

The Cycloaddition Reaction of N-Sulfinylaniline with Norbornene

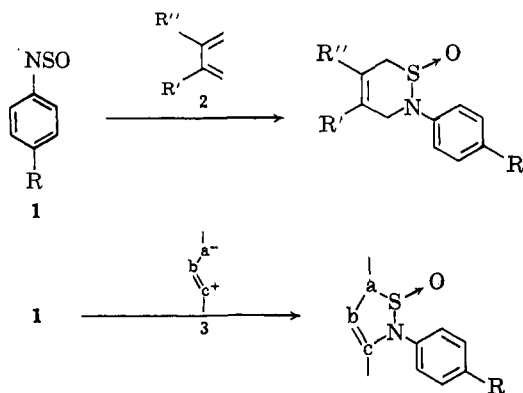
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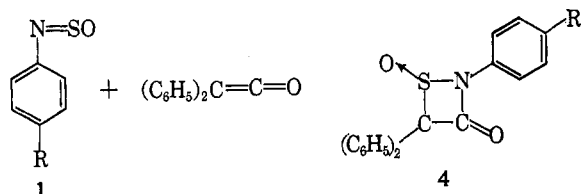
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N-Sulfinylaniline reacts with norbornene in a novel manner to yield 1,2,3,4,4a,10b-hexahydro-1,4-methano-6H-dibenzo[*c,e*](1,2)thiazine 5-oxide (6, R = H). In analogous reaction with dicyclopentadiene, 5,6a,7,7a,10,10a,11,11a-octahydro-7,11-methanobenzo[*c*]indeno[5,6-*e*](1,2)thiazine 6-oxide (15) is obtained.

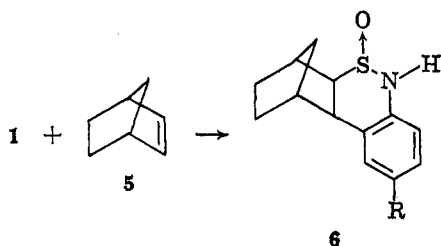
The cycloaddition reactions of N-sulfinylaniline (1, R = H) with 1,3-dienes (2) and 1,3-dipolar systems (3)



have been well documented in recent literature.¹⁻⁵ Further, Beecken and Korte⁶ have reported that N-sulfinylanilines undergo 1,2-cycloaddition with diphenylketene to give thiazetidinone 1-oxides (4). In all cases, the reaction with 1 takes place across the —N=S— bond.

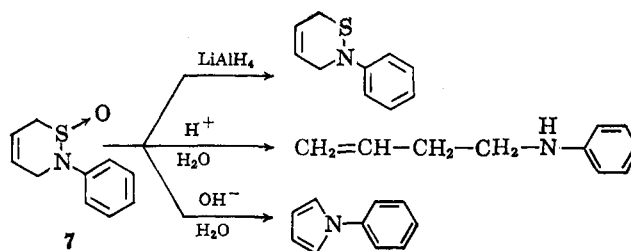


We have now found that, when 1 is treated with norbornene (5) in refluxing toluene, a 1:1 adduct (6) is ob-

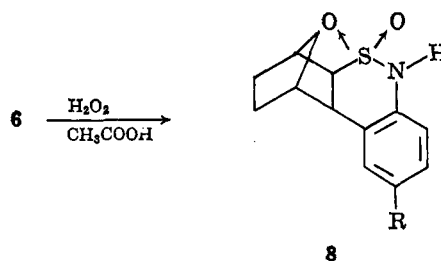


tained in which the N-sulfinylaniline participates as a "diene." The structure of 6 has been established on the basis of its degradation products and derivatives, as well as its infrared and nuclear magnetic resonance (n.m.r.) spectra (Table I). The reaction of 6 with di-

