,

Scheme 10



the tertiary alcohol **6** ionizes initially to the carbocation **i** ($R=CH_3$), from which proton loss gives **20**, and the 1,2-alkyl shift discussed above yields the allylic cation **j** ($R=CH_3$) affording the second product **19**. This type of rearrangement was also observed for nonamethylbicyclo[2.2.2]octa-2,5-diene-7-ol [5]. The preference of the 1,2-alkyl shift to the 1,2-vinyl shift in **i** can be attributed to the stability of the resulting carbocation **j**. The conversion of **20** into **19** by treatment with TsOH is similarly explained by formation of carbocation **i** by protonation of **20**.

While the skeletal rearrangement of **22** to **25** *(cf. Scheme 6)* can be explained similarly to that of **6** to **19**, the mechanism of the unusual formation of the vinylsulfonyl fluorides **24** and **25** from trifluoroacetate **22** by action of FSO_3H is not yet clear and requires further investigation.

It should be noted that the chemical behaviour of the alcohols derived from ketone **1** was quite different from that of the alcohols derived from ketone **2**, participation of the propeno-bridge in the carbocation rearrangement being observed only for the former.

We gratefully acknowledge the support of this work by the *Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung.* We are grateful to Professor *H.-J. Hansen* for useful discussion and encouragement. We thank the Analytical Department of the Institute and Dr. *Gy. Fráter* for the supply of ketones **1** and **2**.

Experimental part

General. M.p. were taken on a *Mettler* FP-2 apparatus. Mass spectra (MS.) were taken on a *CEC*-21-110B mass spectrometer at an ionizing voltage of 70 eV and data are expressed in *m/e* (rel. %). Infrared (IR.) data are expressed in units of frequency (cm^{-1}). UV. spectra were performed in hexane and data (sh = shoulder) are given in nm (ε). Comments on the proton magnetic resonance (^{1}H-NMR.) spectra are given in footnote [2]).

Analytical gas-liquid phase chromatography (GC.) was performed on *C. Erba* apparatus using a glass capillary column [12]. Analytical and preparative thin layer chromatography (TLC. and prep. TLC.) was carried out on Polygram-Kieselgel and Kieselgel 60 F_{254} *(Merck)*-Fertigplatten, respectively. For column chromatography Kieselgel 60 *(Merck)* was used. Distillations were done in a bulb tube (Kugelrohr), using *Büchi* GKR-50 distillation apparatus.

1. Preparation of alcohols 3–8. See [1].

2. General procedure for dehydration of alcohols 3–7. – 2.1. *Procedure A.* A solution of the appropriate alcohol and a 1.7–3.1 fold molar excess of phosphorus oxychloride ($POCl_3$) in pyridine, sometimes diluted with benzene, was heated at 70–80° until the alcohol was completely consumed. The reaction mixture was cooled and poured into ice/water, and the organic layer separated. The aqueous layer was extracted with ether and the combined organic layers washed with 1N aqueous HCl, saturated $NaHCO_3$-solution and water. After drying ($MgSO_4$), the solvent was removed under reduced pressure and the residue subjected to column chromatography and bulb tube distillation. In case of mixtures, further purification was effected by a second column chromatography and/or prep. TLC.

2.2. *Procedure B.* To a solution of the alcohol in benzene a 2.8–3.5 fold molar excess of *p*-toluene sulfonic acid monohydrate ($TsOH.H_2O$) was added. The suspension was heated at 70–80° with stirring until the starting material had completely disappeared. The reaction mixture was cooled and the solvent evaporated under reduced pressure. The resulting residue was directly chromatographed on a silica gel column. If necessary, further column chromatography or prep. TLC. was employed.

3. Dehydration reaction of alcohol 3. – 3.1. *Procedure A.* A solution of 0.5 g (2.45 mmol) of **3** and 700 mg (4.55 mmol) of $POCl_3$ in 2 ml of pyridine and 3 ml of benzene was heated for 3 h at 80°. After work-up the reaction mixture gave 300 mg of oil which was subjected to prep. TLC. on silica gel in hexane to afford 70 mg (17%) of **9** and 91 mg (20%) of **10**.

1,4,5-Trimethyl-tetracyclo[6.3.0.0.^{4,6}0^{5,11}]undeca-2,9-diene (**9**). Colourless oil, b.p. 35–40°/0.008 Torr. – UV.: $\lambda_{max}=213$ (7150). – IR. (film): 3060, 3030, 2980, 2950, 2910, 2880, 2860, 1650, 1600,

1470, 1460, 1450, 1440, 1370, 840, 765, 715, 690. – NMR.: *Table 1.* – MS.: 186 (M^+, 25), 171 (100), 156 (39), 143 (38), 107 (40), 91 (37), 80 (71).

$C_{14}H_{18}$ (186.28) Calc. C 90.26 H 9.74% Found C 90.36 H 9.64%

2,3,10-Trimethyl-tricyclo[5.2.1.1^{4,10}]undeca-2,5,8-triene (**10**). Colourless oil, b.p. 48–50°/0.008 Torr. – UV.: λ_{max}=215 (3410). – IR. (film): 3050, 3020, 2950, 2920, 2860, 1640, 1615, 1460, 1450, 1370, 800, 770, 725, 700. – NMR.: *Table 1.* – MS.: 186 (M^+, 100), 171 (41), 143 (23), 107 (66), 91 (29), 77 (23).

