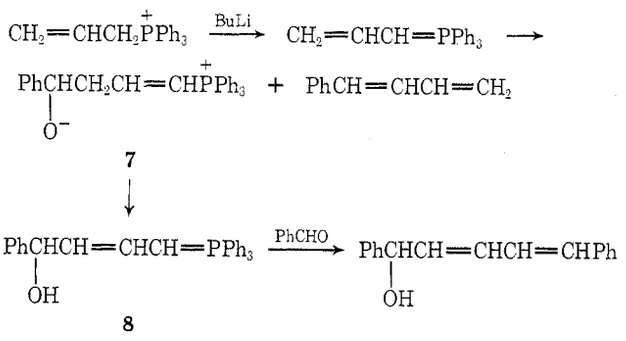
transoid allylic ylide **6**[10] which is incapable of a cycloaddition process.

To determine the generality of γ substitution, we have examined the reaction of allylidenetriphenylphosphorane and benzaldehyde under more typical Wittig conditions. Treatment of allyltriphenylphosphonium fluoroborate with a small excess of *n*-butyllithium (positive Gilman test) in tetrahydrofuran followed by benzaldehyde and aqueous work-up affords 1-phenylbutadiene (65%). Under these conditions, 1,5-diphenylpenta-2,4-dien-1-ol is not formed in amounts detectable by thin layer chromatography. However, the dienol is formed in 11% yield in addition to 1-phenylbutadiene if the same experiment is performed without aqueous work-up and the THF solution is treated with DBU, benzaldehyde, and the flurorboric acid salt of DBU to approximate the latter stages of reactions listed in Table I. Clearly, the γ-substituted vinylphosphonium salt **7** is formed to a small extent even under aprotic Wittig conditions, but requires a proton transfer agent (DBU·HBF_4 or methanol) in order to be converted into the hydroxyl ylide **8**.[11]



Allyl- or crotyltriphenylphosphonium salts also react with isobutyraldehyde (DBU, THF at reflux) to form dienols (10–20%) in addition to the dienes. We conclude that γ substitution of allyl ylides is general and probably has not been observed previously in the Wittig reaction because the initially formed salt (*i.e.*, **7**) is not converted to dienol under aprotic conditions, and is discarded along with other polar byproducts in the course of aqueous work-up.

Experimental Section

2-(2-Butenyl)methyldiphenylphosphonium Fluoroborate.—A 250-ml three-neck flask was equipped with mechanical stirring and argon inlet and outlet. Lithium wire (1.3 g, 0.185 mol) cut into small pieces was added together with dry ether (60 ml) under argon and the mixture was cooled to −30° and stirred vigorously. (*E*)-2-bromobut-2-ene (5.4 g, 0.04 mol) was added dropwise over 20 min and the mixture was stirred for an additional 1 hr at −30°. The ether solution was transferred at −30° by syringe to a second flask, unreacted lithium being left behind. To this solution was added chlorodiphenylphosphine (Aldrich, distilled, 5.5 g, 0.025 mol) and the reaction mixture was stirred at −30° for 3 hr. Excess methyl iodide (17 g) was then added under argon and the reaction was allowed to stand at room temperature for 18 hr. The ether was evaporated to dryness, and the residue was taken up in methanol (*ca.* 100 ml) and stirred vigorously with a large excess of aqueous sodium fluoroborate. The product was then extracted into chloroform (3 × 50 ml), and the chloroform was dried over magnesium sulfate and evaporated under high vacuum. The residual yellow oil could not be crystallized but the nmr spectrum indicated <90% 2-(2-butenyl)methyldiphenylphosphonium fluoroborate, nmr ($CDCl_3$) δ 7.4–8 (10 H, m), 6.2–6.8 (1 H, m), 2.7 (3 H, d, J = 14 Hz), 2.1 (3 H, m), 1.6 (3 H, m).

Reaction of Allylic Phosphonium Salts with Benzaldehyde. General Procedure.—The phosphonium salt (0.005 mol), DBU (0.0055 mol), and benzaldehyde (0.025 mol) were dissolved in the appropriate solvent (dry tetrahydrofuran or reagent grade methanol, 10 ml) and allowed to react under nitrogen as indicated in Table I. The products were then extracted by aqueous pentane work-up. The pentane layer was concentrated, an internal standard (toluene) was added, and the diene yields were determined by glpc on 5 ft × 0.25 in. SE-30. The aqueous layer and all pentane—insoluble residues were then extracted with chloroform, and all of the organic fractions were combined and evaporated. The crude product was separated by preparative layer chromatography over silica gel using 4:1 hexane–ether. Three zones were observed in addition to polar base line material, R_f 0.8 (diene), 0.6–0.7 (recovered benzaldehyde), and 0.2–0.3 (dienol). All dienol products were oils and were characterized by nmr and exact mass. Elution of the base-line material with chloroform–ether afforded the phosphine oxide, generally in 3–8% higher yield than the combined yields of diene and dienol.

