yield of abstraction products in the 147° gas-phase run than in the 147° liquid-phase run are consistent with the increasing tendency of radical–alkene addition products to dissociate at high temperatures and low concentrations and to be superseded by abstraction reactions.[17]

The initial products of the gas-phase oxidation of isobutylene at 293° in clean Pyrex are 80% acetone (and formaldehyde + CO), 17% isobutylene oxide, and methacrolein.[18] In an unpacked quartz reactor at 400–550°, a 60% yield of methacrolein has been reported.[19] Together, these results illustrate again the tendency of higher temperatures to cause more reaction by the abstraction mechanism. However, wall reactions[18] have a still undetermined effect on these high temperature oxidations. That the addition/abstraction ratios are not consistent with our own below 200° may also be due to replacement of alkylperoxy radicals by some other, undetermined, chain carrier at high temperatures.

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Registry No.—Isobutylene, 115-11-7; cyclopentene, 142-29-0.

Supplementary Material Available. Full discussion and experimental data for our oxidations of cyclopentene and the decomposition of cyclopentenyl hydroperoxide will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-885.

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Oxidations of α-Methylstyrene at 110–160°

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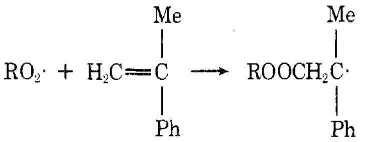
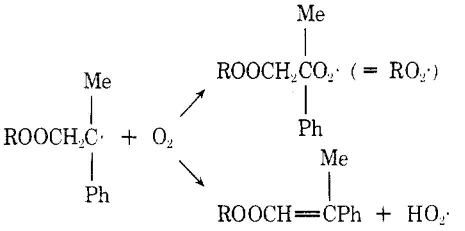
This paper considers the transition between the previously reported oxidations of α-methylstyrene[1] at 50 and 170°, with special attention to the nature of the nonvolatile residue, which changes from an alternating copolymer of α-methylstyrene and oxygen to a very complex mixture. Increasing reaction temperature and rate of oxidation result in lower effective oxygen concentrations, formation of increasing ratios of α-methylstyrene oxide to acetophenone, rapidly decreasing formation of polyperoxide above 100°, increasing involvement of primary products in secondary reactions, and gradual replacements of peroxide groups by ether groups, including $-OCH_2O-$ groups, in the residue. The residues average about two α-methylstyrene units, one ether link, and one hydroxy group per molecule, but contain some vinylidene groups. However, vigorous reduction with HI and red P and then with $LiAlH_4$ gives alkylbenzenes with one to four aliphatic carbon atoms and various dimers of α-methylstyrene.

Previous work[1] on the oxidation of α-methylstyrene showed that the principal products at 50° are a polyperoxide, acetophenone, formaldehyde, and α-methylstyrene oxide. The principal chain propagation steps are shown in eq 1–7.

The competition among these reactions largely determines the products of reaction. Alternation of reactions 1 and 2 produces a polymeric peroxide radical that is stabilized as a polyperoxide molecule by some chain transfer step (not yet established but reaction 3 is suggested). Competition between reactions 2 and 4 depends on oxygen pressure and determines how much acetophenone and epoxide are formed. Whenever reaction 4 occurs, the resulting alkoxy radical (which may contain several alternating C_9H_{10} and O_2 units) "unzips" through all the adjacent polyperoxide groups to give acetophenone, formaldehyde, and a small terminal radical (reaction 5). The ratio of carbonyl compounds to epoxide depends on how many times reaction 2 occurs before reaction 4 occurs. The ratio of polyperoxide to smaller molecules depends on the competition between reactions 3 and 4, the former apparently being independent of oxygen and methylstyrene concen-

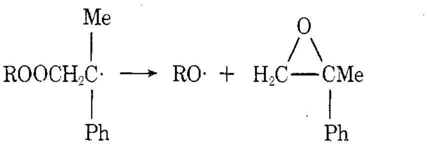


$$RO_2\cdot + H_2C{=}\underset{Ph}{\overset{Me}{C}} \longrightarrow ROOCH_2\underset{Ph}{\overset{Me}{C}}\cdot \qquad (1)$$

