Phenylcycloheptabenzofuran from (2-Phenoxyphenyl)phenylcarbene and Its Photoisomerization

Hideo TOMIOKA,* Hiroshi MURATA, and Shigeru MURATA
Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514
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Synopsis. Photolysis (>350 nm) of (2-phenoxyphenyl)-phenyldiazomethane (**1**) in cyclohexane at 10 °C gave the title compound (**4**), while similar irradiation with a shorter wavelength light (>300 nm) afforded a mixture of the isomers (**5**—**7**), which were shown to be formed by photoisomerization of the initially formed **4**.

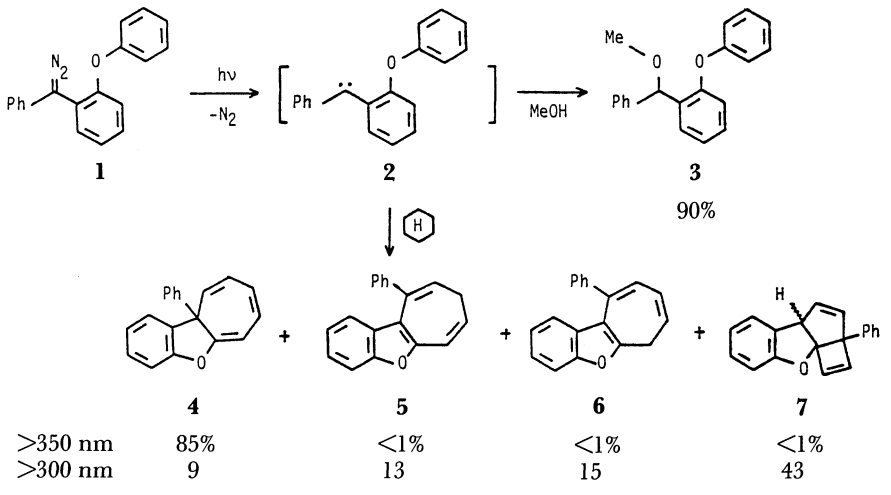
Carbenes can undergo addition to benzene to give bicyclo[4.1.0]heptadienes (norcaradiene) or cycloheptatrienes or both, which rapidly equilibrate even at low temperature.[1,2] The position of the equilibrium is usually affected by the substituents.[3] Even if the divalent carbon is attached to an arene ring, intramolecular addition often takes place to form benzocyclic compounds which are otherwise difficult to synthesize. A literature survey[2] immediately indicates, however, that the reaction is heavily weighted with that of keto carbenoid species generated by catalytic decomposition of the precursory keto diazo compounds, and almost no information is available for similar reactions of other simple free carbenes which can be generated photolytically. During the course of our studies on the effect of proximate substituents on the reaction of arylcarbene systems,[4] we found that phenoxy phenyl group underwent attack by a divalent species at ortho position to give cycloheptatrienes, which were exceptionally susceptible to photomigration.

Results and Discussion

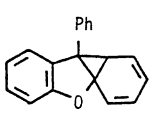
Irradiation of (2-phenoxyphenyl)phenyldiazomethane (**1**) in methanol resulted in the exclusive formation of 2-(α-methoxybenzyl)phenyl phenyl ether (**3**), which was obviously arising from insertion of the photolytically generated carbene (**2**) into the O-H bond of the solvent. No products expected to be formed as a result of the intramolecular interaction of carbene with phenyl ring were detected in the reaction mixtures. This is not surprising since methanol is known as one of the most reactive reagents for carbenes. For example, even carbene having 1,2-H shift channel can be trapped by methanol. The intramolecular products were formed, however, when the irradiation was carried out in a less reactive solvent. Thus, photolysis of **1** in cyclohexane with the light from a 300-W high-pressure Hg lamp through Corning CS-052 filter (>350 nm) gave an intramolecular addition product, which was identified as one of expected intramolecular benzene adducts (**4**) on the basis of the spectroscopic data. The reaction was found to be sensitive to the irradiation wavelength; irradiation with a Pyrex filter (>300 nm) afforded the other adducts (**5**—**7**) at the expense of **4**. Control experiments showed that the initial adduct (**4**) was photolabile and produced these new adducts (**5**—**7**) quite efficiently upon irradiation with the light of the wavelength >300 nm. Monitoring of the reaction as a function of irradiation time revealed that **5** and **6** were formed initially as **4** was consumed and that **7** began to form later at the expense of **5** and **6**, indicating **7** was not formed directly from **4** but formed via **5** and **6**.

The structure of these adducts (**4**—**7**) were determined mainly from their 400 MHz ^{1}H NMR spectra. Thus, analysis of the spectra revealed that **5** and **6** showed three vinyl protons with methylene protons whereas **7** showed four vinyl protons with one methine proton.

The formation of the initial adduct (**4**) is interpreted



Scheme 1. Photolysis of **1** in MeOH and Cyclohexane.



