ALKALOID SYNTHESES USING PHOTOCHEMICAL REACTIONS

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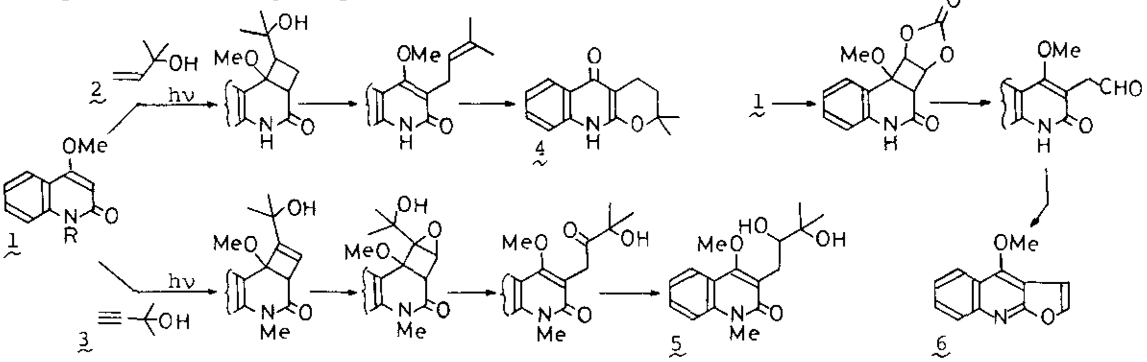
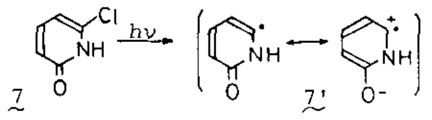
New alkaloid syntheses using two types of photochemical reactions (A and B) are described. A) Photochemical addition of 2-quinolones to alkenes or alkynes:

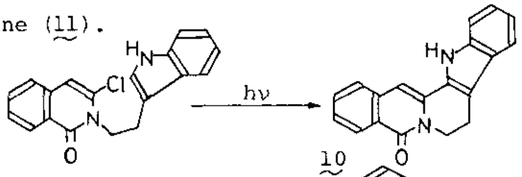
2-Quinolones react photochemically with alkenes or alkynes to give the head-to-tail adducts. Thus, the cycloadducts derived from 1 and unsaturated alcohols (2 and 3) were converted to khaplofoline[1] (4) and edulinine[2] (5) These reactions provide a new isoprenylation method for heteroaromatics. Dictamnine (6) can also be synthesized using vinylene carbonate as an olefin.

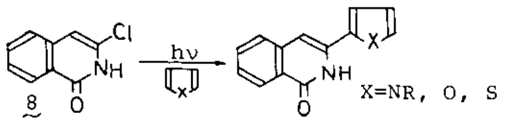


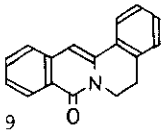
B) Arylation via the radical derived from 6-chloro-2-pyridone system:

The C-Cl bonds in 7 and 8 are readily cleaved photochemically and the resulted radicals (e.g. 7') attack the α-position of 5-membered heteroaromatics both inter- and intramolecularly. Utilizing this type of reactions, 8-oxoprotoberberine[3] (9) and norketoyobyrine (10) were synthesized. Extension of this method to quinazolone series led us find a new route to rutecarpine (11).





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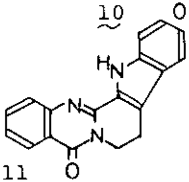
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1) T. Naito, Y. Momose, and C. Kaneko, Chem. Pharm. Bull., 30, 1531 (1982).
2) T. Naito and C. Kaneko, Chem. Pharm. Bull., 31, 366 (1983).
3) C. Kaneko, T. Naito, and C. Miwa, Chem. Pharm. Bull., 30, 752 (1982).