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THE PHOTOCHEMICAL ANTI-MARKOVNIKOV ADDITION OF METHANOL TO AN ACYCLIC OLEFIN

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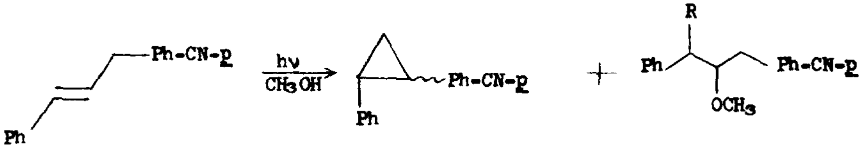
Observations of the photochemical polar addition of methanol to olefins have heretofore been restricted to cases where the double bond is contained within a ring[1] or (in a few examples) where an acyclic double bond is conjugated to a highly polar carbonyl group.[2] We wish to report the anti-Markovnikov photochemical addition of methanol to an acyclic olefin not conjugated with any highly polar group, an addition, therefore, quite different from those previously reported.

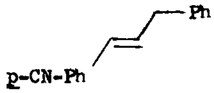
Irradiation[3] of a 2.16×10^{-3} *M* methanol solution of *trans*-3-(*p*-cyanophenyl)-1-phenylpropene[4] (1) for 320 min provided in addition to 40% of a mixture of *cis*- and *trans*-1, 13% of a mixture of *cis*- and *trans*-1-(*p*-cyanophenyl)-2-phenylcyclopropane (2), and 18% of 1-(*p*-cyanophenyl)-2-methoxy-3-phenylpropane (3). Unidentified higher molecular weight materials and very small amounts (4%) of photochemical products of 2 account for the remaining material.



1

2

3, R = H
3d, R = D



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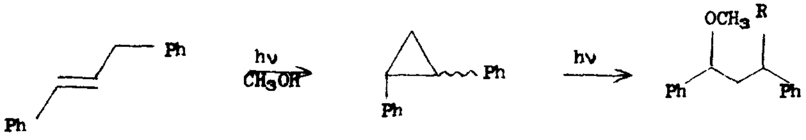
The structure of 3 was established by a satisfactory elemental analysis and spectral data: ir (neat) 2230, 1607, 1093, and 694 cm^{-1}; nmr ($CDCl_3$) δ 2.69-2.87 (m,4), 3.24 (s,3), 3.36-3.64 (m,1), 7.14-7.66 (m,9); mass spectrum (70 ev) m/e 251 (M^+, < 2%), 160 (85), 135 (100), 116 (18), 103 (18), 91 (24).

Irradiation[6] of 1(1.37×10^{-2} M) in the presence of xanthone (1.37×10^{-2} M) led to efficient cis-trans isomerization and little if any of ether 3. No reaction occurred when a methanol solution of 1 was refluxed in the dark. Thus the reaction is a photochemical one most likely proceeding via the singlet state.

Irradiation of either trans-1-(p-cyanophenyl)-3-phenylpropene (4)or 2 in methanol likewise gives ether 3, but in much lower yields than is the case with 1. However, in both cases the addition occurs via prior formation of 1: irradiations of 2 and 4 carried out in CH_3OD gave product (3-d)with essentially all (mass spectral analysis) of the deuterium at the benzylic as opposed to the p-cyanobenzylic position. Moreover, it was found on further examination that 4 on irradiation very rapidly gives 2, which in turn forms 1 more slowly.

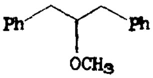
Photolysis of 0.017 M 1,3-diphenylpropene (5) for 2 hrs in methanol led to a 24% yield of an ether 6. However, irradiations carried out in CH_3OD gave 6-d with an nmr spectrum still showing a triplet for the C-1 hydrogen as in 6 but with only three instead of four hydrogens in the δ 1.77-2.76 region assigned to the C-2 and C-3 protons. Thus, 6 must arise via prior isomerization of 5 to 1,2-diphenylcyclopropane (7)[7a,b] followed by photoaddition of methanol to the latter.[8] Indeed, when the irradiation of 5 was followed closely by gas chromatography, a rapid formation of 7 followed by a slower buildup of 6 was observed. No 8 could be detected among the products.



5

7

6, R = H
6-d, R = D



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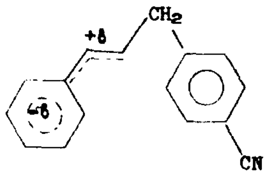
The direction of addition to 1 would seem to imply a species polarized as in 9 was involved. However, the unreactivity of excited 4 and 5 towards methanol addition argues against this. Furthermore, we have found that the singlet of 1 rearranges to cyclopropanes 2 at a faster rate than does the singlet of 5 rearrange to 7 (in cyclohexane),[9] so that the difference between 1 and 5 with respect to methanol addition does not appear to arise simply from a greater rate of cyclopropane formation from 5.

Apparently the p-CN group in 1 causes an excited state interaction to occur which is either not present or is unimportant in 4 and 5. Structure 10 shows such an interaction, involving electron transfer from the vinyl to the p-cyanophenyl group, which could account for the mode of addition. We are in the process of investigating the methanol addition to other 1,3-diarylpropenes.



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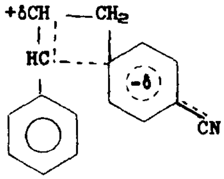

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2. S. F. Nelsen and P. J. Hintz, J. Amer. Chem. Soc., 91, 6190 (1969), and references therein.
3. Samples were irradiated under nitrogen with a Vycor-filtered Hanovia 450 watt mercury arc. Progress of the reactions was monitored closely by gas chromatography.
4. Prepared from trans-3-(p-chlorophenyl)-1-phenylpropene[5] using cuprous cyanide in N-methylpyrrolidone; m.p. 46.5-47.5°.
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