acetonate and also in agreement with the theoretical predictions and evidence from the vibrational spectra for minimal π-interaction in vanadyl β-keto-enolates.

This work was supported by research grants provided by the University of Cape Town and the *South African Council for Scientific and Industrial Research*. We thank Dr. *K. G. Führ* for assistance with the microanalyses. We are indebted to Professors *G. Schwarzenbach, G. Anderegg*, and *W. Schneider* for hospitality extended to one of us (D. A. T.) while on leave for study at the Laboratorium für anorganische Chemie, Eidg. Technische Hochschule Zürich, during 1971.

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246. Photochemical Reactions

Part 67 [1]

Photochemistry of Saturated Aliphatic and Cyclic β-Keto Sulfoxides (C_α–S)- and α-Cleavage – A New Case of Photostereomutation

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(23. VI. 71)

Summary. The photochemical behaviour of saturated aliphatic (**2**, **4**, and **5**) and bicyclic (**18** and **19**) β-keto sulfoxides has been studied. Photostereomutation of the sulfoxide group was observed on irradiation of **4a**, **4b**, **18**, and **19**. Most likely an internal energy transfer from the excited carbonyl to the sulfoxide group is operating on direct irradiation of such compounds.

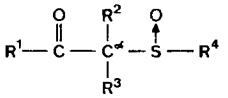
Prolonged photolysis of an aliphatic β-keto sulfoxide, which is nonalkylated at the α-carbon (**2**), yielded a product due to preferential (C_α-S)-cleavage (**24**). Mono- (**4**) and dialkylated- (**5**, **6**, and **8**) analogues primarily afforded products due to α-cleavage (**26–31** and **32**). The carboxylic acid S-methylesters (**26–31**) were exclusively formed by an intermolecular path. Prolonged irradiation of the bicyclic β-keto sulfoxides **18** and **19** favored the formation of a desulfurized compound **34** due to initial (C_α-S)-cleavage.

The scope of the use of β-keto sulfoxides in organic synthesis is considerable, a wide variety of products can be obtained from them by chemical or physical means[1]).

In the present paper we describe the results of photochemical reactions of saturated aliphatic[2]) and saturated cyclic[3]) β-keto sulfoxides.

1. Synthesis of β-Keto Sulfoxides. – a) *Synthesis of the Aliphatic β-Keto Sulfoxides* **1–8** (Chart 1). Aliphatic β-keto sulfoxides are easily obtained by condensation of dimethyl sulfoxide with esters in basic solution according to *Corey* & *Chaykovsky* [6]. The β-keto sulfoxides **3** and **7** were prepared by synthesis analogous to that of **1** and **2** [6].

Chart 1



	R^1	R^2	R^3	R^4
1	$n\text{-}C_5H_{11}$	H	H	CH_3
2	C_6H_{11}	H	H	CH_3
3	C_6H_{11}	H	H	CD_3
4	C_6H_{11}	CH_3	H	CH_3
5	C_6H_{11}	CH_3	CH_3	CH_3
6	$C_6H_{10}D$	CH_3	CH_3	CD_3
7	C_7H_{13}	H	H	CH_3
8	C_7H_{13}	CH_3	CH_3	CH_3

Gassmann & *Richmond* [7] described a general procedure for the alkylation of β-keto sulfoxides; best results had been achieved using dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO) as a solvent and sodium hydride as the added base. The β-keto sulfoxides reacted vigorously yielding their soluble salts which, by treatment with an alkylating agent in the DMF or DMSO solution, gave high yields of crude alkylated β-keto sulfoxides. As purification presented a major obstacle, the crude alkylation products were directly used for further reactions. For the synthesis of the dimethylated β-keto sulfoxides **5** (from **2**) and **8** (from **7**) we chose hexamethylphosphorictriamid (hexametapol, HMPT) as the solvent and a modified work-up which afforded good yields of pure **5** and **8**. The NMR. spectra show singlets at δ 1.51 and 1.55, respectively, for the geminal dimethyl groups.

The tetradeuterio-product **6** was prepared from cyclohexanecarboxylic acid methylester by analogy to the synthesis of **2** [6] but using DMSO-d_6. The product,

[1]) Products which can be derived from β-keto sulfoxides have been recently summarized by *Russell* & *Ochrymowycz* [2]; see also [3].

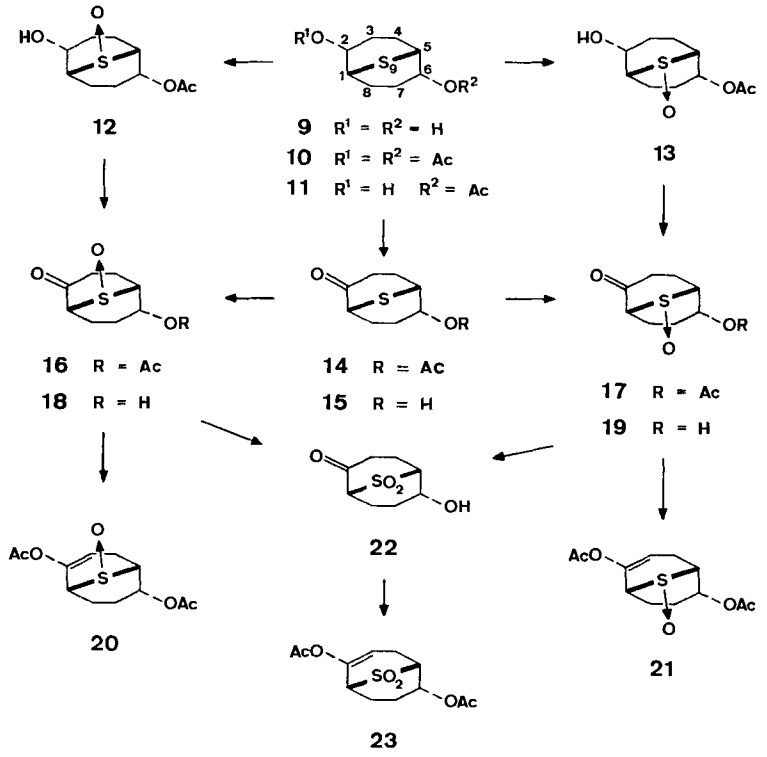
[2]) The results from aliphatic β-keto sulfoxides have partially appeared in a preliminary communication [4].

[3]) The photochemistry of cyclic β-keto sulfoxides was first described by Miss *S. Escher* (Diploma thesis, ETH Zürich 1967; see also footnote 10 in [5]) and by *F. Sitek* (Diploma thesis, ETH Zürich 1968), both in our group.

trideuteriomethyl-sulfinylmethyl cyclohexyl ketone (**3**), was partially deuterated (ca. 50%) at C-1 of the cyclohexyl ring. Subsequent dimethylation was carried out in the usual way (see above), and the dimethylated β-keto sulfoxide was finally treated with $NaOD/D_2O$ in dioxane to afford the tetradeuterio compound **6**.

It remains to comment on the monoalkylated β-keto sulfoxide **4**. Its preparation is described by *Russell* & co-workers [8] who reported that upon cooling the oily product (an equal mixture of the expected two pairs of enantiomers) in an ice bath, one of the pairs of enantiomers crystallized. They controlled this separation by NMR. investigation. Our own experiments largely confirm their results; a 4:1 mixture of the two pairs of enantiomers **4a** and **4b** was obtained by *fractional* crystallization. The NMR. spectra of this and other mixtures of the two pairs of enantiomers show an interesting feature, *viz.*: variation of temperature or concentration causes observable shifts of the resonance signals[4]), best interpreted by assuming a dimerisation of the sulfoxides[5]).

Chart 2



[4]) For accurate determinations of the ratio of the two pairs of enantiomers of **4**, *i.e.*, to assure line separation between the signals of the two pairs of enantiomers (**4a** and **4b**), it is necessary to carry out NMR. measurements with samples of different concentrations and/or at different temperatures.

[5]) The dimeric structure of sulfoxides has already been discussed by several authors, see [9] and [10].

b) *Synthesis of the Bicyclic β-Keto Sulfoxides* **18** *and* **19** (Chart 2). As starting material for the synthesis of **18** and **19** we used *endo*-2-hydroxy-*endo*-6-acetoxy-9-thiabicyclo[3.3.1]nonane (**11**) [5][6]. Treatment of **11** with one equivalent of aqueous hydrogen peroxide in acetic acid yielded almost quantitatively a mixture of the two S-9 epimeric sulfoxides **12** (S-$9_{C\text{-}3}$-oxide)[7] and **13** (S-$9_{C\text{-}7}$-oxide)[7] in the ratio of 8:5. The configuration of the sulfur atom was easily determined by NMR. measurements[8]. The hydrogen atoms CH-2 in **12** and CH-6 in **13**, respectively, are strongly deshielded by the sulfoxide group with the oxygen atom pointing toward these methine groups. The signal of CH-2 appears at δ 4.4–4.8 in **12** and at δ 4.15 in **13**, that of CH-6 at δ 5.15 in **12** and at δ 5.69 in **13**, respectively. The hydroxy acetate **12** was oxidized with *Collins* reagent [15] to the keto acetate **16** (IR.: 1735, 1708; NMR.: δ 5.22 CH-6) and, analogously, **13** to **17** (IR.: 1736, 1710; NMR.: δ 5.77 CH-6).

Yet another means of preparing the keto acetoxy sulfoxides **16** and **17** was by oxidation of the known keto acetoxy sulfide **14** [5][9] with one equivalent of aqueous hydrogen peroxide in acetic acid. A mixture of **16** and **17**, ratio approximately 10:3, was obtained which, in the crude state, was subsequently hydrolyzed with base to afford a mixture of the two keto hydroxy sulfoxides **18** and **19** then separated by column chromatography. In **19** (S-$9_{C\text{-}7}$-oxide) CH-6 is also deshielded by the sulfoxide group (CH-6: δ 4.2–4.5 in **19**, but, in **18** δ 3.8–4.1).

This anisotropic effect of the sulfoxide group is also observed in the corresponding enol acetates **20** and **21** which were easily formed by treatment of the ketones **18** and **19**, respectively, with acetic anhydride in pyridine at room temperature (CH-3 and CH-6: δ 5.87 and 4.8–5.1, resp., in **20**; δ 5.72 and 5.5–5.85, resp., in **21**).

That the two keto-hydroxy sulfoxides **18** and **19** are epimeric only at S-9 was proved by further oxidation of the sulfoxide groups with hydrogen peroxide. The same keto-hydroxy sulfone **22** was obtained from either **18** or **19**. Treatment of the ketone **22** with acetic anhydride in pyridine at room temperature gave the corresponding enol acetate **23**.

2. UV. Spectra of Saturated β-Keto Sulfoxides. – We are not aware that UV. spectra of saturated β-keto sulfoxides have been described, although many β-keto sulfoxides have been prepared and are often used in organic syntheses (see footnote 1 and [6] [7] [8]).

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[6]) Originally [5] the hydroxy acetate **11** was obtained by partial acetylation of the diol **9**, its preparation could be improved, however, by partial hydrolysis of the corresponding diacetate **10** [11], see Experimental Part.

[7]) The indices C-3 and C-7 indicate the carbon atom towards which the oxygen atom of the sulfoxide group is orientated. These indices are used instead of applying each time the complex nomenclature for racemates with several asymmetric centres (sequence-rule method by *Cahn et al.* [12]), *e.g.*, **12**: (1*RS*, 2*RS*, 5*RS*, 6*RS*, 9*SR*)-2-hydroxy-6-acetoxy-9-thiabicyclo[3.3.1]-nonane 9-oxide.

[8]) The extensive application of NMR. measurements on sulfoxy compounds was recently described in "The Configuration of Phenoxymethyl Penicillin Sulfoxide" by *Cooper et al.* [13]. Using the *McConnell* approach to chemical-shift calculations, aromatic solvent-induced shifts, and hydrogen-bonding studies, the sulfoxide configuration could be determined. See also [14].

[9]) Originally **14** was synthesized by *Oppenauer* oxidation of the hydroxy acetate **11** [5]. For an improved preparation of **14** from **11** (oxidation by *Collins* reagent [15]), see Experimental Part.

