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# REACTION OF PHENYLCARBENE FORMED FROM BENZALDEHYDE TOSYLHYDRAZONE IN CERTAIN SOLVENTS

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**Abstract**—Treatment of benzaldehyde tosylhydrazone (I) with sodium methoxide in various solvents under irradiation and/or heating yields products arising from phenylcarbene (IV) which is produced by photolytic or pyrolytic decomposition of initially formed phenyldiazomethane (III). Reaction products originating solely from the tosylhydrazone (I) are (VI ~ XI) while those produced by the interaction with solvents are formulated as addition products of (IV) to olefinic and aromatic C—C bonds and insertion products of (IV) to aliphatic and to aromatic C—H bonds. The reaction with aniline yields an insertion product of (IV) to the N—H bond, or N-benzylaniline, in 26% yield, besides ring-benzylated compounds. *o*-Tolualdehyde and 2,4,6-trimethylbenzaldehyde tosylhydrazones react similarly.

THE basic decomposition of tosylhydrazones[1] (Bamford-Stevens reaction[2]) gives *p*-toluenesulphinate anions and diazoalkanes which decompose either pyrolytically or photolytically in aprotic solvents to afford carbenes and nitrogen.[3–9] Thermal or photochemical decomposition of benzaldehyde tosylhydrazone (I) in the presence of sodium methoxide suspended in aprotic solvents has now been investigated in order to throw light on the behaviour of phenylcarbene (IV) which is produced in this reaction.[10]

[1] Tosylhydrazone(s): for *p*-toluenesulphonylhydrazone(s).

[2a] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.* 4735 (1952); See also [b] D. G. Farnum, *J. Org. Chem.* **28**, 870 (1963).

[3] J. W. Powell and M. C. Whiting, *Tetrahedron* **7**, 305 (1959).

[4] L. Friedman and H. Shechter, *J. Amer. Chem. Soc.* **81**, 5512 (1959); **82**, 1002 (1960); **83**, 3159 (1961).

[5] S. J. Cristol and J. K. Harrington, *J. Org. Chem.* **28**, 1413 (1963).

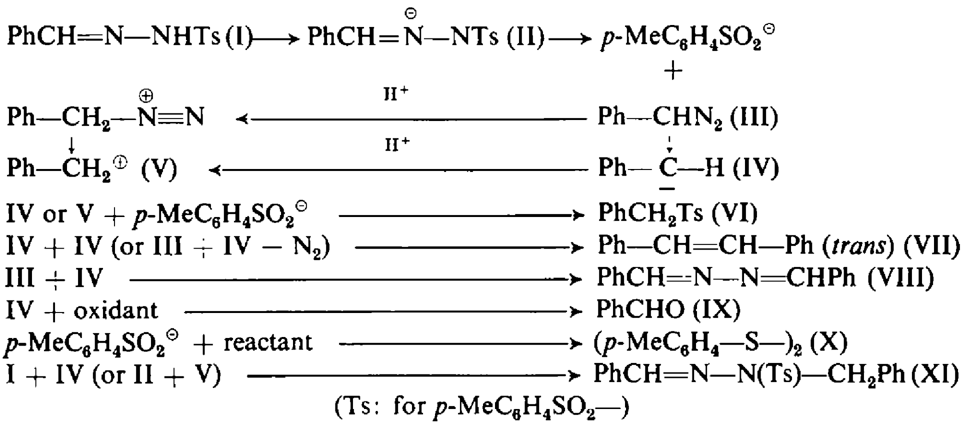
[6] H. N. Frey and I. D. R. Stevens, *J. Amer. Chem. Soc.* **84**, 2647 (1962).

[7] G. L. Closs, *J. Amer. Chem. Soc.* **84**, 809 (1962).

[8] W. G. Dauben and F. G. Willey, *J. Amer. Chem. Soc.* **84**, 1497 (1962).

[9] C. A. Grob and J. Hostynek, *Helv. Chim. Acta* **46**, 1676 (1963).

