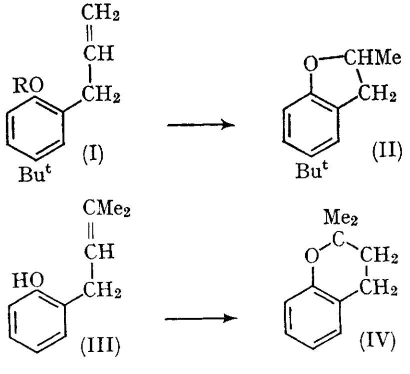
Photochemical Addition of Olefins

By W. M. HORSPOOL and P. L. PAUSON

(*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.*1)

THE appearance of two communications[1,2] describing the photochemically induced addition of alcohols to olefins prompts us to record here our parallel observations on the addition of phenols.

In continuation of our study of the photolysis of aryl formates[3] we examined this reaction in cyclohexene and observed that the products included aryl cyclohexyl ethers, albeit in low yield. Use of 2-methylpent-1-ene with *p*-t-butylphenyl formate gave an ether (9%), shown by its n.m.r. spectrum to be *p*-t-butylphenyl 1,1-dimethylbutyl ether, *p*-$Bu^t{\cdot}C_6H_4{\cdot}O{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}Me$. The addition therefore occurred in a Markovnikov direction, as now reported also for the addition of alcohols.[1,2] This suggested the free phenol as a possible addend, and indeed such addition, *e.g.*, of *p*-t-butylphenol to cyclohexene, was observed under the same conditions but in lower yield. More efficient addition (40—50% yields) occurred when we examined intramolecular addition in *o*-allylphenols or their formates. Markovnikov direction was again found, 2-allyl-4-t-butylphenol (I; R = H) or its formate (I; R = CHO) giving 2,3-dihydro-2-methyl-5-t-butylbenzofuran (II), whereas *o*-(3-methylbut-2-enyl)phenol (III) yielded 2,2-dimethylchroman (IV).



The available evidence does not permit a decision between a homolytic and a heterolytic mechanism. The former would account *inter alia* for the improved yields of adducts obtained from formate esters. Photolytic formation of aryloxy-radicals from phenols is known[4] and their addition *via* an intermediate complex could account for the observed direction. Alternatively a heterolytic mechanism could be invoked, possibly involving the highly acidic[5] first excited singlet state of the phenol. The formates are known to be efficiently converted[3] into the free phenols under the reaction conditions and the difference in yield could be an artefact, caused for example by the formate acting as a better photosensitizer. Further experimental evidence is being sought to differentiate between these alternatives.

(*Received, January* 11*th*, 1967; *Com.* 035.)

---

[1] P. J. Kropp, *J. Amer. Chem. Soc.*, 1966, **88**, 4091.

[2] J. A. Marshall and R. D. Carroll, *J. Amer. Chem. Soc.*, 1966, **88**, 4092.

[3] W. M. Horspool and P. L. Pauson, *J. Chem. Soc.*, 1965, 5162.

[4] See *e.g.*, E. J. Land, G. Porter, and E. Strachan, *Trans. Faraday Soc.*, 1961, **57**, 1885; H. I. Joshek and S. I. Miller, *J. Amer. Chem. Soc.*, 1966, **88**, 3273.

[5] See: E. L. Wehry and L. B. Rogers, *J. Amer. Chem. Soc.*, 1965, **87**, 4235, and references quoted there.