

NON-STEREOSPECIFIC 1, 2-PHOTOCYCLOADDITION OF METHYL ACRYLATE  
AND METHYL METHACRYLATE TO BENZENE

R. J. Atkins and G. I. Fray \*

School of Chemistry, The University, Bristol, BS8 1TS

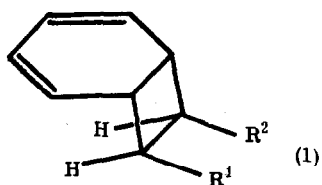
A. Gilbert \* and M. W. bin Samsudin

Department of Chemistry, The University, Reading, RG6 2AD.

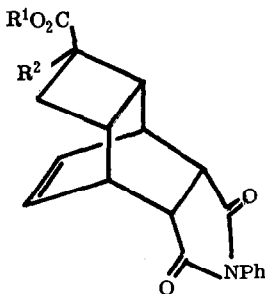
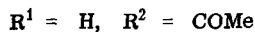
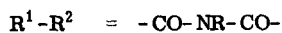
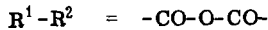
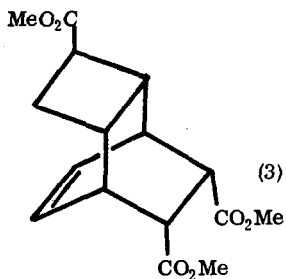
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Electron-deficient ethylenes such as maleic anhydride, maleimides, acrylonitrile, and methyl vinyl ketone undergo exclusive 1, 2-photocycloaddition to benzene.<sup>1</sup> In all these cases the addition reaction is also stereospecific, giving rise to exo adducts (1),<sup>2,3</sup> and it is significant that this stereochemistry is matched by the initial orientation of the addends in the ground state (as indicated by n. m. r. spectroscopy<sup>4</sup>). From these results it would be expected that methyl acrylate and methyl methacrylate would photoadd to benzene in a similar fashion, and that in the products the methoxycarbonyl group would be exclusively exo to the cyclohexa-1, 3-diene moiety. We now report that although 1, 2-cycloadducts do result from the u. v. irradiation of these two systems, unexpectedly and contrary to all other known 1, 2-cycloadditions of ethylenes to benzene, a mixture of exo and endo products is formed in each case.

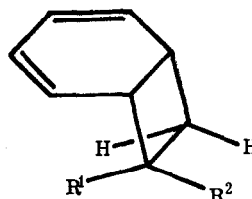
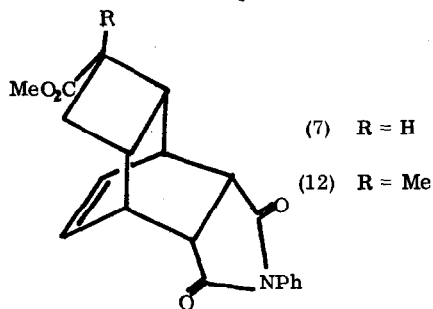
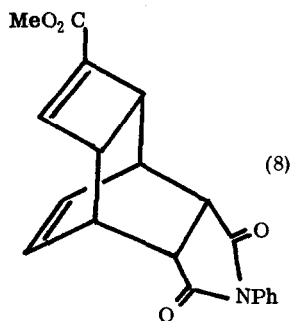
The 254 nm irradiation of an equivolume mixture of benzene and methyl acrylate led to the formation of five products in the approximate ratios 16:4:1:1:1, in order of increasing g. l. c. retention time (Carbowax 20M). Only the major product was an adduct of the starting materials ( $\bar{M}^+ = 164$  m. u.); the other components of the mixture appeared from molecular weight ( $\bar{M}^+ = 172$  m. u.) and spectroscopic properties to be the four possible cyclobutanes resulting from photodimerisation of the substituted ethylene. The 1:1 photoadduct showed  $\lambda_{\text{max}}$  (cyclohexane) 280 nm. ( $\epsilon = 2950$ ), underwent facile retro-addition in the mass spectrometer, and reacted readily and quantitatively with dienophiles to yield 1:1:1 adducts; these properties are indicative of the 1, 2-cycloadduct structure. The n. m. r. spectrum ( $\text{CDCl}_3$ ) of the adduct confirmed this assignment but displayed a split methyl resonance near 3.65 p. p. m., the intensities of the two



