1,2 Migrations in Alkyl Radicals[1]

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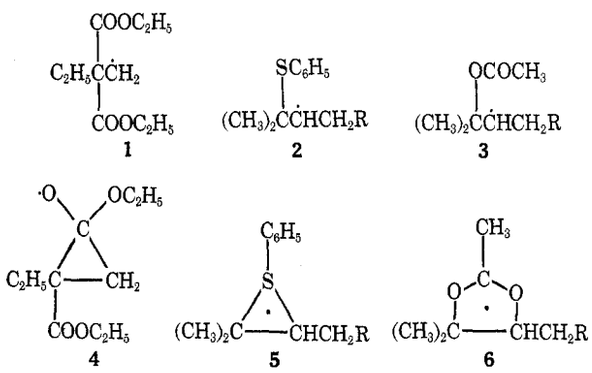
The behavior of three β-substituted alkyl radicals, geometrically and energetically capable of "bridging," has been examined in environments conducive to their rearrangement. Although the β-carbethoxyalkyl radical generated by the decarbonylation of β,β-dicarbethoxyvaleraldehyde produced only unrearranged products, compelling evidence is presented for the 1,2 migration of an acetoxy group during the free-radical initiated addition of butyraldehyde to α,α-dimethylallyl acetate. In contrast, β-thiophenoxyalkyl radicals, similarly generated during addition of both butyraldehyde and thiophenol to α,α-dimethylallyl phenyl sulfide, displayed an overwhelming preference for elimination of the thiophenoxy group.

Since the first reported instances[4,5] of phenyl migration in the "neophyl" radical, there have been numerous attempts to extend this apparent analogy of Wagner–Meerwein carbonium ion rearrangements.[6] Nonetheless, no *bona fide* examples of hydrogen or alkyl migration have surfaced, hardly surprising in view of the vastly different energetic requirements imposed by the odd electron on a transition state or intermediate involved in the actual shift of a migrating group. Indeed it has been suggested that 1,2-alkyl or hydrogen migration in ground-state free radicals is forbidden by orbital symmetry restrictions.[7]

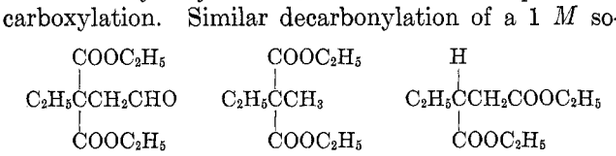
The aromatic nucleus clearly is satisfying some requirement for migration, presumably formation of a bridged species, that hydrogen or alkyl groups cannot. Significantly, the only credible reports of 1,2 migration of substituents other than aryl involve those groups (Cl,[6] Br,[6] SR,[6b] $OCOCH_3$[8,9]) which are also capable of accommodating, both geometrically and orbitally, the odd electron of the adjacent radical center in some kind of bridged intermediate or transition state.

In this paper we wish to report the behavior of three β-substituted alkyl radicals which, by virtue of either valence shell expansion[10] (**5**) or π electron delocalization (**4** and **6**), are theoretically capable of rearrangement *via* bridged species. The β-carbethoxyalkyl radical (**1**) was generated by the decarbonylation of the homologous aldehyde, an elegant method pioneered by Winstein and Seubold[5] for the generation of the "neophyl" radical from β-phenylisovaleraldehyde, and especially effective when the migrating group is resistant to competitive loss by reverse Michael reaction. Alternatively, addition of free radicals (R·) to allylically substituted terminal olefins, a procedure successfully exploited by Weinstock and Lewis[11] for the study of β-phenylbutyl radicals, was selected for the generation of the β-thiophenoxyalkyl (**2**) and β-acetoxyalkyl (**3**) radicals so as to avoid the reported[8,12] nonradical elimination of the corresponding aldehydes. In order to afford the greatest opportunity for observing rearranged products, the concentration and reactivity of the chain-transfer agent RH was manipulated in accord with the ground rules[13] established by comprehensive investigation of phenyl migration in alkyl radicals.[6a]



Results and Discussion

β-Carbethoxyalkyl Radical.—β,β-Dicarbethoxyvaleraldehyde (**7**) smoothly decarbonylated at 130° in the presence of di-*tert*-butyl peroxide (DTBP) to give a >97% theoretical yield of carbon monoxide and a 92% yield of a single product which was characterized as the unrearranged diester **8** by hydrolysis to the known methylethylmalonic acid and its subsequent decarboxylation. Similar decarbonylation of a 1 *M* solution of the aldehyde in diphenyl ether gave >95% carbon monoxide evolution and a 92% yield of the unrearranged diester. Again, no rearranged diester **9** was detected, suggesting that, even in the presence of a sub-



(1) Abstracted in part from the Ph.D. thesis of Sheldon N. Lewis, submitted to the University of California at Los Angeles in Aug 1959.

(2) Eastman Kodak Company Fellow, 1958–1959; Rohm and Haas Co.

(3) Deceased, Nov 23, 1969.

(4) W. H. Urry and M. S. Kharasch, *J. Amer. Chem. Soc.*, **66**, 1438 (1944).

(5) S. Winstein and F. H. Seubold, *ibid.*, **69**, 2916 (1947).

(6) For a comprehensive review of free-radical rearrangements, see (a) C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Part I, Wiley-Interscience, New York, N. Y., 1963, pp 407–450; (b) R. Kh. Freidlina in "Advances in Free Radical Chemistry," G. H. Williams, Ed., Vol. I, Logos Press, London, 1965, pp 211–278.

(7) M. J. Perkins in "Organic Reaction Mechanisms," B. Capon and C. W. Reese, Ed., Wiley-Interscience, London, 1969, p 293.

(8) D. D. Tanner and F. C. P. Law, *J. Amer. Chem. Soc.* **91**, 7535 (1969).

(9) J. M. Surzur and P. Teissier, *C. R. Acad. Sci.*, **264**, 1981 (1967).

(10) H. H. Jaffe, *J. Phys. Chem.*, **58**, 185 (1954), has reported evidence of sulfur valence shell expansion in radical reactions.

(11) J. Weinstock and S. N. Lewis, *J. Amer. Chem. Soc.*, **79**, 6243 (1957).

(12) S. J. Lapporte, Ph.D. Thesis, UCLA, 1956.

(13) These studies show that, irrespective of bridged intermediacy, product formation results from the reaction of the *classical* unrearranged and rearranged radicals with the chain-transfer agent RH. Thus the lifetime of the unrearranged radical is dictated by the reactivity and concentration of RH and its opportunity for migration is determined not only by the rate (k_1) at which the bridged species is formed but also by the rate (k_2[RH]) at which the unrearranged radical competitively collapses to unrearranged product. Even when migration is feasible, formation of rearranged product *via* the rearranged radical may be precluded if the ratio of k_2[RH]/k_1 is sufficiently large. While increased stability of the rearranged radical need not provide the "driving force" for migration, it does provide the incentive for the bridged species to open to the rearranged rather than the unrearranged radical.

stantially reduced concentration of aldehyde, the unrearranged radical had either insufficient inclination or time to assume the bridged conformation preparatory to migration.

β-Thiophenoxyalkyl Radical.—Pure samples of α,α- (**10**) and γ,γ- (**11**) dimethylallyl phenyl sulfides, prepared by the acid-catalyzed addition of thiophenol to isoprene, were characterized by oxidative ozonolysis to α-phenylsulfonylisobutyric acid and phenylsulfonylacetic acid, respectively. The *tert*-butyl hydroperoxide (TBHP)[14] initiated reaction of the terminally unsaturated isomer **10** with *n*-butyraldehyde, despite no evidence of butyraldehyde decarbonylation, gave only a trace of a ketonic product which boiled in a range considerably lower than that expected for a keto sulfide adduct. Only its primary allylic isomer **11** was pro-

$$(CH_3)_2\overset{SC_6H_5}{\overset{|}{C}}CH{=}CH_2 \;(\mathbf{10}) + R\cdot \rightleftharpoons (CH_3)_2\overset{SC_6H_5}{\overset{|}{C}}\dot{C}HCH_2R \;(\mathbf{2}) \longrightarrow (CH_3)_2C{=}CHCH_2R$$

11, R = SC_6H_5
15, R = COC_3H_7

duced and recovered in high yield with *ca.* 50% of unreacted **10**. Although it was thermally stable, partial isomerization of **10** could be accomplished just by heating at 75° in the presence of a trace of TBHP. Isomerization, dramatically increased by a trace thiophenol, was complete in 30 min at 75° and, in excess thiophenol, afforded considerable primary isomer even at room temperature in the absence of TBHP. Its free-radical character was supported by acceleration with TBHP, suppression with 1,3,5-trinitrobenzene, and an insensitivity to pyridine.