Table 1. *UV. Spectra of β-Keto Sulfoxides*[a])

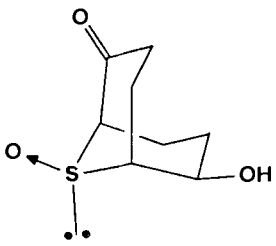
Compound	Cyclohexane	Dioxane	Acetonitrile	Ethanol	Methanol	Water
1		296 (170) 238 (1110)				
2		302 (130) 240 (980)				
7		303 (130) 243 (985)				
4		303.5 (220) 245.5 (1475)				
5	312 (220) 250.5 (1340)	309.5 (200) 250 (1410)	307.5 (140) 245.5 (910)	307.5 (110) 236 (850)[b])	306.5 (100) 232.5 (915)[b])	301.5 (95) 233 (745)[b])
8	310 (210) 250.5 (1390)	310 (190) 250 (1295)	306.5 (135) 244.5 (1030)	304.5 (110) 236.5 (1025)[b])	305.5 (100) 237.5 (670)[b])	300 (86) 234 (715)[b])
18	[c])	315.5 (96) 303.5 (118) 297 (109) 235.5 (565)	304.5 (130) 238 (645)	304.5 (110) 297 (110) 227.5 (655)[b])	304 (105) 297 (105)	297.5 (125) 226 (635)[b])
19	[c])	307 (54)[b]) 298.5 (56) 248 (225)	297 (56) 247 (200)	298 (36) 244 (145)[b])	298 (28) 245.5 (110)[b])	286 (47) 237.5 (175)[b])
15[d])	305.5 (105) 242 (225)	303.5 (155) 245.5 (305)	301.5 (160) 246 (275)	302.5 (205) 247 (270)	302 (190) 246 (265)	299 (280) 245.5 (295)
22		322 (7)[b]) 308 (19)[b]) 300 (26)[b]) 291 (27) 284 (25)[b])		322 (6)[b]) 309 (17)[b]) 298 (26)[b]) 291.5 (29) 285 (27)[b])		

[a]) Measured on a UV. Spectrometer *Cary* 14; [b]) Shoulder; [c]) Insoluble; [d]) See [16].

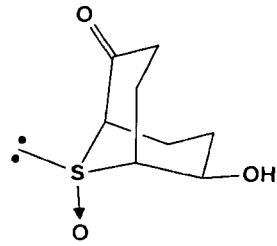
The UV. spectra of the saturated open-chain and bicyclic β-keto sulfoxides **1**, **2**, **4**, **5**, **7**, **8**, **18**, and **19** are listed[10]) in Table 1. Two characteristic absorptions are observed above 225 nm: the carbonyl ($n \rightarrow \pi^*$)-transition in the range of 295–315 nm, which is perturbed by the presence of the sulfoxide group, and the transition of nonbonding electrons of sulfur, in the range of 225–250 nm. Blue-shifts of both transitions, for the aliphatic as well as for the bicyclic compounds, accompany apolar → polar solvent changes. The blue-shift of the 225–250 nm maximum implies that this transition is not due to a charge transfer[11]) in contrast to the electron transfer from sulfur to the carbonyl group in saturated β-keto sulfides (see UV. data of **15** in Table 1). The transition of nonbonding electrons of sulfur in β-keto sulfoxides seems closely related to that of α,β- or β,γ-unsaturated sulfoxides which exhibit an analogous blue-shift by change to polar solvents[12]).

The aliphatic β-keto sulfoxides afford evidence for the pronounced influence of steric effects on UV. absorption. Considerable red-shifts as well as higher ε values are observed for both transitions with increasing substitution of the β-keto sulfoxides (see sequence in dioxane: **1**, **2**, **7**, **4**, **5**, **8** in Table 1)[13]).

Whereas the UV. spectra of the conformationally mobile aliphatic β-keto sulfoxides should reflect the statistically optimal interactions of keto and sulfoxide groups, a marked dependence of the UV. absorption on the spatial orientation of carbonyl and sulfoxide groups in the more rigid bicyclic compounds may be expected. The



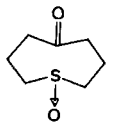
b



c

[10]) For comparison, the UV. spectra of the corresponding bicyclic β-keto sulfide **15** and the β-keto sulfone **22** are included.

[11]) A similar electronic interaction between a sulfoxide and a carbonyl group, albeit across a ring, has already been observed by *Leonard* & *Johnson* [17] in the δ-keto sulfoxide 1-thiacyclooctan-5-one 1-oxide (**a**). Using more highly polar solvents a maximum exhibiting blue-shift appears within the region of 235 nm (in cyclohexane) to 226.5 nm (in water).



a

[12]) α,β- and β,γ-unsaturated sulfoxides have been extensively studied by *Procházka* & *Paleček* [18]. They report absorptions for α,β-unsaturated unsubstituted compounds in the range of 245–249 nm in cyclohexane, 232–235 nm in methanol and 225 nm in water, and for β,γ-unsaturated analogues in the range of 232–238 nm, 222–226 nm, and 217 nm in the same solvents, respectively. UV. data of saturated di-alkyl and alkyl aryl sulfoxides, exhibiting similar behaviour, are discussed by *Mislow et al.* [10].

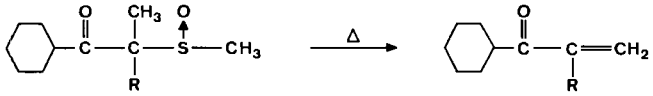
[13]) Analogous steric effects have already been noted by several authors, *e.g.*, see [10] and [18] and references therein.

data for the two epimeric at S-9 products, **18** and **19**, are listed in Table 1. It is of interest that both **18** and **19** show smaller ε values than comparable aliphatic β-keto sulfoxides, such as **4**, also monoalkylated at the carbon atom located between the keto and the sulfoxide group. Furthermore, the difference in spatial relationship of the sulfoxide and carbonyl groups in the two epimers **18** (see **b**) and **19** (see **c**) is clearly reflected in differences relating to structure, energy, and extinction of the ($n \rightarrow \pi^*$)-transitions. Thus, the epimer **18**, in which the sulfoxide oxygen is *syn* and the lone-pair of electrons on sulfur is *anti* to the carbonyl group at C-2, absorbs at higher wavelengths with a greater ε value and exhibits a more highly structured band than **19**.

3. UV. Irradiations of β-Keto Sulfoxides (Results and Discussion)[14]. – The aliphatic β-keto sulfoxides **2** (non-alkylated at the α-carbon), **4** (mono-alkylated), and **5** (di-alkylated), as well as the bicyclic compounds **18** (S-$9_{C\text{-}3}$-oxide) and **19** (S-$9_{C\text{-}7}$-oxide) were irradiated on analytical and preparative scales using 0.02M solutions and light of wave-lengths both 2537 Å (low-pressure mercury lamp, quartz) and > 2850 Å (medium-pressure mercury lamp, Pyrex). For mechanistic studies the aliphatic sulfoxides **6** and **8** as well as photoproduct **26** and mixtures (**5** + **26**, **26** + **29**, **8** + **26** + **29**, **5** + **6**, **6** + **8**) were also photolysed[15]). For the aliphatic compounds irradiation in pentane proceeded more rapidly than in diethyl ether though the product compositions and yields were practically identical. For the bicyclic β-keto sulfoxides in dioxane or ethanol, almost identical results were obtained.

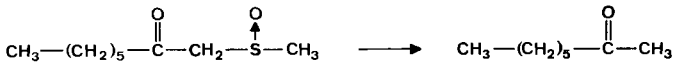
a) *Stereomutation*[16]) *and Products resulting from* (C_α-*S*)-*Cleavage.* On irradiation of mono-alkylated aliphatic β-keto sulfoxides of type **4** and of the bicyclic S-9 epimeric compounds **18** and **19**, photo-induced inversion at the chiral sulfur was the most salient feature observed[17]).

[14]) For comparison brief mention of the pyrolytic and electrolytic cleavage reactions of β-keto sulfoxides may be useful. Ketones **4** and **5** were quantitatively *pyrolysed* in either ether or methylene chloride in the vpc. injector, to give cyclohexyl vinyl ketone (**d**) and cyclohexyl isopropenyl ketone (**e**), respectively (see Exp. Part).



4 R = H **5** R = CH_3 **d** R = H **e** R = CH_3

Electrolytic cleavage of β-keto sulfoxides has recently been described by *Samuelsson & Lamm* [3]: **f** → **g**.



f **g**

[15]) For details and continuous numbering of experiments, see Experimental Part.

[16]) *Mislow et al.* [19] [20] ascribe the term "stereomutation" to interconversion of stereoisomers, i.e., of enantiomers (inversion, racemization) or of diastereomers (epimerization, *cis-trans* interconversion) using the term "diastereomer" in its most general sense (see [21]).

[17]) For a preliminary note on our observations, see [5] footnote 10.

Chart 3

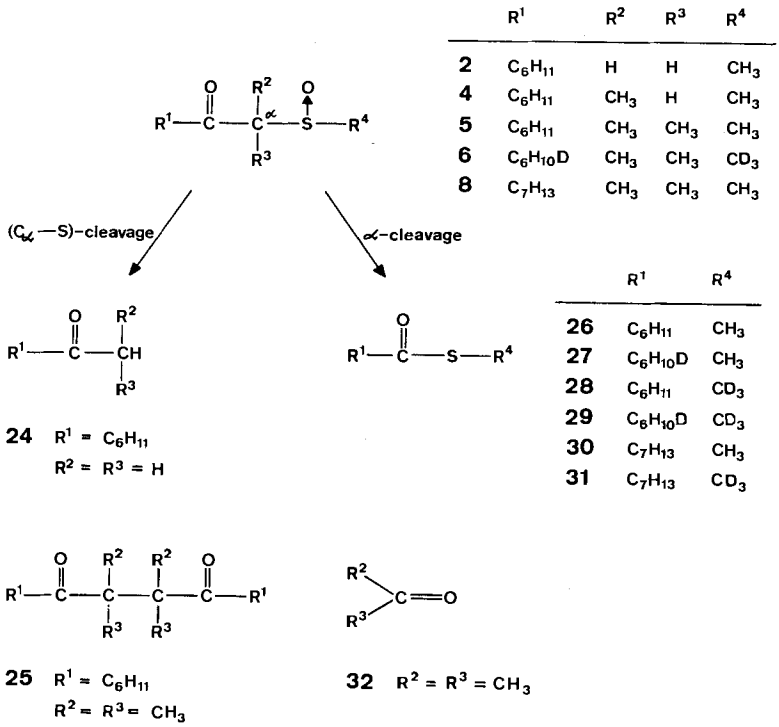
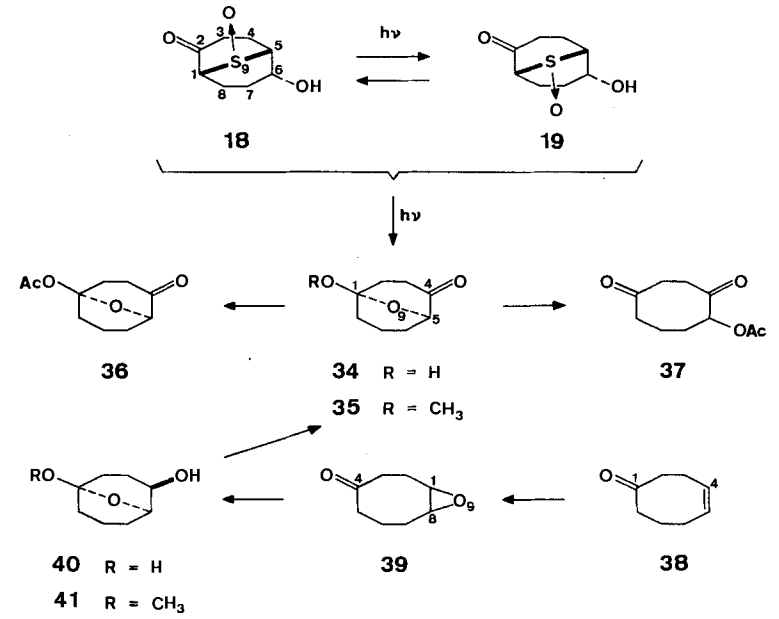


Chart 4



Short-period photolysis[18]) of a 4:1 mixture (Exp. 7, > 2850 Å) and of a 2:1 mixture (Exp. 8, 2537 Å) of the two pairs of enantiomers **4a** and **4b** gave mixtures from which "starting material" could be recovered in 60% and 35% yields[19]). In both cases NMR. measurements indicated the presence of a 1:1 mixture of **4a** and **4b**. In a control experiment (Exp. 5, > 2850 Å) a 1:1 mixture of **4a** and **4b** was similarly irradiated. In the recovered "starting material" (approx. 60%) the ratio of **4a** and **4b** was still 1:1. This clearly indicates that the formation of a 1:1 mixture from a 4:1 mixture is not due to accidentally faster decomposition of one pair of enantiomers but rather that stereomutation to a photostationary mixture of epimers has occurred.

Results of irradiation of the bicyclic β-keto sulfoxides **18** and **19** (Exp. 30–35, > 2850 Å) are listed in Table 2 (see Exp. Part). Again a configurational change of the sulfoxide pyramid by photochemical interconversion of the two isomers **18** and **19** was observed. Photolysis in ethanol (Exp. 36 and 37) as well as in dioxane (Exp. 41 and 42) at > 2850 Å and 2537 Å, resp. (Exp. 41 and 42) afforded qualitatively the same results. Epimerization was the predominant reaction, but other products accumulated upon prolonged irradiation[19]); for this reason the photostationary state was not determined.

