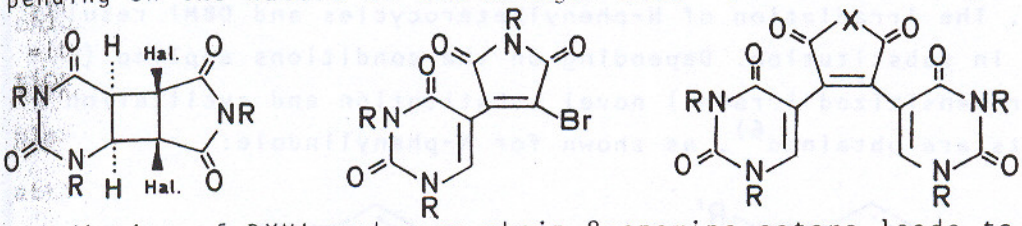
New Photoreactions of Dihalomaleimides

H. Wamhoff, H.J. Hupe, A.A. Nada, P. Sohár, G. Szilágyi, and K. Wald

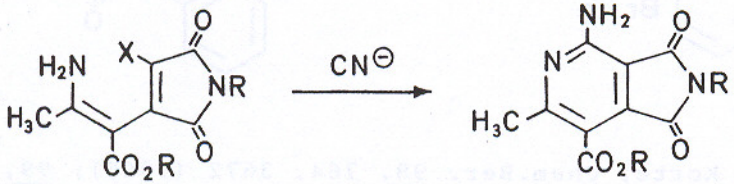
Institut für Organische Chemie und Biochemie der Universität Bonn
Gerhard-Domagk-Straße 1, D 5300-Bonn-1 (Bundesrepublik Deutschland)

Dihalomaleimides (DXMI) are known as photocyclophiles. The 2+2→ 4-cycloaddition of DXMI to olefinic double bonds has been repor= ted[1].

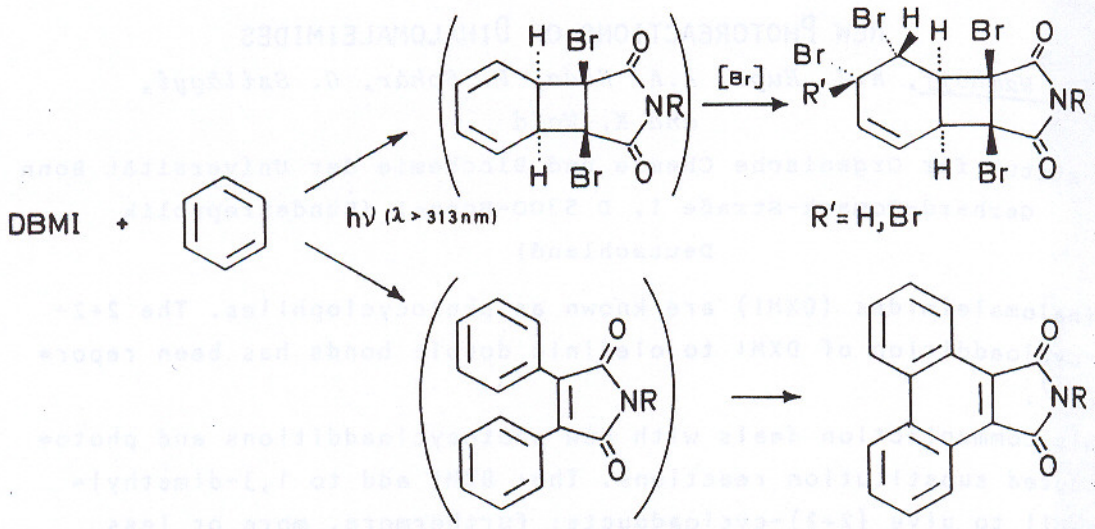
This communiaction deals with new photocycloadditions and photo= induced substitution reactions. Thus DXMI add to 1,3-dimethyl= uracil to give (2+2)-cycloadducts; furthermore, more or less amounts of 5-mono- and 5,5-disubstitution products are formed de= pending on the nature of the halogen atom[2]: X = O, NH, NR



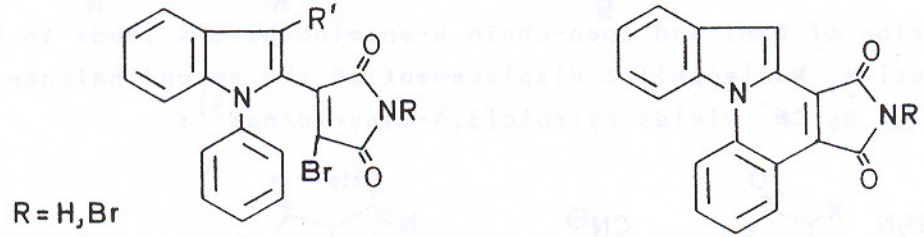
Irradiation of DXMI and open-chain ß-enamino esters leads to C_β-substitution. Nucleophilic displacement of the second halogen atom, e.g. by CN^- yields pyrrolo[3,4-c]pyridines[3]:



While UV-irradiation of DXMI and furan or thiophene gives without exception the fluorescing 2-mono- and 2,2-disubstitution pro= ducts[4], photoreaction with aromatic hydrocarbons, as e.g. phe= nanthrene, indene and naphthalene affords mainly *syn*- and *anti*-(2+2)-cycloadducts. Employing benzene it appears that the prima= ry 1:1-adduct is intercepted *in situ* by bromination[5]:



As a side reaction the phenanthra[9,10-c]pyrrole system arises through the photophenanthrenization of the intermediary diphe= nyl-MI. The irradiation of N-phenylheterocycles and DBMI results solely in substitution. Depending on the conditions applied (di= rect or sensitized irradn.) novel substitution and cyclization products are obtained[6], as shown for N-phenylindole:



BIBLIOGRAPHY:

1) H.D. Scharf, F. Korte, Chem.Ber. 98, 764, 3672 (1965); 99, 1299 (1966); Angew.Chem. 77, 452 (1965), Int.Ed. 4, 429 (1965).
2) G. Szilágyi, H. Wamhoff, P. Sohár, Chem.Ber. 107, 1265 (1974).
3) G. Szilágyi, H. Wamhoff, P. Sohár, Chem.Ber. 108, 464 (1975).
4) H. Wamhoff, H.J. Hupe, Tetrahedron Lett. 1978, 125.
5) H. Wamhoff, H.J. Hupe, Chem.Ber. 111, 2677 (1978).
6) K. Wald, A.A. Nada, H. Wamhoff, Chem.Ber. in preparation.

The support of this work by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknow= ledged.