oberhalb 240°. Leicht löslich in Wasser; wenig löslich in Methanol; unlöslich in Alkohol, Äther, Chloroform.

$C_{11}H_{12}Cl_2N_2$	Ber.	C 54,33	H 4,97	N 11,52	Chlorid 29,16%
(243,17)	Gef.	,, 54,35	,, 4,82	,, 11,22	,, 29,65%

Die Substanz enthält nach *Karl-Fischer*-Bestimmung 6,09% Wasser (Ber. für 1 mol: 6,89%); die Analysenwerte sind auf Trockengewicht korrigiert. – IR. (KBr): 3440, 3390, 3020, 2995, 2950, 2865, 1630, 1575, 1490, 1380, 1355, 1295, 1235, 1220, 1175, 1015, 840, 825, 780, 765, 690, 670, 565, 555, 470 cm^{-1}. – NMR. (D_2O): 9,6–8,2 (10 H, *m*, Pyridinreste); 7,48 (2 H, *s*, $-CH_2-$); 4,65 (*s*, H_2O, HDO).

Pikrat: Smp. 245° (aus Wasser), (Lit. [8] 245–249°).

3. Weisse rhombische Kristalle aus Äthanol/Äther, hygroskopisch. Smp. 184–185°. Leicht löslich in Wasser, Methanol; heiss löslich in Äthanol; unlöslich in Äther, Chloroform.

$C_6H_{13}Cl_2NO \cdot H_2O$	Ber.	C 35,31	H 7,41	Chlorid 17,37%	
(186,09)	Gef.	,, 35,35	,, 7,54	,, 17,65%	

IR. (KBr): 3430, 2980, 2870, 1465, 1425, 1410, 1350, 1285, 1260, 1230, 1200, 1115, 1050, 1035, 1015, 1000, 945, 895, 850, 825, 775, 705, 620, 505 cm^{-1}. – NMR. $(CD_3)_2SO$: 5,72 (2 H, *s*, $-CH_2Cl$); 3,81 (8 H, *m*, $-CH_2-CH_2-$); 3,30 (3 H, *s*, CH_3-).

Pikrat: Smp.: 230–231° (aus Wasser).

$C_{12}H_{15}ClN_4O_8$ (378,74) Ber. C 38,05 H 3,99 N 14,79% Gef. C 38,15 H 4,25 N 14,56%

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259. Specifically $\pi \rightarrow \pi^*$ Induced Photoreactions of α,β-Unsaturated Ketones: Hydrogen Abstraction by the α-Carbon[1])

(Preliminary Communication)

by **Jean Gloor, Gérald Bernardinelli, Raymond Gerdil,** and **Kurt Schaffner**

Département de Chimie Organique, Université de Genève, 1211 Genève 4

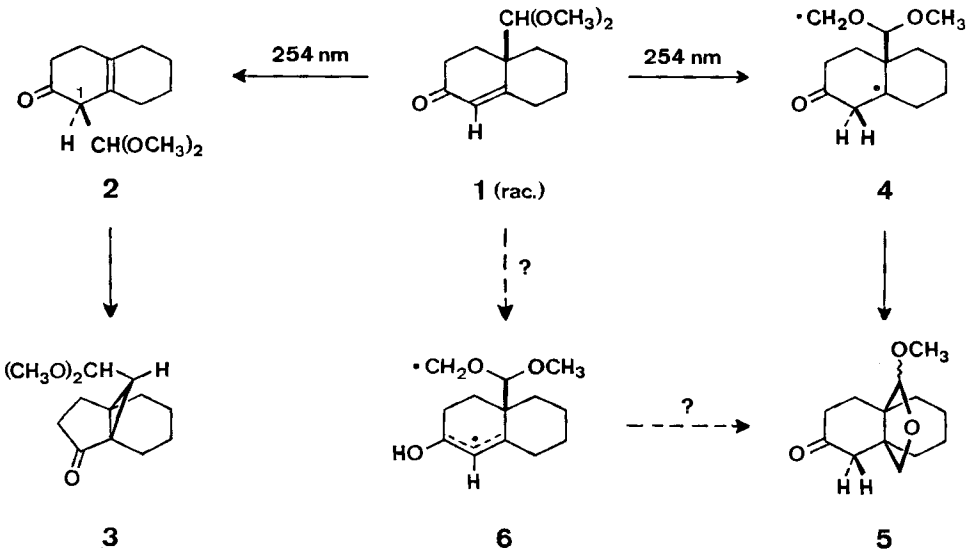
(4. X. 73)