Stereomutation of sulfoxides is a well known phenomen[20]) and has been accomplished by a variety of methods. That induced by chemical means or heating has received considerable attention. The photochemically induced pyramidal inversion of sulfoxides was first observed by *Mislow et al.* in 1965 [19]. *Cooke & Hammond* [22] reported: "Direct irradiation of alkyl aryl or diaryl sulfoxides leads to racemization with concurrent decomposition whereas dialkyl sulfoxides are decomposed but not racemized by direct irradiation. Both intra- and inter-molecular sensitization by naphthalene lead to stereomutation of diaryl and aryl alkyl sulfoxides with little decomposition, however, di-alkyl sulfoxides are not inverted."

All compounds so far described, which underwent photochemically induced sulfoxide inversion, were mono- or diaryl sulfoxides[21]). The stereomutation of the saturated β-keto sulfoxides **4a**, **4b**, **18**, and **19** (containing no aryl groups), by direct photolysis, now constitutes *a new example of photoinduced configurational inversion of sulfoxides.*

Two mechanistic paths are possible to explain such stereomutation: simple sulfur pyramidal inversion and homolytic cleavage of the (C_α-S)-bond to a radical pair (aliphatic β-keto sulfoxides), or diradical formation (bicyclic compounds) followed by recombination. The present results do not yet permit a distinction between these paths. The simultaneous operation of both mechanisms has recently been described by *Schultz & Schlessinger* [23]. The photoracemization of the sulfoxides **h** and **i** involves both sulfur pyramidal inversion and reversible sulfenate ester (**k**) formation *via* a diradical species **j**. Several features indicate that the photostereomutation of β-keto sulfoxides here described, also involves possibly both paths.

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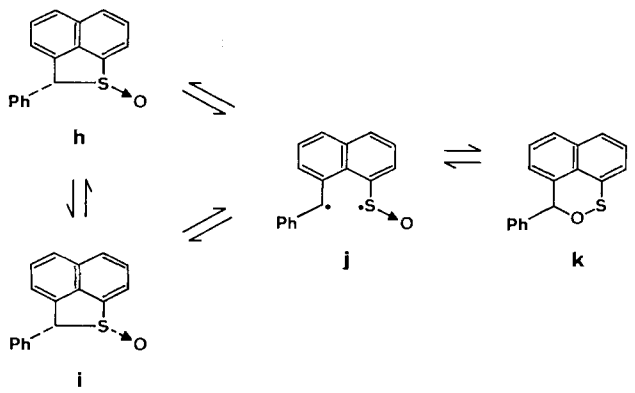
[18]) Comparable fast decomposition was also observed in the photolysis of the di-alkylated compound **5** (see Exp. 15 and 16, 2537 Å).

[19]) The remaining fraction contained products of further photoreactions. Their formation and structure determination is discussed below.

[20]) For an extensive review see [20].

[21]) See [22] and the sulfoxide photoracemizations described by *Schlessinger et al.* [23].

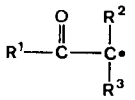


On the one hand, the results resemble the intramolecularly naphthalene-sensitized photoracemizations of alkyl aryl sulfoxides. *Cooke* & *Hammond* [22] proposed an exciplex mechanism to account for the observed non-exothermic singlet energy-transfer from excited naphthalene. A similar intramolecular energy-transfer from the excited carbonyl group may also be responsible for the sulfur pyramidal inversion in β-keto sulfoxides. The following results lend support to this possibility. On irradiation the hydroxy acetoxy sulfoxide **12** in acetone at > 2850 Å and 2537 Å, no stereomutation was observed in either case (Exp. 44 and 45). The two epimers **12** and **13** were also photolysed in the presence of the bicyclic β-keto sulfoxides **17** and **16**, resp. (Exp. 46 and 47) and sulfoxide **13** in the presence of the β-keto sulfoxide **19** (Exp. 48). Although epimerization of **16**, **17**, and **19** occurred, each of the sulfoxides **12** and **13** was again unchanged. In this connection it is noteworthy that excitation of the non-bonding electrons on sulfur in **4a** and **4b** (Exp. 8), in **18** (Exp. 41), and in **19** (Exp. 42) at 2537 Å, leads qualitatively to the same results; most likely an intramolecular energy-transfer is operative as well.

Another factor to be considered is that photostereomutation is invariably accompanied by formation of decomposition products which can be derived from a diradical (for aliphatic β-keto sulfoxides) or a radical pair (for bicyclic compounds) formed by scission of the (C_α-S)-bond. It can therefore be expected that epimerization on sulfur may be equally well operative by (cage) recombination of such radical primary photoproducts. The photolytic products of the bicyclic compounds **18** and **19** can be taken as support for this path; a re-formation of the (C_α-S)-bond should be highly favored because of the conformational rigidity of such bicyclic β-keto sulfoxides. Indeed, the predominating products on irradiation of either the S-$9_{C\text{-}3}$-oxide **18** or the S-$9_{C\text{-}7}$-oxide **19** for up to 8 h, are in each case mixtures of these two epimers (see Table 2, Exp. 30–35), whereas similar irradiation of the aliphatic compounds **4a** and **4b** (Exp. 3, 4, and 6) as well as of **2** (Exp. 1 and 2), of **5** (Exp. 9, 10, 12, and 13), of **6** (Exp. 17 and 18), and of **8** (Exp. 19 and 20) furnished much less unchanged or epimerized starting material after identical irradiation times. Instead, the major part of each compound had already been transformed to other products resulting from either (C_α-S)- or α-cleavage.

Preference for either (C_α-S)- or α-cleavage strongly depends on the substitution at the α-carbon atom. The non-alkylated aliphatic β-keto sulfoxide yielded products

due to both (C_α-S)- and α-cleavage in a 9:1 ratio (Exp. 1 and 2: **2** → 86.5% of **24** and 9% of **26**) whereas mono- and di-alkylated β-keto sulfoxides afforded predominantly α-cleavage products (*e.g.*, Exp. 3 and 6: **4** → 50–54% of **26**, Exp. 12: **5** → 4.5% of **25** and 60% of **26**). The compounds **24** and **25** resulting from an initial (C_α-S)-cleavage are both attributable to a common intermediate radical **1**: – **24** by hydrogen



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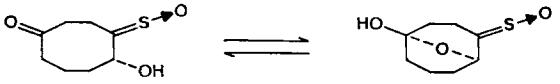
addition to radical **1**, and **25** by combination of two such radicals. The structural assignment of **25** is based on ample spectral evidence.

Prolonged irradiation of the bicyclic β-keto sulfoxides **18** and **19** led to the appearance of a new product, the desulfurized ketone **34**[22]) (Exp. 38–40). Its generation is most plausibly explained by an initial (C_α-S)-cleavage followed by a transanular hydrogen shift affording a sulfine **33**. Compounds of this type are known to photo-



33a **33b**

decompose into ketones by loss of sulfur[23]). The structure of **34** is based on spectral evidence, chemical transformations, and independent synthesis (see Chart 4).

In the mass spectrum (MS.) of **34** a molecular ion of *m/e* 156 ($C_8H_{12}O_3$) is found. The IR. spectrum exhibits absorption bands for hydroxyl (3565 and 3400 cm^{-1}) and keto functions (1725 cm^{-1}). The NMR. spectrum shows only two protons at field lower than δ 2.6, one at δ 3.56 (1-OH) and the other at δ 4.29 (CH-5). It follows that the hydroxyl group is tertiary which leads to the conclusion that **34** exists as a bicyclic hemiketal. This was confirmed by the facile transformation of **34** to the corresponding methoxy derivate **35** (NMR.: δ 3.44/*s* 1-OCH_3; 4.3/*m* CH-5) by treatment with methanolic HCl. Acetylation of **34** yielded two compounds, the bicyclic acetate **36** (NMR.: δ 4.16/*m* CH-5) and the monocyclic diketo acetate **37** (NMR.: δ 5.00 doublet of a doublet, CH-5).

A conclusive proof for the structure of **34** was finally obtained by a partial synthesis starting from 4-cycloocten-1-one (**38**) [25] (see Chart 3). Epoxidation of **38** with *m*-chloroperoxybenzoic acid afforded the keto epoxide **39** [26], which was converted to the bicyclic dihydroxy compound **40** by treatment with 0,1 N aqueous H_2SO_4. The bicyclo[3.3.1]nonane skeleton of **40** is evident from its IR. spectrum, especially from the absorption bands at 2995 and 1490 cm^{-1}, characteristic for a chair-chair conformation of this ring system[24]); furthermore, no carbonyl absorption band is observable. The hemiacetal **40** was subsequently converted by methanolic HCl to **41** (NMR.: δ 3.33/*s* 1-OCH_3) which by oxidation with *Collins* reagent [15] yielded 1-methoxy-4-oxo-9-oxabicyclo[3.3.1]nonane (**35**). The compound was identical with that prepared from the photoproduct **34**.

b) *Products resulting from α-cleavage.* – As briefly mentioned above, products due to α-cleavage also resulted by photolysis of β-keto sulfoxides. The three aliphatic

[22]) Ketone **34** is moderately photostable (see Exp. 43).

[23]) See *Schultz & Schlessinger* [24] for photodesulfurization of sulfoxides and references cited therein.

[24]) See *Brown et al.* [27] and footnote 3 in [5].

cyclohexyl-substituted compounds **2**, **4**, and **5** decomposed to cyclohexanecarboxylic acid S-methylester (**26**) (R^1–CO–S–R^4) and to the corresponding carbonyl compounds of type $R^2R^3C{=}O$, *e.g.*, acetone (**32**) from **5**. Whereas the non-alkylated β-keto sulfoxide **2** afforded product **26** as a minor component (Exp. 1 and 2: **24**:**26** = 9:1), **26** could be isolated in yields up to 60% from the mono- and di-alkylated analogues **4** and **5**, resp., (Exp. 3, 4, 6, 9, 10, 12, and 13).

The structure of the S-methylester **26** was elucidated by spectroscopy and by its synthesis from cyclohexanecarboxylic acid chloride. This ester is photochemically stable at wavelengths > 2850 Å under irradiation in ether for 8 h (Exp. 21)[25]. Photolysis of a 1:1 mixture of **26** and the corresponding tetradeuterio(d_4) compound **29**[26] caused no exchange (Exp. 24), *i.e.*, no trace of the mono(d_1)- and trideuterio(d_3) S-methylesters **27** and **28**, resp., could be detected, and **26** and **29** were quantitatively recovered. **26** is also photostable in the presence of starting material as shown by its irradiation in the presence of **5** (Exp. 23) which yielded 56.5% of newly formed **26** in addition to the unchanged S-methylester **26** initially present. Photolysis of a 1:1 mixture of **26** with the corresponding tetradeuterio(d_4) compound **29** in the presence of the cycloheptyl-substituted β-keto sulfoxide **8**[27] (Exp. 25) gave a 1:1 mixture of unchanged **26** (d_0) and **29** (d_4) and, from **8**, cycloheptanecarboxylic acid S-methylester (**30**). No cross exchange occurred between **26**, **29**, and **30**. These last two experiments (Exp. 23 and 25) demonstrate furthermore that the presence of S-methylesters in the photolysis mixture does not alter the nature of the products formed nor their distribution.

It remains to comment on the formation of the carboxylic acid S-methylester **26**. The fact that it was obtained not only from the mono- and di-alkylated β-keto sulfoxides **4** and **5** but also from the non-alkylated **2**, led to the probable assumption that the methyl group of **26** was identical with that attached to the sulfur atom in the starting materials. This was confirmed by irradiation of the tetradeuterio(d_4) di-alkylated compound **6**, bearing an S-trideuteriomethyl group. As expected, cyclohexane(d_1) carboxylic acid S-trideuteriomethylester (**29**) was isolated (Exp. 17 and 18).

The following cross experiments served to distinguish between inter- and intramolecular paths for the formation of the S-methylester **26**. The irradiation of 1:1 mixtures of the two di-alkylated cyclohexyl β-keto sulfoxides **5** (nondeuterated, d_0) with **6** (tetradeuterated, d_4) in ether (Exp. 26) and in pentane (Exp. 27) gave in each case a statistical 1:1:1:1 distribution of the four S-methylesters **26** (d_0), **27** (d_1), **28** (d_3), and **29** (d_4), as determined by MS. In a second series, 1:1 mixtures of the di-alkylated tetradeuterated cyclohexyl β-keto sulfoxide **6** and the di-alkylated non-deuterated cycloheptyl β-keto sulfoxide **8** were photolysed in ether (Exp. 28) and in pentane (Exp. 29). In both cases two fractions were formed, the one a 1:1 mixture of the cyclohexanecarboxylic acid S-methylesters **27** (d_1) and **29** (d_4), and the other a 1:1 mixture of the cycloheptanecarboxylic acid S-methylesters **30** (d_0)

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[25] It should however be noted that photolysis of **26** by 2537 Å resulted in unspecific decomposition after only 1 h (Exp. 22).

[26] **29** was prepared by photolysis of **6** either in ether or in pentane (Exp. 16 and 17).