Significantly, no adduct formation accompanied isomerization even in excess thiophenol at 75°, despite the fact that these adducts, obtained independently[16] (Scheme I), were completely stable under the reaction conditions. Clearly, if free-radical addition proceeded through the expected radical intermediate (**2**), loss of the tertiary thiophenoxy group must have occurred at a rate substantially faster than chain transfer, even in the presence of the highly reactive thiophenol (see ref 26). This behavior is quite consistent with the established reversibility of thiol additions to olefins[17] and also is in accord with the isomerization of α-methylallyl methyl sulfide reported by Huyser and Kellogg.[18] The intermediate **2** (R = SC_6H_5) reversibly formed by the addition of a thiophenoxy radical now, unaware of its ancestry, has a choice of β-thiophenoxy groups to expel. Although simple bond dissociation energy considerations suggest a preference for loss at the tertiary alkyl position, the primary sulfide **11** would accumulate in

(14) An attractive low-temperature initiator (*ca.* 80°) mainly because of its ease of removal by distillation and the innocuous nature of its decomposition products. Its role is obscure, however, since its first-order rate of homolysis at 80° is insufficiently fast to provide radical fragments at these temperatures.[15] It usually does function nonetheless, undoubtedly as a consequence of second-order-induced decomposition (*e.g.*, with RSH) or first-order homolysis of subsequent reaction products [*e.g.*, RCH(OH)OO-*tert*-C_4H_9 from reaction with aldehydes].

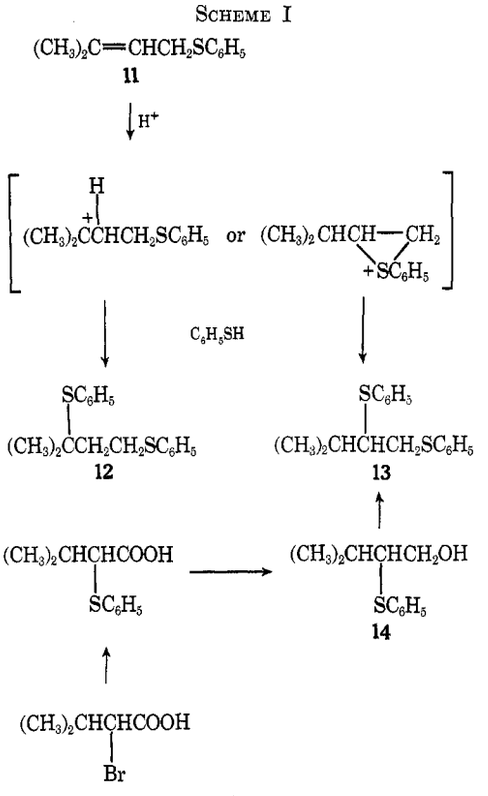
(15) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, pp 403, 404.

(16) The validity of Scheme I as an unambiguous synthesis of **12** *via* orthodox protonation of **11** suffers from the possibility of anomalous protonation induced by thiophenoxy participation to give **13** instead. The unequivocal preparation of **13**, however, established its dissimilarity to **12**.

(17) C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, **81**, 1144 (1959).

(18) E. S. Huyser and R. M. Kellogg, *ibid.*, **87**, 2867 (1965).

SCHEME I



any case since its formation is essentially irreversible under these conditions. Its isolation as the major product, even from the attempted addition of butyraldehyde in the absence of thiophenol, simply attests to the greater efficiency of the thiophenoxy radical in continuing the chain process. After the first few additions of a butyryl radical, the expelled thiophenoxy radical preferentially adds to the olefinic unsaturation of **10** rather than chain transfer with butyraldehyde, and only a small quantity of the unsaturated ketone **15** (R = COC_3H_7) is produced.

The overwhelming preference of the intermediate radical (**2**) for elimination over admittedly rapid chain transfer certainly compromises its opportunity for rearrangement, casting serious doubt on the validity of reports of 1,2-thiophenoxy migration during the reaction of acetone mercaptols with peroxides.[6b] The products observed are probably more appropriately explained by an elimination–addition sequence.

$$CH_3\overset{SR}{\overset{|}{C}}CH_2 \xrightarrow{-RS\cdot} CH_3C{=}CH_2 \xrightarrow{+RS\cdot} CH_3\overset{SR}{\overset{|}{C}}CH_2SR$$

Conceivably, subsequent reaction of thiophenol and **11** to give the expected adduct **13** could have created the misleading impression of thiophenoxy migration

$$(CH_3)_2C{=}CHCH_2R + C_6H_5SH \xrightarrow[75°/24\ hr]{TBHP} (CH_3)_2\overset{H}{\overset{|}{C}}CHCH_2R$$
$$\overset{SC_6H_5}{\overset{|}{}}$$

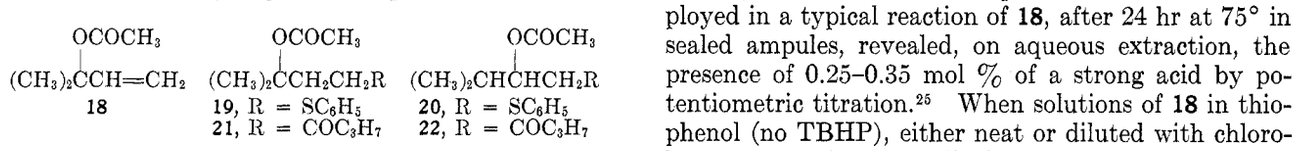
11, R = SC_6H_5
16, R = $OCOCH_3$

13, R = SC_6H_5
17, R = $OCOCH_3$

during isomerization of **10**; none of this adduct was detectable under these conditions, however. In fact, the reaction of **11** with thiophenol was very slow, providing, after 24 hr at 75°, a high recovery of reactants and only

a few per cent of a material which, although analyzing correctly for a 1:1 adduct, appeared to be a mixture of isomers. In sharp contrast, the addition of thiophenol to γ,γ-dimethylallyl acetate (**16**) under similar conditions gave >40% of an adduct identical in all respects with **17** prepared independently by the acetylation of **14**.[19]

β-Acetoxyalkyl Radical.—The TBHP-initiated reaction of α,α-dimethylallyl acetate (**18**) with thiophenol produced essentially equivalent quantities of acetic



18 **19**, R = SC_6H_5; **21**, R = COC_3H_7 **20**, R = SC_6H_5; **22**, R = COC_3H_7

acid and γ,γ-dimethylallyl phenyl sulfide (**11**) as well as a single adduct by vpc which was completely stable under the reaction conditions and identical in all respects with an authentic sample of the unrearranged adduct (**19**) prepared independently by acetylation of the tertiary alcohol obtained from the reaction of methyl β-thiophenoxy propionate with methylmagnesium iodide. The negative trend in adduct formation with increasing dilution of the reactants (Table I)

TABLE I

EFFECT OF CHLOROBENZENE DILUTION ON THE REACTION PRODUCTS OF α,α-DIMETHYLALLYL ACETATE, THIOPHENOL, AND TBHP[a]

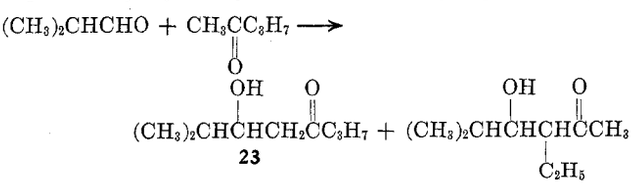
C_6H_5Cl	**11**/CH_3COOH[b]	**19**[c]
0.00	0.53	0.45
1.00	0.58	0.40
2.00	0.68	0.30
4.50	0.74	0.23
7.50	0.79	0.16
10.00	0.80	0.13

[a] Values refer to moles of chlorobenzene and product/mole of acetate employed, after 24 hr at 75°. [b] Titrimetric estimates of acetic acid; distilled recovery of **11** generally >90% of acetic acid titer. [c] Estimated by saponification.

is suggestive of a competitive acetoxy radical elimination from **3** (R = SC_6H_5) in a manner analogous to thiophenoxy loss from **2** (R = SC_6H_5). The stoichiometric isolation of acetic acid, however, is inconsistent with the well-documented rapid decomposition of acetate radicals (CO_2 + $\cdot CH_3$), which is extensive even in the presence of highly efficient radical scavengers.[20] Furthermore, simple thermodynamic calculations[21] lend little encouragement to acetoxy radical loss, indicating that it should occur at a rate 10^{11} slower than thiophenoxy radical loss.

