## THE REACTIONS OF PHENYLCARBENE WITH POLYNUCLEAR AROMATIC COMPOUNDS

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Abstract—The Bamford-Stevens reaction of benzaldehyde tosylhydrazone (I) was carried out in the presence of polynuclear aromatics,—naphthalene, phenanthrene, anthracene or acridine. Products isolated were norcaradiene derivatives with *exo*-phenyl group (II, V, VII) and/or ring-benzylated compounds. In addition, anthracene gave a *meso*-bridged 1,4-adduct (VIII) of phenylcarbene. Diphenylcarbene as produced by the thermal decomposition of diphenyldiazomethane was shown to attack anthracene at the 1,2-position to afford a norcaradiene (X).

REACTIONS of certain organic solvents with phenylcarbene as produced by the Bamford Stevens reaction<sup>1</sup> of benzaldehyde tosylhydrazone  $(I)^2$  were discussed in the previous paper<sup>3</sup> from this laboratory. The investigation on the intermolecular reactions of phenylcarbene has now been extended to several polynuclear aromatic compounds.

Decomposition of I in the presence of sodium methoxide suspended in molten naphthalene at 140° gave a crystalline 1:1 adduct of phenylcarbene and naphthalene in 9% yield.<sup>4</sup> Spectroscopic evidences<sup>5,6</sup> supported the formula II. Hydrogenation



- <sup>14</sup> W. R. Bamford and T. S. Stevens, J. Chem. Soc. 4735 (1952); <sup>b</sup> J. W. Powell and M. C. Whiting, Tetrahedron 7, 305 (1959); <sup>c</sup> L. Friedman and H. Shechter, J. Amer. Chem. Soc. 81, 5512 (1959); 82, 1002 (1960); 83, 3159 (1962).
- <sup>a</sup> Tosylhydrazones for *p*-toluenesulphonylhydrazone.
- <sup>3</sup> H. Nozaki, R. Noyori and K. Sisido, Tetrahedron 20, 1125 (1964).
- <sup>4</sup> All yields are based on the consumed I. The low yields are due to the formation of by-products arising from I only, i.e., *trans*-stilbene, benzalazine, benzaldehyde, benzyl *p*-tolyl sulphone, di-*p*-tolyl disulphide and benzaldehyde N-benzyltosylhydrazone, as discussed in Ref. 3. Descriptions on these by-products are minimized in the present paper.
- <sup>5</sup> NMR spectra in this paper were taken on a Varian A-60 instrument with tetramethylsilane as an internal reference and are given in the order of peak position on ppm from the reference signal, relative area in parentheses, splitting pattern and assignment.
- $\lambda_{\text{max}}^{\text{BioH}}$  in m $\mu$  (log  $\epsilon$ ): 243 (4.47), 276 (3.79) and 310s (2.53). NMR (CCl<sub>4</sub>): 7.40 6.80 (9), multiplet, aromatic protons; 6.35 - 6.10 (2), multiplet, olefinic protons (H<sub>a</sub>, H<sub>b</sub>); 2.64 (1), quartet, H<sub>e</sub>; 2.40 - 2.05 (1), multiplet, H<sub>a</sub>; 1.15 (1), triplet, H<sub>a</sub>. The coupling constant (J<sub>H,H<sub>a</sub></sub> 4 c/s) indicates that H<sub>a</sub> and H<sub>a</sub> protons are *trans* and therefore the phenyl group occupies the *exo* position. For the coupling constants of cyclopropane hydrogens, see U. Schöllkopf and H. Küppers, *Tetrahedron Letters* 105 (1963) and Refs. cited therein.

of II upon 10% Pd—C catalyst gave the hydrocarbon (III) which was obtained independently by the Clemmensen reduction of the known diketone (IV).<sup>7</sup> The IR spectra of both products were completely superimposable.

Reaction of phenylcarbene with phenanthrene under analogous conditions gave 9-benzylphenanthrene<sup>8</sup> (4% yield) and an isomeric hydrocarbon (V; 0.2% yield). The formula V was supported by the light absorptions,<sup>9</sup> which were found quite similar to those recorded by Dewar and Ganellin for compounds VI.<sup>10</sup> The mass spectrum<sup>11</sup> (Fig. 2) indicated the numerical mol. wt. of 268 and the presence of the norcaradiene structure. As summarized in Fig. 1–3, all 7-phenylnorcaradienes obtained in the present investigation showed closely resembled fragmentation patterns. Fragment peaks at m/e M – 16, M – 29, M – 77, M – 90 and M – 103 were commonly observed in each norcaradiene. Attempted thermal isomerization of V into 9-benzylphenanthrene by heating at 180–200° for 2 hr failed to succeed.<sup>12</sup>