Summary. Irradiations at 254 nm of the α,β-unsaturated γ-dimethoxy-methyl ketone **7** in iso-octane and *t*-butyl alcohol afforded in a specifically $\pi \rightarrow \pi^*$ induced process and in high chemical yield the epimeric products **9** and **10**. These products were not formed on $n \rightarrow \pi^*$ excitation of **7** at > 340 nm, but triplet energy transfer to 1,3-cyclohexadiene could be observed. Photolyses of the hexadeuterio analog **7-d_6** at 254 nm led to the fully deuteriated products (*cf.* **9-d_6**) in both solvents, with stereospecific incorporation of a deuterium atom in position C(1α). The structures

[1]) Presented at the VIIth International Conference of Photochemistry, Jerusalem, September 1973.

of **9** and **10** were determined by an X-ray diffraction analysis of **9** and chemical correlations of the two products. The structural constraints in **7** demand a hitherto unprecedented direct transfer of a methoxyl hydrogen to the α-carbon of the excited enone and formation of intermediate **8**.

We have reported previously [1] that selective $\pi \rightarrow \pi^*$ excitation of the α,β-unsaturated ketone **1** effects transformations, **1** → **2**[2]) + **5**, which are not observed on irradiation in the first ($n \rightarrow \pi^*$) absorption band and which differ from the reactions of the lowest-lying triplet state. Mass spectrometric results obtained from experiments with the di-(trideuteriomethoxy) analog of **1** in *t*-butyl alcohol had led to the conclusion that the intramolecular transfer of a methoxyl hydrogen to the α-carbon C(1) in product **5** involves *in part* hydrogen abstraction by the ketone oxygen in an upper excited state of **1** possessing a non-planar enone conformation, and formation of inter-



mediate **6**. *A recent re-examination by NMR. invalidates now the previous experimental evidence taken in favor of path* **1** → **6** → **5**.

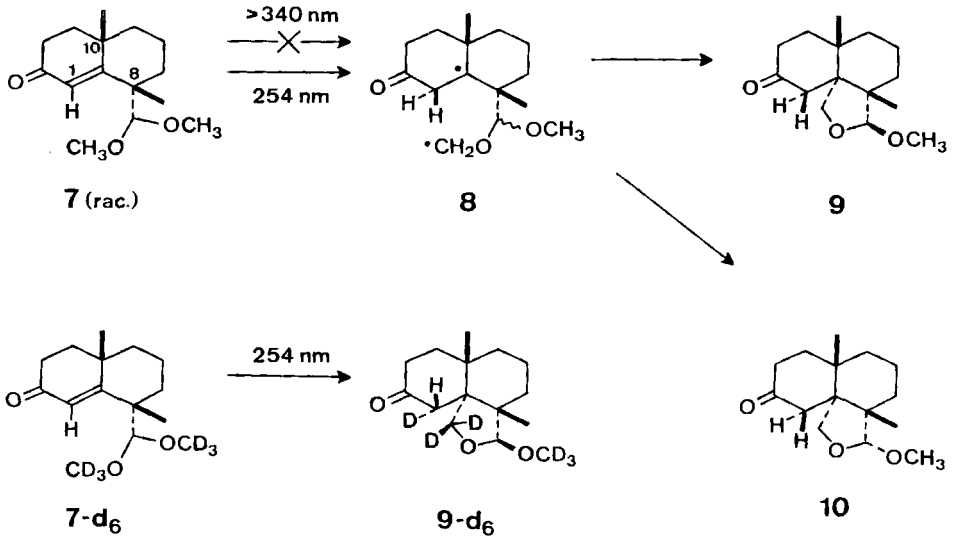
Ketone **7**[3])[4]) was now chosen in order to explore the alternative path **1** → **4** → **5**, involving a direct hydrogen transfer from a methoxy group to the α-carbon. The methoxy groups of this compound are definitely too remote from the ketone oxygen to permit a