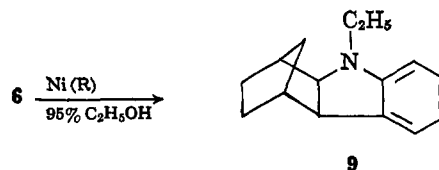
methyl sulfate in aqueous, alkaline tetrahydrofuran gave the N-methyl derivative. This structure assignment was confirmed on the basis of its elemental analysis and infrared spectrum. Compound 6 was found to be stable in the presence of hot 6 N sodium hydroxide and 6 N hydrochloric acid, and to be unattacked by LiAlH₄ in refluxing tetrahydrofuran. The stability of this system is surprising in view of the reactions of 2-phenyl-3,6-dihydro-1,2-thiazine 1-oxide (7) with the same reagents under much milder conditions.¹



Upon reaction of 6 with 30% hydrogen peroxide in glacial acetic acid, 8 is readily obtained. Desulfurization of 6 using degassed Raney nickel in refluxing

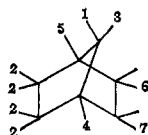


ethanol afforded predominately the N-substituted hexahydrocarbazole (9), characterized by infrared, n.m.r. and elemental analysis.



The desulfurization of 6 was repeated employing freshly prepared Raney nickel in refluxing methanol. The reaction mixture was separated into its three major volatile components, which were characterized as 10, 11, and 12. These three components accounted for 60, 24, and 14%, respectively, of the volatile fraction, as determined by planimeter integration of the g.l.c. spectrum.

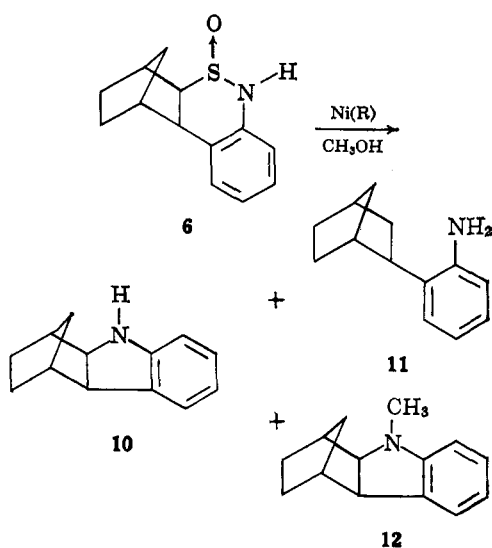
- (1) G. Kresze, A. Maschke, R. Albrecht, K. Bederke, H. P. Patzschke, H. Smalla, and A. Trede. *Angew. Chem., Intern. Ed. Engl.*, **1**, 94 (1962).
- (2) G. Kresze and R. Albrecht, *Angew. Chem.*, **74**, 781 (1962).
- (3) E. G. Kataev and V. V. Plemenkov, *Zh. Obshch. Khim.*, **32**, 3817 (1962).
- (4) P. Rajagopalan and H. U. Daeniker, *Angew. Chem., Intern. Ed. Engl.*, **2**, 46 (1963).
- (5) R. Huisgen, R. Grashy, M. Seidel, H. Knupfer, and R. Schmidt, *Ann.*, **658**, 169 (1962).
- (6) H. Beecken and F. Korte, *Tetrahedron*, **18**, 1527 (1962).

TABLE I
 N.M.R. ASSIGNMENTS^a


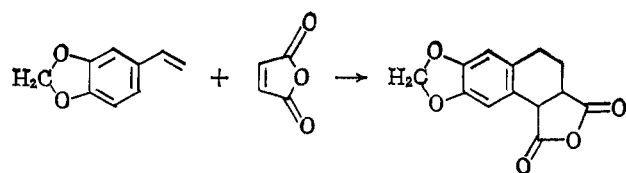
Com- pounds	Solvent	Aromatic protons ^b	Ex- changeable protons ^c	Position						
				1	2	3	4	5	6	7
6	CF ₃ COOH	-7.8, ^b -8.15		-2.02	-2.02	-2.29	-2.82	-3.12	-3.97	-3.97
8	CF ₃ COOH	-7.59, ^b -7.98		-1.42	-1.83	-2.28	-2.8	-3.32	-3.98	-3.98
11	CDCl ₃	-6.67	-3.42	-1.57	-1.57	-1.57	-2.5	-2.5	-1.57 ^d	-2.5
10	CDCl ₃	-6.75, ^b -7.22	-3.57	-1.57	-1.57	-1.57	-2.49	-2.47	-2.9	-2.9
12	CDCl ₃	-7.09		-1.17	-1.47	-1.83	-2.35	-2.22	-3.2	-3.64

