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Reaction of 1-Azirine with Diphenyldiazomethane. On the 1:2 Adducts of 1-Azirine and Diphenylcarbene

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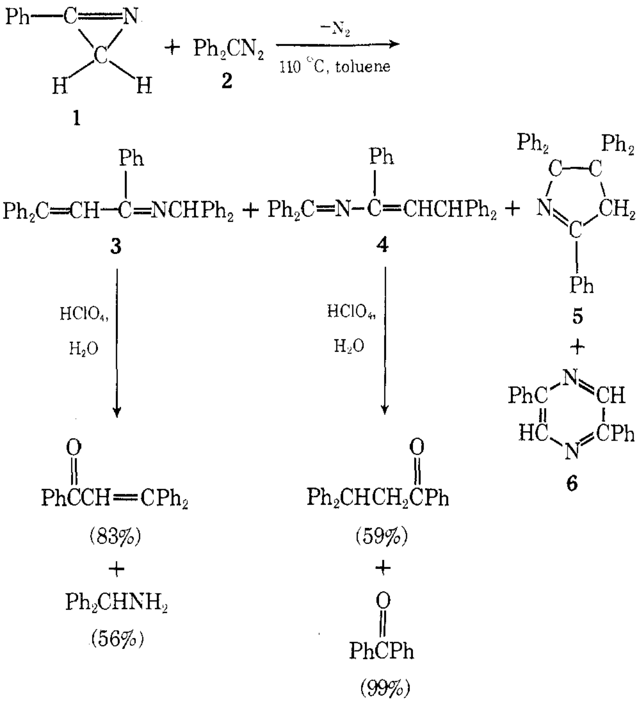
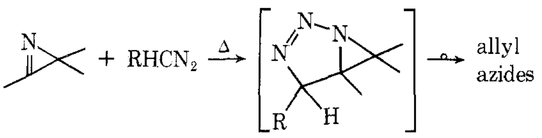
In this paper, we present studies on the reaction of 2-phenyl-1-azirine (**1**) with diphenylcarbene giving rise to 1:2 adducts. In this reaction, diphenyldiazomethane (**2**) was employed as the carbene source and thermolysis of the diazomethane **2** was carried out in refluxing toluene in the presence of the azirine **1** under an atmosphere of nitrogen. The reaction mixture was column chromatographed (aluminum oxide) to give 4-azapenta-1,3-diene **3** (20%), 2-azapenta-1,3-diene **4** (12%), pentaphenylpyrroline **5** (19%), and diphenylpyrazine **6** (17%). The compounds **3**, **4**, and **5** had the same molecular formula of $C_{34}H_{27}N$ and, hence, are 1:2 adducts of the 1-azirine and diphenylcarbene. The structural assignment of these compounds was performed by means of spectrometry. The azadiene structures of **3** and **4** were further ascertained by the chemical evidences, as shown in Scheme I.

The product **5**, on the other hand, resisted hydrolysis under acidic conditions and gave **4** (31%) and tetraphenylethylene (16%) upon heating at 200 °C under reductive conditions (H_2 100 atm in the presence of platinum oxide). Oxidation of the compound **5** with *m*-chloroperbenzoic acid gave the *N*-oxide of **5**. The ir spectrum of the *N*-oxide showed the shift of C=N absorption toward a lower frequency. The pyrazine **6**, which often appears in the reactions of the azirine, was surely formed by the dimerization of **1** followed by dehydrogenation.

The above results are quite different from those of the reactions of simple diazomethane and phenyldiazomethane. These two diazomethanes have been reported to react with the azirines as 1,3-dipoles giving allyl azides.[1a,b] The azides were presumably formed via a five-membered intermediate given by cycloaddition of the 1,3-dipoles across the C=N bond.

Scheme I

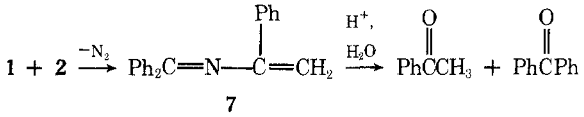




R = H or Ph

It is clear that the 1:2 adducts cannot be produced by such a reaction as above and, therefore, we should assume the reaction of diphenylcarbene. Regarding the reactions of 1-azirines with carbenelike reagents, several reports have been made.[1] Hassner and his co-workers observed the formation of a 1:1 adduct in the reaction with dichlorocarbene.[1d] They gave little consideration to the structure of the minor 1:2 adduct and suggested the structure containing an aziridine ring. However, under the conditions we employed, neither the 1:2 adducts which contain an aziridine linkage nor 1:1 adducts were isolated. Even when the mole ratio of **1** to **2** was greater than a unit, no 1:1 adduct was observed but the 1:2 adducts **3**, **4**, and **5** were obtained.