γ Substitution under Aprotic Conditions.—Allyltriphenylphosphonium fluoroborate (1.8 g, 0.0045 mol) suspended in dry tetrahydrofuran (25 ml) was treated dropwise with *n*-butyllithium (0.0046 mol) in hexane (3 ml) at 0°. Benzaldehyde (2.38 g, 0.0225 mol, freshly distilled) was then added to the homogeneous red solution and the reaction mixture was stored under nitrogen for 18 hr at 25°. Work-up as above afforded phenylbutadiene (65%, cis:trans 1:3) but no dienol by tlc analysis.

The above experiment was repeated. After overnight reaction of benzaldehyde with the ylide, 0.0045 mol each of DBU, DBU·$H^+BF_4^-$, and benzaldehyde was added, and the mixture was heated at reflux for 18 hr. Work-up as before afforded phenylbutadiene (52%) and 1-phenylpenta-2,4-dienol (11%). Addition of 3,4-dichlorobenzaldehyde after the initial Wittig condensation did not alter the product ratios and produced no new products by tlc or glpc analysis.

Registry No.—Benzaldehyde, 100-52-7; (*E*)-2-bromobut-2-ene, 3017-71-8; chlorodiphenylphosphine, 1079-66-9; methyl iodide, 74-88-4; sodium fluoroborate, 13755-29-8.

(10) E. Vedejs, K. A. J. Snoble, and P. L. Fuchs, *J. Org. Chem.*, **38**, 1178 (1973).

(11) It is conceivable that **7** is not formed initially if the Wittig betaine has not completely decomposed to phenylbutadiene at the time that benzaldehyde, DBU, and DBU·HBF_4 are added. Dissociation of the betaine under protic conditions followed by readdition to form **7** could then explain formation of the dienol. To exclude this possibility, we have conducted a crossover experiment where 3,4-dichlorobenzaldehyde is added instead of benzaldehyde after the initial Wittig condensation. The products contain no trace of 3,4-dichlorophenylbutadiene, which would have to be formed if dissociation of the betaine plays any role in the reaction.

The Reaction of Triethylamine with *N*-*p*-Toluenesulfonylarylhydrazidoyl Chlorides

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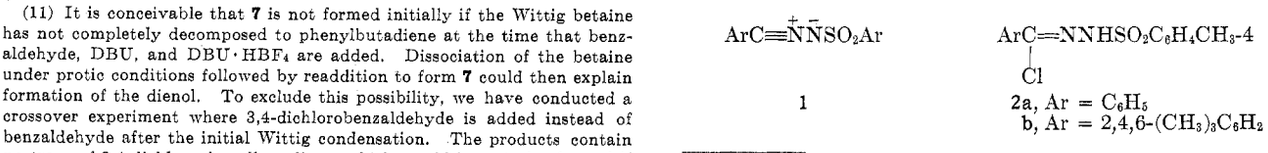
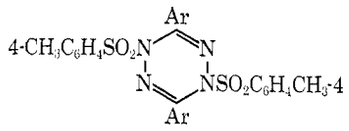
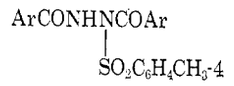
The reaction of triethylamine with *N*-*p*-toluenesulfonylhydrazidoyl chlorides (**2**) was investigated as a method for preparing nitrilesulfonimides (**1**).



(1) Abstracted in part from the Ph.D. Thesis of J. N. K., 1973.

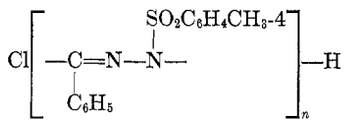
Triethylamine in tetrahydrofuran converted **2** into the 1,4-dihydro-3,6-diaryl-1,4-bis(*p*-toluenesulfonyl)-*s*-tetrazines (**3**). The reaction involving **2a** gave in





3a, Ar = C_6H_5 **4a**, Ar = C_6H_5
b, Ar = 2,4,6-$(CH_3)_3C_6H_2$ **b**, Ar = 2,4,6-$(CH_3)_2C_6H_2$

addition small amounts of 1,2-dibenzoyl-1-*p*-toluenesulfonylhydrazine (**4a**) and two other compounds for which structures **5a** and **5b** were assigned upon the basis of their ir and nmr spectra and elemental analysis.

