193. O-Protonation of α-Diazoketones in Super-strong Acids

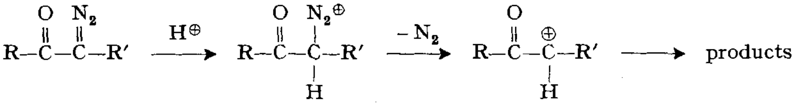
by **C. Wentrup** and **H. Dahn**

Institute of Organic Chemistry, University of Lausanne

(22. VII. 70)

Summary. Primary diazoketones, R–CO–CHN$_2$, are O-protonated in HF–SbF$_5$–SO$_2$ or FSO$_3$H–SbF$_5$–SO$_2$ at –60°, as observed by NMR. The OH-proton resonates at 9.3–9.6 δ and is coupled with H–C1 (J = 1–2.5 Hz). Secondary diazoketones, R–CO–C(N$_2$)–R, when protonated, give an OH-singlet at 8.85 δ. The assignments are corroborated by use of deuterated diazoketones, R–CO–CDN$_2$, or deuterated acid, FSO$_3$D. Primary diazoketones react with FSO$_3$H at –60° to –15°, giving products assigned the fluorosulfate structure, R–CO–CH$_2$–OSO$_2$F; they do not exchange H–C1 with solvent before or during decomposition. Intermediate C-protonated diazonium ions and α-oxo-carbonium ions (vinyl carbonium ions) have not been identified. 3-Diazo-4-methyl-2-pentanone (VIII) reacts with FSO$_3$H at –15°, eliminating N$_2$ and giving protonated mesityl oxide by a strictly intramolecular hydride shift.

In preceding communications [1] we have discussed the acid hydrolysis of secondary α-diazoketones, R–CO–CN$_2$–R', and similar compounds; the reaction proceeds via rate-determining protonation at C, followed by a S_N1-type decomposition of the diazonium ion postulated as an intermediate.



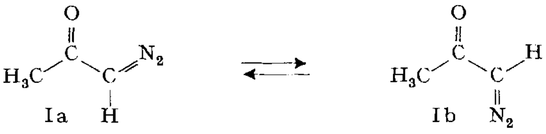
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle N_2}{\|}}{C}-R' \xrightarrow{H^\oplus} R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle N_2^\oplus}{|}}{C}}-R' \xrightarrow{-N_2} R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\oplus}{C}}-R' \longrightarrow \text{products}$$

Arguments in favour of this mechanism were: (a) general acid catalysis; (b) kinetic isotope effect of the solvent $k_{D_2O}/k_{H_2O} = 0.5$; (c) no dependence of product composition on added nucleophiles; (d) hydride shift in olefin formation. Primary α-diazoketones, R–CO–CHN$_2$, and primary α-diazoesters react by a different mechanism [2], *i.e.* by reversible C-protonation, followed by a S_N2-type displacement of N$_2$ by a nucleophile.

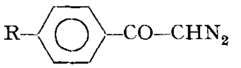
In order to gain further information on the acid hydrolysis of α-diazoketones and related compounds, we have studied their protonation in super-strong acids at low temperatures.

Mohrig & Keegstra [3] have detected the first case of an aliphatic diazonium ion stable at low temperature, namely the 2,2,2-trifluoroethyl-diazonium ion, CF$_3$–CH$_2$–N$_2^\oplus$, formed by protonation of trifluorodiazoethane in HFSO$_3$ at – 60°. *Allard, Levisalles & Sommer* [4] recently published a short communication in which they report results showing O-protonation for various primary and secondary α-diazoketones in FSO$_3$H–SbF$_5$–SO$_2$ at – 60°. Their communication prompts us to publish our own findings.

Spectra in SO$_2$ solution. Diazoketones have been shown [5] to exist as mixtures of *syn-* and *anti*-forms, the *syn*-form usually predominating; stabilisation occurs by the resonance contribution of the diazonium enolate. At low temperatures, the rate of interconversion of these isomers is sufficiently slow for many NMR. spectra to show the presence of both forms.



