by filtration, dried, and compared with an authentic sample of benzoic acid. The ir spectra were superimposable and a mixture melting point showed no depression. The aqueous layer was extracted with methylene chloride and the dried extract was concentrated in vacuo to ~0.3 g of white solid. After recrystallization this solid was identified as dimethyl sulfone by ir and a mixture melting point. Under the conditions described above 3-p-chlorophenylthiete 1,1-dioxide was converted to p-chlorobenzoic acid and dimethyl sulfone.

Reduction of 3-Phenylthiete 1,1-Dioxide (6c) with Lithium Aluminum Hydride.—A solution of lithium aluminum hydride (1.0 g) in 50 ml of freshly distilled THF was refluxed for 30 min. To this was added dropwise with stirring 1.0 g of sulfone (6c) in 50 ml of THF; addition time was 45 min. Stirring was continued at room temperature for 12 hr after which the excess hydride was decomposed with a 20% ammonium chloride solution. The organic layer was filtered and the residue was washed with ether. The dried (MgSO₄) organic solution was concentrated in vacuo to a foul smelling oil which was analyzed as predominantly a single component on vpc. This major component, a colorless oil, was collected from vpc and tentatively identified as 2-phenyl-propanethiol: ir (film) 3000–2850, 1600, 1490, 1440, 1365 (w), 1060 (w), 1010 (w), 905 (w), 755, and 690 cm⁻¹; nmr (CCl₄) δ 1.0 (t, 1), 1.35 (d, 3), 2.5–2.9 (m, 3), and 7.17 (s, 5). On shaking the nmr sample with D₂O the triplet at δ 1.0 disappeared and the multiplet at δ 2.5–2.9 became less complex.

H–D Exchange of α-Methylene Protons of Thietane 1,1-Dioxide.—Sodium (60 mg, 2.5 mg-atoms) was added to 2.60 g (130 mmol) of deuterium oxide; to that solution was added 2.75 mmol of sulfone 4a or 4b in 6 ml of dioxane. The mixture was heated with stirring at 40–50° for 24 hr; stirring was continued at room temperature for an additional 24 hr. Concentrated hydrochloric acid (2.5 ml) was added with stirring. The reaction mixture was evaporated in vacuo to dryness and the residue was extracted with ethyl acetate. The extract was concentrated and the residue was recrystallized from methanol to yield 88% of the α-tetradeuterated sulfone. The melting point and ir spectrum remained very similar to that of starting material. In the nmr

spectrum the signal for the α-methylene protons had disappeared and the multiplet for the methine proton collapsed to a broad singlet.

The α-tetradeuterated thietane derivatives were reacted under the same conditions as their hydrogen analogs.

Oxidation of Thietanes.—The general methods of oxidation employed for the oxidation study were reported earlier.[6] The use of N-chlorotriazole as an oxidant for sulfides has been reported in a more recent communication from this laboratory.[33] Special care was observed to avoid over oxidation to sulfone, less than 1 equiv of oxidant per mole of sulfide was employed. The ratios given in Table I were obtained from planimetric integration of the vpc graphs.

(33) W. D. Kingsbury and C. R. Johnson, *Chem. Commun.*, 365 (1969).

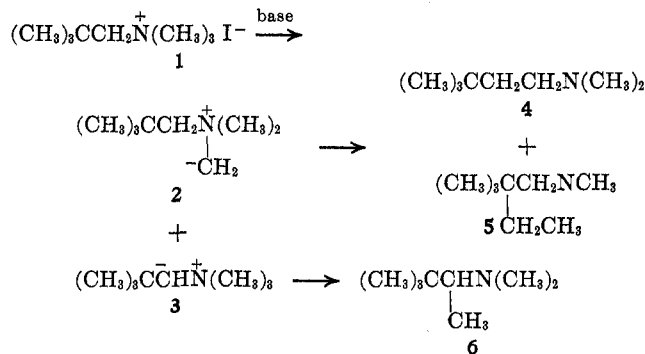# The Stevens Rearrangements of N,N,N-Trimethylneopentylammonium Iodide[1]

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The Stevens rearrangements of N,N,N-trimethylneopentylammonium iodide (1) have been investigated using a series of base–solvent systems. In all cases 3,3,N,N-tetramethyl-1-butylamine (4) is the major rearrangement product, with N-ethyl-N-methylneopentylamine (5) and 3,3,N,N-tetramethyl-2-butylamine (6) being formed in low yields. In addition, N,N-dimethylneopentylamine (7) from a displacement reaction becomes the major product in more acidic solvents. Thermal decomposition (294°) leads to 7 and methyl iodide. An ion-pair rearrangement pathway is proposed consistent with the minor side products, N,N-dimethylbenzylamine (10), from phenyllithium, N,N-dimethyl-1-pentylamine (11) from n-butyllithium, and neopentane (9).