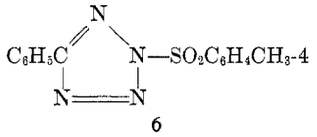


5a, $n = 2$
b, $n = 3$

In agreement with the structure proposed compound **5a**, when refluxed with aqueous ethanol, gave **3a**, the related 3,5-diphenyltetrazine, and **4a**. This reaction confirms the intermediacy of **5a** in the formation of **3a** and **4a** with the latter probably resulting from the action of moisture.

The only by-product isolated when **2b** was treated with triethylamine was **4b**.

The same dihydrotetrazine **3a** has been isolated in the reaction of *p*-toluenesulfonyl chloride with 5-phenyltetrazole in pyridine and has been ascribed to the dimerization of the intermediate nitrile imide (**1**).[2] An alternate and more likely reaction for the formation of the dimer **3a** is the conversion of the nitrile imide **1** by the pyridine hydrochloride into the chloride **2a** which is then converted into the dimer **3a** by pyridine. Evidence for such a pathway was obtained by preparing 2-*p*-toluenesulfonyl-5-phenyltetrazole (**6**) and studying its thermolysis. This labile tetrazole (**6**) decom-



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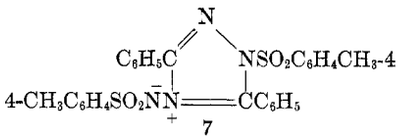
posed in the presence of water and gave the hydration product of the intermediate nitrile imide (**1**), 1-benzoyl-2-*p*-toluenesulfonylhydrazine, the hydrolysis product of **6**, 5-phenyltetrazole, and trace amounts of 3,6-diphenyl-*s*-tetrazine.

Thermal decomposition of the tetrazole (**6**) in anhydrous benzene was complex and gave 1,2-dibenzoyl-1-*p*-toluenesulfonylhydrazine (**4a**), *S*-*p*-tolyl thiobenzoate, *S*-*p*-tolyl *p*-toluenethiosulfonate and *p*-tolyl disulfide as the main products together with traces (less than 2 mg) of 3,6-diphenyl-*s*-tetrazine, the dimer **3a**, and *sym*-dibenzoylhydrazine.

The precursor of the disulfide and toluenethiosulfonate is *p*-toluenesulfinic acid[3] which would arise from the conversion of the dimer **3a** into 3,6-diphenyl-*s*-tetrazine.[2] The total amount of the latter actually isolated was very small and precludes this reaction as the only possibility involved in the formation of *p*-toluenesulfinic acid.

1,2-Dibenzoyl-1-*p*-toluenesulfonylhydrazine (**4a**) is probably formed by the action of traces of moisture on a dimer of the nitrile imide **1**. This dimer may be the [4 + 2] cycloaddition product **7** or the dipolar ion **8**.



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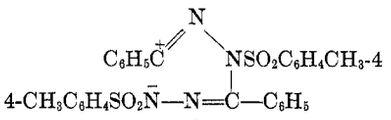

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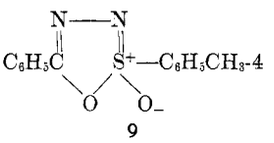
Either one of these could form the dimer **3a** and may be the precursors of *sym*-dibenzoylhydrazine.

The source of *S*-*p*-tolyl thiobenzoate is not known. The dimers **7** and **8** postulated are unlikely intermediates for this compound. A remote possibility which might lead to this compound is the cyclic form **9** of the nitrile imide **1**.



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Experimental Section[4]

1-Benzoyl-2-*p*-toluenesulfonylhydrazine.—A solution of *p*-toluenesulfonyl chloride (85.5 g) in pyridine (175 ml) was added dropwise to a solution of benzhydrazide[5] (61.2 g) in pyridine (200 ml) at 10–15°. The reaction mixture was allowed to come to room temperature and was added to a mixture of 30% hydrochloric acid and ice. The resulting light yellow solid upon crystallization from 70% ethanol melted at 175.5–178.5° (lit.[6] mp 175–176°): yield 106.2 g; ir (Nujol) 3400 (NH), 1670 (CO), 1155 cm^{-1} (SO_2); nmr (pyridine-d_5) δ 11.68 (s, 1, $NHSO_2$), 8.64 (s, 1, CONH), 6.84 (m, 9, C_6H_5, C_6H_4), 2.04 (s, 3, CH_3).