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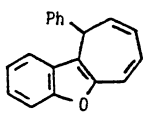

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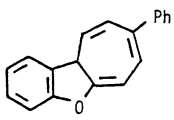

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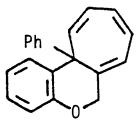

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in terms of the intramolecular addition of **2** on the phenyloxy ring at *o*-position to give norcaradiene derivative (**8**) which is in equilibrium with **4**. One would easily expect that the position of the equilibrium is shifted to **4** because of the strain in **8** due to the tricyclic cyclopropane structure. Photochemical isomerization of **4** to **5** and **6**, on the other hand, must include migration of H and Ph groups. Photochemical isomerizations of arylcycloheptarienes have been studied in detail and it has been suggested[5,6] that either phenyl group or hydrogen undergoes suprafacial 1,7-migration rather than 1,3 shift and that there is little discrimination between the migration in the electronically excited state. One cannot draw any single-step reaction for the formation of **6** and **7** from **5**, indicating several intermediates must be included in the isomerization. If one assumes that all the migration steps occur in the excited state via 1,7-modes, the following mechanism can be proposed. Thus, **5** undergoes 1,7-Ph-migration upon photoexcitation to produce **9** which then undergoes the H migration from C_7 to C_6 and then from C_6 to C_5 by repeating the suprafacial photo 1,7-shift to give **5**. The formation of **6** can be similarly interpreted in terms of the repeated 1,7-H shift of the excited state of **6**. The formation of **7**, on the other hand, must include the photo-electrocyclization reaction across C_1 and C_4 of **10**, which may be formed by two successive 1,7-Ph-shifts, followed by three 1,7-H-migrations upon excitation of **9**. The similar photocyclization reactions of cycloheptatrienes are well-known[7,8] to occur especially when the electron-donating substituents are introduced at these positions.

We were not able, however, to detect or isolate any of the possible intermediates (e.g., **9**, **10**) involved in the reaction mechanism proposed above, and we are not sure why these intermediates are so unstable, although it has been noted[5] that the intermediates involved in the cycloheptatriene migration systems are sometimes elusive. It is possible that the thermal 1,5-shift in the photochemically formed intermediate must also be included. For instance, the 1,5-H-shift of **9** will produce **6** directly without recourse to the intervention of **5** and the other intermediates. Such migration is considered to be thermally favored by the aromatization energy accompanied by the formation of benzofuran ring in **6**.

Finally, it is very interesting to note here that cycloheptatriene (**11**), a homologue of **4**, is completely photostable[9] under the conditions where **4** undergoes the multiple migrations. The results suggest that the aromatization energy gained as a result of migration plays an important role in the photoisomerization of **4**.

Experimental

Instrumentation. The IR spectra were determined with a JASCO A-100 spectrometer, while the ^{1}H NMR spectra were measured on a JEOL JNM-MH-100 and JNM-GX-400 NMR spectrometer with Me_4Si as the internal reference. The mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer. The GC analyses were performed on a Yanagimoto instrument, Model G-80. The GC column A was prepared from 5% SE-30 on Diasolid L (5.0 mm×2.0 m): column B consisted of 5% PEG-20M on Diasolid L (5.0 mm×1.0 m).

2-Phenoxybenzophenone. A mixture of 2-hydroxybenzophenone (2.0 g, 10.1 mmol) and powdered potassium hydroxide (0.67 g, 10.1 mmol) was heated to 150 °C under reduced pressure for 3 h to give the potassium salt as an orange solid. To the dry salt was added 10 mg of copper powder,[10] bromobenzene (1.07 g, 10.1 mmol) and a few drops of the hydroxybenzophenone. The mixture was stirred thoroughly and heated at 200 °C for 2 h. After cooling, the products were extraced from the reaction mixture with successive portions of water and ether. The combined ether and water solutions were steam-distilled to remove the unreacted bromide. The residue was extracted with ether and the ether layer was dried and distilled to give the ketone as a pale yellow oil. Bp 145—150 °C/0.8 mmHg (1 mmHg=133.322 Pa). ^{1}H NMR ($CDCl_4$) δ=6.66—7.74 (m, 14H); IR; MS (70 eV) *m/z* (rel intensity) 274 (M^+), 273 (100).

(2-Phenoxyphenyl)phenyldiazomethane (1). A solution of the benzophenone (10 mmol) and hydrazine hydrate (40 mmol) in anhydrous ethanol (10 ml) was refluxed overnight. The mixture was then evaporated to about 3 ml, poured onto water, and extracted with ether. The extract was dried (Na_2SO_4), and evaporated to give the benzophenone hydrazone (76.0%) as an oily solid of a geometrical isomeric mixture, which was used without further purification.