Although the Stevens rearrangement[2] of quaternary ammonium salts has been the subject of many studies since its discovery in 1932,[3] very little work has been reported using simple alkylammonium systems.[4] As a continuation of our interest in this area, we have studied the Stevens rearrangements of N,N,N-trimethylneopentylammonium iodide (1) with a series of base–solvent systems. The quaternary ammonium salt 1 has the characteristic of being the potential precursor for three different Stevens rearrangement products, 4, 5, and 6, through ylides of similar carbanion stability,[5] 2 and 3,

$$(CH_3)_3CCH_2\overset{+}{N}(CH_3)_3 \; I^- \xrightarrow{\text{base}}$$
$$\mathbf{1}$$

$$(CH_3)_3CCH_2\overset{+}{N}(CH_3)_2$$
$$\underset{-CH_2}{|}$$
$$\mathbf{2}$$
$$+$$
$$(CH_3)_3C\overset{-}{C}H\overset{+}{N}(CH_3)_3 \longrightarrow$$
$$\mathbf{3}$$

$$(CH_3)_3CCH_2CH_2N(CH_3)_2$$
$$\mathbf{4}$$
$$+$$
$$(CH_3)_3CCH_2NCH_3$$
$$\underset{5 \; CH_2CH_3}{|}$$

$$(CH_3)_3CCHN(CH_3)_2$$
$$\underset{CH_3}{|}$$
$$\mathbf{6}$$

but differing steric requirements. In the following we report the results of this study and their relevance to the mechanism of the Stevens rearrangement.

* To whom correspondence should be addressed.

(1) The authors thank the National Science Foundation and the donors of the Petroleum Research Fund for partial support of this work.

(2) T. S. Stevens, E. M. Creighton, A. B. Gordon, and M. MacNicol, *J. Chem. Soc.*, 3193 (1928).

(3) For leading references, see S. H. Pine, *Org. React.*, 18, 403 (1970).

(4) (a) H. Daniel and J. Paetsch, *Chem. Ber.*, 101, 1445 (1968); (b) W. K. Musker, *J. Org. Chem.*, 32, 3189 (1967); (c) G. Wittig and D. Krauss, *Justus Liebigs Ann. Chem.*, 679, 34 (1964).

(5) D. J. Cram in "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 21.

Results

N,N,N-trimethylneopentylammonium iodide (1) was allowed to react with a series of base–solvent systems under dry nitrogen. Products were separated into basic and nonbasic fractions for analysis by gas chromatography. The basic products were positively identified by separation through preparative gas chromatography and comparison of the nmr and ir spectra of the recovered samples with the spectra of independently synthesized materials. The average results of many runs are compiled in Table I.

TABLE I
STEVENS REARRANGEMENTS OF
N,N,N-TRIMETHYLNEOPENTYLAMMONIUM IODIDE

Base–solvent	Basic products, %			
	4	5	6	7
n-C₄H₉Li–hexane[a]	86	5.1	0[b]	9.3
n-C₄H₉Li–hexane, TMEDA[c]	81	2.1	1.3	16
n-C₄H₉Li–HMPA[a]	73	1.2	0.4	25
C₆H₅Li–HMPA[a]	77	2.5	1.2	19
C₆H₅Li–(C₂H₅)₂O, C₆H₆	97	1.0	0	1.7
n-C₄H₉Li–DMSO[a]	0	0.7	0	99
NaNH₂–NH₃ (liquid)	d			d
KOC(CH₃)₃–(CH₃)₃COH				e

[a] Average of runs. [b] In one case a trace peak with the retention time of 6 was observed. [c] Tetramethylethylenediamine. [d] Low yield provided only qualitative data, 4:7 ≈ 1:5. [e] Only basic product observed.