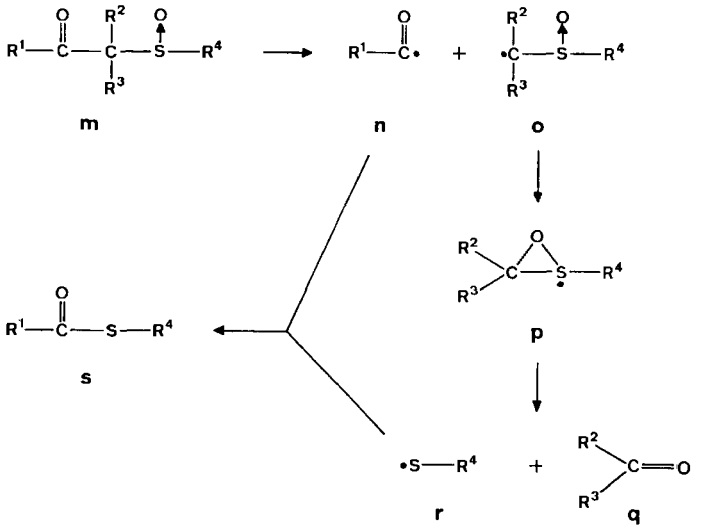
[27] **8** was also separately irradiated affording the S-methylester **30** (Exp. 19 and 20).

and **31** (d_3). These results imply that *the S-methylesters are exclusively formed intermolecularly*.

Acetone (**32**), as a representative of the general type $R^2R^3C{=}O$, also resulting from an initial α-cleavage, was trapped as the 2,4-dinitrophenylhydrazone after irradiation of the di-alkylated β-keto sulfoxide **5** in ether (Exp. 11).

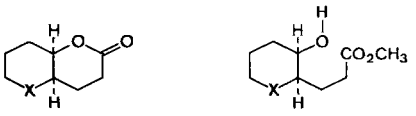
A plausible path for the photolysis involving an initial α-cleavage of compounds of the general type **m** (see **1**–**8**) is given in Chart 5. Thus, scission of the C_α–CO bond can lead to the two radicals **n** and **o**. The latter decomposes to ketone **q** (see **32**) and methyl mercaptyl radical **r**, possibly through an intermediate oxathi-iran radical **p**.

Chart 5



Combination of the acyl radical **n** and the methyl mercaptyl radical **r**, finally affords the carboxylic acid S-methylester **s** (see **26**–**31**).

A marked difference in product distribution is observed in the photolysis of the bicyclic compounds **18** and **19**. As already mentioned above, stereomutation is predominant and **34**, a product due to (C_α-S)-cleavage, is formed only very slowly as the main component among further products arising by prolonged photolysis[28]). Most likely α-cleavage products were also formed, but only to an insignificant amount



42 X = S **43** X = S

44 X = SO **45** X = SO

[28]) This result is in contrast to the photochemical behaviour of the aliphatic α-monoalkyl-β-keto sulfoxide **4** (see above).

and no attempt was made to isolate any. These results differ quite markedly from the photolysis of the corresponding saturated bicyclic β-keto sulfide **15**. Direct ($n \rightarrow \pi^*$)-excitation of **15** mainly led to the selective α-cleavage of the CO–C_α(-S) bond producing ketenes by a secondary intramolecular hydrogen transfer. Depending on the availability of internal (OH-group at C-6) and/or external (*e.g.* methanol) nucleophiles, the compounds **42** and **43** were formed as major products [5] [16] [28]. By analogy one might expect the corresponding lactone **44** (*e.g.*, in ether, pentane or dioxane) and sulfoxy ester **45** (in methanol)[29]) to be formed.

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Experimental Part

General Remarks. – *After working up*, the organic layer containing the products was dried over $MgSO_4$ and the solvent either removed *in vacuo* in a rotary evaporator or carefully distilled through a *Vigreux* column.

Preparative column chromatography was performed (unless stated otherwise) on a 100-fold amount of silicagel *Merck* (0.05–0.2 mm). For *thin layer chromatography* (TLC.), *Merck* TLC-plates Silica Gel F_{254} precoated were used. The spots were located by the use of UV. light or iodine vapors, or by spraying the plates with conc. H_2SO_4 and subsequent heating. *Vapor phase chromatography* (VPC.) was performed on an *Aerograph* Model A-90-P gas-chromatograph (thermal conductivity detector) using a $10' \times {}^3/_8''$ column of 15% SE-52 on 60–80 mesh chromosorb W at 200° unless stated otherwise.

Melting points (m.p.) were measured in open capillaries in an oil bath and are uncorrected. *Ultraviolet spectra* (UV.): λ_{max} are given in nm, ε values added in parentheses. *Infrared spectra* (IR.): ν_{max} are given in cm^{-1}. *Nuclear magnetic resonance spectra* (NMR.) were recorded at 60 or 100 MHz. Chemical shifts are expressed in δ values (ppm) downfield from tetramethylsilane as internal standard. Multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad. Coupling constants (J) are measured in Hertz (Hz). $W^{1/2}$ means line width at half height. Proton integration of each signal is in agreement with the given assignments. Spectra of substances containing hydroxyl groups (easy exchangeable hydrogen atoms) were recorded without and with added D_2O. *Mass spectra* (MS.) were recorded on a *Hitachi-Perkin-Elmer* (RMU-6A or RMU-6D) mass spectrometer.

UV. irradiation. – *Preparative scale* (prep.): The solutions (well flushed with solvent saturated, oxygen free N_2) were irradiated at room temperature in a cylindrical flask equipped with a magnetic stirrer and a central immersion well (pyrex glass) holding a 70 Watt medium pressure mercury lamp (med.) (Q 81, *Quarzlampen GmbH*, Hanau) or a 0.9 Watt low pressure mercury lamp (low) (2537 Å, NK 6/20, *Quarzlampen GmbH*, Hanau); the immersion well was water cooled. – *Analytical scale* (anal.): Degassed (three freeze-thaw cycles at 10^{-5} Torr) solutions in sealed pyrex ampoules or solutions, well flushed with oxygen free N_2, in pyrex or quartz tubes, were irradiated at room temperature under magnetic stirring, using either a 70 Watt medium pressure mercury lamp (med.) (Q 81, *Quarzlampen GmbH*, Hanau) or a 0.9 Watt low pressure mercury lamp (low) (2537 Å, NK 6/20, *Quarzlampen GmbH*, Hanau); the distance of the tubes from the water cooled light source was approx. 5 cm.

Quantitative determinations of yields by VPC. were carried out as follows: Three standard solutions (5 ml each) of the product were prepared, the concentration of one as near as possible to the expected value, the second with slightly smaller and the third with slightly higher concentration. For each of the three standard solutions three times 100 μl were injected and the surfaces on the recorder compared with those of three 100 μl injections of the reaction solution (5 ml).

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[29]) Irradiation of **5** in methanol for $12^1/_2$ h showed only an unspecific product pattern (Exp. 14).

Synthesis of Aliphatic β-Keto Sulfoxides 1–8. – *Methylsulfinylmethyl* n-*Pentyl Ketone* (**1**). Prepared following procedure described in [6]. The crude product was purified by chromatography in $CHCl_3$-C_2H_5OH(19:1) and subsequently recrystallized from isopropyl ether and hexane. M.p. 47–48° (*cf.* [6]). IR. (CCl_4): 2944, 2918, 2860, 2845, 1710, 1469, 1080, 1039 (cf. [6]). UV. (dioxane): see Table 1. MS.: *m/e* 159 (M^+-17), 120 (M^+-46), 113 (M^+-63), 112 (M^+-64); $C_8H_{16}O_2S$ = 176.

Methylsulfinylmethyl Cyclohexyl Ketone (**2**). Prepared following procedure described in [6]. The crude product was purified by chromatography in $CHCl_3$–C_2H_5OH(19:1) followed by three recrystallizations from isopropyl ether and hexane. M.p. 60–61°. IR. (CCl_4): 2922, 2844, 1702, 1450, 1071, 1051, 999, 967 (*cf.* [6]). UV. (dioxane): see Table 1. NMR. (CCl_4, 100 MHz): 1.0–2.1/*m* –$(CH_2)_5$–; 2.3–2.6/m –CO–CH<; 2.56/*s* –SO–CH_3; 3.65/*d* and 3.72/*d* *J* = 14 –CO–CH_2–SO– (cf. [6]). MS.: *m/e* 188 (M^+), 171 (M^+-17), 125 (M^+-63), 124 (M^+-64); $C_9H_{16}O_2S$ = 188.

1-(Methylsulfinyl-)ethyl Cyclohexyl Ketone (**4**). Prepared following procedure described in [8]. The crude product was purified by chromatography in $CHCl_3$–C_2H_5OH(19:1). 7.26 g of the oily product was kept for 3 days at 0° until approximately 50% had crystallized. The oil was decanted and the crystalline residue washed several times at 0° on a sintered glass filter with pentane-ether(2:1). The 775 mg of crystalline product obtained were again liquefied by warming and slowly crystallized at 0°. The crystals were washed at 0° with pentane-ether(2:1) to give 384 mg of a mixture (4:1, determined by NMR.[4]) of the two pairs of enantiomers **4a** and **4b**. UV. (dioxane): see Table 1. NMR. (460 mg in 1 ml CCl_4, 25°, 100 MHz): **4a**: 1.0–2.0/*m* –$(CH_2)_5$–; 1.32/*d* *J* = 7 –CO–CH(CH_3)–; 1.58/*m* –CO–CH<; 2.43/*s* –SO–CH_3; 4.12/*q* *J* = 7 –CO–*CH*(CH_3)–. **4b**: 1.0–2.0/*m* –$(CH_2)_5$–; 1.26/*d* *J* = 7 –CO–CH(CH_3)–; 1.58/*m* –CO–CH<; 2.39/*s* –SO–CH_3; 4.08/*q* *J* = 7 –CO–*CH*(CH_3)–. MS.: *m/e* 202 (M^+, weak), 185 (M^+-17), 138 (M^+-64), 83 (C_6H_{11}); $C_{10}H_{18}O_2S$ = 202.

2-(Methylsulfinyl)-isopropyl Cyclohexyl Ketone (**5**). 958 mg of a sodium hydride dispersion (55–60% in oil) was washed with pentane under nitrogen to remove the mineral oil and the pure NaH suspended in 25 ml of hexamethylphosphorictriamide (hexametapol, HMPT). 1.8 g (9.6 mmol) of methylsulfinylmethyl cyclohexyl ketone (**2**) was slowly added and the reaction mixture kept at 40° for 15 min. After cooling to 0° 1.25 ml (20 mmol) of methyl iodide was added, and after stirring for 30 min at 0°, subsequently for 30 min at room temperature, the mixture was poured onto ice-water and extracted with benzene-ether(1:1). The organic phase was washed twice with a 10% HCl-, once with saturated aqueous NaCl-, once with a 10% aqueous $Na_2S_2O_3$-, again with saturated NaCl- solutions and then yielded 1.756 g of crude product. Chromatography in $CHCl_3$–C_2H_5OH(19:1) afforded 1.645 g (79.5%) of **5** which was recrystallized from isopropyl ether and hexane. M.p. 46–47°. IR.(CCl_4): 2920, 2842, 1692, 1463, 1450, 1080, 1072, 1060, 1003, 988. UV. (different solvents): see Table 1. NMR. (CCl_4, 100 MHz): 1.1–2.1/*m* –$(CH_2)_5$–; 1.27/*s* and 1.51/*s* –$C(CH_3)_2$–; 2.24/*s* –SO–CH_3; 2.6–3.0/*m* –CO–CH<. MS.: *m/e* 152 (M^+-64), 137 (M^+-64-15). 123 (M^+-63-15-15).

$C_{11}H_{20}O_2S$ Calc. C 61.09 H 9.32% Found C 61.02 H 9,35%

2-(Trideuteromethylsulfinyl)-isopropyl 1-Deuteriocyclohexyl Ketone (**6**). – a) *Trideuteriomethylsulfinylmethyl cyclohexyl ketone* (**3**) approx. 50% deuterated at C-1 of the cyclohexyl ring, was prepared by the method based on that for the undeuterated ketone **2** [6]: 1.466 g of a sodium hydride dispersion (55–60% in oil), washed with pentane to remove the mineral oil, 20 g of $(CD_3)_2SO$, 20 ml of THF, and 2.347 g of cyclohexanecarboxylic acid methylester. The crude product (3.855 g) was chromatographed in $CHCl_3$–C_2H_5OH(19:1) to give 2.923 g (81%) of **3**.

b) *The synthesis of* **6** was analogous to that of **5**: 1.38 g of a sodium hydride dispersion (55–60% in oil), washed with pentane to remove the mineral oil, 30 ml of HMPT, 2.70 g (12.3 mmol) of **3** and 1.8 ml (2.89 mmol) of CH_3I. The crude product (2.72 g) was chromatographed in $CHCl_3$–C_2H_5OH(19:1) to yield 2.057 g (66.5%) of product of which 836 mg were treated with 25 ml of D_2O, 28 ml dioxane and 1.8 ml of 1 N NaOD in D_2O. After 16 h of stirring at room temperature, the reaction mixture was acidified with a 10% aqueous HCl solution and extracted with ether-benzene(1:1). The organic layer was washed twice with a 10% HCl-, once with saturated NaCl-, once with a 10% $Na_2S_2O_3$–, and finally with saturated NaCl-solutions. The crude product (760 mg) was chromatographed in $CHCl_3$–C_2H_5OH(19:1) to afford 603 mg (72%) of **6** which was once

recrystallized from isopropyl ether and hexane. M.p. 54–56°. IR. (CCl_4): 2932, 2855, 2660, 1688, 1462, 1450, 1069, 1063, 1033, 1005, 991. MS.: *m/e* 153 (92% d_1, M^+-67)[30]; $C_{11}H_{16}D_4O_2S$ = 220.