Ia Ib



II $R = H$
III $R = Cl$
IV $R = OCH_3$

$ROOC-CHN_2$ V $R = CH_3$
VI $R = C_2H_5$
$CH_3-CO-CN_2-CH_3$ VII
$CH_3-CO-CN_2-CH(CH_3)_2$ VIII

In SO_2 solution at −60° we found spectra similar to those measured previously in $CHCl_3$ solution [5], except that all bands were shifted 0.5 to 1 ppm towards lower field in SO_2 (Table 1). In the *syn*-form (Ia) of diazoacetone the methine proton at C1 comes at lower field than in the *anti*-form (Ib) [5]; this is reasonable since H–C1 in Ib is in the shielding region of the C=O group.

Like diazoacetophenone (II) [5], *p*-chloro-diazoacetophenone (III) and *p*-methoxy-diazoacetophenone (IV) give discreet spectra due either to rapid interconversion of the isomers even at −100°, the lowest temperature applied, or (more probably) to the exclusive presence of the sterically favoured *syn* isomer. *Kaplan* & *Meloy* [5] have shown that in methyl (V) and ethyl diazoacetate (VI), in which steric hindrance is smallest, the *syn*/*anti* ratio is nearly 1:1. In these cases we chose to assign the lowest-field signals to the *syn*-forms.

Secondary diazoketones, 3-diazo-2-butanone (VII) and 3-diazo-4-methyl-2-pentanone (VIII) exhibit a similar general pattern. Using $CD_3-CO-CN_2-CH_3$ (VII-D) we found that in VII the CH_3 group in position 1 resonates at lower field than that in position 4. The ratio of isomers was 4:1 in the case of VII (coalescence temperature ca. +20° in $CHCl_3$), 9:1 in the case of VIII (coalescence temperature ca. +10°). In neither case is it at present clear whether the *syn*-form is still prevalent, or whether steric hindrance has reversed the ratio.

Protonation. We have protonated the α-diazoketones and α-diazoesters I–VIII with strong anhydrous acids at low temperature (−60° to −80°), thus excluding the possibility of uncatalysed thermal decomposition *via* carbene formation [6], and using the poorest possible nucleophiles as anions (SbF_6^-; $SO_3SbF_6^-$) to enable observation of the protonated species by NMR. The mixtures generally used were $FSO_3H-SbF_5-SO_2$ ('magic acid') [7] and the even stronger [8] $HF-SbF_5-SO_2$.

On treatment with $HF-SbF_5$ in SO_2, diazoacetone (I) showed two sets of signals (see Table 1): a) 2.05 (3 H, singlet) and 5.91 δ (1 H, doublet, $J = 2$ Hz); b) 2.19 (3 H singlet) and 6.06 δ (1 H, doublet, $J = 1$ Hz); the two sets are due to the methyl and methine groups of the *syn*- and *anti*-forms (IXa and IXb) of protonated I present in the ratio of about 4:1. In contrast to unprotonated I, the methine H of the major isomer of protonated I (IX) resonates at the higher field. This means either that the

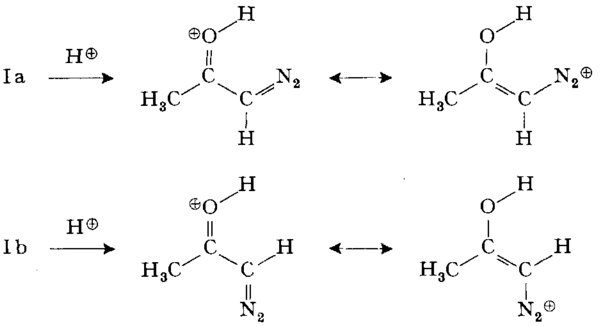
Table 1. *NMR. spectra of diazoketones in SO_2 and SO_2-acid solution at* $-60°$