$C_{14}H_{18}$ (186.28) Calc. C 90.26 H 9.74% Found C 90.07 H 9.93%

3.2. *Procedure B.* A solution of 0.45 g (2.65 mmol) of **3** in 30 ml of benzene and 1.5 g (7.9 mmol) of $TsOH.H_2O$ was heated at 50° for 10 h. After work-up, the residue was chromatographed on a silica gel column in hexane. The first fractions gave 113 mg (23%) of **10** and later fractions 392 mg (72.5%) of **11**.

2,3,3a,6,7,7a-Hexahydro-2,3a,7-trimethyl-2,7-ethano-3,6-methano-benzofuran (**11**). Colourless oil, b.p. 52–55°/0.006 Torr. – UV.: λ_{max}=212 (1180). – IR. (film): 3040, 2990, 2970, 2930, 2890, 2870, 1630, 1490, 1455, 1380, 1370, 1085, 1050, 1020, 990, 870, 860, 810, 710. – NMR.: 6.52 ($d\times d$, $J_{5,4}$=8.0, $J_{5,6}$=6.5, H–C(5)); 5.72 ($d\times d$, $J_{4,5}$=8.0, $J_{4,6}$=1.5, H–C(4)); 3.11 (d, $J_{7a,3}$=2.0, H–C(7a)); 2.16–1.88 (m, H–C(3) and H–C(6)); 1.84–1.28 (m, 5H); 0.92 ($d\times d\times d$, J_{gem}=14.0, $J_{8\beta,9\beta}$=7.0, $J_{8\beta,9\alpha}$=3.0, Hβ–C(8)); 1.38, 1.36 and 0.80 (3 s, H_3C–C(2), H_3C–C(3a) and H_3C–C(7)). – MS.: 204 (M^+, 3.5), 116 (3), 112 (19), 111 (100), 105 (5.5), 93 (5), 91 (10), 77 (7).

$C_{14}H_{20}O$ (204.30) Calc. C 82.30 H 9.87% Found C 82.58 H 9.59%

4. Dehydration of alcohol 4. – 4.1. *Procedure A.* A mixture of 1.25 g (5.73 mmol) of **4** and 1.5 g (9.8 mmol) of $POCl_3$ in 15 ml of pyridine was heated at 70° for 3 h. Work-up gave 515 mg of a mixture subjected to prep. TLC. in hexane to afford 48 mg (4.3%) of **12** in the first fraction and 235 mg (20.4%) of **13** in a later fraction.

1,4,5,11-Tetramethyl-tetracyclo[6.3.0.0.^{4,6}0^{5,11}]undeca-2,9-diene (**12**). Colourless oil, b.p. 48–50°/0.03 Torr. – UV.: λ_{max}=213 (6130). – IR. (film): 3050, 3030, 2980, 2960, 2920, 2880, 2850, 1645, 1605, 1470, 1450, 825, 800, 770, 730, 700, 675. – NMR.: *Table 1.* Decoupling experiment: 2.07→5.77 (d, J=6.0). – MS.: 200 (M^+, 15), 185 (100), 170 (44), 157 (36), 121 (45.5), 94 (67), 91 (59), 77 (48).

$C_{15}H_{20}$ (200.31) Calc. C 89.94 H 10.06% Found C 89.89 H 10.07%

1,3,6-Trimethyl-2-methylidene-tricyclo[5.4.0.0^{3,9}]undeca-5,10-diene (**13**). Colourless oil, b.p. 65–68°/0.05 Torr. – UV.: λ_{max}=218 (3420), 250 (73, sh), 275 (55, sh). – IR. (film): 3080, 3040, 2960, 2930, 2910, 2880, 2820, 1645, 1460, 1450, 1380, 1025, 870, 810, 760, 695. – NMR.: 6.39 ($d\times d$, $J_{10,11}$=8.0, $J_{10,9}$=6.5, H–C(10)); 5.78 ($d\times d$, $J_{11,10}$=8.0, $J_{11,9}$=1.5, H–C(11)); 5.19–5.04 (m, H–C(5)); 4.52 and 4.44 (2 s, 2H–C(2′)); 2.56–2.27 (m, H–C(7) and H–C(9)); 2.14–1.49 (m, 2H–C(4) and 2H–C(8)); 1.80 (small m, H_3C–C(6)); 1.31 and 1.04 (2 s, H_3C–C(1) and H_3C–C(3)). – MS.: 200 (M^+, 14), 185 (6), 144 (8), 120 (13), 119 (100), 91 (18), 81 (12), 77 (14).