All three potential rearrangement products are found, with 3,3,*N,N*-tetramethyl-1-butylamine (4) predominant in all cases. In less basic systems the rearrangements are notably inhibited and the nonrearranged tertiary amine, *N,N*-dimethylneopentylamine (7), pre-

$$(CH_3)_3CCH_2N(CH_3)_2$$
7
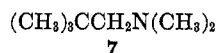
dominates. Additional basic materials, *N,N*-dimethylbenzylamine (10) and *N,N*-dimethyl-1-pentylamine (11), are also observed when the base used is phenyllithium or *n*-butyllithium, respectively.

Discussion

The observation that 4 is the major rearrangement product suggests that the relief of internal nonbonded interactions is significant in directing the reaction pathway. In a related study only the product analogous to 4 was obtained from *N,N,N*-trimethyl-2,2,2-triphenylethylammonium iodide. In this case the authors suggested that a combination of steric and electronic factors may be involved.[6] (It is interesting to note, however, that the reductive cleavage of 1 with sodium-ammonia results principally in methyl cleavage, a result which does not appear to involve significant steric acceleration.[6]) Consistent with this is the formation of only small amounts of 5 which also originates from the ylide 2, but provides little relief of strain. We would not expect electronic factors to be important in directing the rearrangement of ylide 2 in this case, although such control would probably favor methyl over neopentyl migration.

The detection of only minor amounts of 6 in some of the rearrangement system is not surprising since formation of the ylide 3 is expected to be sterically quite hindered. In fact, 6 is observed only with the base–solvent systems generally found to be particularly reactive. This is exemplified by the formation of 6 on the addition of tetramethylethylenediamine (TMEDA) to an *n*-butyllithium–hexane run. TMEDA is known to depolymerize the reagent and markedly increase its activity.[7]

The relatively greater yield of 7 in hexamethylphosphoramide (HMPA), presumably from a methyl displacement, reflects an expected enhancement of nucleophilic reactivity of the base in this polar aprotic solvent. This is further indicated by the comparison of the phenyllithium and *n*-butyllithium results where *n*-butyl is the better nucleophile. Although 1 is thermally stable under our reaction conditions, it does decompose at its melting point (294°) to give 7 and methyl iodide. In the more acidic solvents, dimethyl sulfoxide, ammonia, and *tert*-butyl alcohol, formation of the requisite ylides (2 or 3) is not favored and displacement to give 7 becomes the major pathway. *tert*-Butyl methyl ether from such a displacement was detected when potassium *tert*-butoxide was the base.

Two dissociation–recombination mechanisms are currently being considered for the Stevens rearrangement. The ion-pair pathway (a) initially proposed by Stevens[8] and reintroduced by Jenny,[9] and the radical-pair pathway (b) suggested by Schöllkopf.[10]
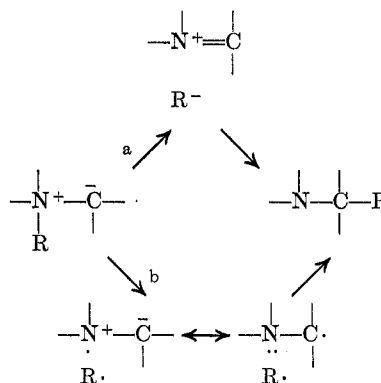
We believe that the ion-pair mechanism is most consistent with our results. Neopentane (9) has been found as a nonbasic product from the rearrangement as expected from collapse of the carbanion portion of the ion-pair 8 with solvent. In addition, the amines 10 and 11, presumed to arise by reaction of the methylene immonium cation portion of 8 with the base, were also detected. Although these products were found in low

(6) E. Grovenstein, Jr, and L. C. Rogers, *J. Amer. Chem. Soc.*, **86**, 854 (1964).
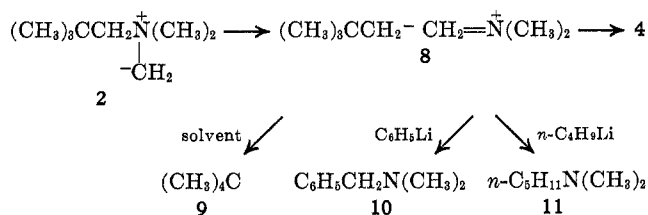
(7) C. G. Screttas and J. F. Eastham, *ibid.*, **87**, 3276 (1965).