Compound	Solvent	Chemical shifts, δ[a]					*Syn*:*anti* ratio
			$CH_3(3)$		CH(1)	$^{\oplus}$OH	
I	SO_2	*syn*	1.34 (*s*)		4.97 (*s*)		4:1
		anti	1.53 (*s*)		4.60 (*s*)		
I	HF–SbF_5	*syn*	2.05 (*s*)		5.9 (*d*, 2)	9.47 (*d*, 2)	4:1
		anti	2.19 (*s*)		6.06 (*d*, 1)	9.29	
I	FSO_3H–SbF_5 or FSO_3D–SbF_5	*syn*	2.05 (*s*)		5.91 (*s*)	–	4:1
		anti	2.19 (*s*)		6.06 (*s*)	–	
I–D	HF–SbF_5	*syn*	2.05 (*s*)		–	9.45 (*s*)	4:1
		anti	2.19 (*s*)		–	9.27 (*s*)	
		OCH_3	aromatic		CH	$^{\oplus}$OH	
II	HF–SbF_5		7.34 (*m*)		6.25 (*d*, 2.5)	9.34 (*d*, 2.5)	–
III	FSO_3H–SbF_5		7.67 (*d*, 9),	7.34 (*d*, 9)	6.34 (*d*, 2.5)	9.36 (*d*, 2.5)	–
IV	SO_2	3.17 (*s*)	7.10 (*d*, 9),	6.34 (*d*, 9)	5.52 (*s*)		–
IV	FSO_3H–SbF_5	4.55 (*s*)	7.51 (*q*, 9)		6.33 (*d*, 2.5)	9.59 (*d*, 2.5)	–
IV	FSO_3D–SbF_5	4.55 (*s*)	7.51 (*q*, 9)		6.33 (*s*)	–	–
IV–D	FSO_3H–SbF_5	4.55 (*s*)	7.51 (*q*, 9)		–	9.59 (*s*)	–
			CH_3	CH_2	CH	$^{\oplus}$OH	
V	SO_2	*syn*[b]	3.07 (*s*)		4.48 (*s*)		1:1
		anti[b]	3.02 (*s*)		4.15 (*s*)		
VI	SO_2	*syn*[b]	0.54 (*t*, 7)	3.44 (*q*, 7)	4.38 (*s*)		1:1
		anti[b]	0.52 (*t*, 7)	3.42 (*q*, 7)	4.04 (*s*)		
VI	FSO_3H–SbF_5		1.17 (*t*, 7)	4.90 (*q*, 7)	5.86 (*s*)	–	–
			$CH_3(1)$	$CH_3(4)$		$^{\oplus}$OH	
VII	SO_2	*syn*	1.52 (*s*)	1.16 (*s*)			4:1
		anti	1.45 (*s*)	1.42 (*s*)			
VII–D	SO_2	*syn*	–	1.16 (*s*)			4:1
		anti	–	1.42 (*s*)			
VII	HF–SbF_5	*syn*	2.14 (*s*)	1.75 (*s*)		8.60 (*s*)	4:1
		anti	2.00 (*s*)	1.76 (*s*)		8.20 (*s*)	
			$CH_3(5)$	$CH_3(1)$	CH(4)	$^{\oplus}$OH	
VIII	SO_2	*syn*[b]	0.40 (*d*, 7)	1.57 (*s*)	2.12 (*m*, 7)	–	9:1
		anti[b]	0.53	1.45			
VIII	FSO_3H–SbF_5		0.79 (*d*, 7)	2.18 (*s*)	2.87 (*m*, 7)	–	–
VIII	HF–SbF_5		0.79 (*d*, 7)	2.18 (*s*)	2.87 (*m*, 7)	8.78 (*s*)	–

[a] Tetramethylsilane as external reference in $CHCl_3$. Coupling constants are given in parenthesis; *s*, singlet; *d*, doublet; *t*, triplet; *q*, quartet; *m*, multiplet.