When the Bamford-Stevens reaction of I was carried out at  $130-140^{\circ}$  in the presence of anthracene dissolved in decalin, two kinds of crystalline 1:1 adducts (VII and VIII) were obtained in 8% and 1% yields, respectively. These compounds did not afford any adducts with maleic anhydride. The norcaradiene structure of VII was supported by the mass (Fig. 3), UV and NMR spectra.<sup>13</sup> Upon catalytic

- <sup>7</sup> G. L. Buchanan and D. B. Jhaveri, J. Org. Chem. 26, 4295 (1961).
- <sup>8</sup> Identified by mixed m.p. and comparison of IR spectra. For the authentic sample, see W. E. Bachmann, J. Amer. Chem. Soc. 56, 1363 (1934).
- \*  $\lambda_{\max}^{\text{ktoH}}$  in mµ (log  $\epsilon$ ): 245s (4.00), 276 (3.98), 286s (3.90), 306 (3.60) and 317 (3.64).
- <sup>10a</sup> M. J. S. Dewar and C. R. Ganellin, J. Chem. Soc. 3139 (1959); <sup>b</sup> C. R. Ganellin, Tetrahedron Letters 2919 (1964).
- <sup>11</sup> All mass spectra were measured with Hitachi RMU-6 mass spectrometer, temp of ionization chamber being kept at 250°, ion accelerating voltage at 1500-2000 V and emission current at 80 μA.
- <sup>12</sup> For thermal isomerization of 9,10-methylene-9,10-dihydrophenanthrene into 9-methylphenanthrene, see Ref. 10b .
- <sup>13</sup>  $\lambda_{\max}^{dioxane}$  in  $m\mu$  (log  $\epsilon$ ): 264 (4.66), 302.5 (4.29), 315 (4.23), 342 (2.83) and 359 (2.83). NMR (CDCl<sub>2</sub>): 7.8 - 7.0 (11), multiplet, aromatic protons; 6.45 - 6.40 (2), multiplet, H<sub>a</sub> and H<sub>b</sub> protons; 2.90 (1), quartet, H<sub>c</sub> proton; 2.50 - 2.10 (1), multiplet, H<sub>a</sub> proton; 1.43 (1), triplet, H<sub>c</sub> proton. The coupling constant (J<sub>H<sub>c</sub>H<sub>c</sub></sub> 5 c/s) indicates that H<sub>c</sub> and H<sub>c</sub> protons are *trans* and, therefore, the phenyl group occupies the *exo* position. IR absorption (KBr disc): 880 cm<sup>-1</sup> (*meso* hydrogens).



FIG. 1. Mass spectrum of 7-exo-phenyl-2,3-benzonorcaradiene-2,4 (II).



FIG. 2. Mass spectrum of 7-phenyl-2,3;4,5-dibenzonorcaradiene-2,4 (V).



FIG. 3. Mass spectrum of 7-exo-phenyl-naphtho[2,3-b]norcaradiene-2,4 (VII).



FIG. 4. Mass spectrum of 7-phenyl-2,3;5,6-dibenzonorbornadiene-2,5 (VIII).



FIG. 5. Mass spectrum of 7,7-diphenyl-naphtho[2,3-b]norcaradiene-2,4 (X).

hydrogenation in the presence of 10% Pd—C the norcaradiene (VII) absorbed two moles of hydrogen to afford a crystalline naphthalene derivative IX.<sup>14</sup>

The structure VIII was based on the UV<sup>15</sup> and mass spectra (Fig. 4). Comparison of the mass spectra of the adducts VII and VIII (both taken under identical conditions with ion-accelerating voltage at 2000 V) showed that VIII gave a remarkably higher anthracene peak at m/e 178 as well as a metastable peak at around m/e 118 indicating the one-step decomposition of the molecular ion to anthracene ion. These can be taken as a token supporting the formula VIII. The formation of this 9,10-bridged dihydroanthracene VIII represents one of the few instances of the 1,4-addition of a carbene.<sup>16</sup>

- <sup>14</sup>  $\lambda_{max}^{dioxane}$  in m $\mu$  (log  $\epsilon$ ): 276.5 (3.34), 287 (3.33), 309 (2.98), 319 (2.67) and 323.5 (2.94). The structure IX was tentatively assigned in analogy to the reduction of II to III.
- <sup>15</sup>  $\lambda_{\max}^{\text{dostane}}$  in m $\mu$  (log  $\epsilon$ ): 266 (3.08), 270 s (2.98) and 273.5 (2.89). The NMR spectrum could not be obtained because of the extremely low solubility. No infrared absorption was observed around 880 cm<sup>-1</sup>.
- <sup>16</sup> For previous records of the possible 1,4-addition of carbenes, see ° M. Orchin and E. C. Herrick, J. Org. Chem. 24, 139 (1959); <sup>b</sup> V. Franzen, Chem. Ber. 95, 571 (1962).