(1)

(2)  $R^1 = R^2 = H$ (6)  $R^1 = Me, R^2 = H$ (11)  $R^1 = Me, R^2 = Me$ 

(3)

(4)  $R^1 = H, R^2 = CO_2Me$ (5)  $R^1 = CO_2Me, R^2 = H$ (9)  $R^1 = Me, R^2 = CO_2Me$ (10)  $R^1 = CO_2Me, R^2 = Me$ (7)  $R = H$ (12)  $R = Me$ 

(8)

signals appearing in an approximate ratio of 2:1. This feature is considered to arise from the methoxycarbonyl protons in the exo and endo isomers (4) and (5) respectively, on the basis of the following observations. Firstly, addition of a europium shift reagent caused a larger movement of the more intense signal than of the less intense one, implying that the  $CO_2Me$  group in the minor isomer is less accessible to the reagent than that in the major isomer and hence that the former has the endo configuration. Secondly, the product reacted quantitatively with dienophiles, including N-phenylmaleimide. In the n. m. r. spectrum of the resulting 1:1:1 adduct, the ester methyl resonance was again split in a ratio of ca. 2:1, with the stronger signal at lower field than the weaker; the protons of the exo  $CO_2Me$  group would be expected to resonate at lower field than those of the endo group, which lies in the shielding region of the ethylenic bond.

Confirmation of this assignment was obtained from the n. m. r. spectra of authentic samples of the two stereoisomers. The exo isomer (6) was prepared by standard procedures from the known<sup>2(c)</sup> tri-ester (3), while the endo isomer (7) was obtained by site-selective and stereospecific catalytic hydrogenation of compound (8), which was prepared from the maleic anhydride adduct of methoxycarbonylcyclo-octatetraene.<sup>5</sup>

It might have been expected that the 1, 2-photocycloaddition of methyl methacrylate to benzene would be more stereoselective than that of methyl acrylate, because from previous work with the cis-but-2-ene - benzene system, in which the 1, 2-cycloadduct has been shown to form with the methyl groups stereospecifically endo,<sup>6</sup> it might be supposed that the non-ester methyl group of the methyl methacrylate residue would lie preferentially endo to the cyclohexa-1, 3-diene ring and hence promote further the degree of exo selectivity of the CO<sub>2</sub>Me group. Irradiation of an equivolume mixture of methyl methacrylate and benzene resulted in the formation of several products, of which one constituted >85% of the mixture and was a 1:1 adduct of the starting materials ( $M^+ = 178$  m. u.). This could be formulated as a 1, 2-cycloadduct from its ready quantitative reactions with dienophiles and its spectroscopic properties. The n. m. r. spectrum, however, again indicated the presence of two stereoisomers, (9) and (10), both methyl signals being split in ratios of ca. 2:1 (CO<sub>2</sub>Me) and 1:2 ( $-\overset{|}{C}-Me$ ) (in order of increasing field). From this and the similar splitting of the methyl signals in the spectrum of the N-phenylmaleimide adduct (mixture of (11) and (12)), it may be deduced that in the minor isomer the ester group is endo, while in the major isomer it is the  $-\overset{|}{C}-Me$  group which lies in the shielding zone of the ethylenic bond.

Thus, although the major isomer from both systems results from exo addition with respect to the ester group (cf. the systems in refs. 2 and 3), for the first time we have noted a lack of stereospecificity in 1, 2-photocycloadditions of ethylenes to benzene.<sup>7</sup> This may result either from two different modes of orientation of the addends in a loose ground-state complex,<sup>4</sup> or from the involvement of triplet intermediates (as has recently been observed in the photoaddition of dimethyl fumarate to phenanthrene<sup>8</sup>); these alternatives are currently under investigation.

### ACKNOWLEDGEMENT

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3. The 1, 2-photocycloadduct of benzene and methyl vinyl ketone was assigned exo stereochemistry on the basis of its conversion of its N-phenylmaleimide adduct into a product (2), identical with that derived from the known<sup>2(c)</sup> tri-ester (3) (R. J. Atkins, G. I. Fray, and A. Gilbert, unpublished observations).
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