Methylsulfinylmethyl Cycloheptyl Ketone (**7**). Prepared by analogy with **2** (see [6]). The crude product was purified by chromatography in $CHCl_3$—C_2H_5OH(19:1) followed by recrystallization from isopropyl ether and hexane. M.p. 54–55°. IR. (CCl_4): 2915, 2842, 1702, 1462, 1055, 1038, 1010, 964, 938. UV. (dioxane): see Table 1. NMR. (CCl_4, 100 MHz): 1.2–2.1/*m* —$(CH_2)_6$—; 2.45–2.8/*m* —CO—CH<; 2.61/*s* —SO—CH_3; 3.81/*d* and 3.88/*d* J = 14 —CO—CH_2—SO—. MS.: *m/e* 202 (M^+, very weak), 185 (M^+-17), 139 (M^+-63), 138 (M^+-64).

$C_{10}H_{18}O_2S$ Calc. C 59.38 H 8.97% Found C 59.37 H 8.91%

2-(Methylsulfinyl)-isopropyl Cycloheptyl Ketone (**8**). Preparation by analogy with **5**: 1.45 g of a sodium hydride dispersion (55–60% in oil), washed with pentane to remove the mineral oil, 25 ml of HMPT, 3.03 g (15 mmol) of methylsulfinylmethyl cycloheptyl ketone (**7**) and 1.87 ml (30 m mol) of CH_3I. The crude product was chromatographed in $CHCl_3$—C_2H_5OH(19:1) to yield 3.11 g (90%) of **8** which was twice recrystallized from isopropyl ether and hexane affording 2.38 g (69%) of **8**, m.p. 37–39°. IR. (CCl_4): 2910, 2843, 1692, 1460, 1076, 1061. UV. (different solvents) see Table 1. NMR. (CCl_4, 100 MHz): 1.1–2.1/*m* —$(CH_2)_6$—; 1.29/*s* and 1.55/*s* —$C(CH_3)_2$—; 2.29/*s* —SO—CH_3; 2.8–3.2/*m* —CO—CH<. MS.: *m/e* 166 (M^+-64), 151 (M^+-64-15).

$C_{12}H_{22}O_2S$ Calc. C 62.58 H 9.63% Found C 62.30 H 9.54%

Synthesis of the Bicyclic β-Keto Sulfoxides 18 and 19. – endo-*2-Hydroxy*-endo-*6-acetoxy-9-thiabicyclo[3.3.1]nonane* (**11**) [5][6]. 11 g (42.6 mmol) of *endo,endo*-2,6-diacetoxy-9-thiabicyclo[3.3.1]nonane (**10**) were hydrolysed during 55 min at 0° with 165 ml of a K_2CO_3-solution (5.4 g of K_2CO_3, 266 ml of CH_3OH, 54 ml of H_2O). The reaction mixture was im mediately neutralized with hydrochloric acid, diluted with 700 ml of saturated aqueous NaCl and extracted with CH_2Cl_2. The crude product was chromatographed in benzene-EtOAc(3:1) to yield 4.67 g (40.5%) of starting material **10** and 3.25 g (35.5%; or 61.5% relative to reacted starting material) of the hydroxy acetate **11**.

endo-*2-Hydroxy*-endo-*6-acetoxy-9-thiabicyclo[3.3.1]nonane* $9_{C\text{-}3}$-*oxide* (**12**) *and* $9_{C\text{-}7}$-*oxide* (**13**). A suspension of 1.007 g (4.67 mmol) of the hydroxy acetate **11** in 30 ml of acetic acid was treated under stirring and cooling, with 550 mg of a 30% aqueous H_2O_2 solution. The clear solution, obtained after 10 min, was left to stand for 16 h at room temperature, and then carefully evaporated to dryness (vacuum, at 50°). The residue was dissolved in EtOAc and the mixture again evaporated to dryness; this procedure was repeated three times. The cristalline residue (1.044 g, 97%) was once recrystallized from EtOAc to yield 1.010 g (93.5%) of a mixture of the two sulfoxides **12** and **13** (ratio approx. 8:5, determined by NMR.), m.p. 151.5–153°. Chromatography in chloroform-ethanol(9:2) afforded 341 mg (31.5%) of **12**, 191 mg (18.5%) of a mixture of **12** and **13** (main component **12**), and 459 mg (42.5%) of **13**.

endo-*2-Hydroxy*-endo-*6-acetoxy-9-thiabicyclo[3.3.1]nonane* $9_{C\text{-}3}$-*oxide* (**12**). Recrystallized from CH_2Cl_2-petrolether, m.p. 171.5–173.5°. IR. (nujol): 3340, 1737, 1482, 1232, 1190, 1064, 1041, 1022, 1007, 988, 959, 920, 879, 860, 780. NMR. ($CDCl_3$, 100 MHz): approx. 1.5–2.75/*m* CH_2-3, -4, -7, and -8; 2.10/*s* 6-OCOCH$_3$; approx. 3.15–3.35/*m* CH-1 and -5; 3.36/*d* $J_{2,2\text{-OH}}$ = 4.5 2-OH; approx. 4.4–4.8/*m* CH-2; 5.15/*t* $J_{6,7}$*endo* = $J_{6,7}$*exo* = 9 (further splitting by $J_{5,6}$ = 3.5) CH-6. MS.: *m/e* 232 (M^+), 215 (M^+-17), 189 (M^+-43), 173 (M^+-59), 172 (M^+-60); $C_{10}H_{16}O_4S$ = 232.

endo-*2-Hydroxy*-endo-*6-acetoxy-9-thiabicyclo[3.3.1]nonane* $9_{C\text{-}7}$-*oxide* (**13**). Recrystallized from CH_2Cl_2-petrolether, m.p. 177.5–179°. IR. (nujol): 3290, 1737, 1486, 1240, 1069, 1038, 1017, 1008, 991, 958, 887, 858, 770. NMR. ($CDCl_3$, 100 MHz): approx. 1.5–2.6/*m* CH_2-3, -4, -7 and -8; 2.08/*s* 6-OCOCH$_3$; approx. 3.25/*m* ($W^{1/2}$ approx. 8) CH-1; approx. 3.35/*m* ($W^{1/2}$ approx. 12) CH-5; 3.37/*d* $J_{2,2\text{-OH}}$ = 4.5 2-OH; 4.15/*t* $J_{2,3}$*endo* = $J_{2,3}$*exo* = 9 (further splitting by $J_{1,2}$ = 3.5 and long range coupling) CH-2; 5.69/*d* $J_{6,7}$*endo* = 11 (further splitting by $J_{6,7}$*exo* = 7, $J_{5,6}$ = 4) CH-6. MS.: *m/e* 232 (M^+), 215 (M^+-17), 189 (M^+-43), 173 (M^+-59), 172 (M^+-60); $C_{10}H_{16}O_4S$ = 232.

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[30] The most suitable fragment that allows a deuterium assay. The minimal deuterium content of **6** can however be determined indirectly from the photoproduct **29** which showed 95% d_4 and 5% d_3.

2-Oxo-endo-*6-acetoxy-9-thiabicyclo[3.3.1]nonane* (**14**) [5][9]. 77.4 mg (0.3 mmol) of *Collins* reagent [15] was added to a solution of 10.8 mg (0.05 mmol) of the hydroxy acetate **11** in 2 ml of CH_2Cl_2. After standing at room temperature for 16 h the mixture was filtered through Celite, the residue washed with CH_2Cl_2 ,and the filtrate several times evaporated to dryness after successive additions of hexane. Filtration of a solution in benzene-EtOAc(3:1) through 1 g of silicagel gave 7.5 mg (72%) of the ketosulfide **14**.

2-Oxo-endo-*6-acetoxy-9-thiabicyclo[3.3.1]nonane* $9_{C\text{-}3}$-*oxide* (**16**). A solution of 12.6 mg (0.545 mmol) of the hydroxy acetoxy $9_{C\text{-}3}$-oxide **12** in 2 ml of CH_2Cl_2 was treated with 80 mg of *Collins* reagent [15] and stirred at room temperature for 2 h and evaporated. The residue dissolved in $CHCl_3$-EtOAc(9:1) was filtered through 1 g of silicagel and the filtrate was several times evaporated to dryness after successive additions of hexane. 10.7 mg (85%) of ketone **16** were obtained which solidified on standing, m.p. 127–129°. IR. (liq.): 1735, 1708, 1440, 1368, 1230, 1190, 1058, 1030, 1013. NMR. ($CDCl_3$, 100 MHz): 1.5–3.2/*m* CH_2-3, -4, -7, and -8; 2.13/*s* 6-OCOCH$_3$; approx. 3.7/*m* ($W^{1/2}$ approx. 12) CH-5; approx. 3.83/*m* ($W^{1/2}$ approx. 8) CH-1; 5.22/*d* $J_{6,7}$*endo* = 11.5 (further splitting by $J_{6,7}$*exo* = 5.5, $J_{5,6}$ = 5) CH-6. MS.: *m/e* 230 (M^+), 213 (M^+-17), 187 (M^+-43), 171 (M^+-59), 170 (M^+-60); $C_{10}H_{14}O_4S$ = 230.

2-Oxo-endo-*6-acetoxy-9-thiabicyclo[3.3.1]nonane* $9_{C\text{-}7}$-*oxide* (**17**). Prepared from 12.4 mg (0.535 mmol) hydroxy acetoxy $9_{C\text{-}7}$-oxide **13** as for **12** → **16**, yielding 9.3 mg (75%) of ketone **13** which crystallized on standing, m.p. 144–146°. IR. (liq.): 1736, 1710, 1440, 1368, 1230, 1190, 1052, 1030, 1014; (nujol): 1728, 1696, 1484, 1238, 1058, 1028, 983, 947, 896, 871. NMR. ($CDCl_3$, 60 MHz): 1.4–3.0/*m* CH_2-3, -4, -7, and -8; 2.08/*s* 6-OCOCH$_3$; 3.5–3.9/*m* CH-1 and -5; 5.77/*d* $J_{6,7}$*endo* = 10.5 (further splitting by $J_{6,7}$*exo* = 5, $J_{5,6}$ = 5) CH-6. MS.: *m/e* 230 (M^+), 213 (M^+-17), 187 (M^+-43), 171 (M^+-59), 170 (M^+-60); $C_{10}H_{14}O_4S$ = 230.

Reaction of the ketosulfide **14** *with hydrogen peroxide.* A solution of 3.044 g (14.2 mmol) of (**14**) in 40 ml of acetic acid and 1.666 g of a 30% aqueous H_2O_2 was left at room temperature for 16 h and the mixture was evaporated to dryness under vacuum. Acetone, EtOAc, and CH_3OH were added to the residue and the mixture again evaporated to dryness; this procedure was repeated several times until all the AcOH was removed. The crude product (3.28 g) was a mixture of the two keto acetoxy sulfoxides **16** and **17** (ratio approx. 3.3:1, determined by NMR.).

Reaction of the mixed keto acetoxy sulfoxides **16** *and* **17** *with base.* 3.27 g of the above crude mixture of **16** and **17** were dissolved in 140 ml of a K_2CO_3 solution (3 g of K_2CO_3, 150 ml of CH_3OH, 30 ml of H_2O). After standing at room temperature for 16 h the solution was concentrated, treated with 150 ml of saturated aqueous NaCl solution, and extracted seven times with CH_2Cl_2 (1200 ml) to afford 1.29 g of crude product. Further continuous extraction (70 h) of the aqueous phase with EtOAc gave a further 1.318 g so that the total yield of the two crude keto hydroxy sulfoxides **18** and **19** was finally 2.608 g (98%). Separation by chromatography in $CHCl_3$-EtOH(9:1) gave 569 mg (21.5%) of **19**, 238 mg (9%) of a mixture of **18** and **19**, and 1.304 g (49%) of **18**.

2-Oxo-endo-*6-hydroxy-9-thiabicyclo[3.3.1]nonane* $9_{C\text{-}3}$-*oxide* (**18**). Recrystallized from acetone-hexane and sublimed (173°/0,03 Torr), m.p. 256–260° (decomp.). IR. ($CHCl_3$): 3590, 3370, 1712, 1469, 1443, 1230, 1120, 1061, 1038, 1009, 946, 906, 885, 868; (nujol): 3285, 1708, 1658, 1470, 1244, 1229, 1118, 1076, 1061, 1018, 1008, 948, 907, 889, 868, 750, 743, 680. UV. (different solvents): see Table 1. NMR. (DMSO-d_6, 100 MHz): 1.3–2.75/*m* CH_2-3, -4, -7, and -8; 3.41/*m* ($W^{1/2}$ approx. 8) CH-5; 3.74/*m* ($W^{1/2}$ approx. 7) CH-1; 3.8–4.1/*m* CH-6. MS.: *m/e* 188 (M^+), 171 (M^+-17), 170 (M^+-18), 153 (M^+-17-18), 139 (M^+-49).

