CHEMISTRY LETTERS, pp. 1551-1554, 1982.

PHOTOCHEMICAL REACTION OF 2-AROYL-3-ARYLNORBORNADIENES[1)]

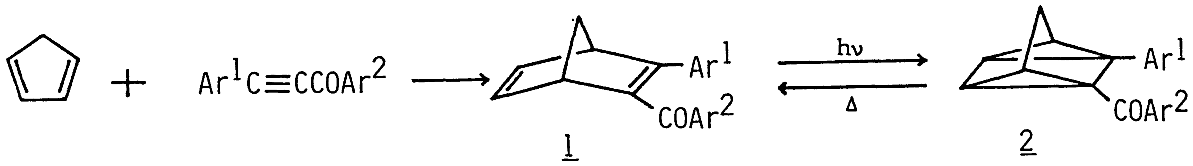
Takashi TODA, Eietsu HASEGAWA, Toshio MUKAI*,
Haruki TSURUTA+, Toshimitsu HAGIWARA+, and Toshio YOSHIDA+
Department of Chemistry and Photochemical Research Laboratory,
Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980
+Research Laboratory, Takasago Perfumary Co., Kamata 5-36-31, Tokyo 144

Irradiation of 2-aroyl-3-arylnorbornadiene derivatives (1) afforded the corresponding quadricyclane derivatives (2) in good chemical yields and with excellent efficiencies (Φ=0.3-0.6). The quadricyclanes were converted to the original norbornadienes by treatment with trifluoroacetic acid, silver perchlorate, and silica gel, or by heating.

Photochemical valence isomerization between norbornadiene and quadricyclane has been investigated extensively from the mechanistic point of view.[2)] In addition, much attention has been focussed recently on this isomerization as a solar energy conversion and storage system, because strain energy stored by quadricyclane can be released as heat on returning back to norbornadiene.[3)] However, norbornadiene does not absorb visible light of the sun, and also direct irradiation of norbornadiene does not give quadricyclane efficiently.[3,4)] To overcome these problems, the introduction of chromophore(s) into norbornadiene skeleton has been attempted,[5,6)] and/or efficient photosensitized isomerization to quadricyclane has been sought.[7)]

For the same purpose, we synthesized 2-aroyl-3-arylnorbornadiene (1), which contain a chalcone chromophore, and investigated photoreaction of these colored norbornadienes. Since the photoisomerization of norbornadiene to quadricyclane occurs from the triplet state,[2,8)] we expected that the aroyl group assists efficiently the intersystem crossing resulting in the transformation to the quadricyclane derivatives (2). Another aim to choose this system 1 is to gain mechanistic insight into (2+2) cyclization in which an internal charge-transfer between the aroyl group and the aryl group would promote the reaction. The valence isomerization causes loss and revival of the conjugation between the aroyl and aryl groups, and therefore, a new photochromic system could be provided.

Norbornadiene derivatives (1) were sysnthsized in good yields by Diels-Alder reaction of cyclopentadiene and dehydrochalcone derivatives[9)] with potassium t-butoxide in t-butylalcohol. Compounds (1a-1k) exhibit electronic spectra possessing absorption maxima shown in the Table and absorption extending over 400 nm region. The electronic spectra of these norbornadienes resemble those of cis-chalcone derivatives in shape.[9)] The nitrobenzoyl derivative 1f shows an end absorption at wave length region longer than 450 nm.



When the irradiation of norbornadiene derivatives (1a-1k) was carried out under the conditions in the Table, the corresponding quadricyclane derivatives (2a-2k) were obtained in good chemical yields (78-91%) and with good efficiencies (Φ=0.3-0.6) with exception of the nirto derivatives 1e and 1f. Introduction of p-methoxy group into the phenyl group (Ar^1) resulted in increase of the quantum yields of quadricyclane formation (2c, 2h, and 2j), whereas a nitro group either in the phenyl (Ar^1) or in the benzoyl group (Ar^2CO) decreased the quatum yields for the formation of 2e and 2f. As shown in the Table, most of the products 2 are colorless, but a week end absorption continues over 350 nm. Wavelength dependency of the photochemical conversion of 1a to 2a was studied using monochromic lights such as 254, 300, and 350 nm, respectively. Although no effect was observed (Φ=0.29-0.30) for the formation of 2a, the equilibrium between 1a and 2a depends on the wavelength of the light. The ratio of 1a to 2a was 1:1 at 254 nm, 2:3 at 300 nm, and 1:9 at 350 nm, respectively. Since this photochemical reaction shows isosbestic points in the electronic spectra and the quantum yield of 2a to 1a is 0.49 at 254 nm, the above equlibrium is apparently controlled by the ε values[10] of each compound at the corresponding light wavelength used for the isomerization. No solvent effect on the photochemical conversion of 1a to 2a was observed in several solvents. The yield of 2a in benzene, carbon tetrachloride, cyclohexane, and acetonitrile was 87, 87, 92, and 89%, respectively under irradiation with Rayonet RUL 3500 Å lamp (100 w) for 3 h. The photoreaction of 1a to 2a was relatively insensitive to the presence of oxygen. When oxygen saturated acetonitrile solution of 1a was irradiated with Rayonet RUL 3500 Å lamp (100 w) for 3 h, the yield of 2a was 87.4%.

Quadricyclane derivatives (2a, 2b, 2c, 2d, and 2g) could be converted readily to the corresponding norbornadiene derivatives (1a, 1b, 1c, 1d, and 1g) in quantitative yields by treatment with trifluoroacetic acid and silver perchloroate, and upon exposure on silica gel at room temperature. However, an analogous compound, 2-methoxycarbonyl-3-phenylquadricyclane[5] did not isomerize to the corresponding norbornadiene by the same treatment with silica gel, and the starting material was recovered quatitatively. Quadricyclanes such as 2a, 2b, 2c, 2d, and 2g upon heating in carbon tetrachloride returned back to the norbornadienes quatitatively, where the half lifetime of 2a and others was 30 min at 80 °C except for that of 2g with 1.5 h at 80 °C.