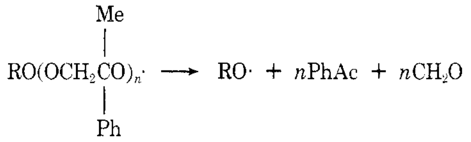


$$ROOCH_2\underset{Ph}{\overset{Me}{C}}\cdot + O_2 \nearrow ROOCH_2\underset{Ph}{\overset{Me}{C}}O_2\cdot\ (= RO_2\cdot) \qquad (2)$$

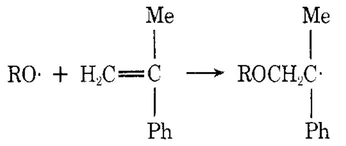
$$ROOCH_2\underset{Ph}{\overset{Me}{C}}\cdot + O_2 \searrow ROOCH{=}\overset{Me}{C}Ph + HO_2\cdot \qquad (3)$$



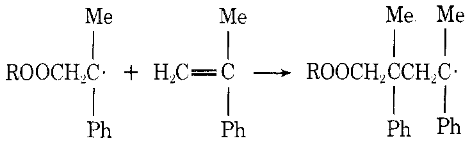
$$ROOCH_2\underset{Ph}{\overset{Me}{C}}\cdot \longrightarrow RO\cdot + H_2C\overset{O}{—}\underset{Ph}{C}Me \qquad (4)$$



$$RO(OCH_2\underset{Ph}{\overset{Me}{C}}O)_n\cdot \longrightarrow RO\cdot + nPhAc + nCH_2O \qquad (5)$$



$$RO\cdot + H_2C{=}\underset{Ph}{\overset{Me}{C}} \longrightarrow ROCH_2\underset{Ph}{\overset{Me}{C}}\cdot \qquad (6)$$



$$ROOCH_2\underset{Ph}{\overset{Me}{C}}\cdot + H_2C{=}\underset{Ph}{\overset{Me}{C}} \longrightarrow ROOCH_2\underset{Ph}{\overset{Me}{C}}CH_2\underset{Ph}{\overset{Me}{C}}\cdot \qquad (7)$$

trations. At low oxygen pressure, the polymer contains $-OCH_2O-$ and other ether groups. Reactions 6 and 7 illustrate how ether links and new carbon–carbon bonds might be formed.

Near 170°, probably with an inadequate supply of oxygen, the products are about one-third each of acetophenone (and formaldehyde), epoxide, and a residue with the average C, H, O analysis of poly(α-methylstyrene oxide). This residue may be formed by repeating sequences of reactions like 6, 2, 1, and 4. This explanation requires that $RO_2CH_2C(MePh)O\cdot$ radicals react at once by 5 but that $ROCH_2C(MePh)O\cdot$ radicals add "as in 1 or 7." The objectives of the present work are to find out how the mechanism of oxidation changes in the intermediate temperature range, to determine what conditions favor formation of residue, and then to investigate the nature of some of these residues. Our conclusions are near the end of the paper.

Oxidations of α-Methylstyrene[2a]

Experimental. Most oxidations were carried out with approximately 0.5 mol of α-methylstyrene in a wide-necked flask with a 170-ml bulb, fitted with a Vibro-Mixer, thermometer, oxygen inlet, and an oxygen outlet through a trap cooled to −78° and through wet glass wool to absorb formaldehyde. Larger runs without solvent in Table I are pairs of similar smaller runs. The oxygen entering and the gas leaving the vessel at 1 atm were usually passed through flow meters, and an effort was made to supply oxygen fast enough so that some excess left the vessel. However, the exit gases contained considerable formaldehyde, which was not readily removed and which partly polymerized on the exit system and flow meter. The reaction mixture was quickly brought to reaction temperature, usually by heating with a gas flame. Thereafter only occasional gentle heating or cooling with water was required to keep the liquid temperatures within about 5° of the stated temperatures, which are weighted averages. The Vibro-Mixer provided a constant fine dispersion of gas bubbles in the liquid.

The products were distilled at reduced pressure, as indicated in Table I. The distillate was analyzed for acetophenone and α-methylstyrene oxide by infrared or gc, using suitable standards. The residues were analyzed for carbon and hydrogen, and sometimes their molecular weights were determined.

