and most of the solvent removed by distillation. Analysis by gc revealed, in addition to solvent, the presence of allylcarbinyl acetate, cyclobutyl acetate, and cyclopropylcarbinyl acetate in the ratio 1:11.0:13.0, respectively. A repeat of this product run where urea was used as the buffer in place of NaOAc gave the same analytical result.

Rate measurements were accomplished by usual techniques.[18] The titrating solutions were, for formolysis, 0.020 *N* sodium acetate in acetic acid and, for ethanolyses and trifluoroethanolyses, 0.020 *N* sodium methoxide in anhydrous methanol. The indicators used were bromphenol blue (in acetic acid), bromthymol blue (in water), and bromphenol blue (in 20% aqueous (EtOH), respectively.

Treatment of Kinetic Data.—The rate constants, k, used in Figure 1 for the acetolysis and 2,2,2-trifluoroethanolysis were calculated according to the following scheme: $k = k_t/(F + F' + F'')$ which was derived from $k_t = Fk + F'k + F''k$ where F = fraction of ion pair yielding solvolysis products, F' = fraction of ion pair collapsing to allylcarbinyl β-naphthalenesulfonate, and F'' = fraction of ion pair collapsing to cyclopropylcarbinyl β-naphthalenesulfonate. It was assumed that the ratio of total anion collapse to solvent collapse is a constant in a given solvent independent of the detailed distribution of charge in the intermediate. For acetolysis, $k = 34.3 \times 10^{-7}$ sec^{-1} compared to $k_t = 24 \times 10^{-7}$ sec^{-1}. For 2,2,2-trifluoroethanolysis, $k = 16 \times 10^{-5}$ sec^{-1} compared to $k_t = 10 \times 10^{-5}$ sec^{-1}.

Registry No.—4-ONas, 26366-58-5.

[18] D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964).

Decomposition of *p*-Toluenesulfonylazoalkenes[1]

Goffredo Rosini* and Raffaele Ranza

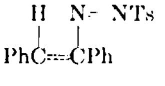
Istituto di Chimica Organica e Industriale, Universita' di Bologna, 40136 Bologna, Italy

Received September 18, 1970

p-Toluenesulfonylazostilbene and 2-*p*-toluenesulfonylazo-1,3-diphenylpropene have been synthesized and decomposed in benzene at 90° and in chloroform at 25°. The results obtained are consistent with a rearrangment of *p*-toluenesulfonylazoenes to the corresponding 2-*p*-toluenesulfonyldiazo compounds and successive protic decomposition. The formation of diphenylacetylene and 1,3-diphenylallene can be ascribed to an internal neutralization of vinyldiazonium ions.

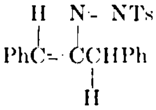
Recently, two papers concerning the reaction of *p*-toluenesulfonylhydrazine with ketones bearing a leaving group on the adjacent carbon have appeared. The first paper[2] reports the formation of diphenylacetylene from benzoin acetate and benzoin benzoate *p*-toluenesulfonylhydrazones with alkali. The proposed mechanism, however, is at variance with experiments previously reported by us.[3,4] The second paper[5] concerns the reaction between *p*-toluenesulfonylhydrazine and α-X ketones *via* *p*-toluenesulfonylazoenes.

We wish to report here some experiments that confirm the peculiar reactivity of the S–N bond in *p*-toluenesulfonylazoalkenes. In aprotic solvents, treatment of α-acetoxydeoxybenzoin and α-acetoxy-1,3-diphenylpropane-2-one *p*-toluenesulfonylhydrazones with bases gives the corresponding *p*-toluenesulfonylazostilbene (I) and 2-*p*-toluenesulfonylazo-1,3-diphenylpropene (II).



$$\mathrm{Ph}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}{=}\overset{\mathrm{N{=}NTs}}{\overset{|}{\mathrm{C}}}\mathrm{Ph}$$

I

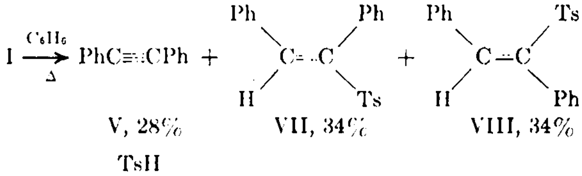


$$\mathrm{Ph}\overset{\mathrm{H}}{\overset{|}{\mathrm{C}}}{=}\underset{\underset{\mathrm{H}}{|}}{\overset{\mathrm{N{=}NTs}}{\overset{|}{\mathrm{C}}}}\mathrm{CHPh}$$