Anal. Calcd for $C_{14}H_{14}N_2O_3S$: C, 57.91; H, 4.86; N, 9.65. Found: C, 58.25; H, 4.92; N, 9.51.

***N*-(*p*-Toluenesulfonyl)benzhydrazidoyl Chloride (2a).**—A solution of 1-benzoyl-2-*p*-toluenesulfonylhydrazine (130.0 g) in thionyl chloride (800 ml) was refluxed for 2 hr. Removal of the thionyl chloride followed by the addition of ethanol (120 ml) and cooling gave a yellow solid. Successive recrystallizations from benzene–hexane and from absolute ethanol gave white crystals melting at 114.5–115.5°: yield 77.2 g (55.5%); ir (Nujol) 3380 (NH), 1595 (C=N), 1165 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 8.36 (s, 1, NH), 7.52 (m, 9, C_6H_5, C_6H_4), 2.34 (s, 3, CH_3).

Anal. Calcd for $C_{14}H_{13}N_2O_2SCl$: C, 54.45; H, 4.24; N, 9.07. Found: C, 54.47; H, 4.29; N, 8.79.

Reaction of *N*-(*p*-Toluenesulfonyl)benzhydrazidoyl Chloride with Triethylamine.—A solution of the chloride (2.0 g) in dry tetrahydrofuran (20 ml) was added to a vigorously stirred solution of triethylamine (1.0 g) in tetrahydrofuran (80 ml) at −10 to 5° over the course of 1 hr. The resulting solution was stirred for 12 hr at room temperature, and the triethylamine hydrochloride was filtered. Removal of the solvent followed by the addition of absolute ethanol (10 ml) gave a yellow solid which after recrystallization from ethanol melted at 153.5–154.5° (lit.[2] mp 156.7°), yield 1.56 g. This compound was identified as 1,4-dihydro-3,6-diphenyl-1,4-bis(*p*-toluenesulfonyl)-5-tetrazene (**3a**) by comparison with an authentic sample.

(2) R. Huisgen, H. J. Sturm, and M. Seidel, *Chem. Ber.*, **94**, 1555 (1961).

(3) E. Vinkler, F. Klivengi, and J. Szabo, *Acta Chim. Acad. Sci. Hung.*, **15**, 384 (1958).

(4) Melting points are corrected. Infrared spectra were obtained using a Perkin-Elmer 137B infrared spectrophotometer and nmr spectra were recorded with a Varian A-60 nmr spectrometer.

(5) G. Struve, *J. Prakt. Chem.*, **50**, 295 (1894).

(6) G. P. Schiemenz and H. Engelhard, *Chem. Ber.*, **92**, 1336 (1959).

The alcohol filtrate upon cooling gave a white solid which after recrystallization from ethanol gave white crystals of the trimer (**5b**) melting at 142–143° dec: yield 0.19 g; ir (Nujol) 3290 (NH), 1565 (C=N), 1165 cm^{-1} (SO_2); nmr ($CDCl_3$) δ, 8.98 (s, 1, NH), 7.35 (m, 27, 3 C_6H_5, 3 C_6H_4), 2.45 (s, 3, CH_3), 2.37 (s, 3, CH_3), 2.23 (s, 3, CH_3).

Anal. Calcd for $C_{42}H_{37}N_6O_6S_3Cl$: C, 59.11; H, 4.37; N, 9.85; S, 11.27; Cl, 4.17. Found: C, 59.16; H, 4.24; N, 9.83; S, 11.22; Cl, 4.18.

Evaporation of the alcohol filtrate gave a solid which upon recrystallization from alcohol gave the dimer (**5a**) melting at 144.5–145.5° dec: yield 0.07 g; ir (Nujol) 3310 (NH), 1560 (C=N), 1165 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 8.65 (s, 1, NH), 7.54 (m, 18, 2 C_6H_5, 2 C_6H_4), 2.41 (s, 3, CH_3), 2.35 (s, 3, CH_3).

Anal. Calcd for $C_{28}H_{25}N_4O_4S_2Cl$: C, 57.87; H, 4.34; N, 9.64; S, 11.04; Cl, 6.10. Found: C, 57.63; H, 4.38; N, 9.55; S, 10.96; Cl, 6.08.

Analysis by tlc on silica gel using chloroform of the ethanol filtrate from the last compound showed the presence of a trace of 1,2-dibenzoyl-2-(*p*-toluenesulfonyl)hydrazine (**4a**). Identification was based on a similar retention time to that of an authentic sample.