(8) (a) T. S. Stevens, *J. Chem. Soc.*, 2107 (1930); (b) T. Thomson and T. S. Stevens, *ibid.*, 55 (1932).

(9) E. F. Jenny and J. Druey, *Angew. Chem., Int. Ed. Engl.*, **1**, 155 (1962).

(10) U. Schöllkopf and U. Ludwig, *Chem. Ber.* **101**, 2224 (1968).

yield, their relevance to the major reaction pathway seems reasonable. The Stevens rearrangement is known to be highly stereospecific[11] and intramolecular[12] and probably occurs within a tight solvent cage. It is not surprising, therefore, that only a small degree of escape from the cage is observed.

The dimer 12 expected from a radical-pair inter-

$$(CH_3)_3CCH_2CH_2C(CH_3)_3$$
12
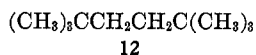
mediate[13a] was shown not to be present by gas chromatographic analysis. An attempt to observe chemically induced dynamic polarization (CIDNP) evidence for a radical pathway[13] was unsuccessful. This may, however, be due to experimental difficulties in this system.

Although the recent observations of CIDNP during product formation in some Stevens rearrangements suggest the involvement of a radical pair,[13] the application of this data to a mechanistic sequence is not clear since substituent effect studies may be consistent with an ionic mechanism.[8b] A competition between the ionic (a) and radical (b) pathways which would result in significant contributions from both seems thermodynamically unreasonable. Possibly both pathways are involved in a sequential rather than competitive pathways. We are currently involved in studies in an attempt to determine the importance of these two potential pathways to the base-promoted rearrangements of quaternary ammonium salts.

Experimental Section

Nmr spectra were obtained using a Varian A-60 spectrometer. Chemical shifts are reported as downfield from internal TMS. Melting points were taken using a Hoover apparatus and are not corrected. Gas chromatographic analyses were obtained on an F & M Model 700 or 720 instrument using a Carbowax 20M or in some cases a Chromosorb 103 column. Peak areas were measured using a Disc integrator and predetermined correction factors for each rearrangement product. Rearrangement products were identified by separation using gas chromatography and comparison of retention times and spectral data with independently synthesized materials.

n-Butyllithium was obtained from Foote Mineral Co. as a solution in hexane. Phenyllithium was obtained from Alfa Chemical Co. as a solution in benzene–ether or was prepared[14] as needed. Potassium *tert*-butoxide was obtained from MSA Corp. Sodium amide was prepared as needed.[15] Solvents were dried and distilled.

N,N,N-Trimethylneopentylammonium Iodide (1).—The reaction of neopentylamine with formic acid–formaldehyde[16] overnight gave a 46% yield of *N,N*-dimethylneopentylamine (7): bp 90–95°; nmr (CCl₄) δ 0.90 [s, 9, (CH₃)₃C], 2.02 (s, 2, CH₂N), 2.28 [s, 6, (CH₃)₂N]. *N,N*-Dimethylneopentylamine (7) was also prepared from pivalyl chloride and dimethylamine[6] in 52% yield.

To 3.0 g (0.026 mol) of tertiary amine in 15 ml of anhydrous acetone was added 8 ml of methyl iodide. After stirring for 24 hr, the solid was recovered by filtration and recrystallized from absolute ethanol to give 6.7 g of 1 as white crystals: mp 293–294° dec; nmr (CDCl₃) δ 1.28 [s, 9, (CH₃)₃C], 3.58 [s, 9, (CH₃)₃N] 3.70 (s, 2, CH₂N).

Anal. Calcd for C₈H₂₀NI: C, 37.37; H, 7.84; N, 5.45. Found: C, 37.41; H, 8.16; N, 5.27.