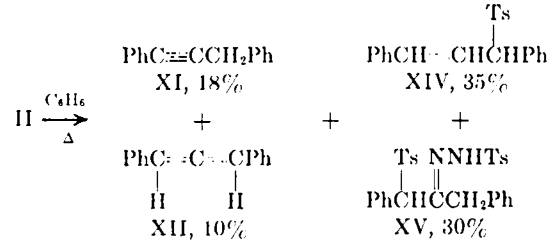
II

The mechanism of the formation of these compounds is consistent with 1:4 elimination of AcOH by basic treatment.[3,4] The *p*-toluenesulfonylazoenes obtained are yellow compounds which decompose on melting, and their structure has been assigned on the bases of analytical and spectroscopic data (Experimental Section).

The thermal decompositions of I and II in dry benzene at 90° resulted in the evolution of nitrogen and the disappearence of the yellow color of the solution. The mixtures obtained by evaporation of the solvent were separated by column chromatography on silica gel to give the compounds shown in eq 1 and 2.



(1)



(2)

The same results were obtained if I or II were allowed to stand at room temperature for several hours in $CHCl_3$ solution. The yields of the products were substantially unchanged compared with those from the thermal decomposition in benzene.

In the case of I, the initial yellow color of the solution turned pink during the first hour of reaction, and then this color slowly disappeared while nitrogen was evolved. A pink compound (mp 95° dec from benzene–*n*-pentane) was obtained by removing the chloroform under reduced pressure, in the cold, when the pink color of the solution had become most intense. The analytical values and the physicochemical data suggest that this compound is 1-*p*-toluenesulfonyl-1,2-diphenyl-2-diazoethane (IV). The rearrangement of I to IV has been followed at 25° by scanning the visible spectrum between 350 and 700 mμ every 16 min. The disappearence of the band at 342 mμ of I is consistent with the formation of the band at 500 mμ of IV. The absorption curves for this transformation carried out at 25° in chloroform are shown in Figure 1.

---

[1] This work was done with financial support of the Italian National Research Council (C.N.R.).

[2] T. Iwadare, I. Adachi, M. Hayashi, A. Matsunaga, and T. Kitai, *Tetrahedron Lett.*, No. 51, 4447 (1969).

[3] L. Caglioti, P. Grasselli, F. Morlacchi, and G. Rosini, *Chem. Ind. (London)*, 25 (1968).

[4] L. Caglioti and G. Rosini, *ibid.*, 1093 (1969).

[5] P. Wieland, *Helv. Chim. Acta*, **53**, 171 (1970).

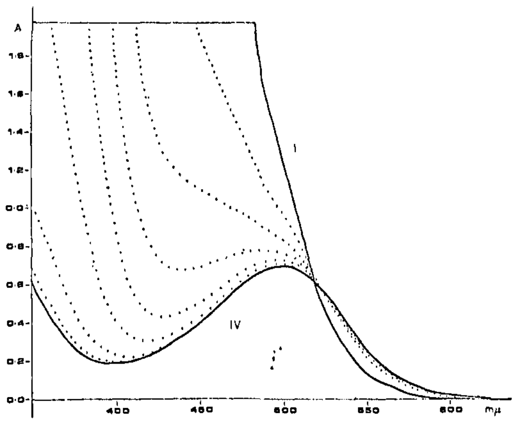
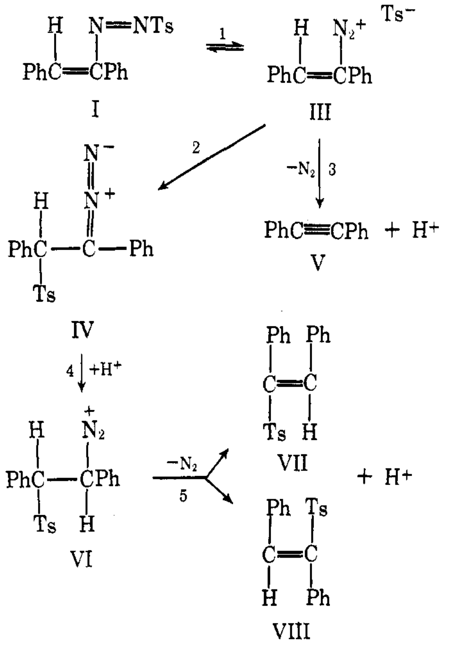


Figure 1.