[2]) Photoproduct **2** has been proposed as an intermediate in the two-step photochemical formation of **3**, but direct evidence for its existence had not been established in [1a]. Compound **2** could now be isolated[3])[4]); it could be converted into **3** only by triplet sensitization using, *e.g.*, acetone solution and 254 nm.

[3]) All new compounds gave satisfactory analytical data. Experimental details, including synthetic and isolation procedures, will be reported in a full paper in this journal.

[4]) Selected characteristic UV. (nm/ε), IR. (cm^{-1}), and/or NMR. (δ) data for this compound are listed below. **2**. IR. (CCl_4): 1720, 1100, 1080, 1060. – NMR. ($CDCl_3$): 2.88/*d*, *J* = 5.5 Hz, H–C(1); 3.38/*s*, 2 CH_3; 4.57/*d*, *J* = 5.5 Hz, H–C(1'). – **7**. UV. (hexane): 230/12600, 334/37. – IR. (CCl_4): 1665, 1595, 1110, 1080. – NMR. (CCl_4): 1.17, 1.32, 3.47, 3.50/4 *s*, CH_3; 4.16/*s*, H–C(8'); 5.76/*s*, H–C(1). – **9**. IR. ($CHCl_3$): 1700, 1095, 1045, 995. – NMR. ($CDCl_3$): 1.05, 1.26, 3.31/3 *s*, CH_3; 4.28/*s*, H–C(8'). – **10**. IR. ($CHCl_3$): 1700, 1110, 1040, 1000. – NMR. ($CDCl_3$): 1.04, 1.26, 3.44/3 *s*, CH_3; 4.64/*s*, H–C(8').

hydrogen transfer to the latter in any conceivable ring conformation. Nevertheless, they are equally favorably positioned as in **1** for an eventual hydrogen transfer to the α-carbon.



On irradiation of a $6 \cdot 10^{-2}$ M solution of **7**[3][4] in iso-octane with >340 nm ($n \rightarrow \pi^*$ excitation) the compound remained unchanged (according to vapor-phase and thin-layer chromatography), whereas in a similar run with added $18 \cdot 10^{-2}$ M 1,3-cyclohexadiene triplet-sensitized diene dimerization [2] was observed. With 254 nm ($\pi \rightarrow \pi^*$ excitation), however, **7** afforded a ca. 3:2 ratio of products **9** (m.p. 126–127°)[4] and **10** (m.p. 162–163°)[4] in 77% total yield after full photochemical conversion and chromatographic separation on silica gel[5]). Qualitatively identical results were also obtained with **7** at 254 nm in *t*-butylalcohol. A product of a sigmatropic 1,3-dimethoxymethyl migration, analogous to **1** → **2**, has not been found.

In view of this result and the structural constraints in **7** we conclude that the specifically $\pi \rightarrow \pi^*$ induced photocyclization to **9** and **10** involves a hitherto unprecedented direct hydrogen transfer to the α-carbon and formation of intermediate **8**. The following additional results comply with this mechanism and are similar in part to previous findings with **1** [1a].

