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A TRANSIENT FORMATION OF N-SUBSTITUTED ISOINDOLE BY MEANS OF PHOTOCHEMICAL INTRAMOLECULAR HYDROGEN ABSTRACTION

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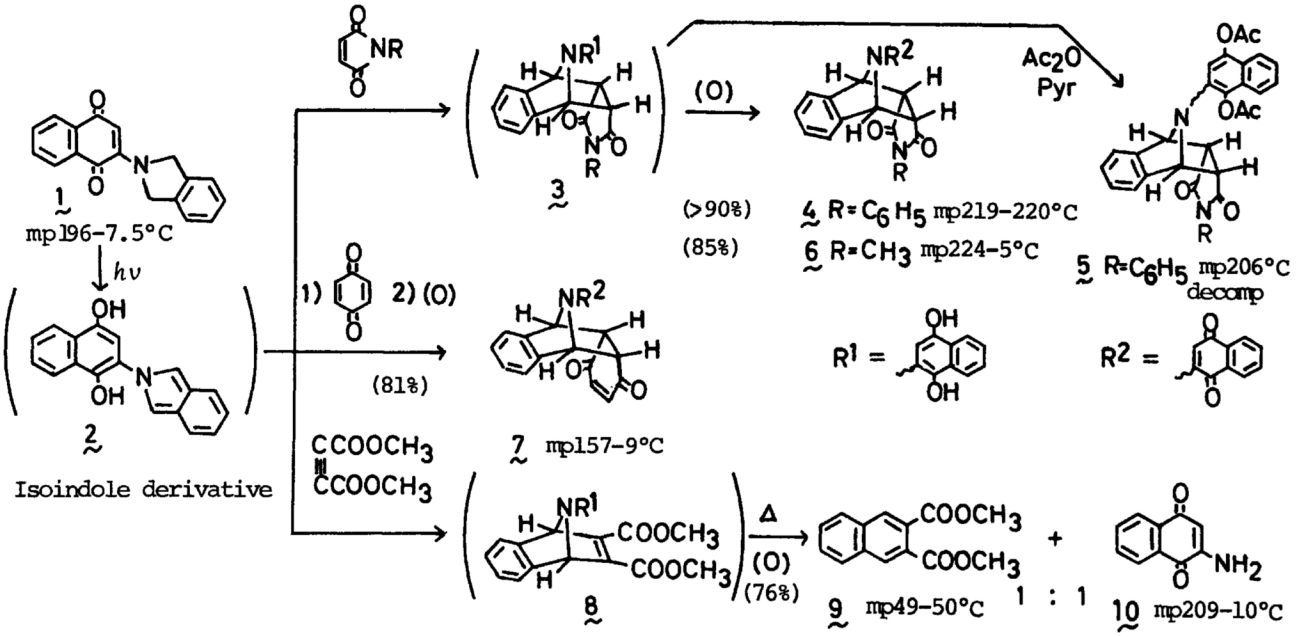
Isoindole derivative 2 was formed transiently by means of intramolecular hydrogen abstraction of 1. The intermediacy of 2 was confirmed by the good yields of Diels-Alder type adducts of it with dienophiles.

The chemistry of isoindoles is sparse, probably because of difficulties of their synthesis.[1 a-o)] Under drastic conditions, e.g. by means of pyrolysis or elimination in the catalysis of strong bases, a transient formation of isoindoles has been reported. We shall disclose here a facile synthesis of N-substituted isoindole 2. The effective formation of the isoindole was confirmative from good yields of coupling products with dienophiles (Scheme).

Upon irradiation of a deaerated benzene solution (50 ml) of 2-(1-isoindolinyl)-1,4-naphthoquinone 1 (275 mg, 1 mmol) and a suitable dienophile (1 mmol) in a Pyrex vessel using 300 W high pressure Hg lamp, a characteristic color (orange-red) of the reaction mixture faded to a light yellow after 1.5 h. In a few case massive adducts were crystallized out from the reacting mixture during irradiation. In a reaction under strictly deaerated conditions, we isolated intramolecular hydrogen abstraction product, i.e., 1,4-naphthohydroquinone derivative 3, as its diacetate 5. The structures of the adducts, 4, 5, 6, and 7, which were all *endo*-adducts, were compatible with their ^{1}H-NMR, IR, and Mass.spectra.[2)]

Since 1,4-naphthoquinonyl group can be removed or substituted by other groups rather easily,[3)] the present reactions will provide a synthetic method of 2,3-benzo-7-azabicyclo[2.2.1]heptane skeleton. In addition, photolysis of 1 in the presence of dimethyl acetylenedicarboxylate gave dimethyl naphthalene-2,3-dicarboxylate 9 in a fairly good yield. The reaction indicates that adduct 8 is thermally unstable in the presence of oxygen, and may present a good synthetic method of naphthalene-2,3-dicarboxylic acid derivatives.



