

Formation of Indan and 2,3-Dihydrobenzofuran *via* Intramolecular Insertion of Phenylcarbene

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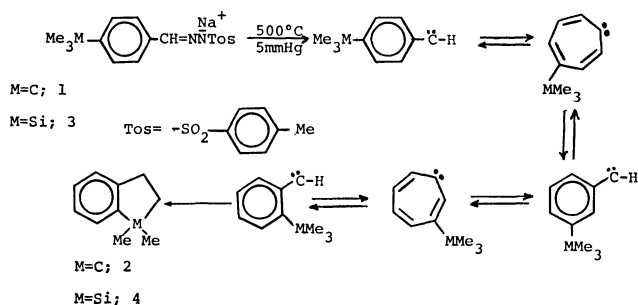
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Synopsis. Pyrolysis of *p*-*t*-butyl- and *p*-trimethylsilylbenzaldehyde tosylhydrazone sodium salts gave indans *via* intramolecular C-H insertions of *o*-substituted phenylcarbenes through carbene-carbene rearrangements. Pyrolysis of *o*- and *p*-alkoxybenzaldehyde tosylhydrazone sodium salts afforded 2,3-dihydrobenzofurans.

Alkylcarbenes react predominantly by insertion into β - and γ -C-H bonds to give olefins and cyclopropanes, respectively.¹⁾ In contrast to the number of studies on the intermolecular reactions of phenylcarbenes,²⁾ seems to have been little reported on the intramolecular insertion reactions of phenylcarbenes³⁾ which are expected to be convenient for the syntheses of cyclic compounds. In this paper, we would like to report on the formation of indan and 2,3-dihydrobenzofuran by insertion of phenylcarbenes.

(*p*-*t*-Butylphenyl)carbene was generated by the pyrolysis of *p*-*t*-butylbenzaldehyde tosylhydrazone sodium salt (**1**) at 500 °C *in vacuo*, the volatile product being trapped in a dry ice acetone trap. 1,1-Dimethylindan (**2**) was obtained in 23% yield by separation of GLC. 1,1-Dimethyl-1-silaindan (**4**)⁴⁾ was also produced in 15% yield by the pyrolysis of *p*-trimethylsilylbenzaldehyde tosylhydrazone sodium salt (**3**) under the above reaction conditions.

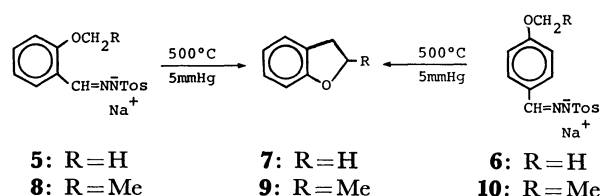


Scheme 1.

A reasonable mechanism probably involves intramolecular insertion of (*o*-*t*-butyl- and *o*-trimethylsilyl-)phenylcarbenes into C-H bonds of *ortho* *t*-butyl and trimethylsilyl groups *via* carbene-carbene rearrangements⁵⁾ of (*p*-*t*-butyl- and *p*-trimethylsilyl-)phenylcarbenes, giving products (**2**) and (**4**) as shown in Scheme 1. This is the first example of the formation of indans from the intramolecular reactions through the carbene-carbene rearrangements of the *p*-substituted phenylcarbenes. The yield is low, but it is a simple and handy method for the synthesis of *o*-substituted cyclic compounds from *p*-substituted phenylcarbenes since the corresponding *p*-substituted benzaldehydes can be easily obtained.

The intramolecular reaction of phenylcarbene containing a hetero atom is important as means for the

synthesis of a hetero cyclic compound. The pyrolysis of *o*- and *p*-anisaldehyde tosylhydrazone sodium salts, (**5**) and (**6**), under the above conditions gave 2,3-dihydrobenzofuran (**7**) in 30 and 7% yields, respectively. The formation of (**7**) from (*p*-methoxyphenyl)carbene might involve the carbene-carbene rearrangement to (*o*-methoxyphenyl)carbene.



In the pyrolysis of *o*-ethoxybenzaldehyde tosylhydrazone sodium salt (**8**), 2-methyl-2,3-dihydrobenzofuran (**9**) was obtained in 69% yield *via* regiospecific intramolecular C-H insertion, without any formation of benzopyran *via* intramolecular β -C-H insertion of (*o*-ethoxyphenyl)carbene. On the other hand, the pyrolysis of *p*-ethoxybenzaldehyde tosylhydrazone sodium salt (**10**) gave *p*-methylphenetole in 2–3% yield in hydrogen abstraction of (*p*-ethoxyphenyl)carbene. The major part is non-volatile substance which might be produced during the course of carbene-carbene rearrangement. In contrast to the carbene-carbene rearrangements of (*p*-alkylphenyl)carbenes, the reason for the unfavorable carbene-carbene rearrangements of (*p*-alkoxyphenyl)carbenes remains unclarified.