Irradiations of **7-d$_6$** with 254 nm in iso-octane and *t*-butyl alcohol afforded the corresponding hexadeuterio products. NMR. analyses of the major compound **9-d$_6$** confirmed that in both solvents the deuterium transfer had occurred essentially without isotopic loss and stereospecifically to the 1α position. Thus, the δ 3.02 doublet (J = 17 Hz) of the 1α methylene proton in **9** is entirely missing in **9-d$_6$**, whereas the δ 2.47 four-line signal (J = 3 and 17 Hz) of the 1β proton in **9** appears as a singlet of equal relative intensity in **9-d$_6$**. Finally, the photolysis of a 1:1 mixture of **7** and **7-d$_6$** in iso-octane gave a kinetic H/D isotope effect of 1.7 for product formation, as measured by mass spectrometry.

[5]) Analogous results were also achieved with the C(8) epimer of **7**[3]).

Acid-catalyzed interconversion of the C(8') epimeric photoproducts **9** and **10**, transformation of both compounds to the same keto-γ-lactone, and the IR., NMR., and mass spectrometric data provide strong support for the constitution of **9** and **10**. The full molecular structure was determined by an X-ray diffraction analysis of **9**. The crystals are monoclinic (a = 7.682, b = 14.448, c = 12.925 Å, β = 108.4°), space group P 2_1/c, with four molecules in the unit cell. Intensity measurements of 1277 reflections were carried out with a *Philips* PW 1100 automatic 4-circle diffractometer with MoKα radiation. Phases were determined by direct methods, and a first *Fourier* synthesis yielded a consistent and well resolved image of the molecule with all atoms present. The positions of all the hydrogen atoms were unambiguously obtained from a difference synthesis at a later stage of the analysis. The final R factor, based on 991 reflections, is 0.049.

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260. Triasteranetrione

by **Ian A. McDonald**[1]) and **André S. Dreiding**

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

(5. IX. 73)

Zusammenfassung. Eine Synthese von Bicyclo[3.3.1]nonan-3,7,9-trion-9-(äthylen)acetal (**6**) durch doppelte *Michael*-Addition von Aceton-dicarbonsäure-dimethylester (**9**) an Benzochinon-mono(äthylen)acetal (**8**) und anschliessende Verseifung und Decarboxylierung des intermediären 2,4-Dicarbomethoxy-bicyclo[3.3.1]nonan-3,7,9-trion-9-(äthylen)acetals (**10**) wird beschrieben. Bromierung des Triketon-monoacetals **6** mit Brom in Eisessig liefert 2α,4β,6α,8β-Tetrabrom-bicyclo[3.3.1]nonan-3,7,9-trion-9-(äthylen)acetal (**12**), dessen Konfiguration sich aus dem NMR.-Spektrum mit Hilfe von Symmetrieargumenten und aus Vergleichen von chemischen Verschiebungen ergibt. Durch Behandlung des rohen Tetrabromids (**12**) mit Triäthylamin entsteht ein Gemisch von 2,4-Dibrom- (**13**) und 2,6-Dibrom-triasteran-3,7,9-trion-9-(äthylen)acetal (**14**), welches sich einerseits mit Säure zu einem 1:2-Gemisch von 2,4-Dibrom- (**15**) und 2,6-Dibrom-triasteran-3,7,9-trion (**16**) hydrolysieren und andererseits mit Tri-*n*-butyl-zinnhydrid zu Triasteran-3,7,9-trion-9-(äthylen)acetal (**17**) reduktiv debromieren lässt. Hydrolyse des Triketon-monoacetals (**17**) oder reduktive Debromierung des Triketodibromid-Gemisches (**15** und **16**) führt zum hochschmelzenden, in den meisten Lösungsmitteln wenig löslichen Triasteran-3,7,9-trion (**4**). Die Spektraleigenschaften der erwähnten Substanzen werden diskutiert und zur Bestätigung der Strukturen zugezogen.

1. Introduction. – The triasterane skeleton (**1**) is of particular interest inasmuch as all six cyclopropyl-methylene bridge bonds ideally 'bisect' [1] a cyclopropane ring. The orbitals of any trigonal bridge carbon atoms are thus favorably disposed for

[1]) Post-doctoral fellow, University of Zürich, 1972–3.