-2.53^e

^a Proton assignments are in parts per million (p.p.m.) with tetramethylsilane at 0. The values given are, in most cases, the centers of complex multiplets. ^b Denotes aromatic proton *ortho* to the nitrogen atom. All examples noted have four aromatic protons. ^c Denotes protons on nitrogen which are readily exchanged when the CDCl₃ solution of the sample is agitated with D₂O. ^d Two protons. ^e >N-CH₃ protons.



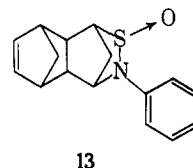
The reaction of 1 with norbornene resembles, in many ways, the reaction of *p*-alkoxy or 3,4-methylenedioxy styrenes with maleic anhydride,⁷ in that an adjacent "double bond" of the phenyl ring is conjugated



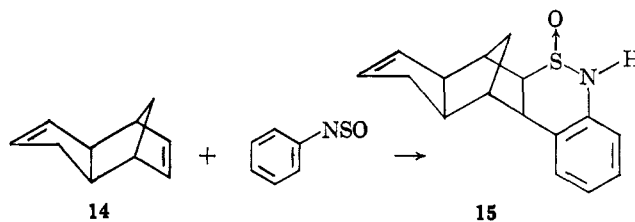
with the vinyl side chain to form a reactive 1,3-diene. A fundamental difference is that, while *p*-alkoxy groups promote the reaction of styrene with maleic anhydride, these same groups in the *para* position of *N*-sulfinylanilines inhibit the reaction with norbornene. Thus far, norbornene and substituted norbornenes are unique in that no other cyclic or acyclic olefins tried would react with *N*-sulfinylanilines. The norbornene moiety would not be expected to rearrange during the reaction, because no Lewis acids are present at any time to promote the formation of carbonium ions. Also, as Huisgen⁸ has found, norbornene can function as a 1,3-dipolaro-

phile under similar reaction conditions with no evidence of rearrangement.

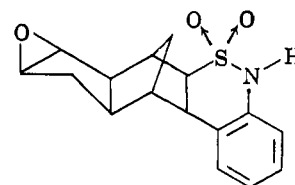
Kataev and Plemenkov have reported³ a reaction between 1 mole of *N*-sulfinylaniline and 2 moles of cyclopentadiene which yielded a solid product, m.p. 190° dec. Their proposed structure (13) is based on the assumption that two cyclopentadiene molecules add to *N*-



sulfinylaniline, sequentially. A repetition of this reaction, following the precise published directions, was found to yield a product which melted, after numerous recrystallizations from ethanol, at 246–248° dec. This compound is identical (infrared spectrum and mixture melting point) with the product (15) obtained from the reaction of 1 mole of dicyclopentadiene (14) with 1 mole of *N*-sulfinylaniline in toluene. This latter structure (which is in complete agreement with both the n.m.r.



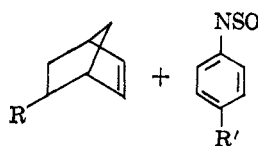
and infrared observations) requires that, in the reaction as described by Kataev and Plemenkov, dimerization had preceded the addition to *N*-sulfinylaniline. Hydrogen peroxide in acetic acid converts 15 to the corresponding epoxy sulfonamide 16.



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(7) M. C. Kloetzel, *Org. Reactions*, **4**, 32 (1948).(8) R. Huisgen, *Angew. Chem.*, **75**, 604 (1963).

TABLE II



E	R'	Carbon, %		Hydrogen, %		Nitrogen, %		% yield	M.p. dec., °C.
		Calcd.	Found	Calcd.	Found	Calcd.	Found		
H	NO ₂	56.10	56.24	5.08	5.17	10.07	10.02	71.5	260.5
H	CH ₃	67.98	67.77	6.92	6.49	5.66	5.86	20.2 ^a	211-214
H	OCH ₃	63.86	63.90	6.52	6.38	5.33	5.21	10.2	188-190
H	Cl	58.08	58.14	5.27	5.16	5.23	5.20	73	196-196.5
CN	H	65.10	65.37	5.47	5.25	10.85	10.79	7.7	259-260

^a Yield was increased to 60%, based on *p*-methyl-*N*-sulfinylaniline, upon changing the mole ratio of norbornene-*p*-methyl-*N*-sulfinylaniline from 1:1 to 10:1.