$C_{15}H_{20}$ (200.31) Calc. C 89.94 H 10.06% Found C 89.81 H 10.09%

4.2. *Procedure B.* A solution of 500 mg (2.3 mmol) of **4** in 25 ml of benzene and 1.5 g (7.9 mmol) of $TsOH.H_2O$ was stirred for 20 h at 60°. After work-up, the reaction mixture was chromatographed on a silica gel column. The first fractions eluted with hexane gave 300 mg (65.4%) of *1,2,3,10-tetramethyl-tricyclo[5.2.1.1^{4,10}]undeca-2,5,8-triene* (**14**). Colourless oil, b.p. 58–60°/0.008 Torr. – UV.: λ_{max}=208 (2410), 216 (2180, sh). – IR. (film): 3040, 3020, 2980, 2960, 2920, 2880, 2860, 1670, 1645, 1620, 1470, 1450, 1380, 1065, 830, 760, 740, 715. – NMR.: *Table 1.* Decoupling experiments: 2.63→6.05 ($d\times d$, J=9.5, J=6.0) and 5.51 (d, J=9.5); 2.37→6.05 ($d\times d$, J=9.5, J=2.0); 1.66→2.37 (d, J=6.0). – MS.: 200 (M^+, 83), 185 (100), 170 (52), 157 (74), 143 (58), 129 (49), 128 (55), 115 (48), 107 (65), 91 (100).

$C_{15}H_{20}$ (200.31) Calc. C 89.94 H 10.06% Found C 90.06 H 10.20%

The later fractions eluted with benzene afforded 18 mg (3.6%) of *2,3,3a,6,7,7a-hexahydro-2,3a,7,7a-tetramethyl-2,7-ethano-3,6-methano-benzofuran* (**15**). Colourless oil, b.p. 50–53°/0.01 Torr. – UV.: λ_{max}=212 (1200). – IR. (film): 3040, 2980, 2960, 2930, 2880, 2870, 1625, 1450, 1380, 1370, 1130, 960, 870, 720, 705. – NMR.: 6.53 ($d\times d$, $J_{5,4}$=8.0, $J_{5,6}$=6.5, H–C(5)); 5.64 ($d\times d$, $J_{4,5}$=8.0, $J_{4,6}$=1.0, H–C(4)); 2.18–0.60 (m, 8H); 1.34, 1.25, 0.99, and 0.76 (4 s, H_3C–C(2), H_3C–C(3a), H_3C–C(7) and H_3C–C(7a)).

Decoupling experiment: 2.05→6.53 (*d*, $J=8.0$). - MS.: 218 (M^+, 2), 145 (8), 126 (11), 125 (100), 119 (9), 117 (5), 107 (11), 105 (12), 93 (7), 91 (25).

$C_{15}H_{22}O$ (218.33) Calc. C 82.51 H 10.16% Found C 82.41 H 9.94%

4.3. *Acid-catalysed isomerization of* **13** *into* **14**. A solution of 20 mg (0.1 mmol) of **13** in 1 ml of benzene and 10 mg (0.05 mmol) of $TsOH.H_2O$ was heated at 50° for 1 h. After filtration through a silica gel column in benzene, the filtrate contained only **14** (TLC., GC.).

5. Acid-catalysed isomerization of tetracyclic undecadienes 9 and 12. - 5.1. *Isomerization of* **9**. To a solution of 18 mg (0.1 mmol) of **9** in 2 ml of benzene, 80 mg (0.42 mmol) of $TsOH.H_2O$ was added and the suspension stirred for 2 h at 60°. After cooling and evaporation of the solvent, the reaction mixture was chromatographed on a silica gel column to give 16.5 mg (91.7%) of **10** as a colourless oil identical (GC., IR., NMR.) with the compound mentioned in 3.1.

5.2. *Isomerization of* **12**. To a solution of 23 mg (0.12 mmol) of **12** in 2 ml of benzene, 70 mg (0.37 mmol) of $TsOH.H_2O$ was added and the suspension stirred for 3 h at 60°. Work-up gave 21 mg (91.3%) of **14** as a colourless oil identical with the compound mentioned in 4.2. (GC., IR., NMR.).

6. Acid-catalysed rearrangement of 1,3,6-trimethyl-tricyclo[5.4.0.0^{3,9}]undeca-5,10-dien-2-one (1). - To a solution of 1.0 g (4.95 mmol) of **1** in 5 ml of CH_2Cl_2 at −78°, 2 ml (34.8 mmol) of fluorosulfonic acid (FSO_3H) was added. The solution was warmed to RT. and stirred for 1 h. The reaction mixture was poured into 100 ml of ice/water, neutralized with $NaHCO_3$, and extracted with ether. The residue was chromatographed on neutral aluminium oxide with benzene/acetone 20:1 to give 465 mg (46.5%) of *2,3,10-trimethyl-tricyclo[5.2.1.1^{4,10}]undeca-2,5,8-trien-1-ol* (**16**). Colourless crystals, m.p. 109–110° (hexane). - UV.: $\lambda_{max}=212$ (3480), 217 (3280, sh). - IR. (KBr): 3320 (OH), 3060, 3040, 3020, 2980, 2920, 2870, 1670, 1640, 1620, 1445, 1390, 1380, 1330, 1100, 1070, 1060, 1020, 990, 915, 840, 770, 740, 720. - NMR: *Table 1*. Decoupling experiments: 2.78→5.45 (*d*, $J=10.0$) and 6.01 (*d*×*d*, $J=10.0$, $J=6.0$); 2.47→6.01 (*d*×*d*, $J=10.0$, $J=2.0$). The assignments are based on peak areas and shift slopes on adding $Eu(fod)_3$[4]) (*Table 3*). - MS.: 202 (M^+, 73), 187 (91), 169 (73), 159 (63), 145 (55), 141 (50), 129 (68), 128 (65), 115 (57), 110 (77), 91 (100).