The oxidations with o-dichlorobenzene as solvent employed similar stirring and arrangements. Experiments 53 and 57 used a little over 0.5 l. of solution in a 1-l. flask. The flask contents were maintained at the stated temperatures by keeping them in oil baths at somewhat higher temperatures.

Results and Discussion. What does happen to the mechanism of oxidation of α-methylstyrene between 50 and 170°? In some unrecorded experiments at 100° considerable polyperoxide was still formed (although its half-life is only a few hours), but very little survived our oxidations at 120°. Somewhere between 100 and 120°, reaction 4 outruns reaction 2, partly because 4 has a higher activation energy, but partly because the oxygen required for 2 is unavoidably depleted by increasingly faster reaction.

Our results at 120° and above are summarized in Table I. Runs without diluent at 120° are considered first. According to our mechanism, the ratio of acephenone to α-methylstyrene oxide formed depends on oxygen pressure and the competition between reactions 2 and 4. If enough oxygen is present, more reactions like 1 and 2, and more acetophenone, can eventually be formed when reaction 4 occurs, but the amount of excess acetophenone is variable and dependent on poorly controlled oxygen concentration.

The next point is that two distillation procedures were used for analyses, as indicated in notes c and d to Table I. Neither is entirely satisfactory, but we can deduce the correct results fairly closely. With procedure c, the distillation residue should not decompose but not all the acetophenone and epoxide are recovered and accordingly the yields of residue are 5–15% higher than with procedure d. Results of distillation of residue 18 by procedure c at 0.05 Torr are shown in Table I. By mass spectrometry, the first fraction was mostly acetophenone not recovered in the first distillation. The second fraction was partly acetophenone, probably partly resulting from pyrolysis of peroxide in the original residue. These figures suggest that, if this experiment had instead been analyzed according to d, the yield of acetophenone might have been about 0.013 mol (7%) higher, two-thirds from incomplete separation and one-third from pyrolysis. Losses of epoxide by poor recovery should be similar since it boils only about 4° lower than acetophenone at 15 Torr. The 5.8% weight loss in the redistillation also sets a low limit on the polyperoxide content of the residue; 20% loss is expected for pyrolysis of polyperoxide into acetophenone and uncondensed formaldehyde.

However, the analyses of the fractions show that they contain about 5% (of the total C_9H_{10}) of unidentified volatile material that contains more hydrogen and more oxygen than acetophenone, α-methylstyrene oxide, or the residues isolated by procedure d; this material is neglected in most analyses. The next section suggests that this material is, or contains, α-methylstyrene glycol. Thus procedure d may overstate the yield of acetophenone by up to 5% at the expense of residue and neglect up to 5% of unidentified volatile products. Procedure c includes 5–8% each of epoxide, acetophenone, and unidentified high boilers as residue.

The epoxide/acetophenone ratios and the yields of residues in expt 45, 48, and 39 are close to those obtained in the oxidation at 50° (6 Torr) of oxygen,[1] although the compositions of the residues may be different. In view of the higher activation energy for epoxide formation,[3] the

