Tetrahedron Letters,Vol.24,No.9,pp 947-950,1983 0040-4039/83/090947-04$03.00/0
Printed in Great Britain

PHOTOLYSIS AND PYROLYSIS PRODUCTS OF ISOGERMACRONE

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Summary. The photolysis and pyrolysis of the title compound leads to, among other products,cyclobutane ring systems with crossed or parallel bonds;photolysis affords also such systems trans-fused to a cyclopentanone. Isogermacrone is found to be present in small amounts in the essential oil of Geranium macrorrhizum L.

The reported isolation from a natural source of the sesquiterpene ketone 1,7-dimethyl-4-isopropylidene-tricyclo[4.4.0.0^{2,7}]decan-3-one(1) named germazone[1] has led us to re-examine the photochemical behaviour of isogermacrone(2), a cyclodecadienone also found to be present in small amounts in the essential oil of Geranium macrorrhizum L.[2a,b]. The absence of the cross-bonded cyclobutane derivative 1 among the photoproducts of 2 observed first by Scheffer and Boire[3] and then also by us initiated molecular mechanics[4] and quantum-chemical[5] studies the results of which indicated that there are no apparent reasons of structural or electronic character which could be put forward to explain for its lack of formation. Under the presently employed conditions 1 was found to be stable to direct irradiation.

Irradiation of 2 under preparative conditions(approx. 4 x 10^{-3} M solutions) with a low- or high-pressure light source(Hanau TNN 15/32 or TQ 150 burners) behind quartz or pyrex in various solvents(n-hexane, benzene, o-xylene, acetone, methanol; all spectroscopic or puriss. grade) and temperatures between -65°C(n-hexane) and 142°C(refluxing o-xylene) resulted qualitatively and quantitatively[6] in the same mixture of photoproducts. The same was also observed on conducting the reaction while bubbling oxygen through an oxygen-equilibrated n-hexane solution of 2.

The reaction mixture consisted, after almost complete conversion of 2, of seven photoproducts(see Scheme 1). Short reaction times(up to 20% conversion of 2), however, led also to the presence of 1. It was found that the concentration of germazone passes through a maximum on prolonging the time of irradiation - reaction times corresponding to almost complete conversion of 2 resulted in only traces of 1. This latter observation seems to indicate that 1 undergoes rearrangement sensitized by some of the compounds present in the reaction mixture.

Under flash-pyrolysis conditions(530°/0,6 mm Hg, nitrogen flow, 300 mm quartz tube with quartz chips filling) 2 formed compounds 1,5 and 6 in a combined yield of 33% and in the ratio of 1:1:2, respectively, as determined by gas chromatography[2a,7].

The following compounds were isolated from the photolysis mixture by preparative tlc as previously described[6].

1,7-Dimethyl-4-isopropylidene-tricyclo[4.4.0.0^{2,7}]decan-3-one(1) showed identical infrared and ^{1}H-NMR spectral characteristics as well as R_f values on tlc(silica gel Merck G, Et$_2$O/petr. ether = 1:10) and gc retention times[2a,b] with an authentic sample[1].

(1R*,2S*,6S*,7S*)-1,7-Dimethyl-4-isopropylidene-tricyclo[5.3.0.0^{2,6}]decan-3-one(3) showed $\nu_{C=O}$/CCl$_4$ 1720 cm^{-1} and $\nu_{C=C}$/CCl$_4$ 1640 cm^{-1}; λ_{max}/EtOH 244 nm(E 6000); MS(70 ev): M$^+$ 218(6%), 81(100%), 96(40%), 122(72%), 203(5%); ^{1}H-NMR(C$_6$D$_6$) δ: 0,84 ppm(s, 3H, 14-Me), 1,17 ppm(s, 3H, 15-Me), 1,22 ppm(m, 2H), 1,47 ppm(bd s, 3H, 13-Me), 1,58 ppm(m, 4H), 1,69 ppm(d, J=16,5 Hz, 1H, C2-H), 1,83 ppm(m, 1H), 1,96 ppm(t, J=13 Hz, C5-H), 2,25 ppm(bd s, 3H,12-Me; d x d, J=5 Hz, other d overlapping with 12-Me signal, 1H, C5-H); ^{1}H-NMR(CDCl$_3$) δ: 0,94 ppm(s, 3H), 1,11 ppm(s, 3H), 1,36 ppm(m, 2H), 1,66 ppm(s, 3H, 13-Me), 1,73 ppm(m, 5H), 1,98 ppm(m,1H), 2,02 ppm(s, 3H, 12-Me), 2,17 ppm(t, J=13 Hz, 1H, C5-H), 2,45 ppm(d x d, J=13 and 5 Hz, C5-H).

