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PHOTOCHEMICAL ADDITION OF BUTADIENE TO ITS HOMOLOGS

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The photochemical dimerisation of butadiene (1, 2), isoprene (2, 3, 4, 5) and piperylene (2) in the presence of a sensitizer lead to the formation of cyclobutane and cyclohexene derivatives and, in the case of isoprene, of cyclooctadiene derivatives too; the dimerisation of 2,3-dimethylbutadiene has been mentioned briefly (2) without separation and characterization of the reaction products.

During our research on the synthesis of non-conjugated dienes we started the study of the photosensitised reaction of butadiene with other conjugated dienes.

In this communication we describe the identification of some of the products obtained in the reaction of butadiene with isoprene, piperylene and 2,3-dimethylbutadiene carried out by irradiation with high pressure mercury lamps in the presence of acetophenone as photosensitizer.

In Table 1 the reaction conditions, the products identified up to now and their content with respect to the total amount of C_8-C_{12} hydrocarbons are reported.

Analysis and physical constants of the compounds, among which only III was already described in the literature (6) are reported in Table 2. The results of NMR analysis of products I, II, IV, V and VI, as well as of trans-1,2-divinylcyclobutane are reported in Table 3.

The IR spectrum of I shows the presence of vinyl (1080, 1632, 995 and 910 cm^{-1}) and methyl (1370 cm^{-1}) groups. The vinyl/methyl group ratio, evaluated using the optical densities of the bands at 910 and 1370

cm^{-1} and the coefficients 2.10^4 $mol^{-1}.ml.cm$ for the methyl group and 12.10^4 $mol^{-1}.ml.cm$ for the vinyl group. (7) is about 2:1.

The NMR spectrum of I shows a symmetrical band at 1.05 p.p.m. from TMS, a complex group having many peaks between 1.2 and 2.2 p.p.m., a group of peaks between 2.5 and 3.0 p.p.m. and two groups of peaks in the olefinic proton region. The relative intensities are nicely close to 3:4:1:6.

By comparing the observed chemical shifts with the chemical shifts of similar compounds (2), the observed peaks have been respectively attributed to methyl protons, ring methylene protons, allylic ring protons, and olefinic protons of vinyl type. On the basis of IR and NMR spectra the formula of methyl-divinyl-cyclobutane has been attributed to I.

The IR spectra of II shows the presence of vinyl (3080, 1635, 992, 910 cm^{-1}), vinylidene (3080, 1647, 885 cm^{-1}) and methyl (1370 cm^{-1}) groups. The vinyl/methyl group ratio, evaluated as in the case of I, is about 1:1.

The NMR spectrum of II shows a symmetrical peak at 1.67 p.p.m., a complex group of peaks between 1.2 and 2.3 p.p.m., a complex group between 2.3 and 3.0 p.p.m. and two complex groups of peaks in the olefinic proton region. The relative intensities of these groups of peaks are close to 3:4:2:5.

By comparing the chemical shifts of II with the chemical shifts of I the observed peaks have been respectively attributed to methyl protons, ring methylene protons, allylic ring protons and olefinic protons. We have therefore attributed to II the structure of vinyl-isopropenyl-cyclobutane.

III is identical with cis, cis-1-methyl-cyclooctadiene-1,5, obtainable by thermal (6) or catalytic (8) addition of butadiene to isoprene. In order to determine the relative position of the ring substituents I and II have been heated to about 140°C. I and II yield III and cyclohexene derivatives. This fact practically excluded 1,3 bisubstituted cyclobutane structures (2).

On the basis of the above data we have attributed to I the formula of 1-methyl-1,2-divinyl-cyclobutane and to II the formula of 1-vinyl-2-isopropenyl-cyclobutane. We have not established whether the two alkenyl groups in I and II are in cis or in trans to one another. However, the fact that by heating I and II both cyclohexene derivatives and III are formed might be taken as an indication of the presence of the trans structure (2).

Compounds IV and V were isolated in the form of a hardly separable mixture, whose IR spectrum shows the presence of vinyl groups (3078, 1633, 990, 910 cm^{-1}) of trans (962 cm^{-1}) and cis (710 cm^{-1}) double bonds and of methyl groups (1370 cm^{-1}).

Among the ozonization products trans-1,2-cyclobutane dicarboxylic acid has been isolated (m.p. 129°C, lit.(9) 131°C, no m.p. depression in mixture with an authentic sample).

The NMR spectrum of the mixture of IV and V shows a group of four peaks near 1.6 p.p.m. due to cis and trans methyl protons coupled with olefinic protons, a complex group of peaks between 1.5 and 2.2 due to ring methylene protons, a complex group of peaks between 1.4 and 1.9 p.p.m. due to ring allylic protons and a complex group of peaks in the olefinic proton region. The intensity ratios are 3:4:2:5.

According to the above data and considering the MW, the analysis and the mode of formation, we have attributed to both IV and V the structure of trans-1-vinyl-2-propenyl cyclobutane, IV and V differing only for the steric configuration of the internal double bond of the propenyl group.

The IR spectrum of VI shows the presence of vinyl (1640, 990, 910 cm^{-1}), vinylidene (885 cm^{-1}) and methyl (1370 cm^{-1}) groups. The methyl/vinyl group ratio, evaluated as in the case of I and II, is about 2:1.