Although the free-radical nature of product formation was implied by the stability of the reactants in the absence of TBHP, the presence of 0.25 mol % pyridine appeared to enhance adduct yield while completely suppressing the production of acetic acid and primary allylic sulfide, thus suggesting strong acid involvement in their formation. Indeed, quantities of thiophenol, TBHP, and chlorobenzene representative of those employed in a typical reaction of **18**, after 24 hr at 75° in sealed ampules, revealed, on aqueous extraction, the presence of 0.25–0.35 mol % of a strong acid by potentiometric titration.[25] When solutions of **18** in thiophenol (no TBHP), either neat or diluted with chlorobenzene were, in turn, spiked with comparable amounts of *p*-toluenesulfonic acid, essentially quantitative conversion to acetic acid and γ,γ-dimethylallyl phenyl sulfide (**11**) was observed after 24 hr at 75°, leaving little doubt that these products derive from the strong acid-catalyzed solvolysis of the allylic acetate in competition with normal radical addition. Accordingly, when the TBHP initiator was replaced by AIBN, only the normal unrearranged adduct **19** was produced, and no acetic acid and primary allylic sulfide were detected by vpc. Chlorobenzene dilution served only to reduce the conversion and consequently the yield of the unrearranged adduct consistent with the trend observed in Table I. Significantly, no rearranged product (**20**) was noted even at the lowest thiophenol concentration examined (1.3 *M*).

Replacement of the thiophenol with butyraldehyde, a much less reactive chain transfer agent,[26] also elicited no migration of the intermediate radical **3** (R = COC_3H_7). The TBHP- or AIBN-initiated reaction of α,α-dimethylallyl acetate (**18**) with pure *n*-butyraldehyde (two and tenfold excesses) gave only a single adduct (vpc) which was characterized as the unrearranged keto acetate **21** by virtue of its elemental analysis, infrared spectrum, and especially its nmr spectrum, which displayed a high-field methyl triplet for the terminal methyl centered at 0.95 ppm, a strong singlet for the *gem*-dimethyl system at 1.5 ppm, and the acetyl methyl at 2.0 ppm. Careful vapor phase chromatography of the reaction mixture indicated the absence of the product of 1,2-acetoxy migration (**22**), obtained independently by acetylation of the major product (**23**)



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of the condensation of isobutyraldehyde and 2-pentanone and characterized by elemental analysis and infrared, mass, and nmr spectra; especially definitive in the nmr was the multiplet at 5.2 ppm due to the single methinyl hydrogen on the carbon adjacent to the

(19) The relatively slow rate of normal addition of thiophenol to **11** suggests that the adduct isolated is at least in part 1,4-dithiophenoxy-3-methylbutane, formed *via* an allylic isomerization [$(CH_3)_2C{=}CHCH_2SC_6H_5 \rightarrow CH_2{=}C(CH_3)CH_2CH_2SC_6H_5$] prior to thiophenol addition in accord with the reported isolation of 1,4-dithiophenoxybutane from the radical-initiated addition of thiophenol to *trans*-crotyl phenyl sulfide (S. J. Cristol, private communication).

(20) J. C. Martin, J. W. Taylor, and E. H. Drew, *J. Amer. Chem. Soc.*, **89**, 129 (1967).

(21) $k_{SC_6H_5}/k_{OCOCH_3} = \exp(E_{OCOCH_3} - E_{SC_6H_5})/RT \cong \exp[D(CH_3\text{–}OCOCH_3) - D(CH_3\text{–}SC_6H_5)]/RT \cong \exp(77.7 - 60.0)/0.69 \cong 1.4 \times 10^{11}$. $D(CH_3\text{–}SC_6H_5)$ has been estimated at 60.0 kcal by M. H. Back and A. H. Sehon, *Can. J. Chem.*, **38**, 1076 (1960), and $D(CH_3\text{–}OCOCH_3)$ was calculated as 77.7 kcal from published thermodynamic data: $\Delta Hf°_{\cdot OCOCH_3}$ (−49.0 kcal),[22] $-\Delta Hf°_{\cdot CH_3}$ (+32.1 kcal),[23] $-\Delta Hf°_{CH_3OCOCH_3}$ (+90.6).[24]

(22) L. Jaffe, E. J. Prosen, and M. Swarc, *J. Chem. Phys.*, **27**, 416 (1957).

(23) J. S. Roberts and H. A. Skinner, *Trans. Faraday Soc.*, **45**, 339 (1949).

(24) Obtained from heats of combustion of reported in International Critical Tables of the National Research Council, Vol. V, McGraw-Hill, New York, N. Y., 1926, p 167.

(25) Most likely benzenesulfinic or benzenesulfonic acid, resulting from the oxidation of thiophenol by TBHP—an unwanted bonus of this unorthodox initiator in this instance (see ref 14).

(26) 100% phenyl migration was observed (ref 11) during the addition of *n*-butyraldehyde to 3,3-diphenyl-1-butene. In contrast, migration was completely suppressed by generation of the β,β-diphenylbutyl radical in the presence of thiols.

acetoxy group. Thus the rearranged keto acetate (22) was readily separable from its unrearranged isomer (21) by vpc and easily distinguishable in mixtures by nmr.

When the butyraldehyde concentration was reduced, 1,2-acetoxy migration was observed. In an AIBN-initiated reaction of α,α-dimethylallyl acetate (18) with butyraldehyde diluted tenfold (on moles of acetate) with chlorobenzene, rearranged adduct (22) (1:5, rearranged/unrearranged) was clearly visible both in the vpc and nmr spectrum of the reaction mixture. Its identity was confirmed by the elemental analysis, nmr, and mass spectra of a pure sample isolated by preparative vpc. Further increasing the chlorobenzene dilution by another factor of five (50-fold) resulted in a depressed yield of products but again clearly indicated the presence of a substantially increased proportion of the rearranged adduct (1:1.6). Both the unrearranged and rearranged keto acetates were stable under the reaction conditions.

The effect of butyraldehyde concentration on the extent of migration is summarized in Table II. It is

TABLE II

EFFECT OF BUTYRALDEHYDE CONCENTRATION ON 1,2-ACETOXY MIGRATION DURING THE ADDITION OF BUTYRALDEHYDE TO α,α-DIMETHYLALLYL ACETATE

$[C_3H_7CHO]$, M	Rearranged (22)/ Unrearranged (21)
9.5[a]	0.00
6.2[b]	0.00
1.5[c]	0.20
0.4[c]	0.63

[a] Neat aldehyde/acetate (10:1); TBHP initiation. [b] Neat aldehyde/acetate (2:1); AIBN initiation. [c] Aldehyde/acetate (2:1) diluted with chlorobenzene; AIBN initiation.

especially interesting to note that a ratio of rearranged/unrearranged product similar to that observed by Tanner and Law[8] during the decarbonylation of β-acetoxyisovaleraldehyde was obtained at *ca.* twice the aldehyde concentration. This reduced influence of the chain transfer agent is likely a reflection of a greater rate constant for the chain transfer of the more reactive primary radical generated by decarbonylation and further attests to the role of the ratio $(k_2[RH]/k_1)$ in determining the extent of migration of classical unrearranged radicals (see ref 13).

There appears to be little question that acetoxy migration during the addition of butyraldehyde to α,α-dimethylallyl acetate must proceed by way of the bridged species 6. Alternative explanations involving an elimination–addition sequence,[6a] even when refined by invoking cage recombination[8] of the dissociated fragments 24 to circumvent the rapid decomposition of

$$(CH_3)_2C{=}CHCH_2R \quad (\cdot OCOCH_3)$$

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the acetoxy radical, are not consistent with the absence of rearranged or unsaturated products from the addition of thiophenol to the allylic acetate. Certainly the nature of R in 3 would not be expected to significantly influence the essentially irreversible formation of 11, and cage recombination, by definition, should be relatively insensitive to the media (thiophenol ~ butyraldehyde). Once generated, 24 must then collapse to either rearranged or unsaturated products.