$C_8H_{12}O_3S$ Calc. C 51.06 H 6.43% Found C 50.55 H 6.48%

2-Oxo-endo-*6-acetoxy-9-thiabicyclo[3.3.1]nonane* $9_{C\text{-}7}$-*oxide* (**19**). Recrystallized from acetone-hexane and sublimed (175°/0.03 Torr), m.p. 238–243° (decomp.). IR. ($CHCl_3$): 3605, 3390, 1710, 1471, 1048, 944, 905; (nujol): 3360, 1708, 1475, 1225, 1200, 1116, 1071, 1058, 1021, 1017, 988, 949, 902, 883, 758, 747, 720, 670. UV. (different solvents): see Table 1. NMR. (DMSO-d_6, 100 MHz): 1.0–2.7/*m* CH_2-3, -4, -7, and -8; 3.40/*m* ($W^{1/2}$ approx. 15) CH-5; 3.64/*m* ($W^{1/2}$ approx. 7) CH-1; 4.2–4.5/*d* $J_{6,7}$*endo* = 11.5 (further splitting by $J_{6,7}$*exo* = 5.5, $J_{5,6}$ = 4) CH-6; 4.9–5.2/*m* 6-OH. MS.: *m/e* 188 (M^+), 171 (M^+-17), 170 (M^+-18), 153 (M^+-17-18), 142 (M^+-18-28), 139 (M^+-49).

$C_8H_{12}O_3S$ Calc. C 51.06 H 6.43% Found C 51.11 H 6.48%

*2,*endo-*6-Diacetoxy-9-thiabicyclo[3.3.1]non-2-ene 9$_{C\text{-}3}$-oxide* (**20**). 30 mg (0.16 mmol) of **18** were acetylated with 0.4 ml of Ac_2O und 0.4 ml of pyridine for 4 days at room temperature. Usual working up and chromatography of the residue (44 mg) in EtOAc on 8 g of silicagel, yielded 40 mg (92%) of crystalline **20** which was once recrystallized from CH_2Cl_2-petrolether, m.p. 132–133°. IR. ($CHCl_3$): 3030, 1745, 1695, 1460, 1375, 1365, 1240, 1179, 1122, 1109, 1063, 1037, 1022, 991, 909; (nujol): 3080, 1762, 1745, 1728, 1697, 1467, 1257, 1217, 1203, 1178, 1122, 1111, 1071, 1064, 1039, 1022, 1010, 991, 909, 884, 792, 780, 743, 701, 658. NMR. ($CDCl_3$, 100 MHz): 1.4–2.5/*m* CH_2-7 and -8; 2.05/*s* 6-OCOCH$_3$; 2.12/*s* 2-OCOCH$_3$; 2.6-2.8/*m* CH_2-4; 3.45–3.75/*m* CH-1 and -5; 4.8–5.1/*m* CH-6; 5.87/*t* $J_{3,4}$*endo* = $J_{3,4}$*exo* = 4 (further splitting by $J \leqslant 1$) CH-3. MS.: *m/e* 272 (M^+), 230 (M^+-42), 170 (M^+-42-60), 153 (M^+-42-60-17); $C_{12}H_{16}O_5S$ = 272.

*2,*endo-*6-Diacetoxy-9-thiabicyclo[3.3.1]non-2-ene 9$_{C\text{-}7}$-oxide* (**21**). 30 mg (0.16 mmol) of **19** were acetylated in a mixture of 0.4 ml of Ac_2O and 0.4 ml of pyridine for 2 days at room temperature. Usual working up gave 43 mg of crude crystalline product which was purified by chromatography in EtOAc on 8 g of silicagel. The eluted product **21** (36 mg, 83%) was once recrystallized from CH_2Cl_2-petrolether, m.p. 133–134°. IR. ($CHCl_3$): 3030, 1745, 1690, 1460, 1372, 1240, 1119, 1049, 1037, 1025, 983; (nujol): 1764, 1746, 1698, 1368, 1247, 1213, 1122, 1109, 1045, 1033, 1027, 991, 984, 918, 898, 880. NMR. ($CDCl_3$, 100 MHz): 1.6–2.9/*m* CH_2-7 and -8; 2.04/*s* 6-OCOCH$_3$; 2.14/*s* 2-OCOCH$_3$; 2.5–2.8/*m* CH_2-4; 3.48/*m* ($W^{1/2}$ approx. 8) CH-1 and -5; 5.5–5.85/*m* CH-6; 5.72/*t* $J_{3,4}$*endo* = $J_{3,4}$*exo* = 4 (further splitting by $J \leqslant 1$) CH-3.

*2-Oxo-*endo-*6-hydroxy-9-thiabicyclo[3.3.1]nonane 9,9-dioxide* (**22**). – a) *From* **18**. 32 mg of perhydrol (31.6%, 0.3 mmol) was added to a solution of 37.6 mg (0.2 mmol) of keto sulfoxide **18** in 1.2 ml of AcOH and the reaction mixture left at room temperature for seven days. Evaporation to dryness under reduced pressure yielded 41 mg of crystalline product which was chromatographed in $CHCl_3$-EtOH(9:1) on 8 g of silicagel. The 30 mg (73.5%) of eluted keto sulfone **22** were recrystallized from EtOAc to afford 29 mg (71.5%) of pure product, m.p. 286–288° (decomp.). IR. (nujol): 3540, 1708, 1671, 1480, 1328, 1302, 1289, 1200, 1125, 1071, 1058, 990, 946, 900, 827, 759. UV. (dioxane and ethanol): see Table 1. NMR. (C_6D_5N, 60 MHz): 1.4–3.1/*m* CH_2-3, -4, -7, and -8; 3.65–3.95/*m* CH-5; 4.10/*d* $J_{1,8}$ = 6.5 (further splitting by $J_{1,8'}$ = 4) CH-1; 4.86/*t* $J_{6,7}$*endo* = $J_{6,7}$*exo* = 10 (further splitting by $J_{5,6}$ = 4 and $J_{6,6\text{-OH}}$) CH-6; (DMSO-d_6, 100 MHz): 1.3–2.9/*m* CH_2-3, -4, -7, and -8; 3.45/*m* ($W^{1/2}$ approx. 12) CH-5; 3.84/*d* $J_{1,8}$ = 7 (further splitting by $J_{1,8'}$ = 3.5) CH-1; 4.29/*d* $J_{6,7}$*endo* = 11.5 (further splitting by $J_{6,7}$*exo* = 5.75, $J_{5,6}$ = 4.25, and $J_{6,6\text{-OH}}$ = 5) CH-6; 5.56/*bd* $J_{6,6\text{-OH}}$ = 5 6-OH. MS.: *m/e* 204 (M^+), 186 (M^+-18), 168 (M^+-18-18), 158 (M^+-18-28), 138 (M^+-66).

$C_8H_{12}O_4S$ Calc. C 47.06 H 5.92% Found C 46.76 H 5.69%

b) *From* **19** (37.6 mg, 0.2 mmol) as from **18** above, but reaction for only six days; yield 44 mg of crystalline product. Chromatography in $CHCl_3$-EtOH(9:1) on 8 g of silicagel gave 26 mg (63.5%) of keto sulfone **22**, recrystallised from EtOAc.

*2,*endo-*6-Diacetoxy-9-thiabicyclo[3.3.1]non-2-ene 9,9-dioxide* (**23**). 102 mg (0.5 mmol) of **22** were acetylated in a mixture of 0.8 ml of Ac_2O and 0.8 ml of pyridine for 2 days at room temperature. Usual working up yielded 148 mg of crude crystalline product which was purified by chromatography in EtOAc to afford 134 mg (93%) of **23** then recrystallized from CH_2Cl_2-petrolether, m.p. 143–144°. IR. (nujol): 3075, 1765, 1740, 1691, 1310, 1241, 1210, 1205, 1180, 1105, 1101, 1039, 916, 901, 879, 860, 857, 822. NMR. ($CDCl_3$, 60 and 100 MHz): 1.5–2.5/*m* CH_2-7 and -8; 2.04/*s* 6-OCOCH$_3$; 2.13/*s* 2-OCOCH$_3$; 2.76/*t* $J_{3,4}$*endo* = $J_{3,4}$*exo* = 4 CH_2-4; 3.2–3.5/*m* CH-1 and -5; 5.35/*d* $J_{6,7}$*endo* = 9.5 (further splitting by $J_{6,7}$*exo* = 7.5, $J_{5,6}$ = 4, and long range couplings $\leqslant 1$) CH-6; 5.74/*t* $J_{3,4}$*endo* = $J_{3,4}$*exo* = 4 CH-3. MS.: *m/e* 288 (M^+), 246 (M^+-42), 228 (M^+-60), 204 (M^+-42-42), 186, 170, 164 (M^+-60-64); $C_{12}H_{16}O_6S$ = 288.

Pyrolysis of 4 and 5. – *Of 1-(Methylsulfinyl)-ethyl Cyclohexyl Ketone* (**4**)[14]. After VPC. control for purity of a sample in either CH_2Cl_2 or ether solution, compound **4** was quantitatively pyrolized in the injector (220–270°). The product isolated was *cyclohexyl vinyl ketone* (**d**). IR. (CCl_4): 2920, 2845, 1698, 1678, 1613, 1452, 1402, 1002, 986, 956. NMR. (CCl_4, 60 MHz): 2.5/*bm* >CH–CO–; 5.5–6.7/*m* –CH=CH_2. MS.: *m/e* 138 (M^+). 109 (M^+-29), 96 (M^+-42), 83 (M^+-55); $C_9H_{14}O$ = 138.

Pyrolysis of 1-(Methylsulfinyl)-isopropyl Cyclohexyl Ketone (**5**)[14]. After VPC. control as for **4** compound **5** was quantitatively pyrolized in the injector (220–270°). The product isolated was *cyclohexyl isopropenyl ketone* (**e**). IR. (CCl_4): 2922, 2842, 1678, 1630, 1453, 930. NMR. (CCl_4, 60 MHz): 1.86/*bs* $-CH_3$; 2.90/*bm* >CH–CO–; 5.7/*m* ($W^{1/2}$ approx. 4) and 5.9/*m* ($W^{1/2}$ approx. 4) $=CH_2$. MS.: *m/e* 152 (M^+), 137 (M^+-15), 123 (M^+-29), 110 (M^+-42), 83 (M^+-69), 69 (M^+-83); $C_{10}H_{16}O$ = 152.

Preparation of Cyclohexanecarboxylic Acid S-Methylester (26), based on a procedure described in [29]. In a 20 ml steel autoclave 1.46 g (10 mmol) of cyclohexanecarboxylic acid chloride were dissolved in 10 ml of anh. ether, cooled to −70° and 5.4 ml of methyl mercaptane added, with a syringe, and then 1.38 ml of triethylamine. After sealing, the autoclave was shaken 4 h at −10°, subsequently 24 h at room temperature, cooled to −70° before opening and the reaction mixture evaporated to dryness at 50°. The residue was extracted with ether and the organic phase washed twice with 10% HCl-, once with 2 N NaOH-, and twice with saturated NaCl-solution. The product was distilled (*Vigreux* column, 88–90°/12 Torr) to yield 520 mg (30%) of **26**. The purity was checked by VPC. IR. (CCl_4): 2910, 2840, 1690, 1448, 1306, 1138, 1110, 1048, 1027, 975, 892, 853. UV. (C_2H_5OH): 232. NMR. (CCl_4, 60 MHz): 0.9–2.6/*m* $-(CH_2)_5-$ and –CO–CH<; 2.22/*s* –S–CH_3. MS.: *m/e* 158 (M^+), 143 (M^+-15), 111 (M^+-47), 83 (M^+-47-28).

$C_8H_{14}OS$ Calc. C 60.74 H 8,92% Found C 60.82 H 8.97%

UV. Irradiations of Aliphatic β-Keto Sulfoxides 2, 4, 5, 6 and 8, and some of their Photoproducts (see General Remarks). – *1. Of* **2**. – *1.1. Ether, prep. scale, 5 h, med.* (Exp. 1). 188 mg (1.0 mmol) of **2** in 50 ml (0.02 M). The solvent was carefully removed by distillation through a *Vigreux* column, the residue containing **24** and **26** in a ratio of approximately 9:1 (determined by VPC.) was chromatographed in CH_2Cl_2-pentane(9:1). The first fraction contained cyclohexyl methyl ketone (**24**) [30] and the second one cyclohexanecarboxylic acid S-methylester (**26**)[31]), the yields of **24** and **26** were not determined on account of their high volatility.

