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THE PHOTO-FRITSCH-BUTTENBERG-WIECHELL REARRANGEMENT

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The dehydrohalogenation of olefins, bearing hydrogen and halogen on the same carbon, to acetylenes under basic conditions has been known for a long time as the Fritsch-Buttenberg-Wiechell rearrangement[1,2,3] and has been studied in detail[4,5,6]. Irradiation of 1,1-di/p-methoxyphenyl/-2-bromoethylene with sunlight in acetic acid resulted in the formation of the dimeric product 1,1,4,4-tetrasubstituted butadiene[7].

We now report the results of irradiation of 1,1-diphenyl-2-halogensubstituted ethylenes /1/ in ether. A 15-hr irradiation of /1/ /0.023 M/ at 2537 Å in ether resulted in a crude reaction mixture of three compounds, i.e. diphenylacetylene /2/, 1,1-diphenylethylene /3/ and 1,1,4,4-tetraphenylbutadiene /4/, which could be separated by preparative t.l.c. and v.p.c. The products were identified by their n.m.r., mass spectral and i.r. data and their distribution is presented in Table 1 /based on isolated products/. Furthermore, 1,1-diphenyl-2-fluoroethylene has been found to undergo rearrangement to cis- and trans-fluorostilbene upon irradiation in ether.

In order to establish the mechanism of photorearrangement to diphenylacetylene, we found it reasonable to irradiate some trans- and cis-halogen-substituted stilbenes /5 and 6/. Irradiation under the above mentioned conditions resulted in a crude reaction mixture of up to four products, i.e. diphenylacetylene /2/, transstilbene /7/, cis-stilbene /8/ and phenanthrene /9/ which could be separated by preparative t.l.c. and v.p.c. However, irradiation of cis- and trans-fluorostilbenes under the above conditions resulted in photoisomerisation and no evidence for photodehydrohalogenation was found.

The available evidence suggests that these photorearrangements of 1,1-diphenylethylenes could occur via the intermediately formed halogen-substituted stilbenes, followed by photodehydrohalogenation to diphenylacetylenes.

Further study of the mechanism of the new photorearrangement is in progress.

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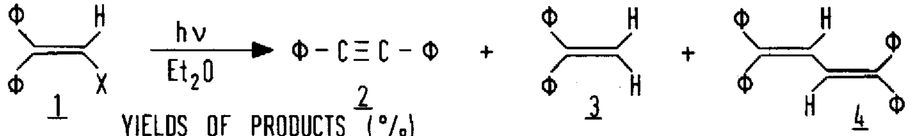
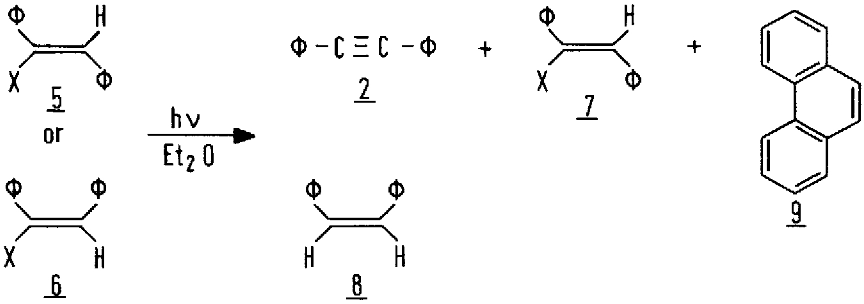


YIELDS OF PRODUCTS (°/o)

X	2	3	4
Cl	25	28	10
Br	23	34	10
I	19	51	6



COMPOUND		2	7	8	9
X = Cl	5	63	16	9	-
	6	57	18	10	-
X = Br	5	30	13	18	10
	6	25	14	19	8