The success of π delocalization in serving as a vehicle for acetoxy and not carbethoxy migration may be a reflection of the geometry of their respective bridged structures [five-membered ring (6) favored over three-membered ring (4)]. More likely, however, it is a manifestation of a greater preference for bond formation at the electron-rich oxygen of the acetoxy carbonyl group to give the relatively stable carbon radical 6 rather than the high-energy oxygen radical required by bond formation at the carbon of the carbethoxy carbonyl group (4); of course, bond formation at the carbonyl oxygen in the latter case is geometrically unfavorable.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were determined on Perkin-Elmer Model 21 and 257 grating spectrometers, mass spectra on a Hitachi RMU-6 double-focusing instrument, and nmr spectra on a Varian T-60 spectrometer using tetramethylsilane as an internal standard.

Diethyl Acetal of β,β-Dicarbethoxy-*n*-valeraldehyde.—To a stirred, refluxing solution of 10.85 g (0.473 g-atom) of sodium in 300 ml of dry ethanol, 89.0 g (0.473 mol) of diethyl ethyl malonate was added, followed by 90 min of reflux. Diethyl bromoacetal, 75.0 ml (0.043 mol), prepared according to the method of McElvain,[27] was added over 12 hr; another 10 ml of the bromoacetal was added after 12 hr and reflux was maintained for a total of 142 hr. Conventional work-up and distillation through a 21-in. Helix-packed column afforded 51.2 g (36%) of the acetal as a colorless liquid, bp 109.0–109.5° (0.5 mm), $n^{25}D$ 1.4304.

Anal. Calcd for $C_{15}H_{28}O_6$: C, 59.19; H, 9.27. Found: C, 59.37; H, 9.18.

β,β-Dicarbethoxy-*n*-valeraldehyde (7).—A vigorously stirred suspension of 13.5 g of the acetal and 40 ml of 50% aqueous citric acid was heated under a 6-in. Vigreux column equipped with a variable take-off head for a total contact time of 50 min; 5.2 ml of ethanol was removed at a head temperature of 77–80°. The colorless residue was diluted with water, extracted with ether, and worked up conventionally. Concentration and distillation in a nitrogen atmosphere through a 6-in. Vigreux column gave 5.30 g of the aldehyde as a colorless liquid, bp 98.0–99.0° (1.5 mm), $n^{25}D$ 1.4350, semicarbazone mp (water) 124.0–124.5°.

Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.16; H, 7.60.

Decarbonylation of β,β-Dicarbethoxy-*n*-valeraldehyde.—The decarbonylation apparatus consisted of a 250-ml flask equipped with a variable reflux distillation head vented *via* an air-cooled safety trap to a water-filled inverted 1-l. calibrated burette; a receiver was fitted onto the stillhead to collect low-boiling material.

Immediately upon distilling the aldehyde into the 250-ml decarbonylation flask, optionally diluted with diphenyl ether, the system was flushed with nitrogen, stirred magnetically, and allowed to equilibrate (10 min) in an oil bath thermostated at 130 ± 1°. Di-*tert*-butyl peroxide, 0.32 g (10 mol %), was quickly injected into the flask and gas evolution began almost immediately. From 5.01 g (0.0218 mol) of the aldehyde a corrected volume of 473 ml (97% of theory) of carbon monoxide was collected over a 6-hr period. Conventional work-up and distillation of the residue through a 6-in. Vigreux apparatus provided the following fractions: (1) 3.85 g, bp 77.0–79.0° (5.0 mm), $n^{25}D$ 1.4167; and (2) 0.20 g, bp 70–90° (5.0–2.5 mm), $n^{25}D$ 1.4150; and 0.28 g of a residue, $n^{25}D$ 1.4470, shown by ir to be starting aldehyde. Fractions 1 and 2 had identical ir spectra and exhibited only a single peak on vapor phase chromatography indicating a 92% recovery of pure unrearranged product 8. Fraction 1 was submitted for analysis and quantitatively hydrolyzed in aqueous NaOH to a white crystalline solid, mp 124.5–125.2° (chloroform–Skelly B) (lit.[28] for methyl ethyl malonic acid, mp 121–122°).

Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.67; H, 8.90.

(27) S. M. McElvain and D. Kunigar, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1943, p 123.

(28) I. Vogel, *J. Chem. Soc.*, 1438 (1929).

Decomposition of 0.37 g of this diacid in a microstill at 170–180° (25 mm) gave 0.129 g of a colorless distillate, n^{25}D 1.4068, neut equiv 102 (lit.[29a] for α-methylbutyric acid, n^{20}D 1.4051, neut equiv 102), *p*-phenylphenacyl ester mp 69–70° (ethanol–water) (lit.[29b] mp 71°).

Decarbonylation of 5.10 g (0.22 mol) of the aldehyde in 17.8 ml (0.11 mol) of diphenyl ether, similarly conducted, evolved a corrected volume of 471 ml (95% of theory) of carbon monoxide over a 9-hr period. Distillation followed by infrared and vpc analysis again confirmed the presence of only the unrearranged ester in 92% yield.

α,α- (**10**) **and** γ,γ- (**11**) **Dimethylallyl Phenyl Sulfides.**—To a solution of 62.4 ml (0.60 mol) of thiophenol, 100 ml (1.0 mol) of isoprene, and 10 ml of dry ether cooled in an ice bath, 20 ml (0.37 mol) of concentrated sulfuric acid was added dropwise with vigorous stirring over a 15-min period. After stirring for another 15 min, 43 g (0.4 mol) of powdered anhydrous sodium carbonate was added followed by 300 ml of ice water. The organic layer was then combined with two ether extracts of the aqueous phase and washed repeatedly with 10% aqueous sodium carbonate and finally with water before drying over magnesium sulfate. Concentration and distillation of the light yellow liquid residue through a 2-ft Podbielniak column afforded 5.5 g of α,α-dimethylallyl phenyl sulfide as a colorless liquid: bp 51.0° (0.5 mm); n^{25}D 1.5447; ir (pertinent absorptions) 1630, 1583 (w), 1412, 908 cm^{-1}.

Anal. Calcd for $C_{11}H_{14}S$: C, 74.13; H, 7.92. Found: C, 74.33; H, 7.87.

Continued distillation provided the isomeric γ,γ-dimethylallyl phenyl sulfide as a colorless liquid: bp 69.0–70.0° (0.5 mm); n^{25}D 1.5635; ir (pertinent absorptions) 1664, 1583 (s), 837 cm^{-1} [lit.[30] for γ,γ-dimethylallyl phenyl sulfide, bp 124–126° (14 mm), n^{25}D 1.5644].

The structure of the low-boiling isomer was confirmed by exposure of 1.0 g to a stream of 3% ozone in 15 ml of acetic anhydride–glacial acetic acid (1:1 v/v) at 0–5°, followed by oxidation with 5 ml of 30% hydrogen peroxide at room temperature. Conventional work-up gave 1.0 g of white needles, neut equiv 224, mp 142–143° (benzene), which was undepressed on admixture with an authentic sample of α-phenylsulfonylisobutyric acid. Similar treatment of the high-boiling isomer (1.0 g) gave 0.33 g of white flakes, mp 110–111° (benzene) (lit.[31] for phenylsulfonylacetic acid, mp 111.5–112.5°), and acetone, isolated as its 2,4-DNPH, mp 124–125° (lit.[29b] mp 126°).

α-Phenylsulfonylisobutyric Acid.—A solution in 50 ml of water of 8.60 g (0.13 mol) of potassium hydroxide, 6.2 ml (0.060 mol) of thiophenol, and 10.0 g (0.060 mol) of α-bromoisobutyric acid, mp 40–42°, prepared according to the procedure of Marvel,[32] was stirred for 1 hr at 0°, heated on the steam bath for 4 hr, and allowed to stand overnight. Conventional work-up and distillation of the liquid residue in a 6-in. Vigreux apparatus afforded 3.30 g of a pale yellow oil, bp 125.0–126.0° (0.8 mm), which solidified completely on standing, mp 68–69° (benzene). Exposure of this solid to a glacial acetic acid solution of 30% hydrogen peroxide for 16 hr gave, after decomposition of excess peroxide with manganese dioxide and acidification with concentrated HCl, white needles, mp 142–143° (benzene).