The NMR spectrum of VI shows two peaks at 1.12 p.p.m. and

1.70 p.p.m. due to methyl protons of different type, a group of peaks between 1.4 and 2.2 p.p.m. due to ring methylene protons, a group of peaks between 2.4 and 3.0 due to allylic ring protons and a group of peaks in the olefinic proton region. The intensity ratios are 3:3:4:1:5.

By heating VI to 140°C, VII (see below) and cyclohexene derivatives are formed. As in the case of I and II, this fact has been taken as an indication that the two alkenyl groups in VI are in 1 and 2 position. On this basis, and taking into account the mode of formation, we have attributed to VI the formula of 1-vinyl-2-methyl-2-isopropenyl cyclobutane. We have not established whether the two alkenyl groups in VI are in cis or trans to one another. However, the fairly high stability of VI and the fact that on heating it rearranges to cyclohexene derivatives besides VII may show (2) that the two alkenyl groups are in trans to one another.

Beside VI, the photochemical addition of butadiene to dimethylbutadiene gives a product (15% wt of the total reaction products), that has been found by v.p.c. of the reaction mixture kept at the reaction temperature, but is unstable even at room temperature and rearranges slowly to a new hydrocarbon VII.

The IR spectrum of VII shows the bands at 3010, 1655 and 715 cm^{-1}, due to the C-H and C=C stretching and to the cis out-of-plane deformation respectively. A very weak band due to the C=C stretching of a tetrasubstituted double bond can be noticed at 1700 cm^{-1}. The presence of methyl groups and the cis,cis-cyclooctadiene-1,5 structure are shown by the bands at 1375 and 1490 cm^{-1} respectively. On this basis, we have attributed to VII the structure of 1,2-dimethyl-cis,cis-cyclooctadiene-1,5. Its unstable precursor might be the cis isomer of VI.

The photochemical addition of butadiene to isoprene and piperylene indicates that the reaction between two vinyl groups is slower than that between a vinyl and vinylidene group and faster than that between a vinyl and an internal double bond. These results are in agreement with those obtained by Hammond (2) in the photochemical dimerisation of isoprene and piperylene.

The photoaddition of butadiene to dimethylbutadiene appears to be strongly favoured in comparison to the dimerisation of the two dienes. This fact shows that, contrary to what has been observed in the dimerisation of isoprene, the addition of a vinylidene double bond to a vinyl double bond is favoured with respect to the reaction between two vinylidene double bonds.

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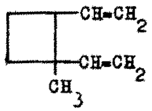
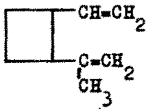
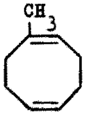
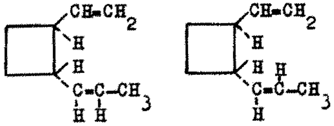
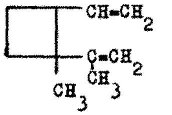
TABLE 1

Photochemical Addition of Butadiene to its Homologs

T= -10°C UV radiation source= 3 Philips HPK 125 W high pressure mercury lamps; sensitizer : acetophenone

C_4H_9 mole	Butadiene Homolog Type	Butadiene Homolog Mole	$PhCOCH_3$ g	Reaction time hrs	Conversion %	Identified Reaction Products (and their wt content in Dimer Mixture by v.p.c.)
3.4	isoprene	3.4	50	150	31	 I (36%)  II (17%)  III (1.5%)
4.6	cis+trans piperylene	4.7	74	190	18	 IV+V (44%)
2.0	dimethyl butadiene	2.3	45	190	37	 VI (58%)  VII (15%) a)

a) Product VII is present only in traces in the reaction mixture; it forms from an unstable precursor by heating.

TABLE 2

Analysis and Physical Constants of Compounds I -VII

Compounds	Analysis				MW[a)]	B.p.(°C/mmHg)	n_D^{20}
	Calc.		Found				
	C	H	C	H			
I	88.45	11.55	88.50	11.50	122	38/24	1.4511
II	88.45	11.55	88.47	11.43	122	40/24	1.4538
III	88.45	11.55	88.49	11.40	122	56.5–57/15	1.4909
IV+V	88.45	11.55	88.51	11.48	122	40/18	1.4559[b)]
VI	88.16	11.84	88.21	11.80	136	47/17	1.4597
VII	88.16	11.84	88.23	11.78	136	73/16	1.4941

a) Determined by mass spectrography.

b) Determined on a nearly equimolecular mixture of IV and V.

TABLE 3

NMR Analysis of Compounds I, II, IV, V and VI

Compound	Methyl Protons		Ring Methylene Protons		Allylic Ring Protons		Olefinic Protons	
	p.p.m.	Relative intensity	p.p.m.	Relative intensity	p.p.m.	Relative intensity	p.p.m.	Relative intensity
t-DVCB*	—	—	1.5–2.2	4	2.4–3.0	2	4.5–6.3	6
I	1.05	3	1.2–2.2	4	2.5–3.0	1	4.5–6.3	6
II	1.67	3	1.2–2.2	4	2.3–3.0	2	4.5–6.3	5
IV+V	1.6	3	1.5–2.2	4	1.4–1.9	2	4.5–6.3	5
VI	1.12	3	1.4–2.2	4	2.4–3.0	1	4.5–6.3	5
	1.70	3						

* trans-1,2-Divinylcyclobutane