[10] For the reactions of phenylcarbene produced by other routes: [a] G. L. Closs and L. E. Closs, *Tetrahedron Letters* No 24, 26 (1960); [b] V. Franzen, H.-J. Schmidt and C. Mertz, *Chem. Ber.* **94**, 2942 (1961); [c] V. J. Hruby and A. W. Johnson, *J. Amer. Chem. Soc.* **84**, 3586 (1962); [d] C. D. Gutsche, G. L. Bachman and R. S. Coffey, *Tetrahedron* **18**, 617 (1962); [e] O. M. Nefedov, V. I. Shiryaev and A. D. Petrov, *Zh. Obshch. Khim.* **32**, 662 (1962) (*Chem. Abstr.* **57**, 14971 (1962)); [f] G. L. Closs and J. J. Coyle, *J. Amer. Chem. Soc.* **84**, 4985 (1962); [g] U. Schöllkopf and M. Eisert, *Liebig's Ann.* **664**, 76 (1963); [h] U. Schöllkopf, A. Lerch and J. Paust, *Chem. Ber.* **96**, 2266 (1963) [see the footnote 4].



$$\begin{aligned}
&\mathrm{PhCH{=}N{-}NHTs\,(I)} \longrightarrow \mathrm{PhCH{=}\overset{\ominus}{N}{-}NTs\,(II)} \longrightarrow p\text{-}\mathrm{MeC_6H_4SO_2^{\ominus}} + \\
&\mathrm{Ph{-}CH_2{-}\overset{\oplus}{N}{\equiv}N} \xleftarrow{\mathrm{H^+}} \mathrm{Ph{-}CHN_2\,(III)} \\
&\mathrm{Ph{-}CH_2^{\oplus}\,(V)} \xleftarrow{\mathrm{H^+}} \mathrm{Ph{-}\underline{\dot{C}}{-}H\,(IV)} \\
&\mathrm{IV\ or\ V} + p\text{-}\mathrm{MeC_6H_4SO_2^{\ominus}} \longrightarrow \mathrm{PhCH_2Ts\,(VI)} \\
&\mathrm{IV + IV\ (or\ III + IV - N_2)} \longrightarrow \mathrm{Ph{-}CH{=}CH{-}Ph\ (\mathit{trans})\ (VII)} \\
&\mathrm{III + IV} \longrightarrow \mathrm{PhCH{=}N{-}N{=}CHPh\ (VIII)} \\
&\mathrm{IV + oxidant} \longrightarrow \mathrm{PhCHO\ (IX)} \\
&p\text{-}\mathrm{MeC_6H_4SO_2^{\ominus} + reactant} \longrightarrow (p\text{-}\mathrm{MeC_6H_4{-}S{-})_2\ (X)} \\
&\mathrm{I + IV\ (or\ II + V)} \longrightarrow \mathrm{PhCH{=}N{-}N(Ts){-}CH_2Ph\ (XI)}
\end{aligned}$$

(Ts: for $p$-$\mathrm{MeC_6H_4SO_2}$—)

The reaction conditions and the products isolated corresponding to formulae VI ~ XI originate solely from I and are listed in Table 1. The most abundant one of these was *trans*-stilbene (VII), which was produced in 40–60% yields by decomposition in cyclohexane or toluene solution. The formation of IX and X should be ascribed to oxygen-disproportionation, as the reaction was carried out in the absence of atmospheric oxygen. The exact nature of this oxidation-reduction reaction is still obscure. The compound XI is new and was characterized by independent synthesis from the sodium salt of I and benzyl chloride in 56% yield. Treatment of XI with 2,4-dinitrophenylhydrazine solution yields benzaldehyde 2,4-dinitrophenylhydrazone. The following products result from the interaction with solvents.

TABLE 1. BASIC DECOMPOSITION OF BENZALDEHYDE TOSYLHYDRAZONE. REACTION CONDITIONS AND PRODUCTS[a]

| Solvent | Method of decomp. | Products (yield in %) | | | | | |
|---|---|---|---|---|---|---|---|
| | | VI | VII | VIII | IX | X | XI |
| Cyclohexene | B | *c* | *d* | 33 | *c* | *c* | *c* |
| Cyclohexane | B | 3 | 46 | 13 | 3 | *d* | *d* |
| DMF | A | 2 | *d* | 59 | *c* | 4 | *d* |
| $\mathrm{(EtOCH_2CH_2)_2O}$ | A | 11 | 12 | *c* | *c* | 9 | *d* |
| PhH | C | 3 | 14 | 4 | 7 | *d* | 41 |
| PhMe | B | 3 | 57 | 4 | *c* | *d* | 14 |
| $\mathrm{PhNH_2}$ | A | 4 | *d* | *c* | *c* | *c* | *c* |
| $\mathrm{PhNMe_2}$ | A | 3 | 4 | *c* | *c* | *c* | 13 |
| Water | B | *c* | 5 | 15 | tr. | *d* | *d* |

[a] Products resulting solely from the hydrazone (I) are listed. For interaction products with solvents, see text.