Anal. Calcd for $C_{10}H_{12}O_4S$: C, 52.63; H, 5.30; neut equiv, 228. Found: C, 52.87; H, 5.00; neut equiv, 228.

1,3-Dithiophenoxy-3-methylbutane (**12**).—To a vigorously stirred solution of 14.6 g (0.082 mol) of γ,γ-dimethylallyl phenyl sulfide and 10.7 g (0.090 mol) of thiophenol in 50 ml of glacial acetic acid cooled in an ice bath, 4.5 ml of concentrated sulfuric acid was slowly added. The ice bath was removed after 10 min and stirring was continued for 27 hr at room temperature. The resulting two-phase solution was poured over crushed ice, diluted with water, and extracted with carbon tetrachloride. Conventional work-up followed by distillation through a 6-in. Vigreux column afforded a 42% recovery of the primary allylic sulfide and 8.8 g of its thiphenol adduct as a very pale yellow liquid, bp 159.0–160.0° (0.7 mm), n^{25}D 1.6041.

Anal. Calcd for $C_{17}H_{20}S_2$: C, 70.81; H, 6.99. Found: C, 70.85; H, 6.96.

A solution of 0.50 g of this material in 15 ml of glacial acetic acid and 5 ml of 30% hydrogen peroxide gave, after 2 hr on a steam bath, the disulfone as long white needles, mp 118.4–119.4° (EtOH–H_2O).

Anal. Calcd for $C_{17}H_{20}S_2O_4$: C, 57.95; H, 5.72. Found: C, 57.72; H, 5.72.

2-Thiophenoxy-3-methylbutanol (**14**).—The crude α-thiophenoxyisovaleric acid (20.1 g), obtained from the reaction[32] in water of thiophenol (12.2 g, 0.11 mol), sodium hydroxide (10.0 g, 0.25 mol), and isovaleric acid (20 g, 0.11 mol), was dissolved in 100 ml of dry ether and slowly added to a vigorously stirred solution of 7.2 g of lithium aluminum hydride in 400 ml of absolute ether cooled in an ice bath. After 15 min the ice bath was removed and the reaction mixture was refluxed on the steam bath overnight. After cooling, 14.4 ml of water and 11.5 ml of 10% aqueous sodium hydroxide were added successively with vigorous stirring and the suspension was filtered. Concentration left 13.8 g of a colorless liquid which on distillation in the 6-in. Vigreux apparatus afforded 8.0 g of the thiophenoxy alcohol as a colorless liquid, bp 93.0–93.5° (0.5 mm), n^{25}D 1.5542. Oxidation with excess 30% hydrogen peroxide in acetic acid followed by reaction with 3,5-dinitrobenzoyl chloride provided the 3,5-dinitrobenzoate of 2-phenylsulfonyl-3-methylbutanol as colorless plates from ethanol, mp 120.0–121.0°.

Anal. Calcd for $C_{18}H_{18}O_8N_2S$: C, 51.19; H, 4.30. Found: C, 50.98; H, 4.17.

1,2-Dithiophenoxy-3-methylbutane (**13**).—To 1.00 g of 2-thiophenoxyisoamyl alcohol in a test tube was slowly added 3.0 ml of thionyl chloride with cooling. After the initial vigorous reaction and copious evolution of gas subsided, the solution was heated in an oil bath at 65° for 10 min and then excess thionyl chloride was removed to give 1.1 g of a pale yellow liquid residue which was then taken up in 5 ml of methanol and refluxed for 2 hr with a solution of 0.61 g of thiophenol and 3 ml of methanol containing 5.00 ml of 1.11 *N* sodium methoxide in methanol. Dilution with water and extraction with pentane gave 1.29 g of the crude 1,2-dithiophenoxy-3-methylbutane as a colorless liquid residue. A solution of 0.50 g of this residue in 15 ml of glacial acetic acid was oxidized with 5 ml of 30% hydrogen peroxide to afford a colorless oil which crystallized to white plates, mp 87.6–89.2° (benzene–hexane); admixture with the disulfone of 1,3-dithiophenoxy-3-methylbutane gave mp 77–107°.

Anal. Calcd for $C_{17}H_{20}S_2O_4$: C, 57.95; H, 5.72. Found: C, 58.08; H, 5.62.

***tert*-Butyl Hydroperoxide Initiated Reaction of α,α-Dimethylallyl Phenyl Sulfide with *n*-Butyraldehyde.**—A solution of 5.00 g (0.028 mol) of the sulfide and 10.0 g (0.140 mol) of freshly distilled *n*-butyraldehyde was stirred in an oil bath for 15 min at 80° while the system was flushed with nitrogen. The nitrogen flow was terminated, 0.25 g (0.003 mol) of *tert*-butyl hydroperoxide was injected, and the reaction mixture was allowed to remain at 80° for 9 hr; a negligible quantity of gas was evolved. Distillation through a 6-in. Vigreux provided the following fractions: (1) 0.85 g, bp 55–70° (750 mm), n^{25}D 1.3790; (2) 3.42 g, bp 70–71° (750 mm), n^{25}D 1.3770; (3) 3.99 g, bp 73–43° (150 mm), n^{25}D 1.3772; (4) 1.15 g, bp 48–53° (0.3 mm), n^{25}D 1.4902; (5) 2.41 g, bp 53–67° (0.3 mm), n^{25}D 1.5320; (6) 1.29 g, bp 67–80° (0.3 mm), n^{25}D 1.5530; and 0.068 g of an amber liquid kettle residue. Fractions 1–3 were essentially butyraldehyde; fractions 4–6 as well as the residue consisted mainly of isomeric mixtures of α,α- and γ,γ-dimethylallyl phenyl sulfides in varying proportions as indicated by ir. The spectrum of fraction 4 also suggested the presence of ketonic material.

***tert*-Butyl Hydroperoxide Initiated Reaction of α,α-Dimethylallyl Phenyl Sulfide with Thiophenol.**—A solution of 3.00 g (0.017 mol) of the tertiary sulfide, 3.70 g (0.034 mol) of thiophenol, and 0.15 g (0.002 mol) of *tert*-butyl hydroperoxide was stirred at 75° for 2 hr. Distillation through a 6-in. Vigreux apparatus revealed a small amount of uncollected volatile material, presumably hydroperoxide and hydroperoxide decomposition products, and provided the following fractions: (1) 3.42 g, bp 59–39° (10–1 mm), n^{25}D 1.5850; (2) 0.46 g, bp 60–64° (0.5 mm), n^{25}D 1.5535; (3) 1.91 g, bp 64–65° (0.5 mm), n^{25}D 1.5629; and 0.61 g of an amber residue which solidified on standing and gave fine white needles, mp 60–61° (MeOH), identified as diphenyl disulfide. Fractions 2 and 3 were identified by ir as γ,γ-dimethylallyl phenyl sulfide.

(29) (a) H. Gilman and R. H. Kirby, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 353; (b) S. M. McElvain, "The Characterization of Organic Compounds," Macmillan, New York, N. Y., 1953.

(30) P. B. de LaMare and C. A. Vernon, *J. Chem. Soc.*, 3555 (1953).

(31) A. C. Cope, D. E. Morrison, and L. Field, *J. Amer. Chem. Soc.*, **72**, 59 (1950).

(32) C. S. Marvel, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1943, p 523.

tert-**Butyl Hydroperoxide Initiated Reaction of γ,γ-Dimethylallyl Phenyl Sulfide with Thiophenol.**—A solution of 5.00 g (0.028 mol) of the sulfide, 6.15 g (0.056 mol) of thiophenol, and 0.50 g (0.006 mol) of *tert*-butyl hydroperoxide was heated at 75° for 24 hr in a sealed ampule. Distillation provided the following fractions: (1) 5.19 g, bp 52–25° (10–0.6 mm), n^{25}D 1.5857; and (2) 4.31 g, bp 70–72° (0.7 mm), n^{25}D 1.5629 (corresponding to an 85 and 87% recovery of thiophenol and the primary allylic sulfide, respectively). The amber residue (1.31 g) which solidified on cooling was chromatographed on a 5 × 1.25 in. column of Alcoa alumina. Elution with 500 ml of pentane provided 0.88 g of diphenyl disulfide, mp 60–61° (ethanol). A yellow liquid, 0.20 g, was then eluted with 250 ml of 50:50 pentane–ether. Distillation in a microstill at a bath temperature of 205° (0.5 mm) provided a small amount of 1:1 adduct, n^{25}D 1.6051.