Decoupling experiments conducted on C$_6$D$_6$ solution of 3. Irradiation centered at 2,25 ppm led to: a)changing the 1H triplet at 1,96 ppm to almost doublet; b)collapse of peaks with J=5 Hz at 1,58 ppm forming discernable doublet with J=16,5 Hz. Irradiation at 1,83 ppm resulted in changes in multiplets for 4H centered at 1,58 ppm and for 2H at 1,22 ppm.

(1R*,2R*,6R*,7S*)-1,7-Dimethyl-4-isopropylidene-tricyclo[5.3.0.0^{2,6}]decan-3-one(4) had the following spectral characteristics: $\nu_{C=O}$/CCl$_4$ 1720 cm^{-1} and $\nu_{C=C}$/CCl$_4$ 1640 cm^{-1}; λ_{max}/EtOH 247 nm(E 9880); MS(70 ev): M$^+$ 218(7%), 81(94%), 96(50%), 122(100%), 203(6%); ^{1}H-NMR(C$_6$D$_6$) δ: 0,85 ppm(s, 3H, 15-Me), 0,86 ppm(s, 3H, 14-Me), 1,21 ppm(m, 1H), 1,36 ppm(m, 1H), 1,42 ppm(s, 3H, 13-Me), 1,50 ppm(m, 1H), 1,59 ppm(m, 3H), 1,69 ppm(d x d x d, J=5, 16,5 and 10 Hz, 1H, C6-H), 1,94 ppm(t, J=13 Hz, 1H, endo-C5-H), 2,17 ppm(d x d, J=13 and 5 Hz, exo-C5-H), 2,25 ppm(m,1H), 2,26 ppm(bd s, 3H, 12-Me); ^{1}H-NMR(CDCl$_3$) δ: 0,95 ppm(s, 3H), 1,01 ppm(s, 3H), 1,38 ppm(m, 2H), 1,62 ppm(m, 1H), 1,65 ppm(s, 3H, 13-Me), 1,76 ppm(m, 4H), 2,03 ppm(bd s, 3H, 12-Me), 2,13 ppm (m, 2H), 2,38 ppm(d, J=13 Hz, 1H).

Decoupling experiments on C$_6$D$_6$ solution of 4. Irradiation centered at 2,17 ppm changed the: a)d x d x d 1H signal at 1,69 ppm to triplet with J=16,5 and 10 Hz; b)triplet at 1,94 ppm to doublet. Irradiation at 2,25 ppm affected the multiplets centered at 1,36 ppm for 1H and 1,59 ppm for 3H.

(1R*,2R*,6S*,7S*)-1,7-Dimethyl-4-isopropylidene-tricyclo[5.3.0.0^{2,6}]decan-3-one(5)[3] exhibited $\nu_{C=O}$/CCl$_4$ 1690 cm^{-1} and $\nu_{C=C}$/CCl$_4$ 1623 cm^{-1}; λ_{max}/EtOH 265 nm(E 12300); ^{1}H-NMR(CDCl$_3$)δ: 1,07 ppm(s, 3H, 14-Me), 1,17 ppm(s, 3H, 15-Me)[8], 1,24 ppm(m, 3H), 1,50 ppm(m, 1H), 1,81 ppm(bd s, 3H, 13-Me), 1,86 ppm(m, 2H), 2,21 ppm(t, J=2 Hz, 12-Me), 2,42 ppm(d x d x d, J=10,9 and 4 Hz, C6-H), 2,51 ppm(d, J=10 Hz, C2-H), 2,60 ppm(m, 2H, C5-2H).

(1R*,2S*,6R*,7S*)-1,7-Dimethyl-4-isopropylidene-tricyclo[5.3.0.0^{2,6}]decan-3-one(6)[3] had the following characteristics: $\nu_{C=O}$/CCl$_4$ 1690 cm^{-1} and $\nu_{C=C}$/CCl$_4$ 1623 cm^{-1}; λ_{max}/EtOH 262 nm(E 7000); ^{1}H-NMR(CDCl$_3$) δ: 0,83 ppm(s, 3H, 15-Me), 0,90 ppm(s, 3H, 14-Me), 1,35 ppm(m, 2H), 1,60 ppm(m,1H), 1,75 ppm(m, 3H), 1,85 ppm(bd s, 3H, 13-Me), 2,27 ppm(m, 4H, 12-Me and C6-H), 2,39 ppm(d, J=8 Hz, C2-H), 2,50 ppm(m, 1H, C5-H), 2,70 ppm(d, J=17 Hz, C5-H).