Experimental

The melting points are uncorrected. All gas chromatograms were determined using a Wilkens Instrument Company Autoprep Model A-700 with helium as the carrier gas. N.m.r. spectra were obtained with the Varian A-60 n.m.r. spectrometer, using tetramethylsilane as an internal standard. The *N*-sulfinylanilines are all known compounds and were prepared from the analogous amines according to the procedure of Michaelis and Herz.⁹

1,2,3,4,4a,10b-Hexahydro-1,4-methano-6H-dibenzo[*c,e*](1,2)-thiazine 5-Oxide (6).—A 500-ml. three-necked flask was equipped with a mechanical stirrer reflux condenser, CaCl₂ drying tube, and nitrogen inlet tube. To the flask was added 13.9 g. (0.1 mole) of *N*-sulfinylaniline, 9.4 g. (0.1 mole) of norbornene, and 300 ml. of anhydrous toluene. The reaction mixture was blanketed with an atmosphere of dry nitrogen while being stirred and refluxed for a period of 72 hr. During this time the reaction mixture became quite dark and the formation of solid particles was noted on the walls of the flask. The reaction mixture was cooled in an ice bath, then filtered, and the filter cake was recrystallized from aqueous ethanol to afford 19.2 g. (81.5%) of the product as colorless needles, m.p. 230–232°, ν_{NH} 3154 and $\nu_{\text{S-O}}$ 1053 cm.⁻¹ in Nujol.

Anal. Calcd. for C₁₃H₁₅NOS: C, 67.01; H, 6.49; N, 6.01. Found: C, 67.00; H, 6.54; N, 5.98.

1,2,3,4,4a-10b-Hexahydro-1,4-methano-6H-dibenzo[*c,e*](1,2)-thiazine 5,5-Dioxide (8).—A mixture of 5 ml. of 30% hydrogen peroxide, 5 ml. of glacial acetic acid, and 2.33 g. (0.01 mole) of 6 was placed in a 50-ml. erlenmeyer flask and allowed to stand overnight at room temperature. Upon pouring the reaction mixture over ice, there was obtained 1.92 g. (77.7%) of a colorless, crystalline compound, m.p. 202–203°; ν_{SO_2} 1151 and 1130, $\nu_{\text{N-H}}$ 3311 cm.⁻¹ (Nujol).

Anal. Calcd. for C₁₃H₁₅N₂O₂S: C, 62.62; H, 6.07; N, 5.61. Found: C, 62.56; H, 6.14; N, 5.28.

5,6a,7,7a,10,10a,11,11a-Octahydro-7,11-methanobenzo[*c*]indeno[5,6-*e*](1,2)thiazine 6-Oxide (15).—By causing (0.1 mole) of *N*-sulfinylaniline to react with (0.1 mole) of dicyclopentadiene (14) under the same conditions as those employed in the preparation of 6, a dark brown solid was obtained. Crystallization from ethanol afforded 8.75 g. (32.3%) of light tan crystals, m.p. 247°; $\nu_{\text{N-H}}$ 3234 and $\nu_{\text{S-O}}$ 1052 cm.⁻¹ in Nujol; n.m.r. (CF₃CO₂H): three aromatic protons centered at -7.05 p.p.m., one aromatic proton in a multiplet at -6.78 p.p.m., and two olefinic protons—one at -5.55 and one at -5.75 p.p.m.

Anal. Calcd. for C₁₆H₁₇NOS: C, 70.91; H, 6.32; N, 5.17. Found: C, 71.27; H, 6.51; N, 5.26.