Anal. Calcd for $C_{17}H_{20}S_2$: C, 70.81; H, 6.99. Found: C, 70.64; H, 6.81.

Another solution of 3.00 g (0.017 mol) of the primary allylic sulfide, 7.4 g (0.068 mol) of thiophenol, and 0.50 g of *tert*-butyl hydroperoxide was heated at 75° for 48 hr in a sealed ampule. Concentration and chromatography of the residue (1.48 g) in similar fashion provided 0.29 g of 1:1 adduct. Oxidation with excess 30% H_2O_2 in glacial acetic acid gave a gummy white solid which defied numerous attempts at crystallization, even when seeded with crystals of authentic disulfones of 1,2- (**13**) and 1,3-dithiophenoxy-3-methylbutane (**12**).

α,α- (18) and γ,γ- (16) Dimethylallyl Acetates.—These acetates were prepared according to the procedure of Young and Webb[33] from 236 ml (2.5 mol) of freshly distilled acetic anhydride and 172 g (2.0 mol) of α,α-dimethylallyl alcohol, bp 96.5°, n^{25}D 1.4140, prepared by hydrolysis of a mixture of dimethylallyl chloride isomers obtained from the hydrochlorination of isoprene by the method of Goodman.[34] Distillation through a 21-in. helix-packed column afforded 54.3 g of the pure (vpc) tertiary allylic acetate, bp 49.0–50.0° (40 mm), n^{25}D 1.4098; continued distillation gave the primary isomer, γ,γ-dimethylallyl acetate, bp 75.0–76.0° (45 mm), n^{25}D 1.4287.

2-Acetoxy-2-methyl-4-thiophenoxybutane (19).—An ethereal solution of 15.0 g (0.077 mol) of methyl β-thiophenoxypropionate, bp 91.5–92° (0.6 mm), n^{25}D 1.5480, prepared from β-thiophenoxypropionic acid which was obtained by reaction of thiophenol with β-chloropropionic acid, was added with stirring to a solution of 0.23 mol of methylmagnesium iodide. The mixture was refluxed for 1 hr, poured into 100 ml of saturated aqueous ammonium chloride, extracted with ether, washed with water, and dried over magnesium sulfate. Concentration left 10.8 g of liquid which was diluted with an equal volume of acetic anhydride and stirred for 4 hr at 80° and 30 min at 105° in the presence of a small crystal of zinc chloride. Work-up and distillation afforded the colorless acetate, bp 99.5° (0.5 mm), n^{25}D 1.5307.

Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.63; H, 7.61. Found: C, 65.49; H, 7.51.

Hydrolysis of this ester with methanolic sodium hydroxide followed by oxidation with hydrogen peroxide in acetic acid and the reaction with 3,5-dinitrobenzoyl chloride provided the 3,5-dinitrobenzoate of 2-methyl-4-phenylsulfonylbutan-2-ol as fine white needles, mp 147.5–148.2° (EtOH).

Anal. Calcd for $C_{18}H_{18}N_2O_8S$: C, 51.19; H, 4.30. Found: C, 50.97; H, 4.28.

tert-**Butyl Hydroperoxide Initiated Reaction of α,α-Dimethylallyl Acetate with Thiophenol.**—A solution of 5.00 g (0.039 mol) of the tertiary allylic acetate, 8.60 g (0.078 mol) of thiophenol, and 0.35 g (0.0039 mol) of *tert*-butyl hydroperoxide was heated at 75° for 20 hr. Distillation of the reaction product through a 6-in. Vigreux column afforded a small amount of uncollected volatile material and the following fractions: (1) 1.02 g, bp 41° (41 mm), n^{25}D 1.3780; (2) 2.88 g, bp 49–42° (10–1 mm), n^{25}D 1.5753; (3) 2.55 g, bp 72–74° (1–0.8 mm), n^{25}D 1.5629; (4) 0.77 g, bp 75–110° (0.8 mm), n^{25}D 1.5529; (5) 3.46 g, bp 110–111° (0.8 mm), n^{25}D 1.5390; and 2.0 g of diphenyl disulfide residue, mp 60–61° (EtOH). Fraction 1 consisted mainly of acetic acid (87% by titration), confirmed by conversion to its *p*-phenylphenacyl ester, mp 112–112.5° (EtOH) (lit.[30] mp 111°). Fractions 3 and 5 were identified as γ,γ-dimethylallyl phenyl sulfide and 2-acetoxy-2-methyl-4-thiophenoxybutane, respectively, by comparison of ir spectra with those of authentic specimens. The spectrum of fraction 4 was consistent with that of a binary mixture. The identity of fraction 5 was established by quantitative saponification with ethanolic potassium hydroxide (sapon equiv 238), followed by oxidation with 30% hydrogen peroxide in acetic acid, and conversion to a 3,5-dinitrobenzoate ester, mp 148.2–148.8° (MeOH), which was identical with the 3,5-dinitrobenzoate of 2-methyl-4-phenylsulfonylbutan-2-ol.

The influence of chlorobenzene dilution on the product distribution of this reaction was determined in the following manner: 2.00 g (0.0156 mol) of α,α-dimethylallyl acetate, 3.44 g (0.0312 mol) of thiophenol, 0.28 g (0.003 mol) of *tert*-butyl hydroperoxide, and an appropriate quantity of chlorobenzene (1:1 to 10:1 molar ratio to acetate) were placed in sealed tubes and immersed in an oil bath thermostated at 75° for 24 hr. The contents were then washed into a distilling flask with enough chlorobenzene to bring the total chlorobenzene content to 20 ml. This solution was then distilled at reduced pressure through a 6-in. Vigreux column and 10 ml of distillate, free of thiophenol, was collected [bath temperature <75° (60–70 mm)] and acetic acid content was determined by titration with methanolic sodium methoxide. The residual chlorobenzene and thiophenol were removed by continued distillation at increasingly diminished pressure until thiophenol ceased to distil [bath temperature 75° (0.5 mm)]. The bath temperature was raised to 100° and the distillation was terminated at a head temperature of 50° (0.5 mm). Infrared spectra of the residues indicated essentially binary mixtures of γ,γ-dimethylallyl phenyl sulfide and 2-acetoxy-2-methyl-4-thiophenoxybutane in varying proportions contaminated by small quantities of diphenyl disulfide. Adduct content was determined by quantitative saponification with methanolic sodium hydroxide. Results are summarized in Table I.

Azoisobutyronitrile-Initiated Reaction of α,α-Dimethylallyl Acetate with Thiophenol.—A solution of 5.2 g (0.04 mol) of the acetate, 9.0 g (0.08 mol) of thiophenol, and 0.33 g (0.002 mol) of azoisobutyronitrile (DuPont) was heated at 75° for 5 hr. Another 0.33 g of AIBN was charged and the solution was maintained at 75° for a total of 28 hr, at which time vpc on a 4-ft 20% Se-30 Chromosorb W column at 120° with a 60-ml/min helium flow indicated 80% consumption of the tertiary allylic acetate. The vpc displayed two minor unidentified peaks and peaks for α,α-dimethylallyl acetate, thiophenol, tetramethylsuccinonitrile (a decomposition product of AIBN), and diphenyl disulfide as well as a single major product peak at the retention time of the unrearranged 1:1 adduct; no acetic acid or γ,γ-dimethylallyl phenyl sulfide was evident. Removal of excess acetate and thiophenol and distillation of the residue in a 6-in. Vigreux column provided the following fractions: (1) 3.6 g, bp 30–75° (0.4 mm), containing mostly allylic acetate and thiophenol; (2) 0.7 g, bp 75–90° (0.04 mm); and (3) 6.3 g, bp 90–93° (0.04 mm), consisting mainly of the 1:1 adduct (60% yield) contaminated with about 10% diphenyl disulfide. The nmr of fraction 3 corroborated the presence of 2-acetoxy-2-methyl-4-thiophenoxybutane (**19**) as the major component, displaying phenyl absorption centered at 7.17 ppm, the acetyl methyl at 2.0 ppm, and the *gem*-dimethyls at 1.5 ppm; the methylene protons are centered at 2.05 and 2.97 ppm in the proper ratios.