Table I
Oxidation of α-Methylstyrene at 120–170°

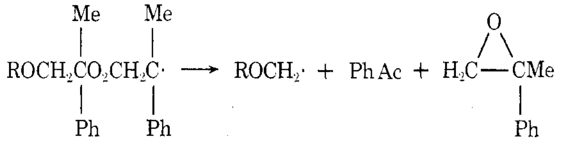
		Reaction			Products, mol (% of C_9H_{10} reacting)			Residue	
Expt no.	C_9H_{10},[a] mol (g)	Av temp, °C	Time, min	Conversion, %	$\overset{O}{PhC—CH_2}$[b] Me	PhAc[b]	Residue	Av composition	Mol wt[a]
45	1.098 (128.8)	120	12	13.6	0.062 (41)	0.066 (44)	0.021[d] (14)	$(C_9H_{10.3}O_{1.67})_{1.69}$	246
4	0.501 (59.2)	120	37	25.7	0.054 (41)	0.049 (38)	0.027[c] (21)	$(C_9H_{12.0}O_{2.00})_x$	
18	0.525 (62.0)	120	36	37.2	0.070 (36)	0.092 (47)	0.034[c] (17)	$(C_9H_{11.14}O_{2.16})_x$	
				Distillation of 5.16 g of residue at 0.05 Torr gave					
					1.52 g to 95°			$(C_9H_{10.2}O_{1.53})_{1.02}$	146
					1.70 g to 155°			$(C_9H_{11.3}O_{2.0})_{1.43}$	217
					1.33 g to 250°			$(C_9H_{11.3}O_{1.56})_x$	
					0.31 g residue			$(C_9H_{10.9}O_{0.98})_{2.95}$	389
					0.30 g loss				
48	0.534 (63.1)	125	36	46.8	0.117 (47)	0.121 (48)	0.012[d] (5)	$(C_9H_{10.4}O_{1.57})_x$	
39	1.018 (120.2)	120	36	51.1	0.214 (41)	0.266 (51)	0.041[d] (8)	$(C_9H_{10.5}O_{1.46})_{2.60}$	369
57	1.01 (119.2 + 512 g o-$C_6H_4Cl_2$)	120	5	3.30	0.0127 (38)	0.020 (60)	0.0006[d,e] (2)	$(C_9H_{10.5}O_{1.66})_{1.54}$	220
53	0.986 (116.5 + 507 g o-$C_6H_4Cl_2$)	118	58				0.0780[d]	$(C_9H_{10.1}O_{1.44})_{1.66}$	236
61	0.489 (57.8 + 263.5 g o-$C_6H_4Cl_2$)	110	58	30.9	0.0284 (19)	0.113 (75)	0.0093[d] (6)	$(C_9H_{9.8}O_{1.22})_{3.49})$	480
8	0.507 (59.9)	140	15	3.3	0.030 (41)	0.028 (37)	0.017[c] (22)	$(C_5H_{11.30}O_{1.26})_x$	
22	0.562 (66.5)	140	18	12.1	0.029 (43)	0.020 (31)	0.018[c] (26)	$(C_9H_{10.8}O_{1.61})_x$	
26	0.516 (60.9)	160	8	5.1	0.0097 (37)	0.0084 (32)	0.0081[c] (31)	$(C_9H_{10.7}O_{1.92})_x$	
Ref 1	0.764 (90.4)	167–168	30	26.5	0.077 (38)	0.066 (33)	0.059 (29)	$\sim(C_9H_{10}O)_x$	

[a] Molecular weight of α-methylstyrene is 118.18. [b] Values obtained by ir analysis, except 39, 45, 48, and 57 by gc. [c] Material not distilled at 70–100° (0.10 Torr). Residue contained some PhAc and epoxide. Moles based on C content, assuming C_9 units. [d] Material not distilled from 180° bath at 0.10 Torr. Moles based on C content assuming C_9 units. [e] After molecular distillation at 180° had removed 33% of material from an ordinary residue.

effective oxygen pressure at 120° must be higher than 6 Torr, but we do not know how much higher.

The average compositions of the residues (and fractions from expt 18) show that nearly all of them have both higher H:C and higher O:C ratios than α-methylstyrene units, the polymer of its epoxide, or acetophenone. The only obvious oxidation product with both higher H and O ratios is formaldehyde.[1] In the absence of a better explanation, we propose that the residues, and even the distillates, in expt 18 contain more $-CH_2O-$ residues than acetophenone residues, or some $-CH_2O-$ units in the α-methylstyrene or 1:1 peroxide residues, the $-CH_2O-$ units being left by "unzipping" of polyperoxide units (see below) or incorporated by condensation, copolymerization, or as paraformaldehyde.

The H:C in the first residue (expt 18) corresponds to almost two formaldehyde units per methylstyrene unit (more if some hydrogen has been lost from the latter) and would account for 60% of the formaldehyde expected from the yield of acetophenone found. Although this high proportion suggests some paraformaldehyde in this residue, not much was found. Samples of this residue were heated with concentrated aqueous hydrochloric acid for 3 hr at 90° or with 2 *M* acid for 2 hr at 70°; 0.83 and 0.68 wt % formaldehyde (about 4 mol %) was found by the dimedon and chromatrophic acid methods, respectively, but this low result could be due to incomplete hydrolysis. Table I shows that the last residue (expt 18) contains lower proportions of both hydrogen and oxygen than the first residue. These observations suggest that the residues contain some peroxide or formal groups that pyrolyze to formaldehyde or one of its condensation products and are lost during distillation (although excess hydrogen persists in the final residue). Such groups could arise by incomplete unzipping of structures containing ether groups, which may also protect peroxide groups in R. The resulting alkoxy-