$C_{14}H_{18}O$ (202.28) Calc. C 83.12 H 8.97% Found C 83.27 H 8.89%

Table 3. *^{1}H-shifts in NMR. spectra of* **16** *in the presence of $Eu(fod)_3$*[a])

$\frac{[Eu(fod)_3]}{[16]}$= Position	0	0.03	0.08	0.14	0.20	0.24	multiplicity and coupling constants
H–C(4)	2.42	2.53	2.71	2.91	3.08	3.24	*m*
H–C(5)	5.99	6.08	6.22	6.37	6.51	6.62	*d*×*d*×*d* ($J=10$, $J=6$, $J=2$)
H–C(6)	5.44	5.51	5.65	5.81	5.95	6.06	*d*×*d* ($J=10$, $J=4$)
H–C(7)	2.76	2.88	3.10	3.32	3.55	3.72	*m*
H–C(8)	5.68	5.73	5.92	6.10	6.28	6.42	*d*×*d* ($J=6$, $J=3.2$)
H–C(9)	5.68	5.96	6.44	6.96	7.44	7.82	*d* ($J=6$)
Hα–C(11)	-	1.78	1.96	2.20	2.42	2.59	*d*×*d* ($J=12$, $J=3$)
Hβ–C(11)	-	1.94	2.30	2.71	-	3.38	*d*×*d* ($J=12$, $J=3$)
H_3C–C(2)	1.72	1.93	2.30	2.69	3.05	3.35	*s*
H_3C–C(3)	1.72	1.77	1.90	2.04	2.16	2.26	*s*
H_3C–C(10)	1.16	1.40	1.80	2.24	2.65	2.98	*s*
OH	1.52	3.28	6.29	-[b])	-[b])	-[b])	*s*

[a]) See footnote [2]).

[b]) Very broad signal beyond 10 ppm.

7. Dehydration of alcohol 5. – 7.1. *Procedure A.* A solution of 500 mg (2.45 mmol) of **5** and 1.0 g (6.54 mmol) of $POCl_3$ in 5 ml of pyridine was stirred for 20 h at 60°. After work-up, the reaction mixture was chromatographed on silica gel in hexane to give 30 mg (6.6%) of **17** in the first fractions and 40 mg (8.7%) of **18** in later fractions. Then elution with benzene gave 64 mg of a mixture of several alcohols not isolated in pure form.

2,5-Dimethyl-11-methylidene-tricyclo[4.3.2.0^{5,9}]undeca-2,7-diene (**17**). Colourless oil, b.p. 35–38°/0.008 Torr. – UV.: λ_{max} = 213 (3586), 237 (1863); λ_{min} = 231 (1793). – IR. (film): 3060, 2980, 2950, 2920, 2890, 1650, 1462, 1433, 1068, 888 (C=CH_2), 710. – NMR.: 6.14–5.88 (*m*, H–C(7) and H–C(8)); 5.42–5.29 (*m*, H–C(3)); 4.68 (*t*, *J* = 2.2, H–C(11')); 4.57 (*t*, *J* = 2.0, H–C(11')); 2.57 (small *m*, H–C(6)); 2.35–1.00 (*m*, 6H); 1.70 (br. *s*, overlapped, H_3C–C(2)); 1.06 (*s*, overlapped, H_3C–C(5)). Decoupling experiments: 2.57 → 6.14–5.88 (changed); 6.02 → 2.57 (br. *s*). – MS.: 186 (M^+, 35), 171 (73), 157 (15), 156 (12), 143 (34), 131 (15), 129 (26), 128 (23), 115 (21), 107 (40), 106 (36), 105 (26), 91 (52), 80 (100), 79 (34), 77 (33).

$C_{14}H_{18}$ (186.28) Calc. C 90.26 H 9.74% Found C 90.23 H 9.86%

2,5,11-Trimethyl-tricyclo[4.3.2.0^{5,9}]undeca-2,7,10-triene (**18**). Colourless oil, b.p. 43–46°/0.005 Torr. – UV.: λ_{max} = 211 (3510), 219 (3024, sh), 235 (810, sh). – IR. (film): 3060, 3020, 2963, 2915, 2875, 2850, 2830, 1447, 1435, 1375, 1325, 890, 820, 770, 760, 732, 702. – NMR.: 6.45 and 5.68 (2 *d* × *d*, *J* = 6.0, *J* = 3.0, H–C(7) and H–C(8)); 5.53–5.36 (*m*, H–C(3)); 4.86–4.73 (*m*, H–C(10)); 2.41–1.82 (*m*, 5H); 1.81 and 1.73 (2 br. *s*, H_3C–C(2) and H_3C–C(11)); 1.03 (*s*, H_3C–C(5)). – MS.: 186 (M^+, 58), 171 (56.5), 157 (34), 143 (38), 139 (39), 138 (49), 115 (54), 107 (38), 91 (100), 77 (83).