It was also possible to follow the rearrangement by observing the infrared spectrum. The band at 1630 cm^{-1} characteristic of I disappears, while a strong band at 1960 cm^{-1} ($>C=\overset{+}{N}=\overset{-}{N}$)[6] characteristic of IV appears. The kinetics of the reaction of IV to form VII and VIII in chloroform were followed by observing the band at 500 mμ, and the results obtained are consistent with a first-order reaction with respect to IV. Duplicate runs at 25° gave $k = 1.5 \times 10^{-5}$ sec^{-1}. On the basis of the above-reported experiments, the course of decomposition of *p*-toluenesulfonylazostilbene (I) can be depicted as in Scheme I.

SCHEME I



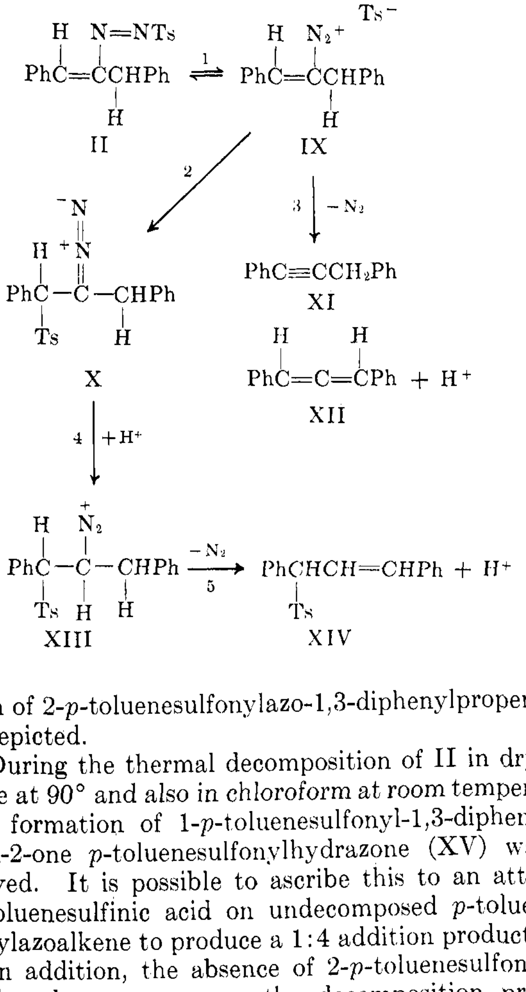
The covalent *p*-toluenesulfonylazoenic form I, by dissociation into diazonium *p*-toluenesulfinate III, rearranges to 1-*p*-toluenesulfonyl-1,2-diphenyl-2-diazoethane (IV), while a fraction of the vinylic diazonium ion undergoes an internal neutralization leading to diphenylacetylene (V), nitrogen, and H$^+$ ions. The latter protonate the diazo group of IV and, by nitrogen expulsion, *p*-toluenesulfonyl-*cis*-stilbene (VII), *p*-toluenesulfonyl-*trans*-stilbene (VIII), and further H$^+$ ions are formed.

A carbenic pathway from IV to VII and VIII is also possible; however, pure IV, when dissolved in chloroform at 25°, is stable. If acetic acid is added, a rapid decomposition is observed. This suggests to us that ionic decomposition should largely overwhelm the carbenic pathway. Extensive mechanistic studies of steps 3 and 5 of this reaction have not been carried out, and, consequently, the decomposition of the diazonium ions of III and IV *via* vinyl carbonium ions is, at present, as likely as the one depicted.

The yields in which compounds IV was obtained suggest that the alternative route *via* displacement of the diazonium ion by the *p*-toluenesulfonyl anion leading to the formation of VII and VIII is not possible in this case.

In Scheme II the probable course of the decomposition of 2-*p*-toluenesulfonylazo-1,3-diphenylpropene (II) is depicted.