This observation prompted the authors to examine the reaction of anthracene with diphenylcarbene, one of the typical triplet carbenes. A mixture of diphenyldiazomethane and anthracene (1:1.5 mole ratio) suspended in benzene was heated at  $160-170^{\circ}$  in an autoclave. Careful examination of the reaction products led to the isolation of a norcaradiene (X; 0.1% yield), the structure being assigned on the basis of UV, IR<sup>17</sup> and mass spectra (Fig. 5). No 9,10-bridged dihydroanthracene could be isolated in the diphenylcarbene reaction.



When the Bamford-Stevens reaction of I was carried out at  $130-140^{\circ}$  in the presence of acridine dissolved in decalin, 9-benzylacridine (XI)<sup>18</sup> was obtained in 4% yield. Neither norcaradiene analogous to VII nor 9,10-bridged dihydroacridine could be isolated.

Summarizing these results, it is concluded that phenylcarbene as produced by the Bamford-Stevens reaction of I shows remarkably selective reactivity and is electrophilic in nature. The aromatic hydrocarbons are attacked at the site of highest double bond character to give norcaradienes, which are fairly stable at higher temperature. Benzylation of acridine at 9-position or the formation of XI would probably proceed through an unstable N-ylide (XII). This assumption is in accord with the previously observed<sup>3</sup> high *ortho:para* ratio in the ring-benzylation of aniline and dimethylaniline with phenylcarbene. This electrophilic nature of phenylcarbene as well as the absence of bibenzyl among the reaction products of phenylcarbene with cyclohexene or toluene<sup>3</sup> are incompatible with the radical character of triplet carbenes. The formation of VIII could be regarded as indicating the phenylcarbene reacting from its triplet state,<sup>19</sup> but the typical triplet diphenylcarbene does not afford an analogous *meso*-bridged compound, the norcaradiene type adduct X being formed. The behaviours of phenylcarbene under our conditions strongly point to the electrophilic, singlet-like character.<sup>20</sup>

## EXPERIMENTAL

All temp were uncorrected. Microanalyses were performed by the late Miss K. Ogawa and by the staff at Elemental Analyses Centre of Kyôto University.

- <sup>17</sup>  $\mathcal{I}_{max}^{\text{discasse}}$  in m $\mu$  (log  $\epsilon$ ): 252 s (4.57), 261 (4.58), 303 (4.15), 316 (4.12), 343 (3.31) and 360 (3.28). IR absorption (Nujol): 890 cm<sup>-1</sup> (*meso* hydrogens).
- <sup>18</sup> A. Bernthsen, Liebigs Ann. 224, 1 (1884).
- <sup>19</sup> W. Kirmse, Carbene Chemistry p. 77. Academic Press, New York (1964).
- <sup>30</sup> For reactions of phenylcarbene as a singlet, see <sup>a</sup> C. D. Gutsche, G. L. Bachman and R. S. Coffey, *Tetrahedron* 18, 617 (1962); <sup>b</sup> G. L. Closs and R. A. Moss, J. Amer. Chem. Soc. 86, 4042 (1964). Triplet phenylcarbene is produced from benzyl tosylate and n-butyllithium (U. Schöllkopf, A. Lerch and J. Paust, Chem. Ber. 96, 2266 (1963) foot-note 4).

Benzaldehyde tosylhydrazone (I) was prepared by the method of Bamford and Stevens.<sup>1a</sup> In all reactions described below, products originating from the starting tosylhydrazone alone, i.e., *trans*-stilbene, benzalazine, benzaldehyde, benzyl *p*-tolyl sulphone, di-*p*-tolyl disulphide and benzaldehyde N-benzyltosylhydrazone, etc, were obtained. Those arising from phenylcarbene and benzene as a solvent were also produced. As details on these products were described in the previous paper,<sup>3</sup> the following descriptions were confined largely to the products resulting from phenylcarbene and polynuclear aromatics.