A solution of 5.2 g (0.04 mol) of α,α-dimethylallyl acetate and 9.0 g (0.08 mol) of thiophenol in 45 ml (0.4 mol) of chlorobenzene was stirred at 75° for 28 hr and catalyzed with a total of 0.66 g (0.004 mol) of AIBN in two portions in the manner described above. Vapor phase chromatography showed only 16% consumption of the allylic acetate with production of a similar product distribution as that observed above but in much lower yield; again only the normal 1:1 adduct **19** was observed.

tert-**Butyl Hydroperoxide Initiated Reaction of γ,γ-Dimethylallyl Acetate with Thiophenol.**—A solution of 5.00 g (0.039 mol) of the acetate, 8.60 g (0.078 mol) of thiophenol, and 0.70 g (0.008 mol) of *tert*-butyl hydroperoxide was heated for 24 hr at 75° in a sealed ampule. Volatiles were removed to a bath temperature of 110° (0.06 mm). The infrared spectrum of the light yellow kettle residue (6.11 g) was essentially identical with that of an authentic sample of 2-thiophenoxy-3-methylbutyl acetate (**17**). Saponification (indicating 41% yield of adduct), followed by oxidation with hydrogen peroxide in acetic acid, and finally reaction with 3,5-dinitrobenzoyl chloride, gave the 3,5-dinitrobenzoate of 2-phenylsulfonyl-3-methylbutanol, mp 121.0–121.4°, undepressed on admixture with authentic material.

2-Methyl-3-hydroxy-5-octanone (23).—A solution of 86 g (1

(33) W. G. Young and I. D. Webb, *J. Amer. Chem. Soc.*, **73**, 780 (1951).
(34) L. Goodman, Ph.D. Thesis, UCLA, 1950.

mol) of 2-pentanone and 17 ml of 1 *N* alcoholic potassium hydroxide was stirred in an ice bath and 23 g (0.32 mol) of isobutyraldehyde was added over a 2-hr period according to the procedure of Powell and Hagemann.[35] Neutralization with 2.5 g of tartaric acid, filtration, and concentration gave 41.6 g of a liquid which by vpc showed only a trace of isobutyraldehyde and three products in a ratio of 7.3:2:9.7. Distillation through a spinning band column provided ten fractions, the first three of which (combined weight 8.2 g) were discarded. The remaining fractions (combined weight 22.5 g), boiling range 55–58° (0.015 mm), were shown by vpc and nmr to be binary solutions of 2-methyl-3-hydroxy-5-octanone (**23**) and its lower boiling isomer, 2-methyl-3-hydroxy-4-ethyl-5-hexanone, in proportions varying from 54:46 to 97:3; the higher boiling isomer was produced in the largest amounts. The final fraction [97% pure 2-methyl-3-hydroxy-5-octanone, bp 58° (0.015 mm)] was submitted for elemental analysis. Its nmr spectrum was consistent with the structural assignment, displaying a multiplet at 3.8 ppm for the methinyl proton adjacent to the hydroxyl function. The significant acetyl methyl proton of the contaminating low boiler, seen to decrease as boiling point increased, was virtually absent; strong hydroxyl and carbonyl absorptions were evident in the infrared at 3460 and 1712 cm^{-1}, respectively.

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.46. Found: C, 68.47; H, 11.62.

2-Methyl-3-acetoxy-5-octanone (22).—To a refluxing solution of 5.9 g (0.074 mol) of pyridine and 9.0 g (0.057 mol) of a 82:18 isomeric mixture of 2-methyl-3-hydroxy-5-octanone and 2-methyl-3-hydroxy-4-ethyl-5-hexanone in 25 ml of dry benzene was added 7.0 g (0.0685 mol) of acetic anhydride over a 15-min period. The mixture was refluxed for 1.5 hr and allowed to cool and stand overnight; vpc revealed two products in the expected 4:1 ratio, confirming that acetylation was accomplished with essentially no change in isomer distribution. Distillation in a spinning band column provided five fractions with a combined weight of 12.6 g, boiling range 60–79° (0.75 mm), containing 30–90% of the higher boiling component. A pure sample of the high-boiling material [2.0 g, bp 78–79° (0.75 mm)] was collected by preparative vpc; the nmr spectrum displayed the *C*-methyl protons split and centered at 0.9 ppm and the acetyl methyl protons at 2.05 ppm, consistent with assignment as 2-methyl-3-acetoxy-5-octanone. The most definitive portion of the spectrum is the multiplet due to the single methinyl hydrogen on carbon adjacent to the acetoxy group at 5.2 ppm. A mass spectrum indicated that the most predominant cleavage is loss of acetic acid to give the conjugated olefin to which can be assigned the major ions observed in the spectrum, *m/e* 140, 97, 71, 43; *m/e* 97 is the most abundant. Although the neat keto acetate tended to lose acetic acid *via* reverse Michael reaction on prolonged standing, it was completely stable under the conditions employed for the butyraldehyde-α,α-dimethylallyl acetate reactions. Neither loss of keto acetate nor appearance of its ketonene decomposition product was evident in the vpc.

***tert*-Butyl Hydroperoxide Initiated Reaction of α,α-Dimethylallyl Acetate with *n*-Butyraldehyde.**—A solution of 5.2 g (0.04 mol) of the acetate, 28.8 g (0.4 mol) of *n*-butyraldehyde, and 1.14 g (0.009 mol) of *tert*-butyl hydroperoxide was maintained at 78° for 32 hr, at which time vpc indicated an 80% conversion of the allylic acetate. Concentration gave 5.1 g of a residue which on distillation through a 6-in. Vigreux column provided (1) 1.0 g, bp 90–93° (0.5 mm); (2) 1.5 g, bp 93–95° (0.5 mm); (3) 1.6 g, bp 90–92° (0.45 mm); and (4) 0.6 g, bp 95–97° (0.45 mm). Vpc on a 6-ft 10% Carbowax 20M Anakrome Q column operated isothermally at 165° with a 60-ml/min helium flow of these fractions showed them to contain, respectively, 57, 75, 85, and 91% of the unrearranged 1:1 adduct (22% yield) with a retention time of 12.25 min in addition to a substantial amount of material with high retention time. No product was observed at the retention time (10.15 min) expected for the rearranged 1:1 adduct, 2-methyl-3-acetoxy-5-octanone. A sample of the major product in fraction 4 was isolated by preparative vpc as a colorless liquid, bp 58° (0.05 mm).

Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.83; H, 10.11.

The nmr of fraction 4 was consistent with its 2-methyl-2-acetoxy-5-octanone (**21**) assignment, displaying a high-field methyl triplet for the terminal methyl centered at 0.95 ppm, a strong singlet for the *gem*-dimethyl system at 1.50 ppm, and the acetyl methyl at 2.0 ppm. A split carbonyl absorption in the infrared at 1715 and 1732 cm^{-1} supported the presence of ketone and ester groups, respectively.

Azoisobutyronitrile-Initiated Reaction of α,α-Dimethylallyl Acetate with *n*-Butyraldehyde.—A solution of 5.2 g (0.04 mol) of the acetate, 5.75 g (0.08 mol) of *n*-butyraldehyde, and 0.33 g (0.002 mol) of azoisobutyronitrile was heated at reflux (90°) for 4 hr, another 0.33 g of azoisobutyronitrile was charged, and the reaction mixture was maintained at 90° for a total of 28 hr. Vpc analysis showed the unrearranged 1:1 adduct as the major product with no trace of the rearranged isomer. Distillation provided (1) 1.6 g, bp 28–55° (2.0 mm); (2) 2.5 g, bp 55–60° (2.0 mm); (3) 0.5 g, bp 60–65° (2.0–0.06 mm); and (4) 3.0 g, bp 65° (0.06 mm). All cuts were impure; however, fraction 4 was estimated (vpc) to contain 89% of 2-methyl-2-acetoxy-5-octanone. A pure sample of the major product isolated from fraction 4 by vpc possessed an nmr superimposable with that of the product of the *tert*-butyl hydroperoxide initiated reaction.