SCHEME II



During the thermal decomposition of II in dry benzene at 90° and also in chloroform at room temperature, the formation of 1-*p*-toluenesulfonyl-1,3-diphenylpropan-2-one *p*-toluenesulfonylhydrazone (XV) was observed. It is possible to ascribe this to an attack of *p*-toluenesulfinic acid on undecomposed *p*-toluenesulfonylazoalkene to produce a 1:4 addition product.[3]

In addition, the absence of 2-*p*-toluenesulfonyl-1,3-diphenylpropene among the decomposition products seems to exclude nucleophilic displacement on the diazonium ion.

The results reported here are in good agreement with the experiments performed on the decomposition of *p*-toluenesulfonylazocyclohexene in acidic conditions.[7]

Experimental Section

All melting points are uncorrected. Spectra were recorded on Beckman IR-5A, UNICAM SP-800, and MiNiMar Jeolco

---

[6] P. Yates, B. L. Shapiro, N. Yoda, and J. Fugger, *J. Amer. Chem. Soc.*, **79**, 5756 (1957).

[7] Work is in progress in our laboratory.

spectrometers. Band relative intensity of ir spectra is indicated as follows: vs, very strong; s, strong; m, medium; w, weak; and vw, very weak. Nmr spectra were recorded using TMS as internal standard. Microanalyses were performed using C, H, and N Analyzer Model 185 of Hewlett-Packard Co. Benzoin, 1,3-diphenylpropan-2-one, and *p*-toluenesulfonylhydrazine are commercial materials. Analytical grade solvents were purified by standard methods[8] and distilled through a Vigreux column before use.

α-Acetoxydeoxybenzoin *p*-Toluenesulfonylhydrazone.—α-Acetoxydeoxybenzoin (10 g, 3.9 × 10^{-2} mol) was dissolved in ethanol and 7.34 g (3.9 × 10^{-2} mol) of *p*-toluenesulfonylhydrazine added. The solution was allowed to stand until precipitation was judged complete (about 3 days). The crystals were collected, washed with alcohol, and dried (mp 130–132°, yield, 85%). In the infrared spectrum, bands were observed at 3200 (NH), 1720 (>C=O), 1600 (phenyl), and 1160 cm^{-1} (SO_2). Nmr ($CDCl_3$) signals appeared at δ 7.75–6.9 (multiplet, 1 H) for aromatic protons, 6.75 (multiplet, 1 H) for the proton on C bearing acetoxy, 6.20 (singlet, 1 H) for the NH proton, 2.35 (singlet, 3 H) for the methyl of *p*-toluenesulfonyl, and 1.95 (singlet, 3 H) for the methyl of acetoxy.

Anal. Calcd for $C_{23}H_{22}N_2O_4S$: C, 65.39; H, 5.25; N, 6.63. Found: C, 65.20; H, 5.32; N, 6.62.

***p*-Toluenesulfonylazostilbene (I).**—α-Acetoxydeoxybenzoin *p*-toluenesulfonylhydrazone (5.0 g, 1.2 × 10^{-2} mol) was dissolved in dry benzene and 1.0 g of LiH was added. The mixture was allowed to stand at room temperature with occasional stirring. After about 20 min the yellow solution was filtered and washed several times with water, dried over Na_2SO_4, and filtered, and finally evaporation of benzene gave a yellow product (mp 95° dec, yield 65%). In the infrared spectrum, bands were observed at 3000 (vw), 1630 (w), 1580 (m), 1480 (vw), 1430 (s), 1370 (m), 1335 (vs), 1320 (m), 1300 (m), 1220 (vw), 1180 (m), 1160 (vs), 1130 (w), 1080 (vs), 1065 (s), 1025 (w), 928 (m), 892 (m), 865 (w), 840 (s), 810 (s), 760 (vs), and 735 cm^{-1} (s). Uv (benzene) showed λ_{max} 342 mμ (ε 19,700). Nmr signals ($CDCl_3$) appeared at δ 7.8–6.9 (multiplet, 14 H) for aromatic protons, 6.84 (singlet, 1 H) for the vinylic proton, and 2.34 (singlet, 3 H) for the methyl of *p*-toluenesulfonyl.

Anal. Calcd for $C_{21}H_{16}N_2O_2S$: C, 69.60; H, 5.0; N, 7.73. Found: C, 69.95; H, 5.1; N, 7.63.