1,2-Dibenzoyl-1-(*p*-toluenesulfonyl)hydrazine (4a).—A mixture of sodium benzoate (0.5 g) and *N*-*p*-toluenesulfonylbenzhydrazidoyl chloride (1.0 g) in tetrahydrofuran (100 ml) was refluxed for 5 hr. Filtration of the solution followed by removal of the solvent gave a solid which was extracted first with chloroform and water and then recrystallized from absolute ethanol. The white crystals obtained melted at 225° dec: yield 0.31 g; ir (Nujol) 3400 (NH), 1705, 1655 (CO), 1155 cm^{-1} (SO_2); nmr (DMSO-d_6) δ 11.93 (s, 1, NH), 7.82 (m, 14, 2 C_6H_5, C_6H_4), 2.43 (s, 3, CH_3).

Anal. Calcd for $C_{21}H_{18}N_2O_4S$: C, 63.94; H, 4.60; N, 7.10. Found: C, 64.23; H, 4.56; N, 7.07.

Dehydrohalogenation of Dimer (5a).—A solution of the dimer (**5a**) (0.061 g) in 95% ethanol (10 ml) was refluxed for 12 hr. The solution became red in color which indicated the formation of 3,6-diphenyl-*s*-tetrazine. Analysis by tlc on alumina using chloroform indicated the presence of 3,6-diphenyl-*s*-tetrazine, 1,4-dihydro-3,6-diphenyl-1,4-bis(*p*-toluenesulfonyl)-*s*-tetrazine (**3a**), dimer (**5a**), and 1,2-dibenzoyl-1-(*p*-toluenesulfonyl)hydrazine (**4a**).

1-(2,4,6-Trimethylbenzoyl)-2-(*p*-toluenesulfonyl)hydrazine.—This compound was prepared from 2,4,6-trimethylbenzhydrazide[7] and *p*-toluenesulfonyl chloride using the procedure given for 1-benzoyl-2-*p*-toluenesulfonylhydrazide. Recrystallization from aqueous ethanol gave white crystals melting at 206–270°: yield 91.7%; ir (Nujol) 3420, 3200 (NH), 1670 (CO), 1155 cm^{-1} (SO_2); nmr (DMSO-d_6) δ 10.22 (s, 1, $NHSO_2$), 10.02 (s, 1, NHCO), 7.60 (q, 4, C_6H_4), 6.78 (s, 2, C_6H_2), 6.78 (s, 3, C_6H_4-CH_3), 2.18 (s, 3, $C_6H_2CH_3$), 2.07 (s, 6, $C_6H_2(CH_3)_2$).

Anal. Calcd for $C_{17}H_{20}N_2O_3S$: C, 61.42; H, 6.06; N, 8.43. Found: C, 61.49; H, 6.10; N, 8.19.

***N*-(*p*-Toluenesulfonyl)-2,4,6-trimethylbenzhydrazidoyl Chloride (2b).**—A solution of 1-(2,4,6-trimethylbenzoyl)-2-(*p*-toluenesulfonyl)hydrazine (38.0 g) in thionyl chloride (250 ml) was refluxed for 4 hr. Cooling gave white crystals melting at 185–186° dec: yield 19.1 g; ir (Nujol) 3225 (NH), 1620 (C=N), 1170 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 8.20 (s, 1, NH), 7.58 (q, 4, C_6H_4), 6.82 (s, 2, C_6H_2), 2.44 (s, 3, $C_6H_4CH_3$), 2.28 (s, 3, $C_6H_2CH_3$), 2.00 [s, 6, $C_6H_2(CH_3)_2$].

Anal. Calcd for $C_{17}H_{19}N_2O_2SCl$: C, 58.19; H, 5.46; N, 7.99. Found: C, 58.46; H, 5.35; N, 7.93.

Reaction of *N*-*p*-Toluenesulfonyl-2,4,6-trimethylbenzhydrazidoyl Chloride with Triethylamine.—A solution of triethylamine (1.52 g) in tetrahydrofuran (250 ml) was treated with the chloride (5.26 g) in tetrahydrofuran (150 ml) dropwise at −5 to 0°. The resulting mixture was stirred at room temperature for 12 hr and filtered. Removal of the solvent followed by the addition of absolute ethanol (20 ml) gave a white solid (**3b**, 1.71 g) melting at 230° dec: ir (Nujol) 1605 (C=N), 1180 cm^{-1} (SO_2); nmr ($CDCl_3$) δ 7.31 (q, 8, 2 C_6H_4), 6.82 (s, 4, 2 C_6H_2), 2.40 (s, 6, 2 $C_6H_4CH_3$), 2.32 (s, 6, 2 $C_6H_2CH_3$), 1.90 [s, 12, 2 C_6H_2-$(CH_3)_2$].