$C_{14}H_{18}$ (186.28) Calc. C 90.26 H 9.74% Found C 90.13 H 9.56%

7.2. *Procedure B.* To a solution of 300 mg (1.47 mmol) of **5** in 10 ml of benzene, 800 mg (4.21 mmol) of $TsOH.H_2O$ was added and the suspension stirred for 50 h at 70°. After evaporation of the solvent, the residue was chromatographed on silica gel in benzene to give 256 mg (85.3%) of starting alcohol **5**.

8. Dehydration of 6. – 8.1. *Procedure A.* A solution of 320 mg (1.47 mmol) of **6** and 700 mg (4.58 mmol) of $POCl_3$ in 5 ml of pyridine was heated at 80° for 20 h. After work-up, the mixture was chromatographed in hexane on silica gel impregnated with silver nitrate (4%). The first fractions gave 59 mg (20%) of *2,5,6-trimethyl-7-methylidene-tricyclo[4.4.1.0^{5,10}]undeca-2,8-diene* (**19**). Colourless oil, b.p. 48–52°/0.006 Torr. – UV.: λ_{max} = 205 (11900), 242 (16700), 251 (7220, sh); λ_{min} = 213 (9690). – IR. (film): 3100, 3030, 2990, 2970, 2950, 2930, 2880, 2840, 1640, 1600, 1450, 1440, 1380, 1060, 880, 810, 790, 650. – NMR.: 6.09–5.78 (*m*, H–C(8) and H–C(9)); 5.10–4.98 (*m*, H–C(3)); 4.70 (*t*, *J* = 1.0, H–C(7')); 4.59 (*d*, $J_{7,8}$ = 1.5, H–C(7')); 2.41 (*d* × *m*, J_{gem} = 16.5, H–C(4)); 2.26–1.88 (*m*, 4H); 1.65 (*d*, $J_{CH_3\text{-}2,3}$ = 2.0, H_3C–C(2)); 1.55 (*d* × *d*, J_{gem} = 20.0, $J_{11a,1}$ = 8.0, H*a*–C(11)); 1.11 and 0.87 (2 *s*, H_3C–C(5) and H_3C–C(6)). – MS.: 200 (M^+, 23), 185 (21), 172 (10), 157 (16), 143 (22), 129 (12), 120 (17), 119 (100), 108 (12), 105 (14), 91 (26), 81 (12), 79 (15), 78 (13).

$C_{15}H_{20}$ (200.31) Calc. C 89.94 H 10.06% Found C 90.26 H 10.18%

The following fractions gave 158 mg (53.8%) of *1,3,6-trimethyl-2-methylidene-tricyclo[5.3.1.0^{3,8}]-undeca-5,9-diene* (**20**). Colourless oil, b.p. 50–53°/0.004 Torr. – UV.: λ_{max} = 213 (3400), 234 (340, sh). – IR. (film): 3080, 3040, 2960, 2920, 2880, 2860, 1640, 1450, 1440, 1375, 1150, 885, 800, 720, 700. – NMR.: 6.25 (*d* × *d*, $J_{9,10}$ = 8.0, $J_{9,8}$ = 6.5, H–C(9)); 5.95 (*d* × *d*, $J_{10,9}$ = 8.0, $J_{10,8}$ = 1.5, H–C(10)); 5.22–5.10 (*m*, H–C(5)); 4.86 and 4.76 (2 *s*, 2H–C(2')); 2.48–2.12 (*m*, 3H); 1.96 (*d* × *m*, J_{gem} = 11.5; H*β*–C(4)); 1.78–0.90 (*m*, partially overlapped, 2H–C(11); 1.67 (small *m*, H_3C–C(6)); 1.27 and 0.99 (2 *s*, H_3C–C(1) and H_3C–C(3)). – MS.: 200 (M^+, 7), 185 (8), 157 (7.5), 143 (7), 119 (100), 105 (8), 91 (7.5), 81 (6), 79 (6), 77 (6).

$C_{15}H_{20}$ (200.31) Calc. C 89.94 H 10.06% Found C 89.97 H 9.95%

8.2. *Procedure B.* A solution of 420 mg (1.93 mmol) of **6** in 15 ml of benzene and 1.3 g (6.84 mmol) of $TsOH.H_2O$ was stirred for 5 h at 60°. After work-up, the reaction mixture was chromatographed in hexane on silica gel impregnated with silver nitrate (4%). The first fractions contained 295 mg (76.6%) of **19** and the later fractions 27 mg (7%) of **20**.

8.3. *Acid-catalysed isomerization of* **20** *into* **19**. A mixture of 10 mg (0.05 mmol) of **20** and 5 mg (0.025 mmol) of $TsOH.H_2O$ in 1 ml of benzene was heated at 50° for 2 h. After filtration through a silica gel column in benzene, the filtrate contained only **19** (TLC., GC.).