[b] Methods of decomposition of the intermediary phenyldiazomethane (III) are classified as follows: A: pyrolysis at 140–180° under nitrogen atmosphere, B: irradiation with a 500 W tungsten lamp at 60–100°, C: irradiation with direct sunlight for two weeks. For details, see Experimental.

[c] No evidence against the formation of each product is available, but the compound failed to be isolated.

[d] The presence of each compound has been disproved.

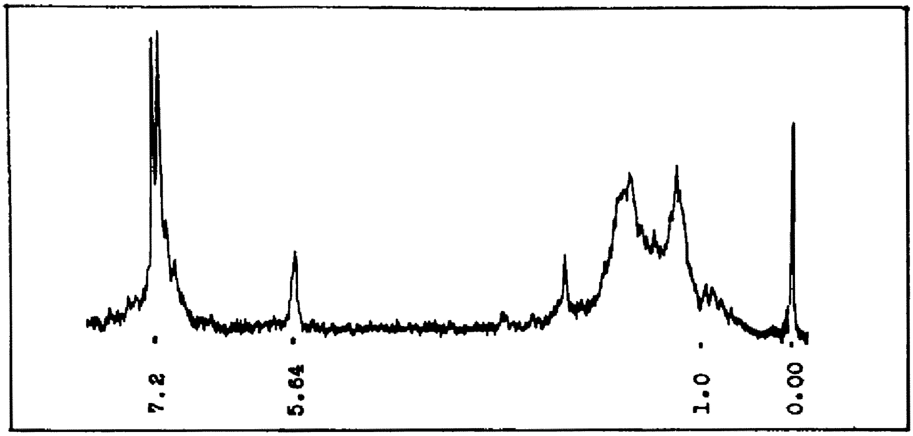


FIG. 1. 7-Phenylnorcarane and benzylcyclohexene(s) (1 : 1)

A *cyclohexene* suspension of I and sodium methoxide, upon irradiation with a tungsten lamp at 70° for 12 hr gave an oil, $C_{13}H_{16}$, in 7% yield. Gas chromatography indicated the presence of two components in approximately equal amounts. NMR (Fig. 1) and IR spectra of this mixture showed one component to be 7-phenylnorcarane[10a] (methine hydrogens at higher fields than $\delta$ 1 ppm from tetramethylsilane, cyclopropane-ring frequency at 1030 cm$^{-1}$); and the other possibly to be 3-benzylcyclohexene[10a] (olefinic protons at $\delta$ 5·64 ppm, ethylene bond stretching at 1645 cm$^{-1}$). The presence of other isomers cannot be completely excluded.

Pyrolysis or photolysis of I in *cyclohexane*, *dimethylformamide* or in *diethyl Carbitol* in the presence of sodium methoxide gave negligible amounts of products arising from the interaction of solvents, although higher yields of such products were obtained in some aromatic solvents.

A *benzene* suspension of I and sodium methoxide, upon irradiation with sunlight for two weeks, gave an oily fraction. The NMR spectrum (Fig. 2) proved this to be

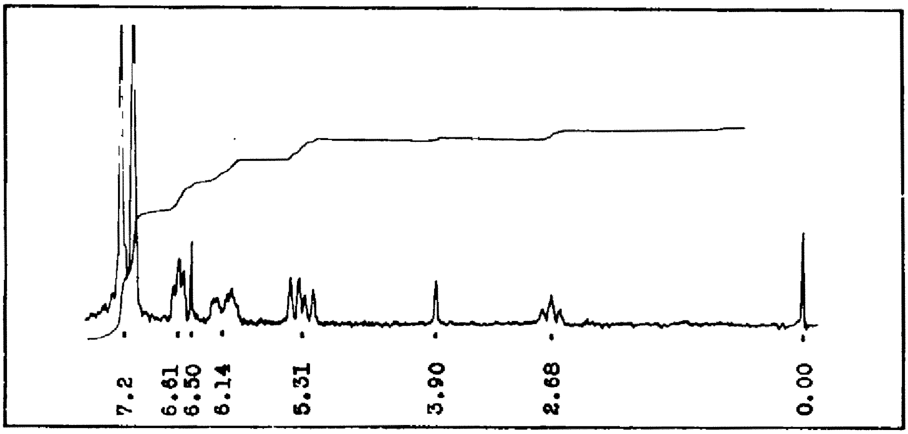


FIG. 2. 7-Phenylcycloheptatriene-1,3,5, diphenylmethane and *cis*-stilbene (4 : 1 : 1)