Reaction of phenylcarbene and naphthalene. A mixture of 100 g naphthalene, 13 g (0.048 mole) benzaldehyde tosylhydrazone (1) and 4 g (0.07 mole) sodium methoxide was heated at 140-150° for 2 hr with vigorous stirring under N<sub>2</sub> atm. After completion of gas evolution, heating and stirring were continued for an additional 1 hr. The mixture coloured pinkish first and then yellowish. From the reaction mixture ca. 95 g naphthalene was recovered by distillation at red. press. The residue was treated with water and extracted with benzene. The combined benzene solution was washed (H<sub>2</sub>O, dil. HCl and H<sub>2</sub>O), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The residue was dissolved in a small amount of benzene and chromatographed on an alumina column. Elution with benzene gave unchanged naphthalene incipiently and then the naphthalenephenylcarbene 1:1 adduct which was contaminated with a small amount of *trans*-stilbene. Recrystallization from EtOH gave 0.9 g (9% yield based on the tosylhydrazone) an analytical sample of 7-exo-phenyl-2,3-benzonorcaradiene-2,4 (II), (Found: C, 93.57; H, 6.69. C17H14 requires: C, 93.53; H, 6.47%). This adduct (II) took up 2 moles H<sub>2</sub> upon 10% Pd—C to afford colourless crystals of 4-phenyl-1,2-benzocycloheptene (III), quantitatively. (Found: C, 91.64; H, 8.22.  $C_{17}H_{18}$  requires: C, 91.84: H, 8.16%).  $\lambda_{max}^{ktoH}$  in  $m\mu$ (log e): 254 s (2.72), 260 s (2.83), 266 (2.88) and 274 (2.86). The IR and UV spectra of this hydrocarbon (III) were completely superimposable on those of an authentic sample obtained by the Clemmensen reduction of 2-phenyl-4,5-benzocycloheptene-1,3-dione (IV)<sup>7</sup> in ca. 20% yield as follows: To a mixture of 13 g Zn-Hg and 1.5 g IV dissolved in 10 ml toluene, 8 ml water and 18 ml conc. HCl aq were added and the mixture stirred while heating under reflux for 25 hr. The crude reduction product was purified by distillation followed by column chromatography on an alumina column with n-hexane as an eluant. The compound III melts at 37-38°.

Reaction of phenylcarbene and phenanthrene. A mixture of 50 g phenanthrene and 5 g (0.08 mole) sodium methoxide was heated at 130-140° with stirring under N2 atm. To this suspension, 13 g (0.048 mole) benzaldehyde tosylhydrazone (I) dissolved in 80 ml dry benzene was added dropwise, meanwhile benzene was distilled off into an ice-cooled trap. When the addition of the benzene solution was completed, stirring and heating were continued for an additional 1 hr. After cooling, the reaction mixture was treated with water and extracted with benzene. The combined extracts were washed (H<sub>2</sub>O, dil. HCl and H<sub>2</sub>O), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in vacuo. Unchanged phenanthrene was largely removed by recrystallization of the mixture from benzene. Further removal was effected by distillation in vacuo. The residue was taken up in a small amount of n-hexanebenzene (1:1 mixture) and passed through an alumina column to remove N- and/or S-containing by-products. The eluant contained phenanthrene, phenylcarbene-phenanthrene 1:1 adducts and a small amount of trans-stilbene. After removal of phenanthrene and trans-stilbene by distillation below 100° at 1 mm with minimal heating, a mixture of phenanthrene-phenylcarbene adducts distilled below 200° (bath temp) under 0.06 mm weighed 600 mg (ca. 5% yield based on the tosylhydrazone). Recrystallization from n-hexane gave two kinds of crystals, or needles and large square plates, both being picked apart. The needles were found to be 7-phenyl-2,3;4,5-dibenzonorcaradiene-2,4 (V), m.p. 125-126° (20 mg or ca. 0.2%). The parent peak at m/e 268 was consistent with phenylcarbene-phenanthrene 1:1 adduct and the formula C<sub>\$1</sub>H<sub>16</sub> was further supported by the relative intensities of M and M + 1 peaks (100 and 22.5, respectively). The plates were shown to be 9-benzylphenanthrene by comparison with an authentic specimen,<sup>8</sup> m.p. and mixed m.p. 151-152°, 450 mg or ca. 4% yield.