9. Dehydration of 7. – 9.1. *Procedure A.* A solution of 500 mg (2.45 mmol) of **7** and 1.0 g (6.54 mmol) of $POCl_3$ in 5 ml of pyridine was heated at 60° for 5 min. After work-up, the residue was chromatographed on silica gel in hexane to give 305 mg (66.9%) of *2,5-dimethyl-7-methylidene-tricyclo-[4.4.1.0^{5,10}]undeca-2,8-diene* (**21**). Colourless oil, b.p. 45–48°/0.005 Torr. – UV.: λ_{max} = 204 (6700), 238 (15440); λ_{min} = 210 (6328). – IR. (film): 3080, 3040, 2990, 2960, 2950, 2930, 2870, 2830, 1640, 1600, 1455, 1440, 1380, 875, 850, 810. – NMR.: 6.02–5.74 (*m*, H–C(8) and H–C(9)); 5.08–4.96 (*m*, H–C(3)); 4.58–4.48 (small *m*, 2H–C(7′)); 2.26 (*d*×*m*, J_{gem} = 20.0, H–C(4)); 2.29–1.60 (*m*, 6H); 1.63 (small *m*, H_3C–C(2)); 0.93 (*s*, H_3C–C(5)). – MS.: 186 (M^+, 19), 171 (14), 157 (11.5), 143 (11.5), 130 (13), 118 (10), 115 (11.5), 106 (21), 105 (100), 91 (22), 81 (64), 79 (31), 77 (21.5).

$C_{14}H_{18}$ (186.28) Calc. C 90.26 H 9.74% Found C 90.31 H 9.78%

9.2. *Procedure B.* To a solution of 300 mg (1.47 mmol) of **7** in 10 ml of benzene, 800 mg (4.21 mmol) of $TsOH.H_2O$ was added and the suspension stirred for 50 h at 70°. After evaporation of the solvent, chromatography on silica gel in benzene afforded 258 mg (86%) of product mixture which consisted (GC.) of the starting alcohol **7** (38%) and four other alcohols. These products were not isolated.

10. Reaction of 1,3,6-trimethyl-tricyclo[5.3.1.0^{3,8}]undeca-5,9-dien-2-one (2) with trifluoracetic acid. – 330 mg (1.63 mmol) of **2** was dissolved in 3 ml (39.3 mmol) of trifluoracetic acid (CF_3COOH) and the solution stirred for 20 h at RT. After evaporation of CF_3COOH, the residual solid was chromatographed on silica gel with hexane/benzene 1:5 to give 316 mg (61.2%) of *6-trifluoroacetoxy-1,3,6-trimethyl-tricyclo[5.3.1.0^{3,8}]undeca-9-en-2-one* (**22**). Colourless crystals, m.p. 98–99° (hexane). – UV.: λ_{max} = 209 (2800). – IR. (KBr): 3000, 2980, 2960, 2940, 1780 ($OCOCF_3$), 1710 (CO), 1475, 1465, 1450, 1390, 1380, 1375, 1220, 1155, 1120, 1085, 1040, 885, 840, 780, 750, 730, 700. – NMR.: 6.43 (*d*×*d*, $J_{9,10}$ = 8.0, $J_{9,8}$ = 6.5, H–C(9)); 5.93 (*d*×*d*, $J_{10,9}$ = 8.0, $J_{10,8}$ = 1.5, H–C(10)); 2.72 (*d*×*d*×*d*, $J_{8,9}$ = $J_{8,7}$ = 3.0, $J_{8,10}$ = 1.5, H–C(8)); 2.56 (*d*×*m*, J_{gem} = 12.0; Hα–C(5)); 2.19 (*d*×*m*, $J_{7,11}$ = 10.0, H–C(7)); 1.96–1.05 (*m*, Hβ–C(5), 2H–C(4), and 2H–C(11)); 1.60 (*s*, H_3C–C(6)); 1.22 and 1.02 (2 *s*, H_3C–C(1) and H_3C–C(3)). – MS.: 316 (M^+, 2), 202 (8), 174 (21), 173 (19), 159 (56), 145 (28), 132 (100), 131 (24), 119 (41), 117 (39), 105 (24), 91 (48), 79 (21), 77 (25).

$C_{16}H_{19}F_3O_3$ (316.31) Calc. C 60.75 H 6.05% Found C 60.87 H 6.06%

11. Reactions of ketoester 22. – 11.1. *Saponification.* To a solution of 500 mg (1.58 mmol) of **22** in 10 ml of *t*-butyl alcohol, 100 mg (0.89 mmol) of potassium *t*-butoxide was added and the solution stirred for 20 h at RT. After evaporation of the solvent, the residual solid was chromatographed on silica gel with hexane/benzene 1:15 to afford 330 mg (94.8%) of *6-hydroxy-1,3,6-trimethyl-tricyclo-[5.3.1.0^{3,8}]undeca-9-en-2-one* (**23**). Colourless needles, m.p. 125–126° (hexane). – UV.: λ_{max} = 211 (2280). – IR. (KBr): 3380 (OH), 2970, 2960, 2940, 2930, 1715 (CO), 1470, 1450, 1380, 1250, 1170, 1035, 915. – NMR.: 6.46 (*d*×*d*, $J_{9,10}$ = 8.0, $J_{9,8}$ = 7.0, H–C(9)); 5.90 (*d*×*d*, $J_{10,9}$ = 8.0, $J_{10,8}$ = 2.0, H–C(10)); 2.97 (*d*×*d*×*d*, $J_{8,9}$ = 7.0, $J_{8,7}$ = 3.0, $J_{8,10}$ = 2.0, H–C(8)); 1.96–1.26 (*m*, 7H); 1.42 (*s*, OH); 1.21, 1.18, and 0.99 (3 *s*, H_3C–C(1), H_3C–C(3), and H_3C–C(6)). – MS.: 220 (M^+, 15), 191 (6), 158 (13), 133 (100), 131 (45), 127 (22), 120 (33), 118 (30), 92 (28), 90 (26).