$$ROCH_2\underset{Ph}{\overset{Me}{C}}O_2CH_2\underset{Ph}{\overset{Me}{C}}\cdot \longrightarrow ROCH_2\cdot + PhAc + H_2\overset{O}{C—}\underset{Ph}{C}Me \quad (8)$$

methyl radical might react with oxygen (eventually releasing formaldehyde) or with methylstyrene to give C_{11} units (see next section), or possibly with some form of formaldehyde. The alternating polyperoxide of α-methylstyrene has the same H:C ratio as the hydrocarbon and does not account for the high H:C ratios in residues.

The experiments in *o*-dichlorobenzene in Table I were carried out to slow the oxidation and thus to increase the concentration of oxygen in solution. Experiment 57 shows that this effort was successful, as measured either by the higher acetophenone/epoxide ratio or by the small proportion of residue, all after pyrolysis as in expt 48 and 37. The less epoxide that is formed, the fewer should be the ether links to stabilize the decomposing peroxy radicals.

Experiment 53 was carried to 58% conversion to supply the residue for the investigation in a later section. Experiment 61 was carried out to obtain full data on a duplicate of expt 53, but, because of difficulties in temperature control, expt 61 shows mostly the effects of a higher oxygen supply and a low temperature (110°): the highest yield of acetophenone after strong heating and the lowest proportions of hydrogen and oxygen in the residues listed in Table I, indicating low incorporation of formaldehyde. We do not know how much polyperoxide was formed and pyrolyzed during analysis.

Comparison of the incomplete data for expt 53 and 57 at 120° suggests that a tenfold increase in reaction time increased the yield of residue about 100-fold and therefore that part of the residue is a secondary product. This latter suggestion has been supported by oxidizing α-methylstyrene in the presence of added p-chloroacetophenone. A mixture of 0.426 mol of α-methylstyrene and 0.124 mol of distilled Eastman p-chloroacetophenone was stirred in a stream of oxygen for 73 min at 120°. A weight gain of 4.13 g corresponded to 0.30 mol of oxygen/mol of α-methylstyrene initially present. Distillation at reduced pressure gave 3.16 g of residue not distillable at 180° (0.4 Torr). This residue contained no free chloroacetophenone (23.0% Cl) by gc but it contained 6.83% chlorine (29% p-chloroacetophenone units), 4.9% of all the chlorine added initially. By ultraviolet absorption, at least 65% of the incorporated p-chloroacetophenone appeared as p-chlorobenzoyl groups. The nmr spectrum of this residue differed from typical residues in that it contained about 1.0 (instead of 0.75) aromatic per aliphatic proton and in that -OCHO- and PhCHO- protons were missing.

Treatment of the distillate from expt 39 with small amounts of formic acid in the absence of oxygen, with and without paraformaldehyde to duplicate some of the conditions during an oxidation, failed to produce significant amounts of residue. These results seem to exclude the possibility of an acid-catalyzed condensation of primary products to residue.

In comparison with expt 4 and 18 in Table I, which employed the same analytical procedure, experiments at 140–168° show very similar results, although there may be some tendency for acetophenone to decrease, for residue to increase, and the hydrogen and oxygen content to decrease with increasing oxidation temperature. Since the rates of oxidation (conversion/time) are lower at the higher temperatures, oxygen supply must have been more limited than at 120°. Since the residues of these high-temperature runs cannot contain peroxides, similarity in products supports our conclusion that the 120° residues did not contain much peroxide.