5,6a,7,7a,8,9,10,10a,11,11a-Decahydro-7,11-methano-8,9-oxirenobenzo[*c*]indeno[5,6-*e*](1,2)thiazine 6,6-Dioxide (16).—When 5 g. of 15 was oxidized by treating it with hydrogen peroxide in glacial acetic acid, as in the preparation of 8, there was obtained 4.5 g. (82.5%) of a colorless crystalline product. This compound decomposed without melting, beginning at 232°.

Anal. Calcd. for C₁₈H₁₇N₂O₂S: C, 63.33; H, 5.66; N, 4.62. Found: C, 63.20; H, 5.64; N, 4.37.

1,2,3,4,4a,10b-Hexahydro-1,4-methano-6-methyldibenzo[*c,e*](1,2)thiazine 5-Oxide.—A mixture of 2.33 g. (10.0 mmoles) of 6 and 0.6 g. (15.0 mmoles) of sodium hydroxide was dissolved in

100 ml. of hot water and enough tetrahydrofuran to form a homogeneous solution. To this stirred mixture was added 1.8 g. (15.6 mmoles) of dimethyl sulfate and the solution was heated and stirred for 1 hr. To the solution was added 100 ml. of water and the resulting mixture was chilled, filtered, and the solids were washed with cold water. The filter cake was recrystallized from ethyl acetate to afford 1.2 g. of colorless needles, m.p. 230–231°, identified as starting material (6). The filtrate was evaporated to dryness under reduced pressure and a residue was obtained which, upon recrystallization from methylenecyclohexane, gave colorless needles, m.p. 140–142°. The infrared spectrum (Nujol) confirmed the structural assignment.

Anal. Calcd. for C₁₄H₁₇NOS: C, 68.00; H, 6.93; N, 5.67. Found: C, 68.17; H, 6.98; N, 5.51.

Table II outlines the reactions of some substituted *N*-sulfinylanilines with norbornene and of *N*-sulfinylaniline with 5-cyanonorbornene.

1,2,3,4,4a,10b-Hexahydro-6H-9-amino-1,4-methanodibenzo[*c,e*](1,2)thiazine 5-Oxide.—Following the procedure for the reduction of aromatic nitro compounds to the corresponding amines, outlined by Surrey and Cutler,¹⁰ a 3-l., three-necked flask was equipped with a reflux condenser and a stirrer. To the flask was added 15.5 g. (55 mmoles) of 1,2,3,4,4a,10b-hexahydro-6H-9-nitro-1,4-methanodibenzo[*c,e*](1,2)thiazine 5-oxide, 62 g. (1.06 g.-atoms) of iron filings, 1.55 g. (25.8 mmoles) of glacial acetic acid, 186 g. (2.48 moles) of ethanol, and 93 ml. of water. The mixture was stirred at reflux temperatures for 6 hr. The reaction mixture was filtered while still hot, then made alkaline with 3.4 g. (60 mmoles) of solid potassium carbonate, and filtered again. Evaporation of the solvent afforded 11 g. (80.4%) of a light brown solid. This product was recrystallized from ethyl acetate to yield 9.8 g. (73.0%) of cream-colored needles of 1,2,3,4,4a,10b-hexahydro-6H-9-amino-1,4-methanodibenzo[*c,e*](1,2)thiazine 5-oxide, m.p. 198–200° dec.; infrared (split mull) ν_{NH_2} asymmetrical and symmetrical 3432 and 3340, S-O stretching frequency 1050, and out-of-plane hydrogen deformation for 1,2,4-trisubstituted benzene near 830 and 860 cm.⁻¹.

Anal. Calcd. for C₁₃H₁₆N₂OS: C, 62.89; H, 6.50; N, 11.28. Found: C, 63.24; H, 6.64; N, 10.68.

Reaction of Cyclopentadiene with *N*-Sulfinylaniline.—Following the work of Kataev and Plemenkov,³ 36.9 g. (0.6 mole) of 1,3-cyclopentadiene (98+% pure) and 27.8 g. (0.2 mole) of *N*-sulfinylaniline were sealed in a Pyrex Carius tube and heated in an oven at 105° for 21 hr. At the end of that time the tube was chilled, opened, and the solid product, which had formed as dark brown crystals, was removed. There was obtained 44.2 g. (81.8%) of material, the infrared spectrum of which was identical with 15, prepared from the reaction of 14 with *N*-sulfinylaniline. A portion of this material was recrystallized from ethanol to afford a light brown solid, m.p. 213–218° dec. Two more recrystallizations raised the melting point to 246–248° dec.