Experimental

General. The IR and NMR data were recorded on Hitachi 215 and Hitachi R-24A spectrometers, respectively. Gas chromatographic analyses were made on an Ohkura 802 gas chromatograph with use of a 1.5 m \times 5 mm stainless column packed with 15% SF-96 on Celite 545. All melting points are uncorrected.

Pyrolysis Procedure. Pyrolysis was performed with a vertical tube oven (inside diameter, 3 cm; length, 33 cm). The pyrolysis apparatus consists of a Pyrex tube, diam. 1 cm, length 18 cm. The powdered tosylhydrazone sodium salts were dropped into the pyrolysis apparatus heated at 500 °C *in vacuo*, and the product was trapped in a dry ice acetone trap.

Reagents. Tosylhydrazones were prepared in the conventional way. *p*-*t*-Butylbenzaldehyde tosylhydrazone was prepared in 71% yield by dissolving *p*-*t*-butylbenzaldehyde (14 g, 86 mmol) in MeOH, adding an equivalent of tosylhydrazine (16 g, 86 mmol) and refluxing for 30 min. Recrystallization from MeOH gave pure *p*-*t*-butylbenzaldehyde tosylhydrazone; mp 143.5–144.5 °C. Found: C, 65.68; H, 6.72; N, 8.78%. Calcd for C₁₈H₂₂N₂SO₂: C, 65.43; H, 6.71; N, 8.48%. *p*-Trimethylsilylbenzaldehyde tosylhydrazone; mp 155–156 °C. Found: C, 58.49; H, 5.96%. Calcd for C₁₇H₂₂N₂SO₂Si:

C, 58.93; H, 6.40%. *p*-Anisaldehyde tosylhydrazone; mp 114–115 °C. Found: C, 59.42; H, 5.25; N, 9.51%. Calcd for $C_{15}H_{16}N_2SO_3$: C, 59.19; H, 5.30; N, 9.20%. *o*-Anisaldehyde tosylhydrazone; mp 169.5–172 °C. Found: C, 59.07; H, 5.27; N, 9.47%. Calcd for $C_{15}H_{16}N_2SO_3$: C, 59.19; H, 5.30; N, 9.20%. *p*-Ethoxybenzaldehyde tosylhydrazone; mp 157–158 °C. Found: C, 60.23; H, 5.66; N, 9.07%. Calcd for $C_{16}H_{18}N_2SO_3$: C, 60.36; H, 5.70; N, 8.80%. *o*-Ethoxybenzaldehyde tosylhydrazone; mp 142–144 °C. Found: C, 60.44; H, 5.70; N, 9.15%. Calcd for $C_{16}H_{18}N_2SO_3$: C, 60.36; H, 5.70; N, 8.80%. Sodium salt (**1**) was obtained in 87% yield by dissolving the *p*-*t*-butylbenzaldehyde tosylhydrazone (6.0 g, 18 mmol) in dry THF and adding an equivalent of sodium hydride (0.88 g, 50% in mineral oil) slowly with stirring. Petroleum ether was added, and the resulting precipitate filtered. The sodium salts, (**3**), (**5**), (**8**), and (**10**) were also prepared from the above tosylhydrazones and sodium hydride in THF.

Pyrolysis of Tosylhydrazone Sodium Salts. Tosylhydrazone sodium salt (**1**, 1.61 mmol) was pyrolyzed by means of the pyrolysis apparatus at 500 °C, 5 mmHg. Dimethylindan (**2**)⁶ was obtained in 23% yield by GLC analysis. The pyrolysis of (**3**, 0.99 mmol) afforded silaindan (**4**)⁴ in 15% yield under the above reaction conditions. 2,3-Dihydrobenzofuran

(**7**)⁷ was formed by the pyrolysis of (**5**, 1.04 mmol) and (**6**, 1.01 mmol) in 30 and 7% yields, respectively. The pyrolysis of (**8**, 1.18 mmol) gave 2-methyl-2,3-dihydrobenzofuran (**9**)⁷ in 69% yield, while that of (**10**) gave *p*-methylphenetole.

References

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