Reaction of phenylcarbene and anthracene. To a vigorously stirred mixture of 13 g (0.073 mole) anthracene, 4 g (0.07 mole) sodium methoxide and 200 ml dry decalin kept at 130-140° was added dropwise a solution of 13 g (0.048 mole) benzaldehyde tosylhydrazone (I) in 150 ml dry benzene during 3 hr under N<sub>2</sub> atm., benzene meanwhile being distilled off. After the addition was completed, stirring and heating were continued for an additional 1 hr. Decalin was removed by steam distillation and the non-volatile products were extracted repeatedly with benzene. The combined benzene extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. Unchanged anthracene was converted into

the Diels-Alder adduct with 27 g maleic anhydride dissolved in 150 ml dioxane by heating the mixture under reflux for 30 hr. Excess maleic anhydride and the Diels-Alder adduct was saponified with 40% KOH aq and the non-acidic products extracted thoroughly with benzene, washed (H<sub>2</sub>O, dil HCl and H<sub>2</sub>O, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The remaining residue was dissolved in a small amount of benzene and subjected to chromatography on an alumina column. Elution with benzene gave ca. 1.5 g anthracene-phenylcarbene adducts contaminated with *trans*-stilbene and/or benzalazine. Careful fractional recrystallizations of the mixture gave two kinds of adducts: 7-phenyl-2,3;5,6-dibenzonorbornadiene-2,5 (VIII), m.p. 240-241°, 130 mg or ca. 1% yield. (Found: C, 93·79; H, 6·32. C<sub>21</sub>H<sub>16</sub> requires: C, 93·99; H, 6·01%) and 7-exo-phenylnaphtho [2,3-b]norcara-diene-2,4 (VII), m.p. 194-195°, 1·1 g or 8% yield. (Found: C, 93·95; H, 6·12. C<sub>21</sub>H<sub>16</sub> requires: C, 93·99; H, 6·01%). The adduct (VII) took up 1 mole H<sub>2</sub> smoothly and another mole rather sluggishly upon 10% Pd—C. By analogy with the transformation of II to III the resulting colourless crystalline product is considered to be 4-phenyl-naphtho[1,2-b]cycloheptene (IX), m.p. 97-97·5°. (Found: C, 92·36; H, 7·38. C<sub>21</sub>H<sub>20</sub> requires: C, 92·60; H, 7·40%-) No further attempt to establish the structure of this hydrocarbon could be made because of the small quantity.

Reaction of diphenylcarbene and anthracene. A mixture of 13 g (0.073 mole) anthracene, 5 g (0.025 mole) diphenyldiazomethane prepared by the method of Miller<sup>21</sup> and 150 ml dry benzene was placed in a stainless steel autoclave and heated at 140° for 3 hr with stirring under N<sub>2</sub> atm. After cooling benzene was removed *in vacuo* and the residue treated with maleic anhydride to remove anthracene. Upon recrystallization of the non-acidic products from benzene ca. 3 g benzophenone azine was separated. After concentration of the mother liquor, the residual mixture was dissolved in benzene and chromatographed on a silica gel column. Elution with benzene gave tetraphenylethane containing the diphenylcarbene–anthracene 1:1 adduct. Fractional recrystallization of this mixture from *n*-hexane–benzene gave colourless prisms, 7,7-diphenyl-naphtho[2,3-b]norcaradiene-2,4 (X), m.p. 202–204°, 10 mg or 0.1% yield. The parent peak appeared at m/e 344 and the relative intensities of M and M + 1 peaks (100 and 29.3, respectively) supported the formula C<sub>27</sub>H<sub>20</sub>. Further investigations were impossible due to the extremely low yield.

Reaction of phenylcarbene and acridine. To a mixture of 20 g (0.12 mole) acridine, 4.5 g (0.08 mole) sodium methoxide and 100 ml dry decalin, was added a solution of 13 g (0.048 mole) benzaldehyde tosylhydrazone in 80 ml dry benzene dropwise during 2 hr at 130–140° with vigorous stirring under N<sub>2</sub> atm., benzene meanwhile being distilled into an ice-cooled trap. Stirring and heating were continued for an additional 2 hr. Decalin was then removed by stream distillation and the residue extracted with benzene. The combined benzene solutions were treated with 2 N HCl, the aqueous layer was made slightly alkaline by adding NaOH aq and the basic precipitates were extracted again with benzene. Upon distillation of this basic mixture *in vacuo* unchanged acridine was recovered and the residual crystalline mixture was subjected to chromatography on an alumina column. Elution with benzene afforded yellow crystals of 9-benzylacridine,<sup>18</sup> m.p. and mixed m.p. 173–174°, ca. 500 mg or 4% yield. Thin layer chromatography gave a single spot.

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<sup>21</sup> J. B. Miller, J. Org. Chem. 24, 560 (1959).