7-phenylcycloheptatriene-1,3,5[11] contaminated with diphenylmethane and *cis*-stilbene, the abundance ratio being approximately 4:1:1.[12] The signal at δ 3·90 ppm was ascribed to methylene protons of diphenylmethane and that at δ 6·50 ppm to the olefin protons of *cis*-stilbene. These conclusions are supported by gas chromatographic comparison with known samples. The formation of *cis*-stilbene is unexpected in this series of experiments and may be attributed to prolonged irradiation causing rearrangement of the *trans*-stilbene (VII) initially formed.[13]

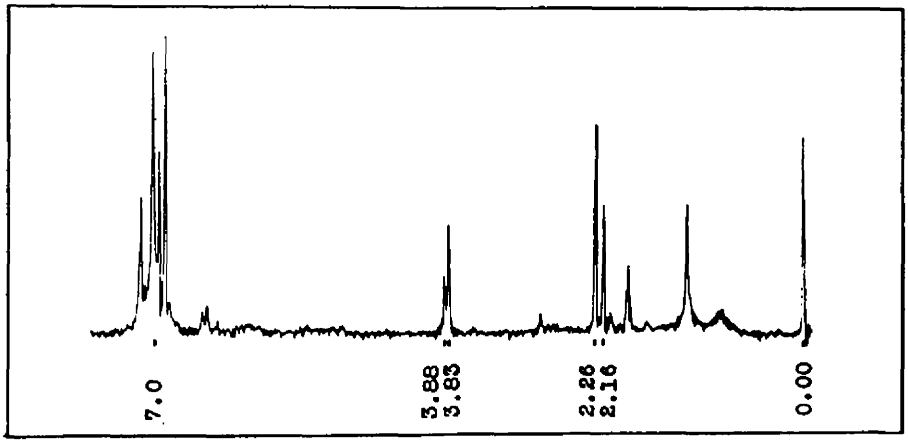


Fig. 3. Unidentified 1:1 adduct, 2- and 4-methyldiphenylmethanes (3:2:4)

In *toluene* suspension irradiation with a tungsten lamp at 90° for 3 hr gave an oil, $C_{14}H_{14}$, in 3% yield. Catalytic hydrogenation over 10% palladium-charcoal resulted in absorption of one mole of hydrogen.[14] The NMR spectrum (Fig. 3) and gas chromatography indicated that the product was a mixture of this "unsaturated" phenylcarbene–toluene adduct and 2- and 4-methyldiphenylmethanes in 3:2:4 ratio, respectively.

In *aniline* suspension, heating at 160° for 1 hr gave N-benzylaniline in 26% yield together with a mixture of *o*- and *p*-benzylaniline in 9% yield. The NMR (Fig. 4) and IR spectra of the mixture of *o*- and *p*-benzylacetanilides prepared showed that the *o*/*p* ratio was approximately 6:1. A similar reaction with N,N-*dimethylaniline* afforded a mixture of *o*- and *p*-benzyl-N,N-dimethylanilines in 8% yield, the NMR spectrum of which (Fig. 5) showed the *o*/*p* ratio to be 5:2.

No cycloheptatriene compounds could be detected among reaction products of both amines. The predominance of *o*-substituted aniline derivatives might tentatively

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[11] Comparison of Fig. 2 with the NMR spectrum of cycloheptatriene-1,3,5 (N. S. Bhacca, L. F. Johnson and J. N. Shoolery, *NMR Spectra Catalog*, Varian Associates, Palo Alto, Calif., 1962) gave an unambiguous assignment of peaks originating from this hydrocarbon.

[12] Liquid phase photolysis of diazomethane in benzene gives a mixture of cycloheptatriene-1,3,5 and toluene in a ratio of 32:9 (W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* **75**, 297, 1953) or of 3·5:1 (R. M. Lemmon and W. Strohmeier, *J. Amer. Chem. Soc.* **81**, 106, 1959).

[13] [a] J. Saltiel and G. S. Hammond, *J. Amer. Chem. Soc.* **85**, 2515, 2516 (1963); [b] R. Srinivasan and J. C. Powers, Jr., *J. Amer. Chem. Soc.* **85**, 1355 (1963) and previous papers.

[14] It is still obscure whether this hydrogen-absorbing hydrocarbon is methylphenylcycloheptatriene, or a norcaradiene derivative or a mixture of both. Detailed work has been abandoned in view of the low yield.