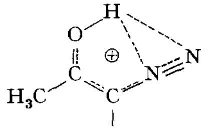
[b] Assignments of signals to *syn*- resp. *anti*-forms uncertain.

isomer ratio is exactly reversed on protonation, or that the major isomer is still in the *syn*-form, but that the methine proton of the *anti*-form (IXb) is now being more strongly deshielded than that of the *syn*-form (IXa). The latter explanation is the more likely one since H–C1 in IXb is closer to the positive charge than in IXa. The enol



IXa

IXb



IXc

$CH_3–CO–CH_2–N_2^{\oplus}$ X

$CH_3–CO–CH_2^{\oplus}$ XI

resonance formulae of IXa and IXb show why the shielding effect of the C=O group is diminished.

Protonation did not lead to a major change either in chemical shifts or in isomer ratio. The 3:1 ratio of the methyl and methine signals excludes C-protonated forms such as the diazonium ion X or the carbonium ion XI. Furthermore, in $HF–SbF_5–SO_2$ at $-60°$ to $-80°$ we observed a doublet at 9.47 δ (1 H; $J = 2$ Hz) caused by the acid proton located on the oxygen atom of the *syn*-form. A minor O–H signal (singlet or slightly split doublet) due to the protonated *anti*-form appeared at 9.29 δ. The methine proton of the two protonated stereoisomers IXa and IXb couple differently with O–H (see Table 1), the *syn*-form IXa having the largest coupling, consistent with *trans*-coupling in IXa, but *cis*-coupling in IXb. This is strong evidence in favour of O-protonation and against N-protonation: the latter should not cause such a difference in coupling constants. Furthermore, EHMO. calculations [9] have shown that the oxygen atom of diazoketones is by far the most negative. The fact that the OH-signal is a sharp doublet, and not a quartet, indicates that IX exists in the *s-syn*-form shown: *Olah et al.* [10] have shown that O-protonated ketones couple only to the side of the OH-proton. When diazoacetone-1-d_1 (I-D) [11] was used, the OH-signal collapsed to a singlet, confirming that at least the major coupling is with H–C1. IXa seems thus to be specifically protonated on the side of the stronger steric hindrance; this might be due to hydrogen bonding such as in IXc (cf. vinyl ethers [12])[1].

With the somewhat weaker protonating agent $FSO_3H–SbF_5–SO_2$, the spectrum of diazoacetone at $-60°$ did not differ substantially from that in HF, except that no HO-proton and no H–H coupling was observed; apparently the compound was protonated, but exchanged the HO-proton rapidly with solvent under these conditions. In accordance with this, the spectrum did not change when FSO_3H was replaced by FSO_3D.

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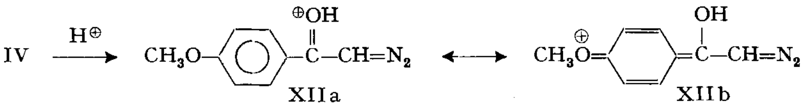
[1] *Levisalles et al.* [4] have given another explanation for the larger coupling in the *syn* isomers, ascribing it to their W-shape: this gives opposite conformations for the OH-hydrogens in IXa–b

In the case of *p*-methoxy-ω-diazoacetophenone (IV) the O-protonated ion XII was formed quantitatively already in $FSO_3H–SbF_5$ and was stable at –60°. The OH-signal was observed as a doublet in the usual position, 9.59 δ; (J = 2.5 Hz); it collapsed to a singlet (slightly broadened due to H–D coupling) when the methine proton was replaced [13] by deuterium (XII-D). The methine proton appeared as a doublet in $FSO_3H–SbF_5$ (J = 2.5 Hz), but as a singlet when FSO_3D was used. The aromatic protons and the OCH_3-protons in the ion XII were strongly deshielded relatively to the unprotonated IV, indicating that the aromatic ring and the methoxy group are involved in resonance, as in the formula XIIb. Consistent with this stabilisation by the methoxy group, the *p*-chloro analogue III gave a similar protonated species with the HO-signal at 9.36 δ (doublet, J = 2.5 Hz; see Table 1), but it was much less stable, disappearing in $^1/_2$ h at –80°; and the unsubstituted diazoacetophenone (II) did not give any observable protonated species in $SbF_5–FSO_3H$; only in the stronger acid $HF–SbF_5$ was O-protonation observed (see Table 1).