The hydrazone (4.4 mmol), anhydrous ether (20 ml), anhydrous sodium sulfate (1.0 g), yellow mercury(II) oxide (4.6 mmol) and saturated ethanolic pottasium hydroxide (0.5 ml) were stirred in the dark at 10 °C for 10 h. After filtration, the solvent was removed on a rotary evaporator at 10 °C to afford essentially quantitative yield of the crude diazo compound as a dark red oil. The crude material was dissolved in pentane (5—10 ml). The solution was cooled to −10 °C and decanted from solid ketazine and hydrazone. The solid was removed to afford the diazo compound (**1**, 200 mg, 95.9%) as a viscous red oil. ^{1}H NMR ($CDCl_4$) δ=6.78—7.44 (m, 14H); IR (neat); 2050 (C=N_2).

Preparative Scale Irradiations. In a typical run, a solution of the diazomethane (**1**, ca. 100 mg) in a solvent (10 ml) was placed in a Pyrex tube and irradiated with a high-pressure, 300-W, mercury lamp at room temperatures until all the diazomethane was destroyed. The irradiation mixture was concentrated on a rotary evaporator below 10 °C. Individual components were isolated by preparative TLC (silica gel) and identified by NMR and MS spectrometry. These fully characterized products were then used as "authentic" compounds for product identification by coinjection in GC-MS. The following products were isolated and characterized.

2-(α-Methoxybenzyl)phenyl Phenyl Ether (3): ^{1}H NMR (CCl_4) δ=7.51—6.65 (m, 14H), 5.52 (bs, 1H), 3.27 (s, 3H); MS *m/z* (rel intensity) 291 (M^++1, 2), 290 (M^+, 12), 275 (26), 257 (42), 181 (base peak).

10*H*-Phenyl-10a*H*-cyclohepta[*b*]benzofuran (4): ^{1}H NMR

($CDCl_3$) δ=7.24—6.97 (m, 9H), 6.45 (dd, J=6.4 and 10.6 Hz, 1H), 6.37 (d, J=6.4 Hz, 1H), 6.31 (dd, J=6.4 and 10.6 Hz, 1H), 6.23 (dd, J=6.4 and 10.6 Hz, 1H), 5.72 (d, J=10.6 Hz, 1H); MS (70 eV) m/z (rel intensity) 259 (M^++1, 5), 258 (M^+, 26), 257 (M^+−1, 12), 181 (base peak).

10*H*-Phenyl-8*H*-cyclohepta[*b*]benzofuran (5): ^{1}H NMR ($CDCl_3$) δ=7.64—6.68 (m, 9H), 6.83 (d, J=10.3 Hz, 1H), 5.88 (td, J=6.7 and 10.3 Hz, 1H), 5.54 (t, J=6.7 Hz, 1H), 2.60 (dd, J=6.7 and 6.7 Hz, 2H); MS (70 eV) m/z (rel intensity) 259 (M^++1, 2), 258 (M^+, 26), 257 (M^+−1, base peak), 181 (99).

10*H*-Phenyl-6*H*-cyclohepta[*b*]benzofuran (6): ^{1}H NMR ($CDCl_3$) δ=7.64—6.54 (m, 9H), 6.66 (d, J=6.7 Hz, 1H), 6.23 (dd, J=6.7 and 10.3 Hz, 1H), 5.61 (td, J=6.7 and 10.3 Hz, 1H), 3.46 (d, J=6.7 Hz, 2H); MS (70 eV) m/z (rel intensity) 259 (M^++1, 2), 258 (M^+, 26), 257 (M^+−1, base peak), 181 (99).

12-Phenyl-8-oxatetracyclo[7.5.0.$0^{2,7}$.$0^{9,12}$]tetradeca-2,4,6,10,13-pentaene (7): ^{1}H NMR ($CDCl_3$) major isomer δ=7.32—6.86 (m, 9H), 6.51 (d, J=2. 9 Hz 1H), 6.28 (d, J=5.9 Hz, 1H), 6.15 (dd, J=2.5 and 5.9 Hz, 1H), 5.63 (d, 2.9 Hz, 1H), 3.72 (d, J=2.5 Hz, 1H); minor isomer δ=7.32—6.86 (m, 9H), 6.60 (d, J=2.9 Hz, 1H), 6.42 (dd, J=5.9 and 2.5 Hz, 1H), 6.15 (d, J=5.9 Hz, 1H), 5.72 (d, J=2.9 Hz, 1H), 3.69 (d, J=2.5 Hz, 1H); MS (70 eV) m/z (rel intensity) 259 (M^++1, 18), 258 (M^+, base peak), 257 (M^+−1, 83), 181 (55).

Irradiation for Analytical Purposes. All irradiations outlined in Scheme 1 were carried out with or without Corning CS-052 filter in a Pyrex tube of 5.0 ml capacity below 10 °C. In order to avoid ambiguity of the yields due to oxidation, the solution was degassed by subjecting the sample to a minimum of three freeze-degas thaw cycles at pressure near 10^{-5} mmHg before irradiation and the tube was sealed under reduced pressure. Irradiation was generally continued until all the diazomethane was destroyed. Product identifications were established by GC-MS comparisons with the samples separated as described above and product yields were conveniently determined by standard GC techniques. Control experiments showed that no reaction occurred in the absence of light and also ruled out the interconversion of the products during analyses.

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