It is reasonable to consider that the above three 1:2 adducts arose from the single 1:1 adduct **7**, which was isolated from the reaction mixture at a lower temperature. We obtained 2-azabutadiene **7** in 71% yield by treating the azirine **1** with the diazomethane **2** in refluxing ether for 40 h. An increase in the amount of **2** relative to that of **1** caused a decrease in the yield of **7** and the formation of **5**. The structure of the compound **7** was determined by analytical data and also by the acidic hydrolysis giving acetophenone (67%) and benzophenone (87%).



$$1 + 2 \xrightarrow{-N_2} Ph_2C{=}N{-}\overset{Ph}{\overset{|}{C}}{=}CH_2 \xrightarrow[H_2O]{H^+,} Ph\overset{O}{\overset{\|}{C}}CH_3 + Ph\overset{O}{\overset{\|}{C}}Ph$$

7

Although it is uncertain whether the carbene is formed in refluxing ether or not, the structure of **7** corresponds to the 1:1 adduct of an azirine and dichlorocarbene.[1d] Furthermore, the reaction of 2-phenyl-3-methyl-1-azirine, which gave allyl azides upon treatment with diazomethane,[1a] with diphenyldiazomethane (**2**) in refluxing toluene and ether was studied. In both solvents, the 1:1 adduct corresponding to **7**, 1,1,3-triphenyl-2-azapenta-1,3-diene, and no allyl azides were found. This also shows that diphenyldiazomethane has the stronger tendency of acting as a carbene source rather than as a 1,3-dipole.

As interconversions among these 1:2 adducts were not observed under the same conditions, three independent paths of giving them from the 1:1 adduct should be taken into account. We can assume that electrophilic attack of diphenylcarbene to the nitrogen atom of the azirine **1** in the initial step of the reaction will lead to the 1:1 adduct **7**. The electrophilic attack of the second molecule of the carbene to this adduct will occur on the vinyl carbon. This is perhaps followed by rearrangement which will give rise to the products **3** and **4**. The compound **5** is considered to be formed as a result of ring expansion of a vinyl aziridine or an iminocyclopropane. Though it was found that **3** and **5** were formed by treating the 1:1 adduct **7** with the diazomethane **2** in refluxing toluene, **4** was not detected and, hence, the process of its formation is still ambiguous.

Experimental Section

All melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Ir, NMR, and mass spectra were obtained on a JASCO IR-E spectrophotometer, JEOL LNM-3H-60 and JEOL JNM-PS-100 spectrometers, and a Hitachi RMU-6E spectrometer, respectively.

2-Phenyl-1-azirine (**1**) was prepared by thermolysis of α-azidostyrene[2] in the presence of triethylamine.[3] Diphenyldiazomethane (**2**) was obtained by the usual way of oxidation of benzophenone hydrazone with mercuric oxide.

Reaction of 2-Phenyl-1-azirine (1) and Diphenyldiazomethane (2) in Refluxing Toluene. In a well-dried atmosphere of nitrogen, 20.1 g (104 mmol) of the diazomethane **2** was added dropwise over 4 h to a refluxing solution of the azirine **1** (5.15 g, 44 mmol) in toluene (100 ml). The reaction mixture was concentrated and then column chromatographed (aluminum oxide) to give 3.6 g (20%) of 1,1,3,5,5-pentaphenyl-4-azapenta-1,3-diene (**3**), 2.1 g (12%) of 1,1,3,5,5-pentaphenyl-2-azapenta-1,3-diene (**4**), 3.5 g (19%) of 2,4,4,5,5-pentaphenylpyrroline (**5**), 0.85 g (17%) of 2,5-diphenylpyrazine (**6**), 0.22 g of tetraphenylethylene, 0.49 g of benzophenonazine, and 2.0 g of benzophenone.

The azadiene **3** was recrystallized from benzene–hexane to give colorless plates: mp 157–158 °C; ir (Nujol) 1615 (C═C) and 1570 cm^{-1} (C═N); NMR ($CDCl_3$) δ 5.93 (s, 1, $CHPh_2$), 6.57 (s, 1, ═CH), 6.8–7.9 (m, 25, 5 Ph); mass spectrum *m/e* 449 (M^+), 282 ($M^+ - CHPh_2$), 269 ($M^+ - Ph_2CN$ or $Ph_2C{=}CH_2$).

Anal. Calcd for $C_{34}H_{27}N$: C, 90.83; H, 6.05; N, 3.12. Found: C, 90.97; H, 5.85; N, 3.13.

The azadiene **4**: pale yellow granules (benzene–hexane); mp 192–193 °C; ir (Nujol) 1615 (C═C) and 1565 cm^{-1} (C═N); NMR ($CDCl_3$) δ 4.80 (d, 1, $CHPh_2$), 5.60 (d, 1, ═CH), 6.6–7.8 (m, 25, 5 Ph); mass spectrum *m/e* 449 (M^+), 282 ($M^+ - CHPh_2$), 269 ($M^+ - Ph_2CN$ or $Ph_2C{=}CH_2$).

Anal. Calcd for $C_{34}H_{27}N$: C, 90.83; H, 6.05; N, 3.12. Found: C, 90.58; H, 6.12; N, 2.86.