Raney Nickel Desulfurization of 1,2,3,4,4a,10b-Hexahydro-1,4-methano-6H-dibenzo[*c,e*](1,2)thiazine 5-Oxide.—To a 1-l. three-necked flask, equipped with a stirrer and reflux condenser, was added 27 g. (0.115 mole) of 6, 520 g. of wet, degassed Raney nickel (65% by weight of Ni) and 500 ml. of 95% ethanol. The reactants were stirred and heated at reflux temperature for a period of 26 hr. At the end of this time, the nickel was separated

(9) A. Michaelis and R. Herz, *Ber. deut. chem. Ges.*, **23**, 3480 (1890).

(10) A. R. Surrey and R. A. Cutler, *J. Am. Chem. Soc.*, **73**, 2413 (1951).

by filtration and the ethanol was evaporated under reduced pressure. Fractionation of the residue, utilizing a semimicro Vigreux column, afforded 17.3 g. (70.2%) of a water-white, rather viscous liquid, which was identified by infrared and n.m.r. as 9-ethyl-1,2,3,4,4a,9a-hexahydro-1,4-methanocarbazole (9), b.p. 166–170° (14–15 mm.). Using a standard technique,¹¹ the methiodide salt was prepared as colorless crystals from ethanol, m.p. 165–166°.

Anal. Calcd. for C₁₆H₂₂IN: C, 54.09; H, 6.25; N, 3.95. Found: C, 54.31; H, 6.74; N, 3.98.

The desulfurization reaction was then repeated utilizing 2.5 g. (0.01 mole) of 6, 40 g. of freshly prepared Raney nickel (wet), and 300 ml. of methanol. Upon evaporation of the methanol, 1.82 g. of a water-white, viscous liquid was obtained. A portion of this liquid mixture was separated into its individual components by g.l.c. at 170°, employing a 5 ft. × 0.375 in. column packed with 20 M Carbowax 60–80 on acid-washed Chromosorb W.

(11) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 180.

These major volatile components were thus isolated and characterized by n.m.r. and infrared as 1,2,3,4,4a,9a-hexahydro-9H-1,4-methanocarbazole (10), infrared ν_{N-H} 3360, ν_{C-N} 1285, and C–H out-of-plane deformation at 739 cm.⁻¹; *o*-(2-norbornyl)-aniline (11), infrared ν_{NH_2} asymmetrical and symmetrical 3380 and 3300, ν_{C-N} 1283, and C–H out-of-plane deformation at 740 cm.⁻¹. The third major volatile component was identified as 9-methyl-1,2,3,4,4a,9a-hexahydro-1,4-methanocarbazole (12), infrared C–H out-of-plane deformation at 740, and >N–CH₃ stretching frequency at 2732 cm.⁻¹. Based upon measurement of their respective peak areas, gas-liquid chromatography indicated that the mixture of amines was 60% 10, 24% 11, and 14% 12, with the remaining 2% unidentified.

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Migratory Aptitudes of Unsaturated Groups¹

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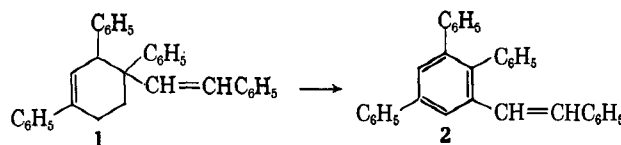
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The quinone-induced dehydrogenative rearrangement of 1,1-disubstituted 1,2-dihydronaphthalenes containing phenyl, vinyl, and styryl groups has been studied. The observed order of migratory aptitudes, methyl < phenyl < styryl = vinyl, is in accord with the hypothesis that the rearrangement involves electrophilic attack by a carbonium ion intermediate.