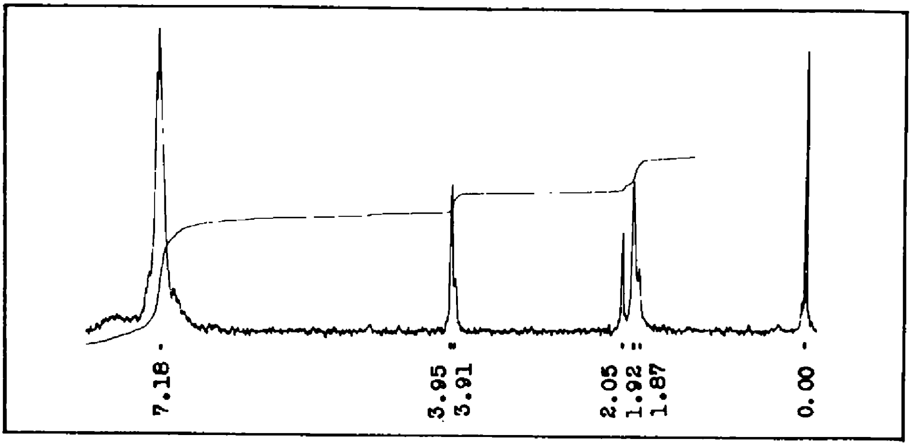

FIG. 4. *o*- and *p*-Benzylacetanilides (6:1)

be interpreted by assuming the initial formation of N-ylides produced by the electrophilic attack of phenylcarbene (IV) on the lone pair electrons of the nitrogen atom and followed by rearrangement of the ylides.[15]

When the decomposition of I was carried out in aqueous sodium hydroxide solution under irradiation with a tungsten lamp at 100° for 1 hr, besides the products listed in Table 1, benzyl alcohol was obtained in 63% yield.

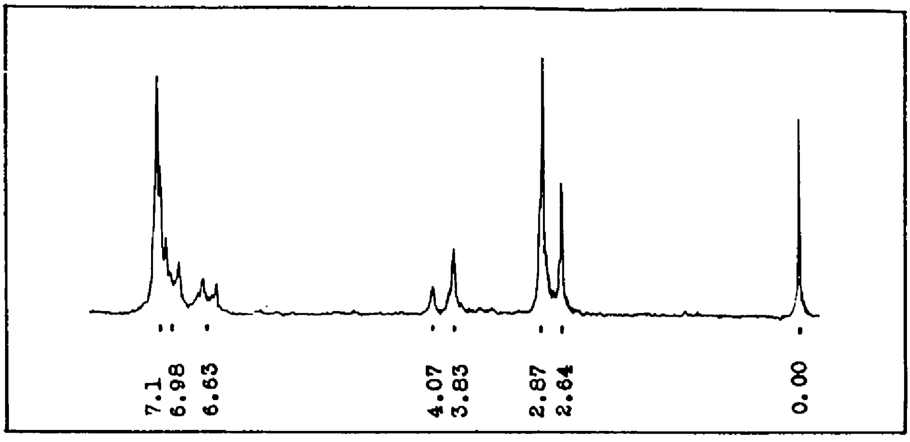

FIG. 5. *o*- and *p*-Benzyl-N,N-dimethylanilines (5:2)

In anticipation of the possible formation of benzocyclobutene[16] from *o*-tolylcarbene by intramolecular carbene-insertion into the methyl C—H bond, photolysis

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[15] For N-ylide formation with carbenes: [a] P. A. S. Smith and N. W. Kalenda, *J. Org. Chem.* **23**, 1599 (1958); [b] V. Franzen and H. Kuntze, *Liebig's Ann.* **627**, 15 (1959); [c] M. B. Frankel, H. Feuer and J. Bank, *Tetrahedron Letters* No 7, 5 (1959); [d] W. Walter and G. Maerten, *Angew. Chem.* **73**, 755 (1961); [e] M. Saunders and R. W. Murray, *Tetrahedron* **6**, 88 (1959); **11**, 1 (1960). S-Ylide formation and the subsequent rearrangement have been recorded: W. E. Parham and R. Koncos, *J. Amer. Chem. Soc.* **83**, 4034 (1961); W. E. Parham and L. D. Huestis, *Ibid.* **84**, 813 (1962).

[16] For benzocyclobutene: [a] M. P. Cava and D. R. Napier, *J. Amer. Chem. Soc.* **78**, 500 (1956); **80**, 2255 (1958); [b] A. P. ter Borg and A. F. Bickel, *Proc. Chem. Soc.* 283 (1958); [c] M. P. Cava and A. A. Deana, *J. Amer. Chem. Soc.* **81**, 4266 (1959); [d] W. Baker, J. F. W. McOmie and D. R. Preston, *J. Chem. Soc.* 2971 (1961); [e] K. Alder and M. Fremery, *Tetrahedron* **14**, 190 (1961).