α-Acetoxy-1,3-diphenylpropan-2-one *p*-Toluenesulfonylhydrazone.—α-Acetoxy-1,3-diphenylpropan-2-one (10 g, 3.7 × 10^{-2} mol) was dissolved in ethanol and 6.9 g (3.7 × 10^{-2} mol) of *p*-toluenesulfonylhydrazine added. The solution was allowed to stand until precipitation of the product was judged complete (about 20 hr). The crystals were collected (mp 132–134°, yield 85%), washed with alcohol, and dried. In the infrared spectrum, bands were observed at 3220 (NH), 1730 (>C=O), 1600 (phenyl), and 1165 cm^{-1} (SO_2). Nmr signals ($CDCl_3$) appeared at δ 8.2–7.0 (multiplet, 14 H) for aromatic protons, 6.70 (multiplet, 1 H) for the proton on C bearing acetoxy, 6.18 (singlet, 1 H) for the NH proton, 3.35 (singlet, 2 H) for benzilic protons, 2.36 (singlet, 3 H) for the methyl of *p*-toluenesulfonyl, and 1.92 (singlet, 3 H) for the methyl of acetoxy.

Anal. Calcd for $C_{24}H_{24}N_2O_4S$: C, 66.04; H, 5.54; N, 6.42. Found: C, 66.24; H, 5.53; N, 6.20.

2-*p*-Toluenesulfonylazo-1,3-diphenylpropene (II).—α-Acetoxy-1,3-diphenylpropan-2-one *p*-toluenesulfonylhydrazone (5.0 g, 1.1 × 10^{-2} mol) dissolved in 500 ml of ether was placed in a separatory funnel, shaken with an aqueous solution of 10% NaOH, and then washed several times with water. The ethereal solution was dried over Na_2SO_4, the ether evaporated, and a yellow compound was obtained (mp 78–80°; yield 60%). Infrared spectrum bands were observed at 3000 (vw), 1600 (w), 1490 (w), 1450 (w), 1340 (s), 1295 (w), 1165 (s), 1085 (w), 970 (vw), 895 (m), 830 (w), 805 (w), 785 (w), 760 (m), and 695 cm^{-1} (vs) in KBr. Uv (benzene) showed λ_{max} 360 mμ (ε 24,340). Nmr spectrum ($CDCl_3$) showed signals at δ 7.8–6.9 (multiplet, 14 H) for aromatic protons, 6.87 (singlet, 1 H) for the vinylic proton, 3.73 (singlet, 2 H) for allylic protons, and 2.42 (singlet, 3 H) for the methyl of *p*-toluenesulfonyl.

Anal. Calcd for $C_{22}H_{20}N_2O_2S$: C, 70.2; H, 5.36; N, 7.44. Found: C, 69.95; H, 5.45; N, 7.40.

Decomposition of *p*-Toluenesulfonylazostilbene. Route A.—(3.0 g, 8.3 × 10^{-3} mol) dissolved in 100 ml of dried benzene in a sealed tube was heated in an oil bath at 90°. After a few minutes the benzene solution turned red and this color disappeared rapidly with evolution of nitrogen. The colorless solution was cooled and concentrated under reduced pressure, and then a chromatographic separation was performed on a silica gel column using benzene as eluent. The products obtained were identified as diphenylacetylene (V)[9] (28% yield) and, from the second set of fractions, a 1:1 mixture of the two *p*-toluenesulfonylstilbene isomers (cis and trans). The separation of these was carried out on another silica gel column using [benzene (70%)–cyclohexane (30%)] as eluent.

***p*-Toluenesulfonyl-*cis*-stilbene (VII).**—VII had mp 179–180°. Ir and uv spectra were identical with those of an authentic sample of *p*-toluenesulfonyl-*cis*-stilbene independently prepared.[10] Nmr spectrum ($CDCl_3$) showed signals at δ 8.2 (singlet, 1 H) for the vinylic proton, 7.6–6.7 (multiplet, 14 H) for aromatic protons, and 2.31 (singlet, 3 H) for the methyl of *p*-toluenesulfonyl.

Anal. Calcd for $C_{21}H_{18}O_2S$: C, 75.41; H, 5.38. Found: C, 75.47; H, 5.48.