XIIa XIIb

The secondary diazoketones VII and VIII were protonated in a manner similar to the primary compounds I to IV: in $HF–SbF_5–SO_2$ at –60° a singlet signal was observed at 8.60 and 8.78 δ, resp. (Table 1). The minor (*anti*) form of VII gave a singlet at 8.20 δ. The HO-signals were not detectable in the weaker acid $FSO_3H–SbF_5–SO_2$ at –60°.

The OH-signals reported here are at considerably higher field than found [10] [14] for O-protonated ketones (12–15 δ). This difference is readily explained in terms of the enol resonance forms, *e.g.* IXa–b. O-protonated amides, capable of similar resonance, absorb in the same region [15].

The α-diazoesters were presumably protonated on oxygen, but reacted rather rapidly with $HF–SbF_5–SO_2$ or $FSO_3H–SbF_5–SO_2$ even at –80°; decomposition occurred invariably to some extent on mixing. Decomposition products (fluorosulphates, *vide infra*) were formed, but intermediate protonated species were not observed. These intermediates, which must be formed, react too fast to allow observation, and/or exchange rapidly with solvent as in the case of diazoacetone (I) in $FSO_3H–SbF_5–SO_2$.

It is well known [2] that primary α-diazo-ketones and -esters, $R–CO–CHN_2$, exchange the α-hydrogen for D rapidly in acidic D_2O, a reaction which is interpreted as reversible C-protonation. In none of the cases described above was H/D exchange observed. Diazoacetone (I) in $FSO_3D–SbF_5$ did not incorporate D in several weeks at –80°, nor did diazoacetone-1-d_1 (I-D) exchange D for H in $HF–SbF_5$. VIII in FSO_3D did not incorporate deuterium. Likewise, *p*-methoxy-ω-diazoacetophenone-ω-d_1 (IV-D) did not exchange in $FSO_3H–SbF_5$ at – 60°. This means that in these acid systems there is no equilibrium between O- and C-protonated ions at temperatures well below that of nitrogen evolution; when diazoacetone in $FSO_3D–SbF_5–SO_2$ decomposed at –15°, no H/D exchange in the protonated diazoacetone was observable.

Table 2. *NMR. spectra of decomposition products of diazoketones*

Starting compound	Product	Solvent	Chemical shifts, δ				
			OCH_3	aromatic			CH_2
IV	XIII	FSO_3H–SbF_5–SO_2[a]) (−60°)	3.55 (*s*)	7.94 (*d*, 9)	6.66 (*d*, 9)		5.75 (*s*)
IV	XIII	$CDCl_3$[b]) (37°)	3.88 (*s*)	7.88 (*d*, 9)	7.00 (*d*, 9)		5.55 (*s*)
IV-D	XIII-D	$CDCl_3$[b]) (37°)	3.88 (*s*)	7.88 (*d*, 9)	7.00 (*d*, 9)		5.55 (*m*, 1H)
			CH_3	CH_2			CH_2
VI	XIV	FSO_3H–SbF_5–SO_2[a]) (−60°)	1.20 (*t*, 7)	4.67 (*q*, 7)			5.26 (*s*)
VI	XIV	CCl_4[b]) (37°)	1.34 (*t*, 7)	4.32 (*q*, 7)			4.85 (*s*)
XV	XVI	FSO_3H–SbF_5–SO_2[a]) (−60°)	1.43 (*t*, 7)	5.00 (*q*, 7)			5.30 (*s*)
V	XVII	CF_3COOH–SO_2[a]) (−60°)	3.28 (*s*)	4.40 (*s*)			
			CH_3	CH_3	CH_3	CH	$^{\oplus}OH$
VIII or XX	XXI	FSO_3H–SO_2[a]) (−60°)	2.07 (*s*)	2.20 (*s*)	2.37 (*s*)	6.50 (*s*)	12.3 (*s*)

[a]) Tetramethylsilane in $CHCl_3$ as external reference.
[b]) Tetramethylsilane as internal reference.