of *o*-tolualdehyde tosylhydrazone was carried out in cyclohexane solution. The product actually isolated in 41 % yield was 2,2′-dimethyl-*trans*-stilbene, *o*-tolualdehyde (8 %), 2-methylbenzal azine (15 %) and *o*-tolualdehyde N-(2-methylbenzyl)tosylhydrazone (analogous to XI) (5 %) being obtained as by-products. Similar decomposition of 2,4,6-trimethylbenzaldehyde tosylhydrazone afforded the corresponding N-substituted tosylhydrazone in 26 % yield together with 2,4,6-tri-methylbenzaldehyde (4 %) and its azine (2 %). In both cases there was no sign of benzocyclobutene formation.[17]

## EXPERIMENTAL

All temperatures are uncorrected. Microanalyses were preformed by Miss K. Ogawa. IR spectra are consistent with assigned structures. All NMR spectra were taken in $CCl_4$ solutions on 60 Mc. machines and are given in ppm from internal TMS reference.

Benzaldehyde tosylhydrazone (I) was prepared by the method of Bamford and Stevens,[2a] m.p. 128–129° (lit. 128°). In a similar manner, o-*tolualdehyde tosylhydrazone* was prepared (60 % yield), m.p. 143–144° from ethanol. (Found: C, 62·59; H, 5·80. $C_{15}H_{16}N_2O_2S$ requires: C, 62·47; H, 5·59 %). 2,4,6-*Trimethylbenzaldehyde tosylhydrazone* (40 % yield), m.p. 158–160° was crystallized from ethanol. (Found: C, 64·77; H, 6·53. $C_{17}H_{20}N_2O_2S$ requires: C, 64·52; H 6·37 %).

*Decomposition of benzaldehyde tosylhydrazone* (I) *in cyclohexene*. A mixture of 12·0 g (44 mmoles) of I and 4·0 g (74 mmoles) sodium methoxide suspended in 160 ml dry cyclohexene was vigorously stirred at 10° for 1 hr ($N_2$ atm.), and then irradiated with a 500 W tungsten lamp at 70° for 12 hr, until no more evolution of $N_2$ was observed. After cooling, the reaction mixture was treated with water, and the organic layer separated, dried and concentrated *in vacuo*. Distillation of the residue gave 0·8 g of an oily product, b.p. 90–92°/4 mm, which was purified by passing through an alumina column and then by short-path distillation to give 0·5 g (7 %) of a colourless oil. (Found: C, 90·57; H, 9·60. Calc. for $C_{13}H_{16}$: C, 90·64; H, 9·36 %). Gas chromatography and NMR spectrum (Fig. 1) showed this to be a 1:1 mixture of 7-phenylcycloheptatriene-1,3,5 and benzylcyclohexene(s), IR absorptions (neat): 1645 (double bond) and 1030 cm$^{-1}$ (cyclopropane ring).

The distillation residue was dissolved in benzene and passed through an alumina column to afford 1·5 g (33 % yield) benzal azine (VIII), m.p. and mixed m.p. 92–93°.

*Decomposition of* I *in cyclohexane*. A mixture of 10·0 g (36 mmoles) of I and 3·5 g (65 mmoles) sodium methoxide suspended in 250 ml anhydrous cyclohexane was stirred at room temp under $N_2$, and then irradiated with a 500 W tungsten lamp at 60° for 5 hr. Recrystallization of the crude reaction product from ethanol gave 1·0 g *trans*-stilbene (VII). The mother liquor was concentrated and distilled to give 0·1 g (3 %) benzaldehyde (IX) which was identified as 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. 235°), and an additional 0·2 g *trans*-stilbene. The residual oily material was dissolved in n-hexane and subjected to chromatography on alumina. Elution with n-hexane gave 0·3 g *trans*-stilbene (VII) in a total yield of 1·5 g (46 %), m.p. and mixed m.p. 123–124°. Further elution with benzene gave 0·5 g (13 %) benzal azine (VIII), m.p. and mixed m.p. 92–93°, and final elution with ethanol gave 0·3 g (3 %) benzyl *p*-tolylsulphone (VI), m.p. 144–145°(lit.[2a] 144°).