Anal. Calcd for $C_{34}H_{36}N_4O_4S_2$: C, 64.94; H, 5.77; N, 8.91. Found: C, 64.87; H, 5.78; N, 9.12.

Removal of the ethanol from the filtrate followed by the addition of chloroform gave 1,2-di(2,4,6-trimethylbenzoyl)-2-*p*-toluenesulfonylhydrazine (**4b**, 2.13 g) melting at 221–222°. The ir and nmr spectra were similar to those of an authentic sample.

Evaporation of the chloroform filtrate gave an oil from which no crystalline compounds could be isolated.

1,2-Di(2,4,6-trimethylbenzoyl)-2-*p*-toluenesulfonylhydrazine (4b).—A mixture of sodium 2,4,6-trimethylbenzoate (0.47 g) and *N*-*p*-toluenesulfonyl)-2,4,6-trimethylbenzhydrazidoyl chloride (0.88 g) in tetrahydrofuran (100 ml) was refluxed for 2 hr. Filtration followed by removal of the solvent gave a solid which was dissolved in chloroform. The resulting solution was washed with water and upon removal of the chloroform gave a solid which was recrystallized from absolute ethanol: mp 221.5–223.5°; yield 1.0 g; ir (Nujol) 3360 (NH); 1705, 1685 (CO), 1165 cm^{-1} (SO_2); nmr (DMSO-d_6) δ 11.27 (s, 1, NH), 7.82 (q, 4, C_6H_4), 6.80 (s, 4, 2 C_6H_2), 2.05 [m, 21, 2 $C_6H_2(CH_3)_3$, $C_6H_4CH_3$].

Anal. Calcd for $C_{27}H_{30}N_2O_4S$: C, 67.76; H, 6.32; N, 5.85. Found: C, 67.79; H, 6.51; N, 5.84.

2-*p*-Toluenesulfonyl-5-phenyltetrazole (6).—A solution of 5-phenyltetrazole (0.73 g) and *p*-toluenesulfonyl chloride (0.95 g) in tetrahydrofuran (25 ml) at 5–10° was treated with triethylamine (1.4 ml) in tetrahydrofuran (20 ml), and the resulting solution was stirred for 5 hr. The resulting triethylamine hydrochloride (0.64 g) was filtered and the filtrate was evaporated to dryness under reduced pressure at room temperature. The resulting solid was extracted with absolute ether and filtered. Concentration of the ether under reduced pressure gave 2-*p*-toluenesulfonyl-5-phenyltetrazole (**6**, 1.12 g): mp 92° (explosive); ir (Nujol) 1530 (C=N), 1180, 1190 cm^{-1} (SO_2); nmr ($CDCl_3$)[8] δ 2.46 (s, 3, CH_3), 7.56 (m, 7, C_6H_5, $CH_3C_6H_2$), 8.17 (d, 2, $C_6H_2SO_2$).

Anal. Calcd for $C_{14}H_{12}N_4SO_2$: C, 56.00; H, 4.00; N, 18.66. Found: C, 55.93; H, 4.55; N, 18.51.

Thermolysis of 2-*p*-Toluenesulfonyl-5-phenyltetrazole (6). A.—A solution of **6** (0.99 g) in a mixture of tetrahydrofuran (50 ml) and water (45 ml) was refluxed for 40 min. Partial removal of the solvent gave a pink solid (0.52 g) which was treated with a small amount of benzene and filtered. The solid (0.36 g) obtained had a wide melting point range, 145–185°, and was extracted with hot benzene. The insoluble portion (0.087 g) melted at 210–212° dec and was identified as 5-phenyltetrazole by its ir spectrum. The benzene filtrate upon cooling gave crystals (0.187 g) which upon crystallization from water gave 1-benzoyl-2-*p*-toluenesulfonylhydrazide (0.1 g), mp 174.5–176.5°. The residue obtained from the first benzene extraction was extracted with petroleum ether (bp 60–68°) and gave 3,6-diphenyl-*s*-tetrazine which upon recrystallization from methanol melted at 190–192°, yield 0.002 g. The mixture melting point with an authentic sample[2] melted at the same point.