$C_{14}H_{20}O_2$ (220.30) Calc. C 76.32 H 9.15% Found C 76.04 H 9.08%

11.2. *Acid-catalysed rearrangement.* To a solution of 500 mg (1.58 mmol) of **22** in 2 ml of CH_2Cl_2, 1 ml (17.4 mmol) of fluorosulfonic acid (FSO_3H) was added at −78°. After stirring for 3 h at −78°, the solution was warmed to RT. and stirred for additional 3 h. The reaction mixture was poured into 100 ml of ice/water, neutralized with $NaHCO_3$ and extracted with ether. The residue was chromatographed on silica gel in benzene to give 100 mg (22.3%) of **24** in the first fractions and 80 mg (17.8%) of **25** in the following fractions.

5-Fluorosulfonyl-1,3,6-trimethyl-tricyclo[5.3.1.0^{3,8}]undeca-5,9-dien-2-one (**24**). Colourless crystals, m.p. 78–80° (hexane). – UV.: λ_{max} = 217 (4770). – IR. (KBr): 3070, 2980, 2940, 2880, 1720 (CO), 1645, 1455, 1435, 1395 (*as* SO_2), 1220, 1200 (*sym* SO_2), 760, 730. – NMR.: 6.43 (*d*×*d*, $J_{9,10}$ = 8.0, $J_{9,8}$ = 6.5, H–C(9)); 6.05 (*d*×*d*, $J_{10,9}$ = 8.0, $J_{10,8}$ = 2.0, H–C(10)); 2.96 (*d*×*m*, J_{gem} = 18.0, Hβ–C(4)); 2.74–2.40 (*m*, 3H); 2.20 (br. *s*, H_3C–C(6)); 1.98 (*t*, J_{gem} = $J_{11\alpha,7}$ = 12.0, Hα–C(11)); 1.27 (*d*×*d*, J_{gem} = 12.0, $J_{11\beta,7}$ = 3.0, Hβ–C(11)); 1.21 and 1.10 (2 *s*, H_3C–C(1) and H_3C–C(3)). – MS.: 284 (M^+, 46.3), 257 (15), 256 (88), 241 (14), 173 (100), 159 (10), 158 (80), 157 (47), 144 (22), 143 (47), 142 (22), 131 (46), 91 (30).

$C_{14}H_{17}FO_3S$	Calc.	C 59.13	H 6.02	S 11.27	F 6.68%
(284.34)	Found	C 59.43	H 6.03	S 11.32	F 6.47%

8-Fluorosulfonyl-1,7,10-trimethyl-tricyclo[4.4.1.0^{5,10}]undeca-3,7-dien-2-one (**25**). Colourless crystals, m.p. 115–117° (hexane). – UV.: λ_{max} = 220 (11570). – IR. (KBr): 3060, 2980, 2940, 1695 (CO), 1650, 1395 (*as* SO_2), 1385, 1375, 1205 (*sym* SO_2), 1190, 830, 800, 780, 755. – NMR.: 6.97 (*d*×*d*, $J_{4,3}$ = 10.0, $J_{4,5}$ = 7.0, H–C(4)); 6.05 (*d*, $J_{3,4}$ = 10.0, H–C(3)); 2.82 (*d*×*m*, J_{gem} = 18.0, Hβ–C(9)); 2.70–2.24 (*m*, 3H); 2.27 (br. *s*, H_3C–C(7)); 2.10 (*d*×*d*, J_{gem} = 14.0, $J_{11\alpha,6}$ = 7.5, Hα–C(11)); 1.69 (*d*×*d*, J_{gem} = 14.0, $J_{11\beta,6}$ = 1.5, Hβ–C(11)); 1.16 and 1.00 (2 *s*, H_3C–C(1) and H_3C–C(10)). – MS.: 284 (M^+, 61), 269 (6), 216 (7), 201 (25), 173 (12), 133 (19), 122 (77), 97 (8), 96 (100), 91 (37).