Decomposition. When the solutions of protonated diazo-ketones and -esters were allowed to warm up to ca. −25°, N_2 evolution occurred and deamination products were formed. In the case of CF_3CHN_2, *Mohrig & Keegstra* [3] showed the product to be a fluorosulfate, CF_3–CH_2OSO_2F. We found that the product formed from *p*-methoxy-diazoacetophenone (IV) showed a peak corresponding to two protons in the ω-position (5.75 δ, singlet) (see Table 2). To confirm the constitution XIII (Scheme 1), the product was isolated by pouring into ice-water, extracting with ether, and distilling the solvent[2]). The NMR. spectrum ($CDCl_3$) of the product resembled that obtained in FSO_3H–SbF_5–SO_2 (Table 2). In an analogous way, ethyl diazoacetate (VI) was completely decomposed in 24 h at −25°; the reaction product, EtOOC–CH_2OSO_2F (XIV), characterised by a singlet at 5.26 δ (CH_2) in FSO_3H–SbF_5–SO_2 at −60°, was extracted and showed a similar NMR. spectrum in CCl_4 at 37° (Table 2); its IR. spectrum was close to that of $CF_3CH_2OSO_2F$ isolated by *Mohrig & Keegstra* [3]. For further corroboration, we dissolved ethyl glycolate, EtOOC–CH_2OH (XV), in FSO_3H–SbF_5–SO_2 at −25°; it was found to be very slowly converted to the acid sulfate EtOOC–CH_2OSO_3H (XVI) in a known type of reaction [16]. Its NMR. spectrum (Table 2) was very similar to that of the fluorosulfate XIV. Methyl diazoacetate (V) was converted in trifluoroacetic acid-SO_2 at −60° to an analogous product, presumably the trifluoroacetate MeOOC–CH_2OCOCF_3 (XVII) (Table 2).

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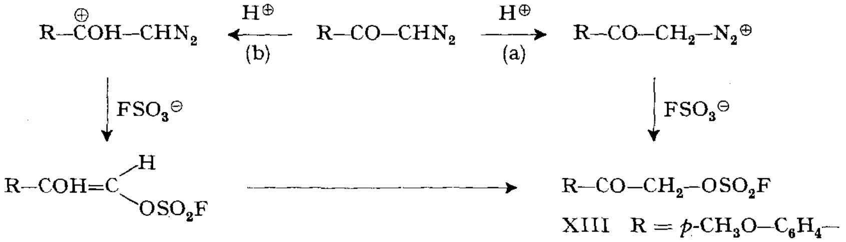
[2]) In the case of simpler diazoketones, this procedure was not applicable due to product solubility in water.

It would normally be assumed [1] [3] that the fluorosulfates were formed from the C-protonated diazo-ketones and -esters (route a, Scheme 1). As we have never observed intermediate carbonium ions, we must assume that they react very rapidly. This is confirmed by the observation that even during decomposition no H/D exchange occurs: IV-D in FSO_3H gave XIII-D with one deuterium in the CH_2 group (Table 2). This means that if a proton is located on carbon, deamination is faster than deprotonation, which is readily explicable for a medium rich in protons and poor in bases. This behaviour contrasts with that in aqueous acids [1] [2], where deprotonation by the base H_2O is much faster than attack on carbon by the same nucleophile; this is equivalent to pre-equilibrium protonation with rate-determining decomposition.