B.—A solution of **6** (1.022 g) in dry benzene (100 ml) was refluxed for 10 min. Removal of the benzene under reduced pressure followed by the addition of dry methanol to the residue gave 0.1 g of 1,2-dibenzoyl-1-*p*-toluenesulfonylhydrazine, mp 214–215° dec. The methanol filtrate was evaporated to dryness and the resulting residue was dissolved in benzene and chromatographed on silica using benzene as the eluent. The first fraction was an oil (0.01 g) which was identified as *p*-tolyl disulfide by its mass and ir spectra. The second fraction was *S*-*p*-tolyl benzoate (0.05 g), mp 75–76° (lit.[9] mp 75°). This structure was substantiated by its mass spectrum. This fraction was contaminated with 3,6-diphenyl-*s*-tetrazine. The third fraction consisted of *S*-*p*-tolyl thio-*p*-toluenesulfonate (0.08 g), mp 73–74° (lit.[3] mp 74–75°). Identification was made by comparison with an authentic sample.

Fractions which did not migrate to any extent with benzene were removed from the silica by extraction with chloroform. Concentration of the chloroform gave a small amount of solid melting at 238–240°. This solid was identified as *sym*-dibenzoylhydrazine by its mass spectrum and comparison of its ir spectrum with that of an authentic sample. Chromatography of the chloroform extract on silica using chloroform as the eluent gave a small amount of the dimer **3a**. Identification was made by its migration time on silica and its decomposition at its melting point to the tetrazine. The other fractions obtained were present in insufficient amounts to be identified.

(7) M. S. Newman and E. G. Caflisch, Jr., *J. Amer. Chem. Soc.*, **80**, 862 (1958).

(8) Nitrogen was evolved slowly during the analysis.

(9) R. Schiller and R. Otto, *Chem. Ber.*, **9**, 1634 (1876).

Registry No.—**2a**, 31910-69-7; **2b**, 41262-87-7; **3b**, 41262-88-8; **4a**, 41262-89-9; **4b**, 41262-90-2; **5a**, 41262-91-3; **5b**, 41262-92-4; **6**, 41262-93-5; 1-benzoyl-2-*p*-toluenesulfonylhydrazine, 3064-19-5; *p*-toluenesulfonyl chloride, 98-59-9; benzhydrazide, 613-94-5; triethylamine, 121-44-8; sodium benzoate, 532-32-1; 1-(2,4,6-trimethylbenzoyl)-2-(*p*-toluenesulfonyl)hydrazine, 41262-95-7; sodium 2,4,6-trimethylbenzoate, 32642-28-7; 5-phenyltetrazole, 18039-42-4; 3,6-diphenyl-*s*-tetrazine, 6830-78-0; *sym*-dibenzoylhydrazine, 787-84-8.

Reactions of Hydroxide Tetrakis(2-hydroxyethyl)ammonium

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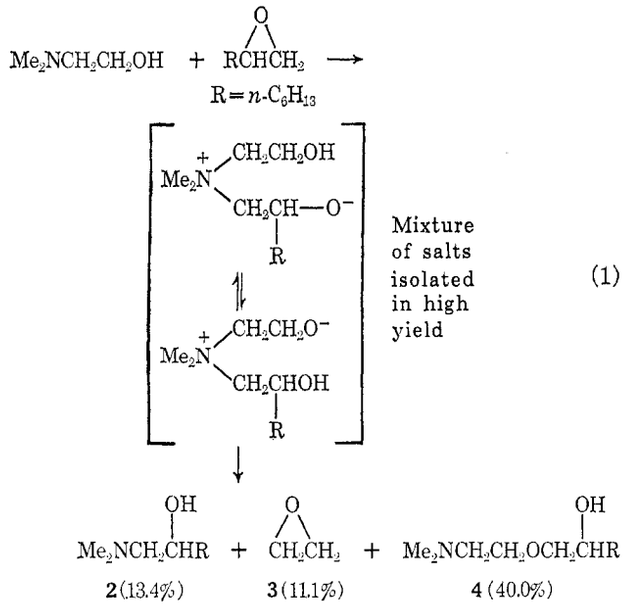
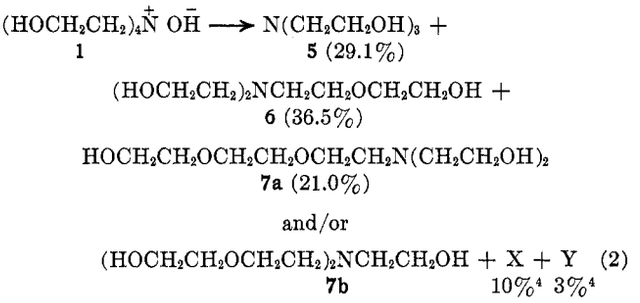
Usually quaternary ammonium hydroxides are considered synthetically useful for olefin formation *via* the Hofmann elimination.[1] However, quaternary ammonium hydroxides bearing one β-hydroxy-substituted side chain thermally decompose to give epoxides, in most cases in high yield to the exclusion of the desired olefin.[1] A paucity of information is available for the chemical reactions and the thermal decomposition of quaternary ammonium hydroxides with more than one β-hydroxy-substituted side chain. Tobler has reported the thermal decomposition of the mixture of quaternary ammonium alkoxides formed by the reaction of 2-(*N*,*N*-dimethylamino)ethanol with 1,2-epoxyoctane.[2] The thermal decomposition of this mixture of quaternary ammonium salts, each species bearing two β-hydroxy-substituted side chains, yields products postulated as occurring *via* intramolecular rearrangements as shown in eq 1.[2] Acetaldehyde formation by a Hofmann-type reaction was not observed.