***p*-Toluenesulfonyl-*trans*-stilbene (VIII).**—VIII had mp 146–148°. Ir and uv spectra were identical with those of an anthentic sample independently prepared.[10] The nmr spectrum ($CDCl_3$) showed signals at δ 7.6–6.5 (multiplet, 15 H) for aromatic protons and a vinylic one and 2.4 (singlet, 3 H) for the methyl of *p*-toluenesulfonyl.

Anal. Calcd for $C_{21}H_{18}O_2S$: C, 75.41; H, 5.38. Found: C, 75.45; H, 5.31.

Decomposition of *p*-Toluenesulfonylazostilbene. Route B. 1-*p*-Toluenesulfonyl-1,2-diphenyl-2-diazoethane (IV).—I (3.0 g, 0.83 × 10^{-2} mol) was dissolved in dried chloroform (300 ml) in a flask. The solution was allowed to stand at 25° in a thermostat bath and the reaction was followed by the visible spectrum change at the same temperature. During *ca.* 1 hr the formation of a band at 500 mμ was observed. When the absorbance of the band at 500 mμ assigned to IV was most intense, 150 ml of solution was removed from the flask and evaporated under reduced pressure at room temperature. The mixture was purified by crystallization from benzene–pentane and a crystalline product was obtained in a 55% yield (mp 95–96° dec). Uv (cyclohexane) showed λ_{max} 282 mμ (ε 14,880) and uv ($CHCl_3$) λ_{max} 500 mμ (ε 613). Ir spectrum bands were observed at 1960 (vs), 1580 (m), 1490 (m), 1440 (w), 1340 (sh, vw), 1310 (s), 1290 (s), 1165 (sh, m), 1140 (s), 1080 (m), 1030 (vw), 880 (vw), 810 (m), 770 (w), 740 (s), 675 (s), and 645 cm^{-1} (s) in KBr. Nmr signals ($CDCl_3$) appeared at δ 8.0–6.7 (multiplet, 14 H) for aromatic protons, 4.83 (singlet, 1 H) for the benzilic proton, and 2.25 (singlet, 3 H) for the methyl of *p*-toluenesulfonyl.

Anal. Calcd for $C_{21}H_{16}N_2O_2S$: C, 69.60; H, 5.0; N, 7.73. Found: C, 69.83; H, 4.92; N, 7.80.

The remaining solution (150 ml) was allowed to stand at 25° until the pink color disappeared, then the solvent was evaporated, and the mixture was taken up in benzene. This solution was placed on a column of silica gel and eluted as for route A. Compounds V, VII, and VIII were obtained in the same yield as in the experiment described above.

Decomposition of 2-*p*-Toluenesulfonyl-1,3-diphenylpropene. Route A.—II (3.0 g, 0.8 × 10^{-2} mol) in 100 ml of dry benzene was sealed in a tube and treated thermally as described before for I. After 15 min the red solution turned colorless; then it was cooled and evaporated. The mixture was taken up in ether and, on adding cyclohexane, a white precipitate was obtained which was filtered off and crystallized from methanol. The spectroscopic results and microanalytical data led to the assignment to this compound as a *p*-toluenesulfonylhydrazone of 1-*p*-toluenesulfonyl-1,3-diphenylpropan-2-one (XV). The residual solution was again evaporated and taken up in benzene (20%) and cyclohexane (80%) (10 ml), and the mixture was separated by chromatography on a silica gel column with cyclohexane as eluent. Three sets of fractions were collected. The purity of these was checked by tlc on silica gel plates using an uv lamp to reveal the spots. By evaporating the solvent at room temperature with a water aspirator, 1,3-diphenylallene (XII) was obtained in 10% yield from the first set of fractions, and from the second set a pale yellow oil, 1,3-diphenylpropyne (XI), was obtained in about 18% yield. The third set of fractions, after evaporation under the

---

[8] A. Weissberger, "Technique of Organic Chemistry," Vol. VII, Interscience, New York, N. Y., 1955.

[9] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1955, p 181.

[10] S. J. Cristol and P. Pappas, *J. Org. Chem.*, **28**, 2066 (1963).

same conditions, gave a white product in 35% yield that furnished analytical data consistent with the structure of 1,3-diphenyl-3-*p*-toluenesulfonyl-1-propene (XIV).