Scheme 1



XIII $R = p\text{-}CH_3O\text{–}C_6H_4\text{–}$
XIV $R = C_2H_5O$

Another explanation for the lack of deuterium exchange in the super-strong acid systems would be that enol-fluorosulfates are formed by attack of FSO_3^- on the O-protonated species, without intervention of C-protonated diazo compounds (route b).

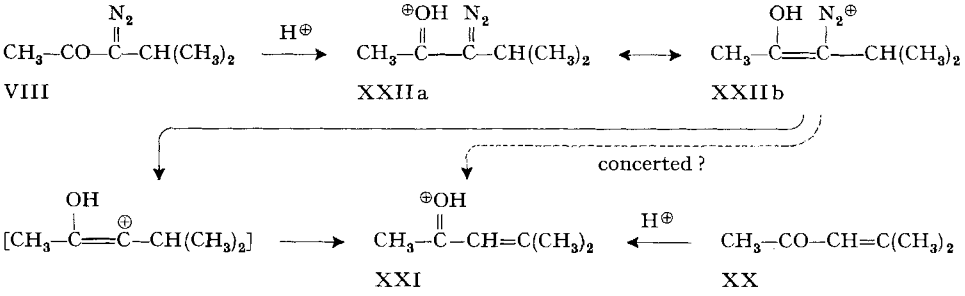
In either case, the decomposition of primary diazonium ions is expected to follow an S_N2-type attack by FSO_3^-, avoiding the formation of primary carbonium ions, as confirmed by the following observations: (a) The decomposition of IV is the faster the higher the concentration of FSO_3H and therefore that of the nucleophile FSO_3^-; (b) all decompositions were very much slower in the more acidic and least nucleophilic system $HF\text{–}SbF_5$, requiring several weeks at −15° (attack by SbF_6^-).

In the secondary diazoketones, C-protonation is rate-determining and irreversible in aqueous acids, and followed by a rapid S_N1-type decomposition [1]. This is not modified in super-strong acids: we found that the rate of decomposition of VII and VIII increased with the acidity of the solvent ($HF\text{–}SbF_5 > FSO_3H\text{–}SbF_5 > FSO_3H$).

Hydride shifts. VIII forms a special case: in aqueous acid, at least 70% of the decomposition products formed are not derived directly from the secondary α-keto-carbonium ion $MeCO\text{–}CH^{\oplus}\text{–}CHMe_2$ (XVIII), but from the tertiary carbonium ion $MeCO\text{–}CH_2\text{–}\overset{\oplus}{C}Me_2$ (XIX) formed by hydride shift [1]. In $FSO_3H\text{–}SO_2$, VIII is converted slowly (5 days at −15°) to protonated mesityl oxide (XXI) (see Scheme 2). This reaction is faster in the stronger acid system $FSO_3H\text{–}SbF_5\text{–}SO_2$, but complicated by further reaction of XXI with acid [17]. In both acid systems the product gave NMR. spectra identical with those of O-protonated mesityl oxide in the same solvent (Table 2). XXI could *a priori* be formed by proton abstraction either from the secondary (XVIII) or the rearranged tertiary carbonium ion (XIX).

When VIII was decomposed by FSO_3D in place of FSO_3H, the protonated mesityl oxide still contained one full vinylic proton (6.50 δ), whereas the carbonyl proton (12.3 δ) had disappeared. This means that the hydrogen at C3 does not come from the solvent, but is exclusively transferred by intramolecular hydride shift from the neighbouring carbon; no proton from the acid is incorporated. To explain this result, one can assume nitrogen elimination from the O-protonated diazoketone (diazonium-enol, XXIIb) either concerted with or followed by intramolecular hydride shift, as shown in Scheme 2.

Scheme 2



The financial support of this research by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* is gratefully acknowledged.