The compound **5** was recrystallized from benzene–hexane to give colorless granules: mp 222–223 °C; ir (Nujol) 1620 cm^{-1} (C═N);[4] NMR ($CDCl_3$) δ 4.15 (s, 2, CH_2), 7.0–7.7 (m, 25, 5 Ph), the singlet of the methylene was observed at δ 3.95 in C_6D_6; mass spectrum *m/e* 449 (M^+), 269 ($M^+ - Ph_2C{=}CH_2$ or Ph_2CN).

Anal. Calcd for $C_{34}H_{27}N$: C, 90.83; H, 6.05; N, 3.12. Found: C, 90.62; H, 6.07; N, 3.13.

Hydrolysis of the Azadienes 3 and 4. To a solution of 870 mg of the compound **3** in 50 ml of isopropyl alcohol, 1 ml of ca. 60% perchloric acid was added and the mixture was refluxed for 2 days. The solvent was removed and extracted with chloroform and dilute hydrochloric acid. The aqueous layer was then made alkaline with aqueous NaOH and again extracted with chloroform. From the first extract, 455 mg (83%) of 1,1,3-triphenylprop-1-en-3-one was obtained and 365 mg (56%) of benzhydrylamine from the second extract. Both of them were identical with authentic samples.[5,6]

The hydrolysis of 460 mg of **4** was carried out in a similar manner to afford 180 mg (59%) of β,β-diphenylpropiophenone and 195 mg (99%) of benzophenone.

β,β-Diphenylpropiophenone: mp 93–94 °C (colorless granules from ether–petroleum ether); ir (Nujol) 1665 cm^{-1} (C═O); NMR ($CDCl_3$) δ 3.68 (d, 2, CH_2), 4.80 (t, 1, $CHPh_2$); mass spectrum *m/e* 286 (M^+), 105 ($PhCO^+$).

Reactions of the Pyrroline 5. Reduction of 750 mg of **5** in 300 ml of EtOH–THF mixture (1:1) was attempted in the presence of 50 mg of platinum oxide at 200 °C and 100 atm H_2 for 20 h and was in vain, but rearrangement and decomposition of **5** occurred to give 230 mg (31%) of **4** and 90 mg (16%) of tetraphenylethylene.

Oxidation was done by treating 1.5 g of **5** in 30 ml of $CHCl_3$ with 1.6 g of *m*-chloroperbenzoic acid for 6 h at a refluxing temperature to obtain 1.22 g (81%) of 2,4,4,5,5-pentaphenylpyrroline *N*-oxide: colorless granules (chloroform–ether); mp 249–252 °C; ir (Nujol) 1545 cm^{-1} (C═N); NMR ($CDCl_3$) δ 4.33 (s, 2, CH_2), 7.0–8.6 (m, 25, 5 Ph); mass spectrum *m/e* 465 (M^+), 449 ($M^+ - O$), 269 ($449 - Ph_2C{=}CH_2$ or Ph_2CN).

Reaction of 2-Phenyl-1-azirine (1) with Diphenyldiazomethane (2) in Refluxing Ether. According to the same procedure as that in toluene, 3.5 g (30 mmol) of **1** and 7.0 g (37.5 mmol) of **2** in 50 ml of ether were allowed to react at a refluxing temperature for 40 h. Column chromatographic treatment of the reaction mixture gave 6.1 g (71%) of 1,1,3-triphenyl-2-azabuta-1,3-diene (**7**): yellow granules (ether–hexane); mp 85.5–86.5 °C; ir (Nujol) 1615 (C═C) and 1560 cm^{-1} (C═N); NMR ($CDCl_3$) δ 4.10 (s, 1, ═CHH), 4.75 (s, 1, ═CHH),[7] 7.0–7.8 (m, 15, 3 Ph); mass spectrum *m/e* 283 (M^+), 180 (Ph_2CN^+).

Anal. Calcd for $C_{21}H_{17}N$: C, 89.01; H, 6.05; N, 4.94. Found: C, 88.71; H, 5.83; N, 4.96.

When twice the amount of **2** was used, the yield of **7** reduced to 33% and the pyrroline **5** was also obtained in 4% yield.

Hydrolysis of the Azadiene 7. To a solution of 400 mg of **7** in 20 ml of ethanol, 2 ml of 16 N sulfuric acid was added and the mixture was refluxed for 5 h. From the ethereal extract of the mixture, 113 mg (67%) of acetophenone and 222 mg (87%) of benzophenone were obtained. The yields were determined by GLC using a 4 mm × 2 m Apiezon L on Diasolid L (60–80 mesh) column.

Registry No.—**1**, 7654-06-0; **2**, 883-40-9; **3**, 59953-62-7; **4**, 59953-63-8; **5**, 59953-64-9; **6**, 5398-63-0; **7**, 59953-65-0; 1,1,3-triphenylprop-1-en-3-one, 849-01-4; benzhydrylamine, 91-00-9; β,β-diphenylpropiophenone, 606-86-0; benzophenone, 119-61-9; tetraphenylethylene, 632-51-9; *m*-chloroperbenzoic acid, 937-14-4; 2,4,4,5,5-pentaphenylpyrroline *N*-oxide, 59953-66-1; acetophenone, 98-86-2.

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