References and Notes

1) a) J.C.Emmett, D.F.Veber, and W.Lwowski, J.Chem.Soc., Chem.Commun. 1965, 272; b) C.O.Bender, R.Bonnett, and R.G.Smith, J.Chem.Soc.,(C). 1970, 1251; c) R.Krecher and J.Seubert, Z.Naturforsch., 206, 75 (1965); d) D.F.Veber and W.Lwowski, J.Am.Chem.Soc., 86, 4152 (1964); e) J.Thesing, W. Schäfer, and D.Melchior, Justus Liebigs Ann.Chem.,671, 119 (1964); f) L.Mandell and W.A.Blanchard, J.Am.Chem.Soc., 79, 6198 (1957); g) G.Wittig and B.Reichel, Chem.Ber., 96, 2851 (1963); h) E. Wolthuis, D.V.Jagt, S.Mels, and A.De.Boer, J.Org.Chem., 30, 190 (1965); i) R.Bonnett and R.F.C. Brown, J.Chem.Soc., Chem.Commun, 1972, 393; j) R.Bonnett, R.F.C.Brown, and R.G.Smith, J.Chem.Soc., Perkin Trans.1, 1973, 1432; k) J.Bornstein, D.E.Remy, and J.E.Shields, J.Chem.Soc., Chem.Commun, 1972, 1149; l) G.M.Pristry and R.N.Warrener, Tetrahedron Lett., 1972, 4295; m) R.Krher and K.J. Herd, Angew.Chem.Int.Ed.Engl., 13, 739 (1974); n) L.J.Kricka and J.M.Vernon, J.Chem.Soc., Perkin Trans.1, 1972, 904; o) J.Bornstein and D.E.Remy, and J.E.Shields, Tetrahedron Lett., 1974, 4247.

2) Physical data of compounds. Compound 1; Prepared essentially by the method of Cameron and Scott from 1,4-naphthoquinone and dihydroisoindole (D.W.Cameron and P.M.Scott, J.Chem.Soc., 1964, 42): IR(KBr); 1677, 1625, 1595, and 1562 cm^{-1}. ^{1}H-NMR($CDCl_3$); δ=5.03(bs,4H), 5.84(s,1H), 7.35(s,4H), 7.67(m,2H), and 8.09(m,2H). MS m/e; 275(M^+). Adduct 4; IR(KBr); 1779, 1718, 1677, 1597, and 1575 cm^{-1}. ^{1}H-NMR($CDCl_3$); δ=4.06(dd,2H), 5.96(dd,2H), 6.11(s,1H), 6.45(dd,2H), 7.36(m,7H),7.71 (m,2H), and 8.05(m,2H). Diacetate 5; IR(KBr); 1780, 1765, 1715, 1370, 1260, and 1195 cm^{-1}. ^{1}H-NMR($CDCl_3$); δ=2.39(s,3H), 2.51(s,3H), 3.95(dd,2H), 5.59(dd,2H), 6.39(dd,2H), 6.88(s,1H), 7.25(m,7H), 7.40(m,2H), and 7.78(m,2H). Adduct 6; IR(KBr); 1779, 1705, 1679, 1645, 1597, and 1560 cm^{-1}. ^{1}H-NMR($CDCl_3$); δ=2.34(s,3H), 3.90(dd,2H), 5.90(dd,2H), 6.10(s,1H), 7.33(m,4H), 7.74(m,2H), and 8.08 (m,2H). MS m/e; 348(M^+). Adduct 7; IR(KBr); 1675, 1640, 1595, and 1562 cm^{-1}. ^{1}H-NMR($CDCl_3$); δ= 3.70(dd,2H), 5.91(dd,2H), 6.06(s,2H), 6.09(s,1H), 7.12(m,4H), 7.60(m,2H), and 7.95(m,2H). Product 9; IR(KBr); 3030, 2980, 1735, and 1725 cm^{-1}. ^{1}H-NMR($CDCl_3$); δ=3.92(s,6H), 7.56(m,2H), 7.83(m,2H), and 8.19(s,2H).

3) Under the catalysis of conc sulfuric acid or a base we can perform the reactions.

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