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FORMATION OF HOMOFULVENES *

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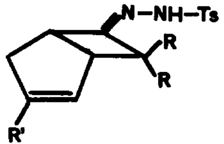
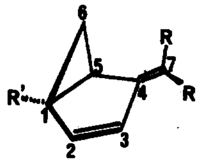
Among several hydrocarbon products (10 to 35 % yield), formed in the thermal decomposition of the sodium salt of the tosylhydrazone of bicyclo(3.2.0)-hept-2-en-6-one *** (Ia) and two of its methylated derivatives (Ib and Ic) in both aprotic and protic solvents (3) at 130 - 150^0 were a group of compounds (1 - 25 % yield), which we call homofulvenes (IIa - IId).



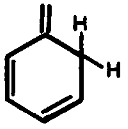
I



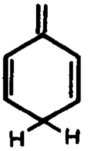
II

a. R = R' = H
b. R = CH$_3$; R' = H
c. R = R' = CH$_3$
d. R = D; R' = H

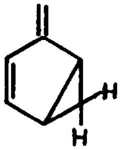
IIa can also be considered as the meta-tautomer of toluene completing the series of ortho- (III)(4) and para-tautomers (IV)(5). The first homofulvene



III



IV



IIa

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* Some of the results have been reported previously in lectures; see for instance (1).

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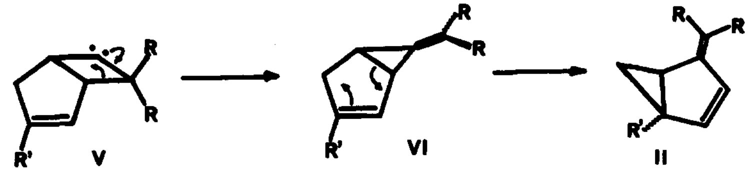
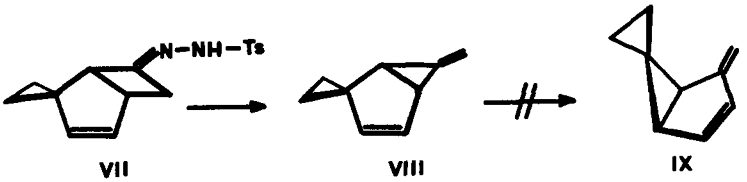
*** Obtained by cycloaddition of cyclopentadienes and ketenes (2); see also the last paragraph of this paper. We are grateful to Dr. R. H. Hasek and the Tennessee Eastman Co. for generous gifts of two dimethylketene adducts.

structure appears to have been found in the skeleton of photodehydroergosterol (6). Other homofulvenes have recently been reported as photoproducts from hexamethylbicyclo(2.2.0)hexa-2,5-diene (7) and 3,3-diphenyl-6-methylenecyclohexa-1,4-diene (8) and the product of dehydrochlorination of 5-chloro-1,2,3,4,5,6-hexamethylcyclohexa-1,3-diene (9).

The homofulvene (II) formation may be explained through the carbene V by ring contraction (10) followed by a thermal rebonding* to release the strain of the alkylidene cyclopropane structure (VI) and to profit from the conjugation of II. This mechanism is supported by the isolation of compound VIII from the sodium salt of VII, the strain inherent in the spiropentane system (11) in IX presumably offsetting the homofulvene advantage, and by the pyrolysis of the sodium salt of the 7,7-dideutero compound (Id) (see below) which yielded the 7,7-dideutero-homofulvene (IId), even under Kirmse's sodium hydride conditions (12).





The UV-spectra of homofulvene (IIa) and its alkylated derivatives are compared to those of the corresponding fulvenes (13) and endo-exocyclic dienes in table 1: The cyclopropane ring appears to have a similar effect on the high intensity low wavelength band (240 - 260 nm) as the third fulvene double bond, but the low intensity high wavelength band (near 360 nm) of the fulvenes is missing in the homo-series (II); it may have become shifted under the low wavelength band **. The ε-values of compounds II in table 1 are not too reliable due to ready polymerizability.

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* Valencetautomeric rearrangement.

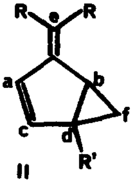
** The detailed geometry, UV-spectra and dipole moments are being calculated by G. Wagnière and W. Hug at the Institute of Physical Chemistry of this University; private communication. Calculations and measurements seem to be in fair agreement.

Table 1:

Compound	Solvent	λ(nm)	ε	λ(nm)	ε	Ref.
IIa	ethanol	245	10900	-	-	-
IIa	n-hexane	246	-	-	-	-
IIb	ethanol	257	12780	-	-	-
IIc	ethanol	257	8940	-	-	-
A	ethanol	260	11300	-	-	(6)
B	n-hexane	255*	10800	-	-	(7)
X	cyclohexane	231	21000	-	-	(14)
XI	n-heptane	234	14300	-	-	(15)
XIIa	ethanol	241.5	11500	360	224	(13)
XIIb	ethanol	268.5	17400	357	381	(13)

A = photodehydroergosterol (6),

B = photoproduct of hexamethylbicyclo(2.2.0)hexa-2,5-diene (7).