$C_{14}H_{17}FO_3S$	Calc.	C 59.13	H 6.02	S 11.27	F 6.68%
(284.34)	Found	C 59.44	H 6.24	S 11.17	F 6.32%

12. Reactions of 11 and 15 with 4-phenyl-1,2,4-triazoline-3,5-dione. – 12.1. *Reaction of* **11**. To a solution of 45 mg (0.24 mmol) of **11** in 5 ml of dry benzene 65 mg (0.37 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione was added and the solution stirred for 20 h at RT. After evaporation of the solvent, the residue was chromatographed on silica gel in chloroform to give 85 mg (97.3%) of *3-(3,5-dioxo-4-phenyl-1,2,4-triazolidine-1-yl)-3,10-dimethyl-2-methylidene-tricyclo[5.2.1.1^{4,10}]undeca-5,8-diene* (**26**)[7]. Colourless prisms, m.p. 171–172° (ethanol). – UV.: λ_{max} = 216 (22100). – IR. (KBr): 3200 (NH), 3060, 2960, 2930, 2870, 1765 (CO), 1695 (CO), 1600, 1510, 1490, 1460, 1430, 790, 770, 700. – NMR.: *Table 2*. Decoupling experiments: 3.67 → 5.88 (changed); 3.11 → 5.92 (*d*×*d*, *J* = 9.0, *J* = 1.5), 5.17 (*s*), 2.21 (*d*, *J* = 13.0), and 1.66 (*d*, *J* = 13.0); 2.73 → 5.92 (*d*×*d*, *J* = 9.0, *J* = 7.5), 5.65 (*d*, *J* = 9.0), and 5.88–5.58 (changed). – MS.: 361 (M^+, 0.8), 303 (0.8), 226 (1.2), 199 (1.3), 186 (8), 185 (100), 184 (6), 177 (6.5), 169 (7.5), 157 (11), 143 (12), 129 (12), 128 (11), 119 (12), 105 (14), 93 (12), 91 (12).

$C_{22}H_{23}N_3O_2$ (361.43) Calc. C 73.10 H 6.41 N 11.63% Found C 73.09 H 6.56 N 11.39%

12.2. *Reaction of* **15**. A solution of 100 mg (0.5 mmol) of **15** and 180 mg (1.03 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione in 5 ml of dry benzene was stirred for 20 h at RT. After evaporation of the solvent, the residual solid was chromatographed on silica gel in benzene/acetone 20:1 to give 125 mg (66.6%) of *3-(3,5-dioxo-4-phenyl-1,2,4-triazolidine-1-yl)-1,3,10-trimethyl-2-methylidenetricyclo[5.2.1.1^{4,10}]-undeca-5,8-diene* (**27**)[7]. Colourless prisms, m.p. 208–210° (ethanol). – UV.: λ_{max} = 214 (16900). – IR. (KBr): 3250 (NH), 1770 (CO), 1700 (CO), 1505, 1430, 1140, 1100, 915, 800, 770, 750. – NMR.: *Table 2*. Decoupling experiments: 3.66 → 5.88–5.57 (changed), 2.40 (*d*, *J* = 14.0), and 1.70 (*d*, *J* = 14.0). – MS.: 375 (M^+, 0.2), 255 (1), 212 (1), 199 (55), 157 (23), 128 (21), 119 (100), 105 (28), 91 (85), 77 (57).

$C_{23}H_{25}N_3O_2$ (375.45) Calc. C 73.57 H 6.71 N 11.19% Found C 73.63 H 6.71 N 11.19%

REFERENCES

[1] *H. Greuter, Gy. Fráter & H. Schmid,* Helv. *55*, 526 (1972).
[2] a) *K. Hayakawa, H. Schmid & Gy. Fráter,* Chimia *29*, 530 (1975); b) Helv. *60*, 561 (1977).
[3] *R. L. Cargill, T. E. Jackson, N. P. Peet & D. M. Pond,* Accounts chem. Res. *7*, 106 (1974).
[4] *M. Kuzuya & H. Hart,* Tetrahedron Letters *1973*, 3887, 3891.
[5] *H. Hart & M. Kuzuya,* J. Amer. chem. Soc. *97*, 2459 (1975).
[6] *Gy. Fráter,* Helv. *57*, 172 (1974).
[7] a) *R. C. Cookson, S. S. H. Gilani & I. D. R. Stevens,* J. chem. Soc. C, *1967*, 1905; b) *R. C. Cookson, S. S. H. Gilani & I. D. R. Stevens,* Tetrahedron Letters *1962*, 615; c) *S. J. Cristol, E. L. Allred & D. L. Wetzel,* J. org. Chemistry *27*, 4058 (1962).
[8] *D. H. Williams & I. Fleming,* 'Spektroskopische Methoden in der organischen Chemie', Georg Thieme Verlag, Stuttgart 1968, p. 37.
[9] *W. H. Sanders, Jr. & A. F. Cockerill,* 'Mechanisms of Elimination Reactions', John Wiley & Sons Inc., New York 1973, p. 221.
[10] a) *H. Hart & G. M. Love,* J. Amer. chem. Soc. *93*, 6264 (1971); b) *H. Hart & M. Kuzuya,* ibid. *95*, 4096 (1973).
[11] *H. G. Richey, Jr.* in 'Carbonium Ions', Vol. III, G. A. Olah & P.v.R. Schleyer, Eds., Interscience Publ., New York 1972, Ch. 25.
[12] *K. Grob,* Helv. *48*, 1362 (1965); *51*, 718 (1968).

[7]) Nomenclature is for compound **b** in *Scheme 7*.