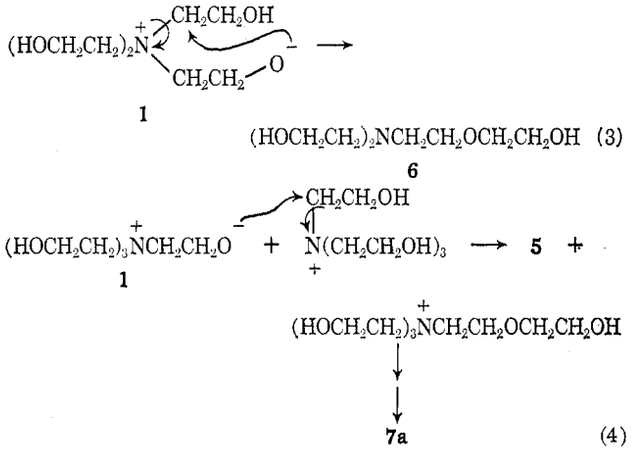


In contrast to the reactions of alkyl-substituted quaternary ammonium salts containing one or two 2-hydroxyalkyl groups, tetrakis(2-hydroxyethyl)-ammonium hydroxide, an easily prepared, stable, white, crystalline compound, behaves somewhat differently. Ethylene oxide and acetaldehyde, expected decomposition products, were not detected in significant quantities under any conditions. Instead the decomposition of **1** was found to take place largely by intermolecular SN2 processes as outlined below.

Thermal decomposition of neat tetrakis(2-hydroxyethyl)ammonium hydroxide (**1**) under nitrogen or high vacuum gives 2,2′,2″-nitrilotriethanol (**5**), 2-(2-hydroxyethoxy)ethyldi(2-hydroxyethyl)amine (**6**), 2-[(2-hydroxyethoxy)ethoxy]ethyldi(2-hydroxyethyl)-amine (**7a**), or di[2-(2-hydroxyethoxy)ethyl]-2-hydroxyethylamine (**7b**), and higher homologs (X, Y) as illustrated by eq 2.[3]



Formation of **6** could occur *via* an intramolecular pathway (eq 3). However, the isolation of the higher ethoxylated products, **7a** and **7b**, provides evidence for the decomposition proceeding at least partially by an intermolecular route (eq 4). In fact, recent work



by Eschenmoser, *et al.*,[5] and earlier work by House and Pitt[6] have shown that, although an endocyclic SN2 displacement reaction is more appealing, the reaction actually proceeds by an intermolecular pathway in many cases. Similar examples of intermolecular attack by various nucleophiles on quaternary am-

(1) A. C. Cope and E. R. Trumbull in "Organic Reactions," Vol. 11, Wiley, New York, N. Y., 1960, Chapter 5.
(2) E. Tobler, *Helv. Chim. Acta*, **52**, 408 (1969).
(3) For simplification **5** will be referred to as NTE and **6**, **7a** and **7b** as the NTE-1-mol and NTE-2-mol ethoxylates, respectively, in the remainder of the text.
(4) Identification of X, Y unknown; yields based on area per cent by vpc.
(5) L. Tenud, S. Farooq, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, **53**, 2059 (1970).
(6) H. O. House, and C. G. Pitt, *J. Org. Chem.*, **31**, 1062 (1966).