1.2. Ether, anal., 6 h, med. (Exp. 2). 18.8 mg (0,10 mmol) of **2** in 5 ml (0.02 M, degassed). Yields (VPC.): 86.5% of **24** and 9% of **26**.

2. Of **4**. – *2.1. Of a 1:1 mixture of 4a and 4b. – 2.1.1. Ether, anal. 13 h, med.* (Exp. 3). 20.2 mg (0.10 mmol) of **4** in 5 ml of (0.02 M, degassed). Yield (VPC.): 54% of **26**.

2.1.2. Ether, prep., 3 h, med. (Exp. 4). 408 mg (20 mmol) of **4** in 100 ml (0.02 M). The solvent was carefully removed by distillation through a *Vigreux* column, and the residue chromatographed in CH_2Cl_2-pentane(9:1) to yield 115.5 mg (38%) of **26** as main fraction.

2.1.3. Ether, prep. 40 min, med. (Exp. 5). 404 mg (2.0 mmol) of **4** in 100 ml (0.02 M). After removal of the solvent by distillation through a *Vigreux* column, the 340 mg of crude product were dissolved in 0.5 ml of CCl_4 for a NMR. measurement (60 MHz) which still indicated the unchanged 1:1 mixture of **4a** and **4b**.

2.1.4. Pentane, anal. 13 h, med. (Exp. 6). 20.2 mg (0.10 mmol) of **4** in 5 ml (0.02 M, degassed). Yield (VPC.): 50% of **26**.

2.2. Of a 4:1 mixture of **4a** *and* **4b**, *ether, prep., 40 min, med.* (Exp. 7). 384 mg (1.90 mmol) of **4** in 90 ml (0.02 M). The solvent was carefully removed by distillation through a *Vigreux* column to yield 352 mg of a product shown by VPC. analysis to contain 60% of **4**. The whole residue was dissolved in 0.5 ml of CCl_4 for a NMR. measurement (60 MHz) which established a 1:1 ratio for the mixture of **4a** and **4b**.

2.3. Of a 2:1 mixture of **4a** *and* **4b**, *ether, prep., 70 min, low* (Exp. 8). 585 mg (2.90 mmol) of **4** in 130 ml (0.02 M). 65% of **4** was transformed to photoproducts (determined by VPC.). Careful evaporation afforded 534 mg of product which was dissolved in 0.4 ml of CCl_4 for a NMR. measurement indicating a 1:1 ratio for the mixture of **4a** and **4b**.

3. Of **5**. – *3.1. Ether, anal., 7 h, med.* (Epx. 9). 21.6 mg (0.10 mmol) of **5** in 5 ml (0.02 M, degassed). Yield (VPC.): 54% of **26**.

3.2. Ether, anal., 8–13 h, med. (Exp. 10). 21.6 mg (0.10 mmol) of **5** in 5 ml (0.02 M, N_2). Yield (VPC.): 54% of **26** after 8 h or 13 h.

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[31]) For analytical and spectroscopical data see above: preparation of **26**.

3.3. Ether, anal., 8 h, med., acetone assay (Exp. 11). 21.6 mg (0.10 mmol) of **5** in 5 ml (0.02M, degassed). The ampoule was opened, 10 drops of a 2,4-dinitrophenylhydrazine solution[32]) were added to the irradiated probe, and after 10 min standing at room temperature, the mixture was evaporated to dryness under reduced pressure. MS. of total residue at n_0 = 85–110°: *m/e* 238 ($C_9H_{10}N_4O_4$).

For control 10 drops of the hydrazine solution[32]) were added to 5 ml of ether. After 10 min standing at room temperature the mixture was evaporated to dryness under reduced pressure. MS. of total residue: only traces of *m/e* 238. This was repeated but with addition of 2 μl of acetone. MS. of total residue: very strong *m/e* 238.

3.4. Ether, prep., 80 min, med. (Exp. 12). 433.5 mg (2.0 mmol) of **5** in 100 ml (0.02M). The solvent was carefully removed by destillation through a *Vigreux* column and the residue (357 mg) chromatographed in CH_2Cl_2-pentane-(9:1). 193 mg (60%) of **26** and 28 mg (4.5%) of *1,4-dicyclohexyl-2,2,3,3-tetramethyl-butan-1,4-dion* (**25**) were eluted. IR. (CCl_4): 1710, 1453, 993, 960, 905, 877, 848. MS.: *m/e* 306 (M^+), 223 (M^+-83), 141 (M^+-83-83+1), 111, 83; $C_{20}H_{34}O_2$ = 306.

3.5. Pentane, anal., 4³/₄ h, med. (Exp. 13). 21.6 mg (0.10 mmol) of **5** in 5 ml (0.02M, degassed). Yield (VPC.): 56,5% of **26**.

3.6. Methanol, anal., 12½ h, med. (Exp. 14). 21.6 mg (0.10 mmol) of **5** in 5 ml (0.02M, degassed). Unspecific reaction, VPC. analysis showed none of the products obtained from the irradiation of **5** in ether or pentane.

3.7. Ether, anal., 2 h, low (Exp. 15). 21.6 mg (0.10 mmol) of **5** in 5 ml (0.02M, N_2). The yellow solution was checked by VPC.: no starting material **5**, unspecific decomposition.

3.8. Pentane, anal., 2 h, low (Exp. 16). 21.6 mg (0.10 mmol) of **5** in 5 ml (0.02M, N_2). The brown solution was checked by VPC.: no starting material **5**, unspecific decomposition.

4. Of **6**. – *4.1. Ether, anal., 6 h, med.* (Exp. 17). 22.0 mg (0.10 mmol) of **6** in 5 ml (0.02M, degassed). *1-Deuteriocyclohexanecarboxylic acid S-trideuteriomethylester* (**29**) was isolated by VPC. MS.: *m/e* 162 (M^+), 112 (M^+-50), 84 (M^+-50-28); $C_8H_{10}D_4OS$ = 162.

4.2. Pentane, anal., 4½ h, med. (Exp. 18). 22.0 mg (0.10 mmol) of **6** in 5 ml (0.02M, degassed) gave **29**, isolated by VPC.

5. Of **8**. – *5.1. Ether anal., 6 h, med.* (Exp. 19). 23.0 mg (0.10 mmol) of **8** in 5 ml (0.02M, degassed). *Cycloheptanecarboxylic acid S-methylester* (**30**) was separated by VPC. MS.: *m/e* 172 (M^+, weak), 157 (M^+-15), 125 (M^+-47), 97 (M^+-47-28); $C_9H_{16}OS$ = 172.

5.2. Pentane, anal., 4½ h, med. (Exp. 20). 23.0 mg (0.10 mmol) of **8** in 5 ml (0.02M, degassed). The photoproduct **30** was separated by VPC.

6. Of **26**. – *6.1. Ether, anal., 1–8 h, med.* (Exp. 21). 10 μl (approximately 10.1 mg) of **26** in 5 ml, N_2. VPC. analysis: stable, quantitatively **26**.

6.2. Ether, anal., 1 h, low (Exp. 22). 10 μl (approximately 10.1 mg) of **26** in 5 ml, N_2. VPC. analysis revealed unspecific decomposition.

6.3. Of **26** *admixed with* **5**, *ether, anal., 8 h, med.* (Exp. 23). 21.6 mg (0.10 mmol) of **5** and 10 μl (approximately 10.1 mg) of **26** in 5 ml, N_2. Yield (VPC.) of newly formed **26**: 56.5%.

6.4. Of **26** *admixed with* **29**, *ether, anal., 8 h, med.* (Exp. 24). 10 μl (approximately 10.1 mg) of **26** and 10 μl (approximately 10.1 mg) of **29** in 5 ml of ether, N_2. The product isolated by VPC. was shown by MS. to be a 1:1 mixture of **26** and **29**.

7. Of a mixture of **8**, **26**, and **29**, *ether, anal., 4 h, med.* (Exp. 25). 23.0 mg (0,10 mmol) of **8**, 5 μl (approximately 5 mg) of **26**, and 5 μl (approximately 5 mg) of **29** in 5 ml, N_2. The product was separated by VPC. into a fraction containing **26** and **29** (ratio 1:1, determined by MS.) and another which was pure **30**.

8. Of a mixture of **5** *and* **6**. – *8.1. Ether, anal., 6 h, med.* (Exp. 26). 10.8 mg (0.05 mmol) of **5** and 11.0 mg (0.05 mmol) of **6** in 5 ml (0.02M, degassed). The product was isolated by VPC., the distribution was shown by MS. to be: **26**:**27**:**28**:**29** = 1:1:1:1.

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[32]) 1 g of 2,4-dinitrophenylhydrazine was dissolved in 12 ml of warm 85% aqueous H_3PO_4, the solution allowed to cool down to room temperature, and after approximately 16 h diluted with 8 ml of abs. C_2H_5OH (*Fluka*, puriss.).

8.2. Pentane, anal., 4½ h, med. (Exp. 27). 10.8 mg (0.05 mmol) of **5** and 11.0 mg (0.05 mmol) of **6** in 5 ml (0.02M, degassed). Isolated by VPC., the product distribution was shown by MS. to be **26**:**27**:**28**:**29** = 1:1:1:1.

9. Of a mixture of **6** *and* **8**. – *9.1. Ether, anal., 6 h, med.* (Exp. 28). 11.0 mg (0.05 mmol) of **6** and 11.5 mg (0.05 mmol) of **8** in 5 ml (0.02M, degassed). The product was separated by VPC. into two fractions the first containing **27** and **29** (1:1) the second containing **30** and **31** (1:1), ratios determined by MS.

9.2. Pentane, anal., 4½ h, med. (Exp. 29). 11.0 mg (0.05 mmol) of **6** and 11.5 mg (0.05 mmol) of **8** in 5 ml (0.02M, degassed). The product separated by VPC. gave a fraction containing **27** and **29** (1:1) and a second containing **30** and **31** (1:1), ratios determined by MS.

UV. Irradiations of Bicyclic β-Keto Sulfoxides 18 and 19, and Sulfoxides 12, 13, 16, and 17. – *1. Of* **18** *and* **19**, resp. – *1.1. Dioxane, anal., med.* (Exp. 30–35). 75.2 mg (0.4 mmol) of **18** and **19**, resp., divided into four samples which each contained 18.8 mg (0.10 mmol) in 5 ml (0.02M, N_2), were each irradiated for 2 h; the experiment was repeated with irradiation for 4 h and again for 8 h. The four probes were combined, evaporated to dryness under reduced pressure in a rotary evaporator, and each residue was chromatographed in $CHCl_3$–C_2H_5OH(9:1). The results are listed in Table 2.

Table 2. *UV. Irradiations of* **18** *and* **19** (*anal., dioxane*)

Exp.	Starting material	Reaction time h	Product distribution*)	
			18	**19**
30	**18**	2	52.5 mg (70%)	22.5 mg (30%)
31	**18**	4	40.0 mg (53%)	29.5 mg (39.5%)
32	**18**	8	28.5 mg (38%)	31.5 mg (42%)
33	**19**	2	10.5 mg (13.5%)	60.0 mg (79.5%)
34	**19**	4	13.5 mg (18%)	50.5 mg (67%)
35	**19**	8	14.5 mg (19%)	42.5 mg (56%)

*) Only the yields of **18** and **19** are given. For the isolation of **34**, a further photoproduct, see Exp. 38, 39, and 40.

1.2. Ethanol, anal., 1½ h, med. (Exp. 36 and 37). 2 mg (0.0106 mmol) of **18** and **19**, respectively, in 1 ml (0.0106M, N_2). The reactions followed by TLC. $CHCl_3$–C_2H_5OH(4:1) gave qualitatively the same results as those in dioxane.

1.3. Dioxane, prep., 16 h, med. (Exp. 38 and 39). 376 mg (2 mmol) of **18** and of **19**, each in 100 ml (0.02M). The reaction mixtures were evaporated to dryness and the residues chromatographed in $CHCl_3$–C_2H_5OH(9:1). **18** (Exp. 38) yielded 62.5 mg of not further examined products, 82.5 mg of crude **34**, 18 mg of not further examined products, 100.5 mg (27%) of **19**, and 97 mg (26%) of **18**. **19** (Exp. 39) yielded 72.5 mg of not further identified products, 89.5 mg of crude **34**, 22.5 mg of not further examined products, 131.5 mg (35.5%) of **19**, and 45 mg (12%) of **18**.

