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PHOTOCHEMICAL ADDITION OF BUTADIENE TO CYCLOPENTADIENE

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Some compounds derived from the sensitized photochemical addition of butadiene to its homologues have been described in a previous communication (1).

In the course of the synthesis of non-conjugated dienes, the study of the sensitized photochemical addition of butadiene to cyclopentadiene was subsequently undertaken.

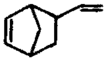
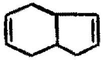
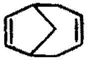
In this communication we describe the mixed addition products obtained from such reaction, using benzophenone as sensitiser, and a product (V) that can be obtained from one of them by thermal re-arrangement. Table 1 reports the reaction conditions, the products identified, their percentage in the total mixture of dimers and physical constants of I, II, III, IV and V, among which I, IV and V have already been described in the literature (2, 6).

All the products I-V have a M.W. of 120 as determined by mass spectrography. The I.R. spectrum of product I is identical with that of a pure sample of 5-vinyl-2-norbornene, prepared by thermal addition of butadiene to cyclopentadiene (2). Moreover the refractive index of I is identical with that already known for vinylnorbornene (2).

The I.R. spectrum of compound II shows the presence of vinyl groups (absorption bands with maxima at 3042, 1635, 992 and 908 cm^{-1}) and of cis double bonds in a 5-membered ring (absorption bands with maxima at 3078, 1605, 725, and 703 cm^{-1}). The N.M.R.

TABLE 1

Photochemical Addition of Butadiene to Cyclopentadiene a)

Reaction Products		Wt. % (by v.p.c.)	B.P. °C/mm.Hg this paper	 literature	n_D^{20} this paper	 literature
	(I)	20	44.5–45/22	67/66 (2)	1.4809	1.4808 (2)
 $CH=CH_2$	(II)	6.5	39/15	-	1.4812	-
 $CH=CH_2$	(III)	19.5	39.5–40/16	-	1.4839	-
	(IV)	1.5	50/16	84–84.2/66 (2)	1.4978	1.4979 (2)
	(V)	(b)	53/16	-	1.5096	1.5045 (6)
butadiene dimers		26.5	-	-	-	-
cyclopentadiene dimers		26	-	-	-	-

a) Reaction conditions: butadiene 3.15 moles, cyclopentadiene 3.15 moles, benzophenone 40 g.; T= -15°C; UV radiation source: 3 Philips HPK 125 W high pressure mercury lamps; reaction time: 200 hrs.; butadiene + cyclopentadiene conversion: 32 % by wt.

b) It is not a primary reaction product; it is obtainable from III by thermal isomerization.

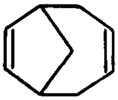
spectrum of II at 100 Mc shows a multiplet around 1.5 ppm with respect to TMS, a complex group of absorptions between 2.04 and 2.86 ppm, a multiplet centered at 3.1 ppm and an unresolved peak at about 3.3 ppm. The presence is also observed of a group of bands between 4.62 and 4.92 ppm, characteristic of terminal vinyl protons and of another group between 5.48 and 5.9 ppm, characteristic of ethylenic protons on the ring and of nonterminal vinyl protons. The observed absorptions and their relative intensities are in good agreement with the formula foreseen for product II resulting from the reaction between a butadiene double bond and one of the cyclopentadiene double bonds.

The I.R. spectrum of III reveals the presence of vinyl groups (absorption bands with maxima at 3042, 1635, 992 and 906 cm^{-1}) and of cis double bonds in a 5-membered ring (absorption bands with maxima at 3070, 1600 and 735 cm^{-1}). The N.M.R. spectrum of III, registered by a 100 Mc/sec apparatus shows a complex group of peaks between 1.62 and 2.1 ppm with respect to TMS, a group of peaks between 2.28 and 3.06 ppm, a group of three peaks between 4.62 and 4.96 ppm, a peak at 5.6 ppm and a multiplet centered at 5.91 ppm. The relative intensities are in the order 3:4:2:2:1. On the basis of the observed positions and the accomplished decouplings, the bands have been attributed, in the order, to cyclic CH_2 and CH, to cyclic allylic CH_2 and CH, to an olefinic CH_2 of vinyl type, to two olefinic CH and to a vinyl CH. On the basis of the I.R. and N.M.R. spectra, the formula of vinylbicyclo-[3,2,0] heptene was attributed to both products II and III; an endo-exo and/or a position (6 or 7) isomerism of the vinyl with respect to the ring double bond might explain the differences between the two products. However, products II and III by complete hydrogenation to ethyl-[3,2,0] bicycloheptane yield two different compounds; therefore it is possible to exclude that a simple isomerism of position exists, as well as that both II and III have the same endo or exo position for the vinyl group. The only possible differences between II and III are therefore a simple endo-exo isomerism or an endo-exo isomerism combined with a position isomerism.