1-*p*-Toluenesulfonyl-1,3-diphenylpropen-2-one *p*-Toluenesulfonylhydrazone (XV).—XV had mp 160–162° from methanol. Ir spectrum showed bands at 3200 (s), 3020 (w), 2880 (w), 1640 (w), 1600 (s), 1480 (s), 1400 (vs), 1335 (vs), 1315 (vs), 1230 (m), 1162 (vs), 1130 (vs), 1080 (vs), 1050 (s), 925 (s), 885 (s), 845 (m), 812 (vs), 790 (s), 760 (s), 740 (m), 705 (vs), and 675 $\mathrm{cm^{-1}}$ (vs) in KBr. Nmr ($CDCl_3$) signals appeared at δ 8.14 (singlet, 1 H) for the NH proton, 7.85–6.5 (multiplet, 14 H) for aromatic protons, 4.7 (singlet, 1 H) for the proton on C bearing *p*-toluenesulfonyl, 3.38 (singlet, 2 H) for benzilic protons, and 2.34 and 2.18 (two singlets, 6 H) for the two methyls of *p*-toluenesulfonyl.

Anal. Calcd for $C_{29}H_{26}N_2O_4S_2$: C, 65.4; H, 5.30; N, 5.26. Found: C, 64.8; H, 5.12; N, 5.31.

1,3-Diphenylallene (XII).—XII had mp 47–50° from *n*-pentane. Ir and uv spectra were in good agreement with the data reported in the literature.[11] Nmr spectrum (C_6D_6) showed signals at δ 7.5–7.1 (multiplet, 10 H) for aromatic protons and at 6.58 (singlet, 2 H) assigned to allenic protons.

Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29; mol wt, 192.25. Found: C, 94.12; H, 6.35; mol wt (mass spectroscopy), 192.

1,3-Diphenylpropyne (XI).—The pale yellow oil distilled at 151–155° (4 mm). Ir and uv spectra were in good agreement with the data reported in the literature.[12] Nmr spectrum (C_6D_6) showed signals at δ 7.5–7.0 (multiplet, 10 H) for aromatic protons and 3.78 (singlet, 2 H) for benzilic protons.

Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29; mol wt, 192.25. Found: C, 94.2; H, 6.05; mol wt (mass spectroscopy), 192.

1,3-Diphenyl-3-*p*-toluenesulfonyl-1-propene (XIV).—XIV had mp 150–153° from CH_2Cl_2–pentane. Ir spectrum showed bands at 3020 (w), 1580 (m), 1480 (m), 1450 (m), 1310 (vs), 1140 (vs), 1080 (m), 1020 (vw), 975 (m), 920 (w), 875 (vw), 810 (m), 780 (m), 750 (vs), 715 (m), and 665 $\mathrm{cm^{-1}}$ (m) in KBr. Nmr ($CDCl_3$) signals appeared at δ 7.5–6.9 (multiplet, 14 H) for aromatic protons, 6.42 (multiplet, 2 H) assigned to vinylic protons, 4.65 (multiplet, 1 H) for the proton on C bearing *p*-toluenesulfonyl, and 2.25 (singlet, 3 H) assigned to the methyl of *p*-toluenesulfonyl.

Anal. Calcd for $C_{22}H_{20}O_2S$: C, 75.84; H, 5.79; S, 9.18. Found: C, 75.9; H, 5.65; S, 9.15.

Decomposition of 2-*p*-Toluenesulfonylazo-1,3-diphenylpropene. Route B.—II (3.0 g, 0.8×10^{-3} mol) in 150 ml of dry chloroform was allowed to stand for several hours until the red color of the solution disappeared. After removal of solvent by evaporation under reduced pressure at room temperature, the mixture was treated as indicated for route A. Compounds XI, XII, XIV, and XV were obtained in yields which were not substantially changed from those observed in route A.

Registry No.—I, 29127-96-6; II, 29127-97-7; IV, 29127-98-8; VII, 29119-39-9; VIII, 29119-40-2; XI, 4980-70-5; XII, 19753-98-1; XIV, 29128-01-6; XV, 29128-02-7; α-acetoxydeoxybenzoin *p*-toluenesulfonylhydrazone, 24854-36-2; α-acetoxy-1,3-diphenylpropan-2-one *p*-toluenesulfonylhydrazone, 29128-04-9.

Acknowledgment.—We are indebted to Professor Luciano Caglioti for his interest and helpful discussion throughout this work.