*Decomposition of* I *in benzene*. An intimate mixture of 20·0 g (72 mmoles) of I, 4·3 g (81 mmoles) sodium methoxide and 200 ml dry benzene was allowed to stand in the sunlight for 2 weeks in $N_2$ atm. The reaction mixture was poured into water and the benzene layer separated, washed, dried and concentrated *in vacuo*. Distillation of the residue gave (a) 0·5 g (7 %) benzaldehyde (IX), b.p. below 70°/4 mm (2,4-dinitrophenylhydrazone, m.p. 235°), (b) 1·2 g of a slightly yellow oil, b.p. 95–105°/3 mm, (c) 0·5 g *trans*-stilbene (VII), b.p. about 120°/3 mm, m.p. and mixed m.p. 123–124° (from ethanol), and (d) 7·4 g residue. The oily fraction (b) was dissolved in a small amount of n-hexane and passed through a short alumina column. Repeated distillation gave 0·8 g (ca. 7 %) a colourless oil, b.p. 96–98°/3 mm, which was shown to be 7-phenylcycloheptatriene-1,3,5 contaminated with diphenylmethane and *cis*-stilbene in roughly 4:1:1 ratio. Identification of these compounds and measurement of the abundance ratio were carried out by means of gas chromatography and NMR spectrometry (Fig. 2). (Found: C, 92·80; H, 7·24. Calc. for $C_{13}H_{12}$: C, 92·81; H, 7·19 %).

The distillation residue was recrystallized from ethanol to afford 4·7 g *benzaldehyde* N-*benzyltosylhydrazone* (XI), m.p. 110–111° from ethanol. (Found: C, 69·40; H, 5·71. $C_{21}H_{20}N_2O_2S$

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[17] For discussions on the possible 1,4-insertion of carbenes, see ref. 10d.

requires: C, 69·20; H, 5·53%). The same hydrazone was obtained in 56% yield by the reaction of sodium salt of I with benzyl chloride in N,N-dimethylformamide at room temp. Upon treatment with 2,4-dinitrophenylhydrazine solution, XI gave benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 235°.

The mother liquor of recrystallization was concentrated, dissolved in a small amount of benzene and subjected to chromatography on alumina. Elution with benzene gave 0·4 g *trans*-stilbene (VII), m.p. and mixed m.p. 123–124° (total yield 0·9 g, 14%), 0·3 g (4%) benzal azine (VIII), m.p. and mixed m.p. 92–93°, and then 0·7 g benzaldehyde N-benzyltosylhydrazone (XI), m.p. 110–111° (total yield 5·4 g, 41%). Final elution with ethanol gave 0·5 g (3%) benzyl *p*-tolylsulphone, m.p. 144–145°.

*Decomposition of* I *in toluene*. A solution of 15·0 g (55 mmoles) of I in 150 ml dry toluene was added dropwise into a suspension of 4·0 g (74 mmoles) sodium methoxide in 100 ml toluene with vigorous stirring during 3 hr at 90° under irradiation with a 500 W tungsten lamp in a $N_2$ atm. Stirring and irradiation were continued for an additional 7 hr. The products were separated by chromatography on alumina. Elution with n-hexane–benzene (1:1) gave (a) 0·3 g a colourless oil, (b) 2·8 g (57%) *trans*-stilbene (VII), m.p. and mixed m.p. 123–124°, and (c) 0·4 g (4%) benzal azine (VIII), m.p. and mixed m.p. 92–93°. The oily fraction (a) was purified by repeated distillation. This oil (Found: C, 92·30; H, 7·83. Calc. for $C_{14}H_{14}$: C, 92·26; H, 7·74%) took up one mole of hydrogen upon hydrogenation over 10% Pd-C. The NMR spectrum (Fig. 3) and gas chromatography indicated this to be a mixture of an "unsaturated hydrocarbon" (methylphenylcycloheptatriene(s) or norcaradiene derivative(s)) (ca. 1% yield) and 2- and 4-methyldiphenylmethanes (0·7% and 1·3% yields, respectively). Elution with benzene gave 1·4 g (14% yield) N-benzyltosylhydrazone (XI), m.p. 110–111°. Final elution with ethanol gave 0·4 g (3%) benzyl *p*-tolylsulphone (VI), m.p. and mixed m.p. 144–145°.

*Decomposition of* I *in aniline*. A mixture of 15·0 g (55 mmoles) of I and 4·0 g (74 mmoles) sodium methoxide in 300 ml dry aniline was well-stirred for 30 min at 10° and then heated at 160° for 1 hr. Aniline was removed by steam-distillation and the residue was extracted with ether. After separating the basic fraction by extraction with 2N HCl, the non-basic fraction was purified by chromatography on alumina to afford 0·5 g (4%) benzyl *p*-tolylsulphone (VI), m.p. and mixed m.p. 144–145°. Distillation of the basic fraction *in vacuo* afforded 3·5 g (35%) of a mixture of benzylanilines (Found: C, 85·06; H, 7·17. Calc. for $C_{13}H_{13}N$: C, 85·20; H, 7·15%). Acetylation of 620 mg of this base with acetic anhydride gave 460 mg N-benzylacetanilide, m.p. and mixed m.p. 57–58°, and 160 mg of a mixture of *o*- and *p*-benzylacetanilides, m.p. 103–108° (Found: C, 79·89; H, 6·90. Calc. for $C_{15}H_{15}NO$: C, 79·97; H, 6·71%). The *o*/*p* ratio of ca. 6:1 was ascertained by IR and NMR spectra (Fig. 4). Yields of N-, *o*- and *p*-benzylanilines were estimated at about 26, 7·7 and 1·3%, respectively.