Some time ago we observed³ that dehydrogenation of the dimer (1) of 1,3-diphenylbutadiene with *o*-chloranil resulted in the formation of 2,3,5-triphenylstilbene (2). Not only were all carbon atoms retained, but it was proved conclusively that the aromatization involved the migration of a styryl group, the latter exhibiting a higher migratory aptitude than phenyl. This paper describes our initial efforts to utilize this reaction for studying migration aptitudes of unsaturated groups in general.

Evidence has been presented⁴ that dehydrogenations of hydroaromatic compounds by quinones are initiated by hydride abstraction which results in a positively charged carbon–negatively charged ion pair. Proton transfer from the carbonium ion to the hydroquinone anion then produces the stable aromatic structure. Recent work^{4b,c} is interpreted as supporting a mechanism which initially involves charge-transfer complex formation followed by hydride abstraction in the rate-determining step.

If this mechanism holds, blocks to aromatization presented by *gem* substitution might be overcome by migration processes similar to Wagner–Meerwein shifts. In fact, dehydrogenation of *gem*-substituted hydroaromatic compounds resulted^{3,4a,d} in rearrangements with retention of all carbon atoms present in the



substrate, a reaction which contrasts with the elimination of blocking groups generally observed during dehydrogenation by conventional methods.

To our knowledge the formation of 2,3,5-triphenylstilbene³ was the first clear demonstration of a 1,2 carbon-to-carbon shift by an unsaturated group under Wagner–Meerwein conditions, since the presence of acids normally precludes any clear-cut investigation of olefinic residues in the Wagner–Meerwein rearrangement.⁵

(5) Styryl migrations have been reported in the Schmidt reaction (carbon → nitrogen)^{6–8} which, however, may be controlled to a large extent by stereochemistry rather than by relative migratory aptitudes. Migration of unsaturated groups has been observed in the course of peracid oxidation (carbon → oxygen).^{9–11} Recent work¹² on the homologation of α,β -unsaturated ketones with diazomethane might be considered as an analogy. More closely related examples are the pinacolic rearrangement of substances containing a propenyl group reported by Deux,¹³ the acid-catalyzed rearrangement of nepenthol to flavanepenthone,¹⁴ and the pinacolic rearrangement of an intermediate hydroxytosylate, in the synthesis of *dl*-longifolene.¹⁵ The former suffers from uncertainty regarding stereochemistry of starting materials and lack of proof for structure of products; the last two deal with rigid systems where stereochemistry might well have been the controlling factor. The subject of rearrangement to electron-deficient atoms has been covered thoroughly in a recent review.¹⁶ Noteworthy is the statement (p. 515, ref. 16) that the styryl group may have a low migration aptitude.

(6) L. H. Briggs, G. C. DeAth, and S. R. Ellis, *J. Chem. Soc.*, 61 (1942).

(7) P. A. Smith and J. P. Horwitz, *J. Am. Chem. Soc.*, **72**, 3718 (1950).

(8) S. C. Bunce and J. B. Cloke, *ibid.*, **76**, 2244 (1954).

(9) J. Boeseken and A. L. Soesman, *Rec. trav. chim.*, **52**, 874 (1933).

(10) H. M. Walton, *J. Org. Chem.*, **22**, 1161 (1957).

(11) E. F. Smitsman and F. B. Block, *J. Am. Pharm. Assoc. Sci. Ed.*, **48**, 526 (1959).

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(2) Abstracted from a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree, Florida State University, April, 1963.

(3) W. Herz and E. Lewis, *J. Org. Chem.*, **23**, 1646 (1958).

(4) (a) R. P. Linstead, E. A. Braude, L. M. Jackman, and A. N. Beames, *Chem. Ind. (London)*, 1174 (1954); (b) E. A. Braude, L. M. Jackman, and R. P. Linstead, *J. Chem. Soc.*, 3548, 3564 (1954); (c) J. P. Barnard and L. M. Jackman, *ibid.*, 3110 (1960); (d) E. A. Braude, L. M. Jackman, R. P. Linstead, and G. Lowe, *ibid.*, 3123, 3133 (1960); (e) E. A. Braude, L. M. Jackman, R. P. Linstead, and J. S. Shannon, *ibid.*, 4794 (1961).