(1R*,2R*,7R*)-2,6-Dimethyl-9-isopropylidene-bicyclo[5.3.0]dec-5-en-10-one(7) showed $\nu_{C=O}/CCl_4$ 1702 cm^{-1} and $\nu_{C=C}/CCl_4$ 1635 cm^{-1}; λ_{max}/EtOH 265 nm(E 12000); MS(70 ev): M^+ 218(100%), 203(25%), 176(40%), 123(30%), 121(60%), 96(35%), 93(35%), 91(34%); ^{1}H-NMR(C_6D_6) δ: 1,30 ppm (d, J=7,3 Hz, 3H, 14-Me), 1,40 ppm(s, 3H, 15-Me), 1,63 ppm(t, J=1,5 Hz, 13-Me), 1,80 ppm(m, 3H), 2,10 ppm(m, 2H), 2,28 ppm(s, 3H, 12-Me), 2,31 ppm(t, J=2 Hz, 1H, C7-H), 2,33 ppm(t, J=2 Hz, 1H, C1-H), 2,25 ppm(m, 2H, C8-2H), 5,32 ppm(t, J=6,5 Hz, 1H, C5-H); ^{1}H-NMR($CDCl_3$) δ: 1,08 ppm(d, J=7,3 Hz, 3H, 15-Me), 1,55 ppm(m, 2H), 1,66 ppm(t, J=1,5 Hz, 3H, 14-Me), 1,75 ppm(s, 3H, 13-Me), 1,81 ppm(m, 2H), 2,02 ppm(m, J=2 and 7,3 Hz, 1H, C2-H), 2,14 ppm(d, J=2,4 Hz, 3H, 12-Me), 2,35 ppm(t, J=2 Hz, 1H, C7-H), 2,38 ppm(t, J=2 Hz, 1H, C1-H), 2,74 ppm(m, 2H, C8-2H), 5,28 ppm (t, J=6,5 Hz, 1H, C5-H).

(1R*,2R*,7S*)-2,6-Dimethyl-9-isopropylidene-bicyclo[5.3.0]dec-5-en-10-one(8) had the following spectral characteristics: $\nu_{C=O}/CCl_4$ 1705 cm^{-1}, $\nu_{C=C}/CCl_4$ 1635 cm^{-1}; λ_{max}/EtOH 256 nm (E 9150); ^{1}H-NMR($CDCl_3$) δ: 0,82 ppm(d, J=7 Hz, 3H, 15-Me), 1,40 ppm(m, 1H), 1,75 ppm(m, 1H), 1,77 ppm(t, J=1,5 Hz, 3H, 14-Me), 1,85 ppm(s, 3H, 13-Me), 2,06 ppm(m, 2H), 2,23 ppm(d, J=3 Hz, 3H, 12-Me overlapping with 1H signal, C7-H, m, J=12 Hz), 2,41 ppm(q, J=7 Hz, 1H, C2-H), 2,80 ppm(m, 2H, C8-2H), 5,59 ppm(t, J=6 Hz, 1H, C5-H).

Compound 9 was found to be identical by ^{1}H-NMR spectrum with reported by Reijnders and Buck[9] 3,7-dimethyl-10-isopropylidene-3(Z),7(E)-cyclodecadien-1-one.

A chemical confirmation of the structures of the strained compounds 3 and 4 was provided by treating them with sodium ethoxide in ethanol at room temperature - they afforded solely compounds 5 and 6, respectively. Irradiation of isogermacrone deuterated at positions C2,C4 and in the C3-methyl group afforded compounds 3 and 4 with deuterium at C2,C10 and 15-Me as well as compound 7 with deuterium at C1,C3 and 15-Me - as evidenced by ^{1}H-NMR spectroscopy.

We believe compounds 3 and 4 are the first cases of a four-membered ring system trans-fused to a five membered one in a tricyclo[5.3.0.0^{2,6}]decan-3-one molecular system.