3,3,*N,N*-Tetramethyl-1-butylamine (4).—To a 100-ml flask equipped with a Dry Ice condenser, stirrer, and dropping funnel, was added *tert*-butylacetyl chloride [prepared from 10.0 g (0.086 mol) of *tert*-butylacetic acid and thionyl chloride] and 20 ml of tetrahydrofuran. The solution was cooled to 0°, and then a solution of 13.0 g (0.29 mol) of dimethylamine in 25 ml of tetrahydrofuran was added dropwise. After stirring an additional 20 min, the solid was recovered by filtration and washed further with solvent. The total solvent was removed under reduced pressure and the resulting liquid distilled to give 8.6 g (71%) of *N,N*-dimethyl-*tert*-butylacetamide: bp 94–97° (23 mm).

To a flask equipped with a stirrer, reflux condenser, and dropping funnel was added 25 ml of anhydrous ether and 2.1 g (0.054 mol) of lithium aluminum hydride (all under nitrogen). *N,N*-Dimethyl-*tert*-butylacetamide (8.6 g, 0.06 mol) in 10 ml of anhydrous ether was added dropwise at a rate to maintain gentle reflux. After refluxing an additional 1 hr, the mixture was cooled and hydrolyzed with 2.1 ml of water, 2.1 ml of 15% sodium hydroxide, and 6.2 ml of water, added in that order.[17] The solids were removed by filtration and washed further with ether. The total ether phase was dried over anhydrous magnesium sulfate and distilled to give 4.5 g (58%) of 4: bp 128–130°; nmr (CCl₄) δ 0.90 [s, 9, (CH₃)₃C], 1.12–1.57 (m, 2, CH₂), 2.04–2.38 (m, 2, CH₂N), 2.13 [s, 6, N(CH₃)₂]; HCl salt mp 260–261° dec.

Anal. Calcd for C₈H₂₀NCl: C, 57.99; H, 12.17; N, 8.45. Found: C, 57.43; H, 11.93; N, 8.24.

N-Ethyl-*N*-methylneopentylamine (5).—*N*-Methylpivalamide was prepared as above from 70.0 g (0.58 mol) of pivalyl chloride[18] and methylamine to give, after recrystallization from petroleum ether (bp 30–60°)–tetrahydrofuran, 53.9 g (81%) of a white solid: nmr (CCl₄) δ 1.17 [s, 9, (CH₃)₃C], 2.73 (d, 3, NCH₃, *J* = 5 Hz), 7.27 (s, 1, NH).

The amide (4.25 g, 0.042 mol) was reduced using 3.66 g (0.094 mol) of lithium aluminum hydride as above. After stirring for 144 hr, work-up and distillation gave 2.41 g (57%) of *N*-methylneopentylamine: bp 88–90°; nmr (CCl₄) δ 0.60 (s, 1, NH), 0.89 [s, 9, (CH₃)₃C], 2.27 (s, 2, CH₂), 2.40 (s, 3, NCH₃).

To 2.4 g (0.024 mol) of *N*-methylneopentylamine in 25 ml of anhydrous acetone was added 1.9 ml (0.024 mol) of ethyl iodide. After stirring for 72 hr, the volume was reduced to 5 ml, and then 25 ml of dilute sodium hydroxide was added and the mixture extracted with pentane. The pentane was dried over anhydrous magnesium sulfate. Distillation yielded 1.1 g (37%) of *N*-ethyl-*N*-methylneopentylamine: bp 110–118°; nmr (CCl₄) δ 0.84 [s, 9, (CH₃)₃C], 0.98 (t, 3, CH₂CH₃, *J* = 7 Hz), 2.05 (s, 2, NCH₂), 2.24 (s, 3, NCH₃), 2.38 (q, 2, CH₂CH₃, *J* = 7 Hz); methiodide mp 261.0–262.0°.

Anal. Calcd for C₉H₂₂NI: C, 39.86; H, 8.18; N, 5.16. Found: C, 40.04; H, 8.28; N, 5.13.

3,3,*N,N*-Tetramethyl-2-butylamine (6).—3,3-Dimethyl-2-butylamine was prepared[19] in 17% yield: bp 102–103°; nmr (CCl₄) δ 0.82 [s, 9, (CH₃)₃C], 0.95 (d, 3, CH₃, *J* = 6 Hz), 1.28 (s, 2, NH₂), 2.56 (q, 1, CH, *J* = 6 Hz).