Azoisobutyronitrile-Initiated Reaction of α,α-Dimethylallyl Acetate with *n*-Butyraldehyde in Chlorobenzene.—A solution of 15.6 g (0.12 mol) of the acetate, 17.4 g (0.24 mol) of *n*-butyraldehyde, and 1.0 g (0.006 mol) of AIBN in 135 g (1.2 mol) of freshly distilled chlorobenzene was heated at 75° for 24 hr, another 1.0 g of AIBN was charged, and the solution was maintained at 75° for another 24 hr. Vpc analysis indicated a 50% conversion of the allylic acetate and the presence of unrearranged 1:1 adduct 2-methyl-2-acetoxy-5-octanone as the major product along with minor quantities of butyric acid and tetramethylsuccinonitrile. The rearranged 1:1 adduct, 2-methyl-3-acetoxy-5-octanone (1:5, rearranged to unrearranged), was clearly evident at a retention time of 10.15 min. Distillation of the crude mixture gave the following fractions: (1) 0.4 g, bp 25–35° (0.25 mm); (2) 0.08 g, bp 35–60° (0.25 mm); (3) 1.0 g, bp 60–61° (0.25 mm); (4) 0.08 g, bp 61–65° (0.25 mm); and (5) 0.5 g, bp 65–68° (0.25 mm). Vpc analysis indicated that fractions 2 and 3 contained, respectively, 1:2 and 1:4 ratios of rearranged to unrearranged adduct contaminated in each case with a trace of the succinonitrile. Fraction 4 appeared to be a 1:4 mixture, while fraction 5 contained a 1:7 ratio plus a small amount of higher boilers. The nmr of fractions 3 and 4 were almost identical and were consistent with a composite spectrum of the pure 2-acetoxy and 3-acetoxy isomers in the indicated ratio. Absorption for the proton α to the 3-acetoxy group is apparent at 5.12 ppm and the *gem*-dimethyls α to the 2-acetoxy group are apparent at 1.5 ppm. Pure samples of the unrearranged and rearranged adducts were separated by vpc and collected. Mass spectral analysis of the pure cuts indicated that material with a 12.25-min retention time was identical in cracking pattern with the product obtained from the neat reactions of α,α-dimethylallyl acetate and butyraldehyde and the cut with the 10.15-min retention time was identical with an authentic sample of 2-methyl-3-acetoxy-5-octanone. A sample of fraction 4 was submitted for analysis.

Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.63; H, 10.23.

A repeat of this reaction employing like amounts of reactants but 575 g (6.0 mol) of chlorobenzene (50-fold dilution) resulted in a much lower conversion of allylic acetate and yield of products. The presence of rearranged and unrearranged 1:1 adducts, however, was clearly evident in the vpc. A substantial increase in the ratio of rearranged to unrearranged adduct was noted (1:1.6).

Registry No.—**1,** 34195-74-9; **2** (R = SPh), 34195-75-0; **3** (R = SPh), 34195-76-1; **3** (R = O=CC_3H_7), 34195-77-2; **7,** 3576-07-6; **7** diethyl acetal, 3494-86-8; **8,** 2049-70-9; **10,** 34043-60-2; **11,** 10276-04-7; **12,** 34224-38-9; **12** disulfone, 34224-39-0; **13,** 34224-40-3; **14,** 34220-15-0; **16,** 1191-16-8; **18,** 24509-88-4; **19,** 34220-19-4; **21,** 34220-20-7; **22,** 34220-21-8; **23,** 34220-22-9; butyraldehyde, 123-72-8; thiophenol, 108-98-5; α-phenylsulfonylisobutyric acid, 34220-23-0; α-phenyl sulfide isobutyric acid, 5219-64-7; 3,5-DNB of 2-phenylsulfonyl-3-methylbutanol, 34220-16-1; 1:1 adduct of 2-methyl-2-butene and diphenyl disulfide, 34220-25-2; 3,5-DNB of 2-methyl-4-phenylsulfonylbutan-2-ol, 34202-01-2.

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Structure and Isomerization Phenomena of Olefin Radical Ions. The 1,2-Bis(*N*-methyl-4-pyridyl)ethylene Tetrafluoroborate Radical Cation

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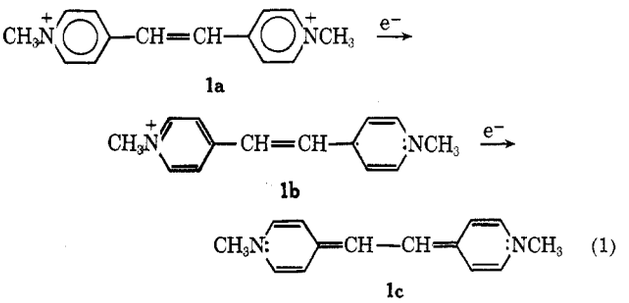
Preparation and structural studies of the radical cation of 1,2-bis(*N*-methyl-4-pyridyl)ethylene tetrafluoroborate by one-electron reduction of the parent diquaternary salt are reported. Both cis and trans isomers of the parent diquaternary are readily reduced to the radical cation by electrolytic reduction at −0.60 V (*vs.* SSCE), by reduction with zinc, or by photolysis in the presence of amines or ethers. The radical is quite stable and structurally similar to the stable methyl viologen radical cation. Cyclic voltammetry experiments indicate that reduction to the radical and neutral species are both reversible; disproportionation of the radical is evidently unimportant. A planar trans structure is indicated for the single form of the radical cation by results of esr and chemical quenching studies. Conversion of cis to trans is very rapid with the lifetime of the cis form evidently being less than 10 μsec at room temperature.

In previous papers[2-5] we have reported on the photochemical isomerization of electron-deficient olefin in various types of molecular complexes. Although in certain cases[3,4] photoisomerization has been found to proceed *via* excited states of the olefin, in other instances[2,4,5] there is strong evidence that electron transfer to the olefin within the excited complex occurs to form a transient radical ion which is the active species in isomerization. Although it has been established that radical anions of stilbene and related olefins can undergo facile geometric isomerization, there has been some uncertainty regarding the structures of these species and the mechanisms and rates for the isomerization. There is good evidence[6] that dianions of stilbene prefer a twisted conformation. The same twisted geometry has been proposed[7,8] for the electronically similar "phantom" excited singlet and triplet states of stilbene on the basis of experimental evidence as well as theoretical considerations. Because of similarities in their electronic structures, the dianion and triplet state of stilbene are predicted by molecular orbital theory to have similar geometric structures.[6] For stilbene radical anion, there is evidence that cis and trans isomers can exist. A difference of 0.03 V has been observed between the half-wave reduction potentials of *cis*- and *trans*-stilbene. In dimethylformamide (DMF), the lifetime of the cis anion is estimated to be in excess of 1 min at room temperature.[9] Furthermore, when *cis*- or *trans*-stilbene is reduced electrolytically in the presence of carbon dioxide in DMF, DL- and *meso*-diphenylsuccinic acid are isolated. Stereochemical analysis of the products indicates that *trans*-stilbene forms a larger proportion of DL acid in relation to meso acid than that formed from *cis*-stilbene.[9] These results are consistent with carboxylation of separate cis and trans radical anions.

Electron spin resonance (esr) experiments[10] have given additional information regarding cis–trans isomerism of stilbene radical anion. The same esr spectrum with roughly uniform line widths is obtained with either *cis*- or *trans*-stilbene over a wide range of temperatures. These results are interpreted in terms of a moderately rapid interconversion of cis–trans isomers which may well occur before esr spectra can be recorded. An interesting result of this work is the finding that rotation about the exocyclic bond joining the ethylenic carbon to the phenyl ring is rather slow and results in an unsymmetrical spin distribution in the phenyl rings. Thus, the bond has a considerable amount of double bond character as predicted by Huckel molecular orbital calculations. Similar hindered rotation is observed for the radical anions of *trans*-1,2-bis(4-pyridyl)ethylene, *trans*-azobenzene, and tolan.[10] Like the stilbene radical anion, only one radical species is observed for each of the above anions.

In the present paper we report an investigation of the structure and isomerization of the radical cation **1b** which is formed by one-electron reduction of 1,2-bis(*N*-methyl-4-pyridyl)ethylene tetrafluoroborate (**1a**) (eq 1). Recently we have found that **1a** undergoes very



(1)

inefficient cis–trans isomerization upon direct or sensitized irradiation in inert solvents such as acetonitrile.[5,11] However, we find that formation of **1b** by one-electron reduction occurs on irradiation of **1a** in the presence of

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