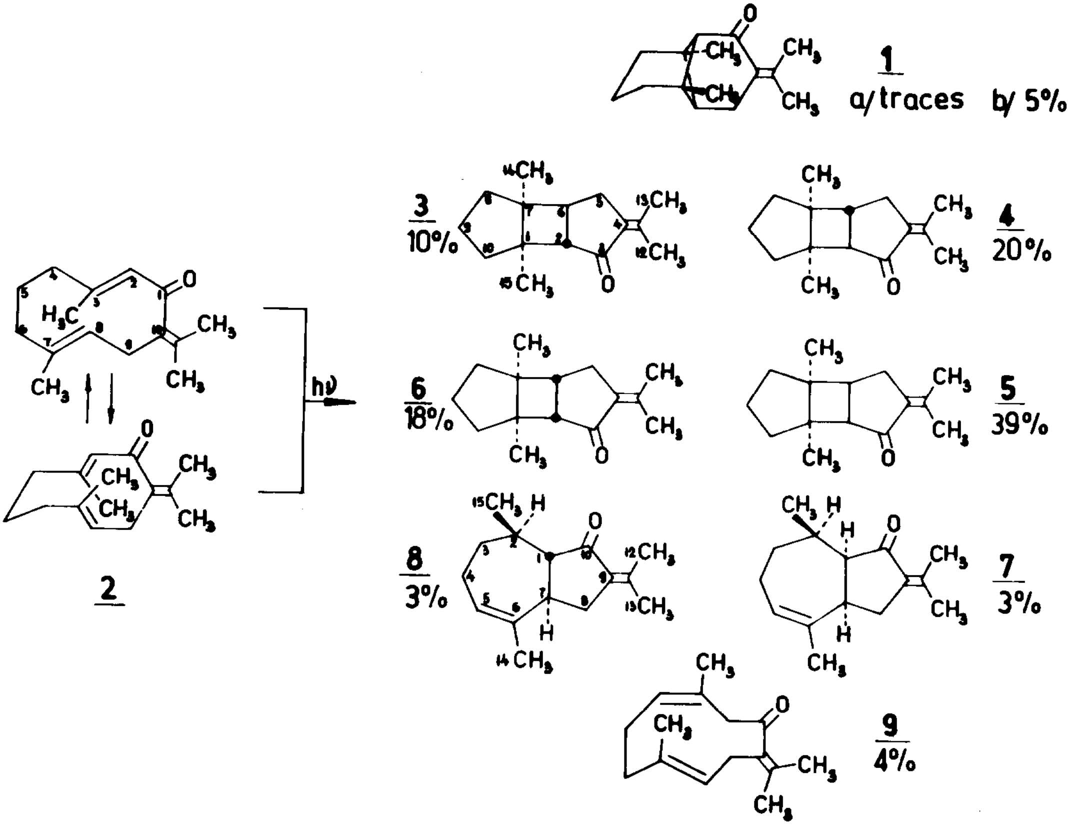
The authors wish to thank Professor André Dreiding for helpful discussions. This work was financially supported in part by UNDP project BUL/77/009 and the Schweizerischen Nationalfonds zur Förderung der wissentschaftlichen Forschung(grant No 2,618-0,80).

References and Notes

1. E.Tsankova and I.Ognyanov, Tetrahedron, 34,603(1978)
2. The gas-chromatographic analyses were conducted on: a)Carlo Erba Model G1 apparatus provided with a glass capillary column(Pluronic 64, 19 m/0,3 cm, oven temp. 125°C); b)Hewlett-Packard instrument with glass capillary column(SP-2100, 15 m/0,3 cm, oven temp. 140°C);both instruments were connected to Spectra-Physics 4100 integrators/FI.
3. J.R.Scheffer and B.A.Boire, Tetrahedron Lett., 1969, 4005
4. P.M.Ivanov, N.V.Bozhkova and A.S.Orahovats, J.Mol.Structure(THEOCHEM), 86,393(1982)
5. G.D.Neykov, N.V.Bozhkova and A.S.Orahovats, ibid., in press
6. N.V.Bozhkova, B.Atanassova and A.Orahovats, Commun.Dept.Chem.,Bulg.Acad.Sci.,13,244(1980)

Scheme 1

Photoproducts and yields obtained on irradiation of isogermacrone



Yields obtained - a)on almost complete conversion of 2; b)on conversion of 2 not exceeding 20%.

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7. The separation was carried out on a Lobar-B column(Merck art.10401).
8. The assignement of the 14-Me and 15-Me signals appears reversed with respect to the one given in ref. 3; this is done on the grounds of the ^{1}H-NMR spectrum of a 15-Me-d_2 sample.
9. P.J.M.Reijnders and H.M.Buck, J.Royal Netherlands Chem. Soc., 97,263(1978).
10. The ^{1}H-NMR spectra were recorded on a Bruker 400 FT(400 MHz) or Bruker HXS-360(360 MHz) instrument against tetramethylsilane as internal standard. The mass spectra were obtained on a MS-Varian MAT 711 apparatus. All new compounds gave satisfactory C and H analyses.

(Received in UK 19 October 1982)