Treatment of the primary amine with formic acid–formaldehyde[16] gave a 50% yield of 6: bp 120–126°; nmr (CCl₄) δ 0.87 (d, 3, CH₃, *J* = 7 Hz), 0.87 [s, 9, (CH₃)₃C], 2.17 (q, 1, CH, *J* = 7 Hz), 2.20 [s, 6, N(CH₃)₂]; methiodide mp 241–242°.

Anal. Calcd for C₉H₂₂NI: C, 39.86; H, 8.18; N, 5.16. Found: C, 40.14; H, 8.22; N, 4.82.

Neopentane (9) was obtained commercially from Cal Biochem.

N,N-Dimethylbenzylamine (10) was obtained commercially from Eastman.

N,N-Dimethyl-1-pentylamine (11) was prepared from 1-pentylamine using formic acid–formaldehyde[16] in 56% yield: bp 118–124°; nmr (CCl₄) δ 0.8–1.1 (m, 3, CH₃), 1.2–1.6 [m, 6, (CH₂)₃], 2.18 [s, 6, N(CH₃)₂], 2.1–2.3 (m, 2, NCH₂).

2,2,5,5-Tetramethylhexane (12).—A mixture of 2 g (0.013 mol) of neopentyl bromide and 0.09 g (0.013 g-atom) of lithium metal in 15 ml of anhydrous ether was refluxed for 4 hr, and then stirred for an additional 16 hr. Addition of water followed by separation of the organic phase, drying (MgSO₄), and distillation gave the crude product, bp 95–105°. Preparative gas chromatography was used to separate starting material from the major product 12: nmr (CHCl₃) δ 0.84 [s, 18, (CH₃)₃C], 1.12 (s, 4, CH₂).

(11) B. J. Millard and T. S. Stevens, *J. Chem. Soc.*, 3397 (1963).

(12) R. A. Johnstone and T. S. Stevens, *ibid.*, 4487 (1955).

(13) (a) U. Schöllkopf, U. Ludwig, G. Ostermann, and M. Patsch, *Tetrahedron Lett.*, 3415 (1969); (b) A. R. Lepley, *Chem. Commun.*, 1460 (1969).

(14) A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1957, p 931.

(15) Reference 14, p 197.

(16) S. H. Pine, *J. Chem. Educ.*, **45**, 118 (1968).

(17) B. M. Micovic and M. L. J. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(18) H. C. Brown, *J. Amer. Chem. Soc.*, **60**, 1325 (1938).

(19) M. L. Moore, *Org. React.*, **5**, 321 (1949).

Typical Rearrangement.—To a constricted tube with a small magnetic stirrer was added 0.26 g (0.001 mol) of 1 followed by 5 ml of dry hexane and 1.3 ml of 1.6 N (0.002 mol) n-butyllithium–hexane. The tube was purged with nitrogen, sealed and placed in a bath at 75 $\pm$ 2° with stirring for 48 hr. Water (3 ml) was added to the reaction mixture, and the organic layer was separated and extracted with 3 N HCl. The remaining nonbasic phase was retained for further analysis. The acid extracts were made basic with 50% sodium hydroxide and the basic products extracted with pentane. Careful distillation to concentrate the product resulted in 0.1–0.2 ml of a products–pentane solution which was analyzed by gas chromatography.

In one run as above, 0.2 ml of TMEDA was added and the reaction time reduced to 1 hr. Controls were also run on solvent plus salt 1 or solvent plus base and analyzed as above.

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o-Quinone Methides. II. Trapping with Production of Chromans
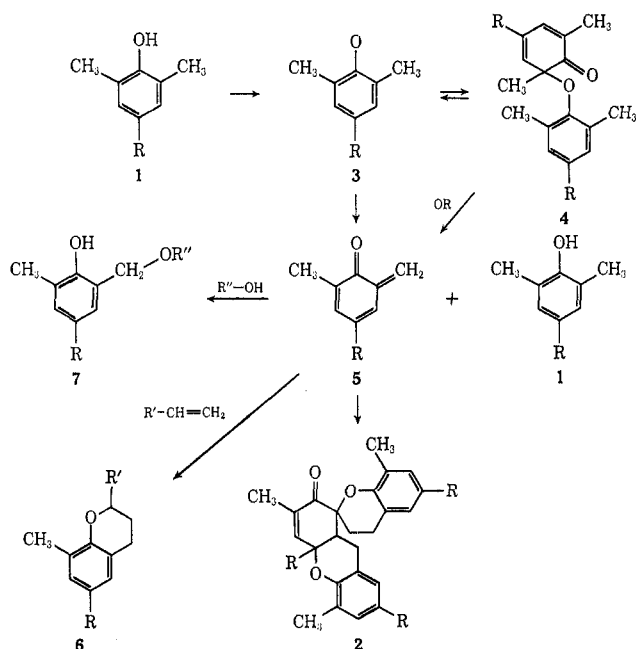
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General Electric Research and Development Center, Schenectady, New York 12301