---

(11) T. L. Jacobs and D. Dankner, *J. Org. Chem.*, **22**, 1424 (1957).

(12) J. R. Johnson, T. L. Jacobs, and A. M. Schwartz, *J. Amer. Chem. Soc.*, **60**, 1885 (1938).

Meisenheimer-Type Compounds from Heteroaromatic Substrates. The Reaction of Methoxide Ion with 2-Methoxy-3,5-dinitrothiophene[1]

GIANCARLO DODDI, GABRIELLO ILLUMINATI,* AND FRANCO STEGEL

Department of Chemistry, University of Rome, 00185 Rome, Italy, and Centro C.N.R. (Rome) dei Meccanismi di Reazione

Received December 1, 1970

The formation and isolation of a Meisenheimer-type adduct from 2-methoxy-3,5-dinitrothiophene and methoxide ion are described. Addition of the nucleophile occurs at the 2 position only, to yield the 2,2-dimethoxy-3,5-dinitrothiacyclopentenate ion. The specific rate and, particularly, the equilibrium constant for the formation of this adduct at 25° are larger than the corresponding values for the formation of the adduct between 2,4,6-trinitroanisole and methoxide ion at the same temperature.

Meisenheimer-type adducts formed from nitro-substituted homocyclic aromatic substrates and methoxide ion have been intensively studied.[2] The formation of similar adducts from pyridine and pyrimidine derivatives has been reported[3–8] and compared with the corresponding reactions of homocyclic compounds. We are now considering the behavior of suitable five-membered ring substrates in order to evaluate the role of the ring size and of the heteroatom in the formation of the adducts. Following a preliminary communication,[9] we report detailed results and additional data for the reaction of 2-methoxy-3,5-dinitrothiophene with methoxide ion.

Experimental Section

Materials.—The methanol used for the rate measurements was purified as described;[3] however, since methanol distilled over magnesium methoxide may still contain traces of basic impurities,[10] that used in the experiments carried out in the presence of sodium acetate was redistilled over *p*-nitrobenzoic acid. 2-Methoxy-3,5-dinitrothiophene ($\epsilon_{max} = 0.92 \times 10^4\ M^{-1}\ \mathrm{cm^{-1}}$ at 243 nm; $\epsilon_{max} = 1.04 \times 10^4\ M^{-1}\ \mathrm{cm^{-1}}$ at 343 nm, in methanol) was prepared by a known procedure[11] and by nitration of 2-methoxy-5-nitrothiophene[12] with 99% nitric acid in acetic anhydride at 0°. Attempts to obtain it by methoxy dechlorination of 2-chloro-3,5-dinitrothiophene were unsuccessful. Other materials used and the analytical and nmr and uv visible spectral

---

(1) Part XXXVI: Nucleophilic Heteroaromatic Substitution.

(2) (a) M. R. Crampton, *Advan. Phys. Org. Chem.*, **7**, 211 (1969); (b) R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966).

(3) P. Bemporad, G. Illuminati, and F. Stegel, *J. Amer. Chem. Soc.*, **91**, 6742 (1969).

(4) C. Abbolito, C. Iavarone, G. Illuminati, F. Stegel, and A. Vazzoler, *ibid.*, **91**, 6746 (1969).

(5) J. E. Dickeson, L. K. Dyall, and V. A. Pickles, *Aust. J. Chem.*, **21**, 1267 (1968).

(6) M. E. C. Biffin, J. Miller, A. G. Moritz, and D. B. Paul, *ibid.*, **22**, 2561 (1969).

(7) M. E. C. Biffin, J. Miller, A. G. Moritz, and D. B. Paul, *ibid.*, **23**, 957 (1970).

(8) R. Schaal, F. Terrier, J. C. Halle, and A. P. Chatrousse, *Tetrahedron Lett.*, 1393 (1970).

(9) G. Doddi, G. Illuminati, and F. Stegel, *Chem. Commun.*, 953 (1969).

(10) E. Grunwald, C. F. Jumper, and S. Meiboom, *J. Amer. Chem. Soc.*, **84**, 4664 (1962).

(11) C. D. Hurd and K. L. Kreuz, *ibid.*, **74**, 2965 (1952).

(12) J. Sicé, *ibid.*, **75**, 3697 (1953).