*Decomposition of* I *in* N,N-*dimethylaniline*. A mixture of 15 g (55 mmoles) of I and 4·5 g (83 mmoles) sodium methoxide in anhydrous N,N-dimethylaniline was stirred at room temp and then heated at 150° for 1 hr under a $N_2$ atm. After removing the solvent by steam-distillation, the residue was extracted with ether. The combined ethereal solutions were extracted with 2N HCl. Distillation of the basic fraction *in vacuo* afforded 1·2 g (8% yield) of a yellowish oil, b.p. 115–120°/0·5 mm, which was shown to be a 5:2 mixture of *o*- and *p*-benzyl-N,N-dimethylanilines by NMR spectrum (Fig. 5). (Found: C, 85·45; H, 8·22. Calc. for $C_{15}H_{17}N$: C, 85·26; H, 8·11%).

Upon chromatography of the non-basic products, 0·2 g (4%) *trans*-stilbene (VII), m.p. and mixed m.p. 123–124°, 1·3 g (13%) benzaldehyde N-benzyltosylhydrazone (XI), m.p. and mixed m.p. 110–111°, and 0·4 g (3%) benzyl *p*-tolylsulphone, m.p. and mixed m.p. 144–145°, were isolated.

*Decomposition of* o-*tolualdehyde tosylhydrazone*. A mixture of 10·0 g (35 mmoles) the hydrazone, 3·2 g (59 mmoles) sodium methoxide and 250 ml dry cyclohexane was stirred at 10° for 1 hr under $N_2$, then irradiated at 70° with a 500 W tungsten lamp until evolution of gas ceased. The reaction mixture was treated as usual and the products were distilled *in vacuo* to afford 0·3 g of *o*-tolualdehyde, b.p. 80–85°/13 mm, which was identified by means of IR. The residue was dissolved in a small portion of n-hexane and chromatographed on alumina. n-Hexane eluted 1·5 g (41%) 2,2-dimethyl-*trans*-stilbene, m.p. 82–83° (lit.[18] 82·5–83°) (from ethanol). Benzene eluted 0·6 g (15%) 2-methylbenzal azine, m.p. and mixed m.p. 99–100° (from ethanol). Finally, ether eluted 0·1 g (5%) o-*tolualdehyde* N-(2-*methylbenzyl*)*tosylhydrazone*, m.p. 159–160° from ethanol. (Found: C, 70·70; H, 6·25. $C_{22}H_{24}N_2O_2S$ requires: C, 70·38; H, 6·16%). The IR spectrum was similar to that of XI in a region of 8 ~ 13 μ.

*Decomposition of* 2,4,6-*trimethylbenzaldehyde tosylhydrazone*. A mixture of 6·1 g (19 mmoles) of the hydrazone, 1·2 g (22 mmoles) sodium methoxide and 200 ml anhydrous cyclohexane was vigorously stirred for 1 hr at room temp and then irradiated at 70° for 3 hr with a 500 W tungsten lamp. After cooling, the mixture was treated with water, and the cyclohexane layer separated, washed, dried and concentrated. Distillation of the residue gave 0·1 g (4%) 2,4,6-trimethylbenzaldehyde, b.p. 100–120°/4 mm, identified by IR. The residue was chromatographed on alumina. Elution with benzene afforded 0·05 g (2%) 2,4,6-trimethylbenzal azine, m.p. 162–163° from ethanol (lit.[19] 167°) (Found: C, 82·16; H, 8·46. Calc. for $C_{20}H_{24}N_2$: C, 82·14; H, 8·27%). Further elution gave 1·0 g (26%) 2,4,6-*trimethylbenzaldehyde* N-(2,4,6-*trimethylbenzyl*)-*tosylhydrazone*, m.p. 173–174° from benzene. (Found: C, 72·21; H, 7·27. $C_{27}H_{32}N_2O_2S$ requires: C, 72·28; H, 7·19%). The IR spectrum was similar to that of the N-benzyltosylhydrazones described.

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