Experimental. – The *materials* used have been described previously [1]. Commercial FSO_3H (*K & K Laboratories*, New York) and SbF_5 (*Koch-Light*, England) were used for spectroscopy. SbF_5 distilled at atmospheric pressure in a glass apparatus contains HF [18]; our '$HF-SbF_5$' was obtained in this way. FSO_3D was prepared by exchange with D_2SO_4 [7].

α-Deuterated primary diazoketones were prepared by base-catalysed exchange with D_2O [11] [13].

3-Diazo-2-butanone-1-d₃ (*VII-D*) was prepared by treatment of acetyl-d_3 chloride with diazoethane in ether at 0°. After standing overnight at –15°, the ether was removed *in vacuo*, and the product distilled in high vacuum. The identity of the product was established by comparison of the IR. and NMR. spectra with those of unlabelled VII.

3-Diazo-4-methyl-2-pentanone (*VIII*). The preparation [1] was improved as follows. A solution of 4.7 g (0.056 mole) diazoisobutane [19] in 82 ml dry ether was treated with 2.2 g (0.028 mole) of acetyl chloride in 35 ml ether at –20° to –15° in the course of 35 min, with stirring. The mixture was then left in the dark at –25° for 12 h. The colour changed from orange to yellow during the first 4 h. Evaporation of the ether below 0° gave 5.6 g of a crude product containing, according to NMR., 66% of VIII. Chromatography on silica gel (0.2–0.5 mm; CCl_4) at 10°, eluting with 2:1 CCl_4–CH_2Cl_2 followed by CH_2Cl_2, gave 2.6 g (74%) of the pure diazoketone. The first fraction contained some mesityl oxide (NMR.) and the last fraction (0.25 g) contained other impurities.

NMR. spectra were recorded on a *Varian* A-60A spectrometer with a variable temperature probe (nr. V6031C) using tetramethylsilane as external reference in $CHCl_3$, unless specifically stated otherwise (see Tables). The diazo compounds were dissolved in SO_2 (ca. 10% solution), and the appropriate acid (excess) added slowly at –80° with shaking, avoiding local overheating. The NMR. spectra were recorded as soon as possible after mixing.

Decomposition (N_2-evolution) was allowed to proceed at temperatures from –80° to –15°. The fluorosulfates XIII and XIV were isolated by pouring the reaction mixtures in ice-water, extracting with ether, washing with water, drying ($MgSO_4$), and evaporating the extracts. The NMR. spectra of the isolated products are given in Table 2.

IR. (CCl_4) of XIII: 2880, 2840, 1695, 1590, 1505, 1440, 1250, 1230, 1050, 965, 827 cm^{-1}.

IR. (CCl_4) of XIV: 1725, 1450, 1230, 1050, 848 cm^{-1}.

Mass spectra of the fluorosulfates could not be obtained, since decomposition and polymerisation took place.

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194. The Conjugative Interaction between π-Orbitals and *Walsh-e*-Orbitals in Bullvalene and Related Systems1)

by **P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung** and **G. Schröder**

Physikalisch-Chemisches Institut der Universität Basel,
and Institut für Organische Chemie der Universität Karlsruhe

(30. VII. 70)

Summary. The photoelectron spectra of bullvalene (**1**), dihydrobullvalene (**2**), tetrahydrobullvalene (**3**), hexahydrobullvalene (**4**), and homotropylidene (**5**) have been recorded. The first bands in these spectra are correlated with orbitals which are linear combinations of the *Walsh-e*-orbitals and of the olefinic π-orbitals. This assignment is based on a qualitative ZDO-molecular orbital model as well as on the results of extended *Hückel* calculations. As anticipated, a large interaction is found between the π- and the *Walsh-e*-orbitals in **1**, **2**, and **3**, indicative of a resonance integral $\beta \approx -2$ eV, *i.e.* of the same order as that between the two double bond π-orbitals in butadiene ($\beta = -2.4$ eV). In **5** the interaction between π- and *Walsh-e*- orbitals is negligible.

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1) Part 14 of 'Applications of Photoelectron-Spectroscopy'. Part 13: [1].