The first paper[1] demonstrated that phenoxy radicals are a precursor to the formation of the trimer 2. They must pass through an *o*-quinone methide which could not be observed. This work demonstrates that the *o*-quinone methide can be trapped by reactive dienophiles and nucleophilic agents. A convenient synthesis of a variety of chromans results from this reaction. Only one isomer is obtained which suggests the similarity to usual diene reactions.

The first paper in this series[1] showed that the oxidation of 2,6-dimethylphenols (1) with metal oxides or basic potassium ferricyanide gave as a product a trimer. The trimer was shown to have the rather complex struc-

ture 2. An examination of the structure suggests that it results from a diene–dienophile addition of three *o*-quinone methides 5. However, spectroscopic evidence demonstrated that both the phenoxy radical 3 and its dimeric *o*-quinol ether dimer 4 were present and were part of the sequence of reactions that resulted in the formation of the trimer. Direct evidence of the existence of the *o*-quinone methide was lacking. It was felt that it should be possible to demonstrate the existence of an *o*-quinone methide by intercepting it with a dienophile more reactive than itself.

There have been a few examples of the presence of an *o*-quinone methide being demonstrated by its being

trapped. Hultzsch[2] heated saligenin in the presence of styrene to form the chroman 8. Other reactions of
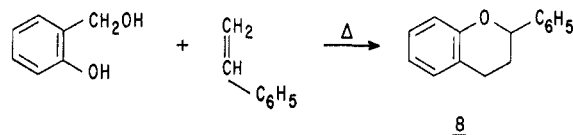
this type have been reported[3,4] but all involve the application of heat to convert the phenol precursor to the *o*-quinone methide.

Near the end of this work, an *o*-quinone methide which is stabilized by trifluoromethyl groups was reported by Sheppard.[5] This was prepared by pyrolysis of the sulfite ester 9. The quinone methide 10 was not isolable but reacted with styrene to give the chroman 11.
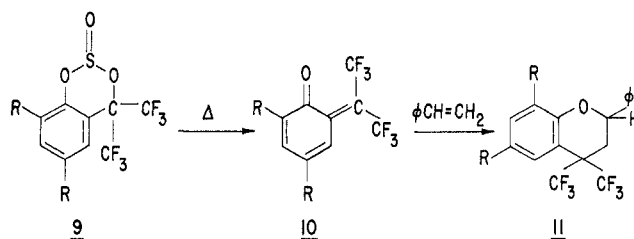
There is another method of trapping quinone methides. This involves the addition of nucleophiles to the conjugated system. Filar and Winstein[6] have studied this addition to *p*-quinone methides, but they had no examples of an *o*-quinone methide. Very little work has been done where *o*-quinone methides have been studied in solution.

With this background of previous work, it was decided to concentrate on the generation of the sus-

(1) D. A. Bolon, *J. Org. Chem.*, **35**, 715 (1970).

(2) K. Hultzsch, *Chem. Ber.*, **74**, 898 (1941), *J. Prakt. Chem.*, **158** 275 (1941).

(3) G. R. Sprengling, *J. Amer. Chem. Soc.*, **74**, 2937 (1952).

(4) M. Wakselman and M. Vilkas, *C. R. Acad. Sci.*, *Ser. C*, **258**, 1526 (1964).

(5) W. A. Sheppard, *J. Org. Chem.*, **33**, 3297 (1968).

(6) L. J. Filar and S. Winstein, *Tetrahedron Lett.*, **25**, 9 (1960).