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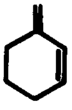
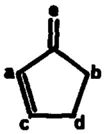
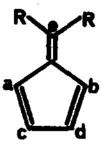


X



XI



XII

a. R = R' = H

b. R = CH_3; R' = H

c. R = R' = CH_3

Table 2: **

	Ha***	Hb	Hc***	Hd	$(CH_3)d$	He	$(CH_3)e$	Hf,endo	Hf,exo
IIa	6.17/D	2.08/DxD	5.66/D	2.08/DxD	-	4.86/M	-	0.37/DxT	0.95/DxT
IIb	5.97/D	2.0/M	5.83/D	2.0/M	-	-	1.82/S 1.73/S	0.14/DxT	0.85/DxT
IIc	5.85/S	1.8/M	5.85/S	-	1.32/S	-	1.81/S 1.73/S	0.37/DxD	0.77/DxD
XIIa (13)	6.44/M	6.44/M	6.11/M	6.11/M	-	5.78/M	-	-	-
XIIb (13)	6.34/S	6.34/S	6.34/S	6.34/S	-	-	2.17/S	-	-
XI (15)	6.09/S	2.49/S	6.09/S	2.49/S	-	4.75/M	-	-	-

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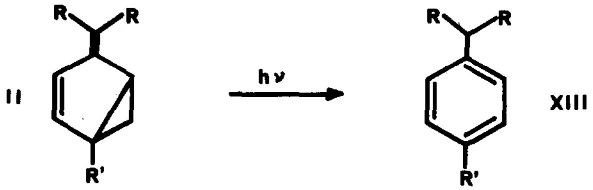
* see footnote on the fifth page of this paper.

** δ-values in ppm relative to TMS = 0 in CCl_4 as solvent. M = multiplet, T = triplet, D = doublet, S = singlet. The integration corresponds to the expected number of protons.

*** These assignments in case of compounds II are uncertain.

In the NMR-spectra of the homofulvenes (table 2) all the proton signals appear at higher field in comparison with fulvenes. In the fulvenes, the side chain substituents (position e) and the ring substituents (positions a, b, c, and d) are deshielded by the high dipole moment (16) and by the ring current respectively. In the homofulvenes (II), the ring current deshielding seems to be decreased (if not absent) in its effect on Ha and Hc and the dipole moments would be expected* to have nearly the opposite direction.

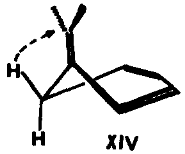
The ortho- and para-tautomers of toluene (III and IV) were reported as unstable, rearranging to toluene already at room temperature or slight warming respectively. The meta-tautomer (IIa) and its higher homologs IIb and IIc on heating without solvent remained unchanged until polymerization. Under no circumstance were any alkylbenzenes observed. Irradiation of homofulvenes IIb and IIc in pentane with a light source emitting 254 nm, however, rapidly produced cumene (XIIIb) and cymene (XIIIc) in 60 and 20 % yield respectively.



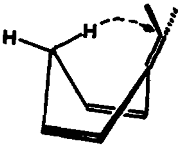
b. R = CH_3; R' = H

c. R = R' = CH_3

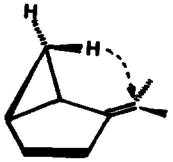
The facile aromatization of the ortho- (III) and para-tautomers (IV) of toluene can be rationalized as thermally allowed (17) antarafacial [1,7]- (XIV) and suprafacial [1,5]- (XV) sigmatropic shifts. If the aromatization of the homofulvenes is a concerted homosigmatropic reaction (18), it must go suprafacially for steric reasons (XVI). As such it may be considered as a 1,5- or a 1,7-shift. Since it was preferred photochemically the longer electron path seems to be favored. It is of interest that the previously described homofulvenes were the result of irradiation (6,8 and 7) and thus could not have been aromatized faster



XIV



XV



XVI

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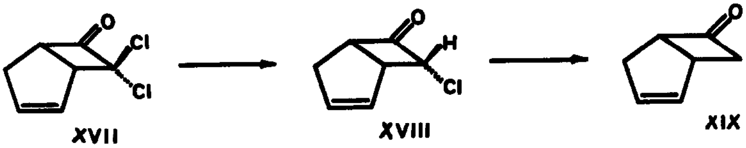
* see footnote ** on the second page of this paper.

than formed. We suggest that an explanation lies in that these homofulvenes do not have endo-hydrogens, capable of migrating by an aromatization mechanism*.

The production of homofulvene (IIa) was made possible only because a new and convenient synthesis of the elusive (2a,b) bicyclo(3.2.0)hept-2-en-6-one (XIX) was developed: The reduction of the dichloro-cycloadduct from dichloroketene and cyclopentadiene (XVII)(19) with zinc in acetic acid or acetic acid-H^2 and pyridine led to an overall yield of 56 % (based on dichloroacetylchloride) of XIX or its 7,7-dideutero derivative. This substitute for the inefficient cycloaddition with ketene itself was also applied to other systems. A milder reduction of XVII yielded the corresponding endo-chloroketone (XVIII).



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* Dr.Hogeveen informed us in a private communication that the cyclopropane proton in their compound IV (7) showed a δ-value of 0.7 ppm (not as reported 0.07); according to our comparisons this is not in contradiction with an exo-position. Incidentally, the UV absorption maximum of their compound IV lies at 255 nm (not as reported at 225 nm), a value in good agreement with our generalization. We thank Dr. Hogeveen for his kind correspondence.

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