Table Photoisomerization of norbornadienes (1) to quadricyclanes (2)

Compound 1	Ar^1	Ar^2	λ_{max}^{MeCN}, nm of 1 (ε/mol^{-1}dm^{3}cm^{-1})	irrad. time[a] h	yields of 2[b] %	quantum yields[c] of 1 to 2	λ_{max}^{MeCN}, nm of 2 (ε/mol^{-1}dm^{3}cm^{-1})
a	C_6H_5	C_6H_5	251 (13000), 325 (4200)	3.5	90.0	0.30[d]	241 (14800)
b	p-Me C_6H_4	C_6H_5	250 (15800), 332 (4880)	3.5	90.0	0.44[d]	240 (15400)
c	p-MeO C_6H_4	C_6H_5	252 (15700), 348 (5250)	2.0	91.0	0.60[d]	239 (17000)
d	p-Cl C_6H_4	C_6H_5	251 (14400), 323 (4920)	4.0	91.0	0.36[d]	243 (18000)
e	p-NO_2 C_6H_4	C_6H_5	249 (12700), 286 (8770), 341 (10000)	5.0	42.0	0.09[d]	255 (14300)
f	p-MeO C_6H_4	p-NO_2 C_6H_4	264 (15300), 370 (4420)	5.0	43.0	0.07[e]	232 (15300)
g	C_6H_5	β-Napht.	221 (30300), 249 (25500), 284 (10500), 330 (5340)	4.0	78.0	0.32[d]	243 (32000), 284 (8300)
h	p-MeO C_6H_4	p-Cl C_6H_4	260 (18500), 353 (5500)	5.0	84.0	0.50[e]	243 (18100)
i	3,4-$(MeO)_2$ C_6H_3	p-Cl C_6H_4	260 (16400), 364 (5350)	4.0	80.0	0.41[e]	245 (17300)
j	p-MeO C_6H_4	p-Br C_6H_4	262 (18600), 353 (5600)	4.0	83.0	0.52[e]	245 (16800)
k	p-Me C_6H_4	p-Br C_6H_4	260 (17600), 337 (4870)	3.5	90.0	0.40[e]	250 (16600)

a) Acetonitrile solution of 1 was irradiated with Rayonet RUL 3500 Å (100 W) in Pyrex vessel.

b) Yields were determined by ^1H NMR spectral measurement. c) Light source was HITACHI MPF-4 Xenon lamp (150 W) and potassium trioxalatoferrate (III) was used as an actinometer.

d) Irradiating light was 350 ± 10 nm. e) Irradiating light was 366 ± 10 nm.

Thus, the photochemically induced isomerization of the norbornadienes 1 to the quadricyclanes 2 and the back reaction induced in dark provide a possible candidate not only for a solar energy conversion and storage system, but also for a novel photochromic system, to which we can readily approach synthetically.

Acknowledgment. The authors (T.T., E.H., and T.M.) gratefully acknowledge a support of this work by the grant-in-aid for "Research on Photosynthesis and Photoconversion of Solar Energy" sponsored by the Ministry of Education, Science and Culture.

References

1) Organic Photochemistry part 61. Part 60; T.Kumagai, K.Murakami, H.Hotta, and T.Mukai, Tetrahedron Lett., 1982. Submitted for publication.
2) N.J.Turro, W.R.Cherry, M.F.Mirbach, and M.J.Mirbach, J. Am. Chem. Soc., 99, 7388 (1977).
N.J.Turro, "Modern Molecular Photochemistry", the Benjamine-Cummings Publishing Co, Inc., Menlo Park, Calif. (1978) p. 247, and references therein.
3) G.Jones II, S.-H.Chiang, and P.H.Xuan, J.Photochem., 10, 1 (1979).
4) W.Dauben and R.L.Cargill, Tetrahedron, 15, 197 (1961). C.F.Wilcox, S.Winstein, and W.G.McMillar, J. Am. Chem. Soc., 82, 5450 (1960).
5) G.Kaupp and H.Prinzbach, Helv. Chim. Acta, 52, 956 (1969).
6) K.Maruyama, K.Terada, and Y.Yamamoto, J. Org. Chem., 46, 5294 (1981).
Z.Yoshida, T.Tsuchiya, Y.Umehara, and S.Miki, 40th General Meeting of Japan Chemical Society at Fukuoka, Oct., 1979, section 3G 34.
7) D.P.Schmendenian and C.Kutal, J. Am. Chem. Soc., 99, 5677 (1977). K.Maruyama, K.Terada, Y.Naruta, and Y.Yamamoto, Chem. Lett., 1980, 1259.
8) G.S.Hammond, N.J.Turro, and A.Fischer, J. Am. Chem. Soc., 83, 4674 (1961).
G.S.Hammond, P.Wayatt, C.D.DeBore, and N.J.Turro, ibid., 86, 2532 (1964).
9) R.E.Lutz, D.F.Hinkly, and R.H.Jordan, ibid., 73, 4674 (1951). W.B.Black and R.E.Lutz, ibid., 77, 5134 (1954).
10) Electronic spectra of 1a and 2a at their excited wavelength; λ_{max}^{MeCN}, nm (ε): 1a; 254 (13000), 300 (3700), and 350 (2700). 2a; 254 (12000), 300 (1500), and 350 (300).

(Received July 12, 1982)