Products II and III show a quite different stability and behaviour on heating. Compound II is stable up to about 150°C; at higher temperatures (170°C), it undergoes a re-arrangement yielding a product, which, by gas chromatography and I.R. spectrography, was recognized to be 5-vinyl-2-norbornene (I) containing a small amount of product IV (see below), which is almost certainly due to a thermal re-arrangement of I (2). On the other hand, compound III is unstable already at temperatures below 100°C and isomerizes from about 80°C yielding an isomer (V).

The I.R. spectrum of V reveals the presence of bands that can be attributed to double bonds present in a ring, whereas no vinyl bands are present. The N.M.R. spectrum of V at 100 Mc/sec shows a peak at 1.48 ppm with respect to TMS, a triplet at 2.06 ppm and bands at 2.19 ppm, 2.75 ppm, 5.15 ppm, 5.53 ppm. The relative intensities are in the order 1:1:4:2:2:2.

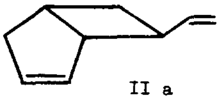
On the basis of the positions observed and decouplings performed, we can propose for V the structure of bicyclo[4,2,1]-nonadiene-3,7:



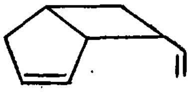
V

This structure is proved by hydrogenation with Pd catalyst at room temperature. In fact product V absorbs 2 moles of hydrogen yielding compound VI, which melts at 95°-96°; no decrease in m.p. is observed by mixing this compound with an authentic sample of bicyclo[4,2,1]-nonane (for bicyclo[4,2,1]-nonane, the following m.p. are reported in the literature: 95-96°C (3); 94-95°C (4); 102-103°C (5)). The N.M.R. spectrum of VI is identical with that of an authentic sample of bicyclo[4,2,1]-nonane (3) and also coincides with the data reported in the literature (4). Product V, although obtained by another method, has been briefly described in a recent patent (6).

The data available did not enable us to attribute definite structures to products II and III. However, by considering that hydrogenation leads to two products, one containing the ethyl group with endo configuration, and the other with exo configuration, and on the basis of their stability and behaviour on heating, it is possible to propose the structure of endo-7-vinyl-bicyclo[3,2,0]-heptene-2 (III a) for product III, and that of exo-7-vinyl-bicyclo[3,2,0]-heptene-2 (II a) for product II :



II a



III a

Structure III a in fact might explain the easy isomerization of the product to bicyclo[4,2,1]-nonadiene-3,7 by a Cope re-arrangement (7); on the other hand, the formation of 5-vinyl-2-norbornene from II a is theoretically possible through a thermal, radical-type isomerization.

The I.R. spectrum of IV is identical with that of a pure sample of 4,7,8,9-tetrahydroindene (bicyclo[4,3,0]-nonadiene-3,7) prepared by thermal addition of butadiene to cyclopentadiene; moreover, it coincides with the data reported in the literature (2). An analogous identity is observed in the N.M.R. spectra of the two samples. Also the refractive index of IV coincides with that of a pure sample of tetrahydroindene.

The results described in this paper show that cyclopentadiene, under the conditions adopted by us, nearly presents the same tendency to give rise to 1,2 and 1,4 photochemical additions. As regards butadiene, the 1,2 addition prevails, as already observed (1) in the photochemical addition of butadiene to its homologues.

The photochemical addition of butadiene to cyclopentadiene is a relatively simple method for the obtainment of compounds containing the skeleton of bicyclo[4,2,1]-nonane.

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