1.4. Dioxane, prep., 16 h, med., isolation of **34** (Exp. 40). 940 mg (5 mmol) of **18** in 250 ml (0.02M). The reaction mixture was evaporated to dryness and the residue chromatographed in $CHCl_3$-C_2H_5OH(9:1) to afford the following: *fraction 1:* 273 mg of a mixture of products which was rechromatographed in $CHCl_3$–C_2H_5OH(19:1). The crude product obtained (227 mg) was treated with charcoal in hot $CHCl_3$, the solution filtered through Celite and evaporated to dryness to give 220 mg (28%) of crystalline *1-hydroxy-4-oxo-9-oxabicyclo[3.3.1]nonane* (**34**) which was further purified by distillation (65–75°/0.02 Torr), m.p. 51–54°. IR. ($CHCl_3$): 3565, 3400, 2995, 1725, 1468, 1120, 1068, 1027, 973, 932, 902, 870; (nujol): 3335, 1709, 1130, 1064, 1025, 979, 938, 904, 870. NMR. ($CHCl_3$, 100 MHz): 1.3–2.6/*m* (9H) and 2.6–3.2/*m* (1H) CH_2-2, -3, -6, -7, and -8; 3.56/*b* 1-OH; 4.29/*m* ($W^{1/2}$ approx. 8) CH-5. MS.: *m/e* 156 (M^+), 138 (M^+-18), 128 (M^+-28).

$C_8H_{12}O_3$ Calc. C 61.52 H 7.75% Found C 61.40 H 7.76%

Fraction 2: 375 mg (40%) of **19**, *fraction 3:* 80 mg (8.5%) of a mixture of **18** and **19** (ratio 5:1), *fraction 4:* 146 mg (15.5%) of **18**.

1.5. Dioxane, anal., 8 h, low (Exp. 41 and 42). 75.2 mg (0.4 mmol) of **18** and of **19**, each divided into four samples containing 18.8 mg (0.10 mmol) in 5 ml (0.02 M, N_2). The four probes were combined, evaporated to dryness and the residues chromatographed in $CHCl_3$-C_2H_5OH(9:1). **18** (Exp. 41) yielded 17.5 mg (23.5%) of **19** and 50.5 mg (67.5%) of **18**. **19** (Exp. 42) yielded 49.5 mg (65.5%) of **19** and 21 mg (28%) of **18**.

2. Of **34**, *dioxane, med.* (Exp. 43). A small sample of **34** was photolyzed as above, and the reaction followed by TLC. Compound **34** was moderately photostable but underwent polymerization.

3. Of **12**. – *3.1. Acetone, anal., 1–10 h, med.* (Exp. 44). 4.3 mg (0.0185 mmol) of **12** in 1 ml (0.0185 M, N_2); followed by TLC. [$CHCl_3$—EtOH(9:1)] there was no reaction.

3.2. Acetone, anal., 1–3 h, low (Exp. 45). 4.3 mg (0.0185 mmol) of **12** in 1 ml (0.0185 M, N_2). The reaction, followed by TLC. [$CHCl_3$—EtOH(9:1)], showed decomposition but no stereomutation.

4. Of admixed **12** *and* **17**, *dioxane, anal., 1–8 h, med.* (Exp. 46). 4.65 mg (0.02 mmol) of **12** and 2.30 mg (0.01 mmol) of **17** in 1 ml (0.01 M relative to **17**, N_2). The reaction, followed by TLC. [$CHCl_3$—EtOH(9:1)], showed no formation of **13** but **17** → **16**.

5. Of admixed **13** *and* **16**, *dioxane, anal., 1–8 h, med.* (Exp. 47). 4.65 mg (0.02 mmol) of **13** and 2.30 mg (0.01 mmol) of **16** in 1 ml (0.01 M relative to **16**, N_2). The reaction, followed by TLC. [$CHCl_3$—EtOH(9:1)], showed no formation of **12** but **16** → **17**.

6. Of admixed **13** *and* **19**, *dioxane, anal., 1–6 h, med.* (Exp. 48). 2.30 mg (0.01 mmol) of **13** and 3.76 mg (0.02 mmol) of **19** in 1 ml (0.02 M relative to **19**, N_2). The reaction, followed by TLC. [$CHCl_3$—EtOH(9:1)], showed no formation of **12** but **19** → **18**.

Structure Elucidation of Photoproduct 34. – *Acetylation of* **34**. 73 mg (0.486 mmol) of **34** were acetylated in 2 ml of Ac_2O and 2 ml of pyridine during 48 h at room temperature. After the usual working-up the residue was chromatographed in $CHCl_3$—EtOAc(19:1) to yield 42.5 mg (45.5%) of *1-acetoxy-4-oxo-9-oxabicyclo[3.3.1]nonane* (**36**) which was distilled at 75°/0.02 Torr. IR. (CCl_4): 1730–1760 (broad), 1467, 1269, 1243, 1235, 1205, 1187, 1151, 1120, 1068, 1050, 1040, 1021, 964, 913, 900, 878. NMR. (CCl_4, 100 MHz): 1.3–2.85/*m* (9H) and 2.9–3.45/*m* (1H) CH_2-2, -3, -6, -7, and -8; 1.99/*s* 1-OCOCH$_3$; 4.16/*m* ($W^{1/2}$ approx. 8) CH-5. MS.: *m/e* 198 (M^+), 170 (M^+-28), 155 (M^+-43), 138 (M^+-60).

$C_{10}H_{14}O_4$ Calc. C 60.59 H 7.12% Found C 60.36 H 7.16%

Further elution gave 18.5 mg (20%) of *1,4-dioxo-5-acetoxy-cyclooctane* (**37**) which was distilled at 85°/0.03 Torr. IR. (CCl_4): 1752, 1711, 1458, 1225, 1100, 1085, 1071, 1042, 1031, 948, 906. NMR. (CCl_4, 100 MHz): 1.6–2.9/*m* CH_2-2, -3, -6, -7, and -8; 2.04/*s* 5-OCOCH$_3$; 5.00/*d* $J_{5,6} = 5.5$ further splitting by $J_{5,6'} = 4$) CH-5. MS.: *m/e* 198 (M^+), 170 (M^+-28), 155 (M^+-43), 138 (M^+-60).

$C_{10}H_{14}O_4$ Calc. C 60.59 H 7.12% Found C 60.36 H 7.21%

4-Oxo-9-oxabicyclo[6.1.0]nonane (**39**) [26]. 2.2 g of 85% *m*-chloroperoxybenzoic acid in 50 ml of $CHCl_3$ were added dropwise to a solution of 1.243 g (10 mmol) of 4-cycloocten-1-on (**38**) [25] in 150 ml of $CHCl_3$ at 0° and the mixture was stirred at 0° for 20 h. The chloroform layer was washed with 10% KI-, saturated aqueous $NaHCO_3$-, 10% aqueous $Na_2S_2O_3$-, and twice with saturated aqueous NaCl-solutions. The solvent was carefully removed by distillation through a *Vigreux* column and the residue distilled (115°/14 Torr) to yield 1.253 g (89.5%) of **39**. An analytical sample was chromatographed in benzene-EtOAc(1:1). M.p. 78–80°. IR. (liq.): 1703, 1471, 1018, 962, 928, 912, 866, 848, 780. NMR. (CCl_4, 60 MHz): 0.8–3.0/*bm*. MS.: *m/e* 140 (M^+), 112 (M^+-28), 96 (M^+-44); $C_8H_{12}O_2 = 140$.

*1,*endo*-4-Dihydroxy-9-oxabicyclo[3.3.1]nonane* (**40**). A solution of 278 mg (2 mmol) of the epoxy ketone **39** in 5 ml of 0.1 N H_2SO_4 was stirred for 2 h at room temperature. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$ and thoroughly extracted with ether to give 298 mg (95%) of crystalline crude **40**. A sample for analysis was chromatographed in EtOAc—CH_3OH(19:1). M.p. 130–132° (after sublimation at 95°/0.01 Torr). IR. ($CHCl_3$): 3605, 3590, 3400, 2995, 1490, 1130, 1074, 1049, 1032, 993, 971, 931, 897, 889, 864. NMR. (C_5D_5N, 60

MHz): 1.3–2.6/*m* CH_2-2, -3, -6, -7, and -8; 4.15–4.65/*m* CH-4 and -5; 6.25/*b* 4-OH; 7.25/*b* 1-OH. MS.: *m/e* 158 (M^+), 140 (M^+-18), 130 (M^+-28), 112 (M^+-18-28), 70 (M^+-18-28-42).

$C_8H_{14}O_3$ Calc. C 60.74 H 8.92% Found C 60.34 H 8.95%

1-Methoxy-endo-*4-hydroxy-9-oxabicyclo*[*3.3.1*]*nonane* (**41**). A solution of 298 mg (1.9 mmol) of **40** in 5 ml of 0.1 N methanolic HCl was allowed to react at 50° for 3 h in a closed system. The reaction mixture was evaporated to dryness under reduced pressure and twice evaporated to dryness after adding a small amount of CH_2Cl_2, to yield 312 mg (96%) of crude **41** which, after chromatography in EtOAc–CH_3OH(19:1), afforded 240 mg (74%) of an oil, further purified by VPC. (20% SE-30). IR. ($CHCl_3$): 3605, 3450, 2995, 2835, 1492, 1120, 1073, 1048, 1032, 1005, 970, 936, 899, 883. NMR. ($CDCl_3$, 60 MHz): 1.4–2.3/*m* CH_2-2, -3, -6, -7, and -8; 3.07/*s* 4-OH; 3.33/*s* 1-OCH_3; 3.8–4.25/*m* CH-4 and -5. MS.: *m/e* 172 (M^+), 155 (M^+-17), 154 (M^+-18), 144 (M^+-28), 143 (M^+-29), 140 (M^+-32), 130 (M^+-42), 112 (M^+-32-28), 72 (M^+-42-58).

$C_9H_{16}O_3$ Calc. C 62.76 H 9.35% Found C 62.85 H 9.41%

1-Methoxy-4-oxo-9-oxabicyclo[*3.3.1*]*nonane* (**35**). – a) *From* **41**. 778 mg of *Collins* reagent [15] was added to a solution of 86 mg (0.5 mmol) of **41** in 11 ml of CH_2Cl_2, the reaction mixture stirred at room temperature for 40 min, and subsequently filtered through Celite. The residue was washed with CH_2Cl_2, the filtrate filtered in EtOAc–CH_3OH(19:1) through 5 g of silicagel and several times evaporated to dryness after successive additions of hexane. The resulting 59 mg (69.5%) of oily **35** was distilled (90°/0.2 Torr). The product solidified at approximately 0°. IR. ($CHCl_3$): 2995, 2838, 2818, 1725, 1470, 1128, 1072, 1050, 1028, 966, 948, 930, 903, 872, 838. NMR. ($CDCl_3$, 60 MHz): 1.4–3.2/*m* CH_2-2, -3, -6, -7, and -8; 3.44/*s* 1-OCH_3; 4.3/*m* ($W^{1/2}$ approx. 7) CH-5. MS.: *m/e* 170 (M^+), 142 (M^+-28), 138 (M^+-32), 128 (M^+-42).

$C_9H_{14}O_3$ Calc. C 63.51 H 8.29% Found C 63.59 H 8.39%

b) *From photoproduct* **34**. A solution of 13.7 mg (0.08 mmol) of **34** in 1 ml of 0.1 N methanolic HCl was allowed to react 6 h at room temperature and subsequently $2^1/_2$ h at 45°. The reaction mixture was evaporated to dryness under reduced pressure to give 11.8 mg (87%) of oily **35**, identification by IR., TLC. in EtOAc–CH_3OH(19:1) and VPC. (20% SE-20).

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247. Etude des composés d'addition des acides de *Lewis* - XXXV [1] Note sur les composés d'addition entre amides et, respectivement, $PdCl_2$ et $PtCl_2$

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(5 VII 71)

Summary. The adducts of dimethylformamide, diethylformamide, dimethylacetamide and diethylacetamide with $PdCl_2$ and $PtCl_2$ have been prepared and the IR. spectra of the compounds in nujol mull or in $CH_2Cl \cdot CH_2Cl$ solution are studied. The lowering of the carbonyl frequency (amide I) shows that the metal is linked by a dative bond to the amide oxygen atom acting as a donor; the lowering is about 33 to 59 cm^{-1}.

The decrease of the frequency of the carbonyl group vibration, observed in these cases as for other addition compounds of *Lewis* acids, is due to an intramolecular electronic displacement in the direction of the amid oxygen atom.

Introduction. – Au cours des recherches du laboratoire de Chimie-Physique de l'Université de Genève sur les composés d'addition entre acides de *Lewis* et donneurs électroniques porteurs de groupe carbonyle: cétones, esters, acides, chlorures d'acyle, aldéhydes et quinones [1] à [4], la présence d'une liaison covalente dative entre l'oxygène du groupe carbonyle et le métal de l'acide de *Lewis* a été confirmée dans chaque cas par un abaissement de la fréquence carbonyle en spectrographie IR.

Penland, Mizushima, Curran & Quagliano [5] ont étudié, entre autres, les complexes de $PdCl_2$ et $PtCl_2$ avec l'urée, molécule dans laquelle un atome d'azote est associé au groupe carbonyle comme donneur électronique potentiel. Basant leur interprétation sur les spectrogrammes IR., ils sont arrivés à la conclusion que pour ces complexes des types, respectivement:

$M(urée)_2Cl_2$ avec M = Pd, Pt, Zn, Cu et $[M(urée)_6]Cl_3$ avec M = Fe, Cr,

la liaison se produisait entre un atome d'azote de chaque molécule d'urée et l'ion