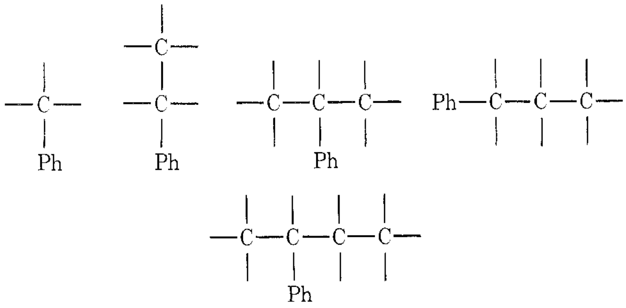
Investigations of Oxidation Residues

Results of investigating two kinds of residues in Table I are summarized. (See paragraph at end of paper regarding supplementary material.) The first kind of residue resulted from high-conversion oxidations of neat α-methylstyrene at 120° where rapid oxidation reduced the availability of oxygen. Most of these data come from the residue of expt 39; some come from expt 18. These residues averaged about one benzoyl and one ester group per molecule, and four aliphatic for three aromatic protons (1:1 in methylstyrene). They also contained methyl, benzyl, and benzyloxy groups. These results, along with the elementary analysis, suggest the incorporation of formaldehyde units in the residues in some form. A similar oxidation to lower conversion (expt 45) gave a similar product except that the molecular weight was lower and the proportion of methyl (end) groups and of ether groups was higher.

In the second kind of oxidation, the methylstyrene was diluted with 3.0 volumes of o-dichlorobenzene, to slow the oxidation and to permit maintaining higher concentrations of oxygen. Residue 57, which was examined most carefully, had an average molecular weight of 220 and an average composition of $C_9H_{10.5}O_{1.66}$. This residue was saponified to give 78% of a neutral, viscous oil, which was a mixture of more than 50 components. The "average" composition of these components was $C_{18}H_{18.4}O_{2.28}$. The "average" molecule contained 1.34 ether oxygen atoms and 0.94 hydroxyl oxygen atom. A small number of hydroxylated eight- to ten-carbon compounds accounts for the low carbon content of the "average" empirical formula. α-Methylstyrene glycol (6%), an expected pyrolysis product of the polyperoxide, was isolated and identified. One out of every four or five molecules contained a terminal $PhC{=}CH_2$ group.

The only other component identified tentatively was ~0.2% of 2,5-diphenyl-1-hexene, a dimer of α-methylstyrene. Fragmentary information was obtained on several other fractions, both single compounds and mixtures. All these materials contained $H_2C{=}C<$, hydroxyl, and phenyl groups; most of them contained ether groups, and the grouping PhC(O–)Me was identified in one case.

Treatment of the neutral mixture with hydriodic acid and phosphorus and subsequently with $LiAlH_4$ gave a mixture of hydrocarbons that was separated into a mixture of five alkylbenzenes and a mixture of α-methylstyrene dimers. The alkylated benzenes resulted from cleavage of the ether molecules. The principal alkylbenzene (75% of the mixture) was cumene; present in much smaller amounts were toluene, ethylbenzene, n-propylbenzene, and *sec*-butylbenzene. These results mean that the following groups could be present in the neutral fraction,



where most of the free valences are attached to hydrogen but at least one in each unit is attached to oxygen. The first two formulas show loss of carbon from α-methylstyrene units; the last shows gain of carbon, and the fourth shows either gain and loss together, or rearrangement. Any -OCH$_2$O- groups would have been lost in the procedure used.

The α-methylstyrene dimer mixture gave ir and nmr spectra that resembled those obtained from a sample of polymerized α-methylstyrene. Eight peaks were obtained on gas chromatography of the α-methylstyrene dimer mixture. One peak, which accounted for about 50% of the mixture, was isolated and was subsequently shown by capillary gas chromatography to consist of two components. No further effort was made to separate these.

The acid fraction recovered from the saponification consisted of a mixture of at least three acids. The major component, and the only one identified, was benzoic acid.

Conclusions

In oxidations of α-methylstyrene with ample oxygen up to 100° the principal product is the alternating polyperoxide, which is reasonably stable at reaction temperature but pyrolyzes cleanly to acetophenone and formaldehyde on heating at reduced pressures. Between 100 and 120°, at 1 atm total pressure, the principal product of oxidation of α-methylstyrene changes from polyperoxide to α-methylstyrene oxide and acetophenone, with minor amounts of residue and still less peroxide. In this range, a combination of a higher activation energy for epoxide formation (reaction 4) in competition with absorption of oxygen (reaction 2) and the difficulty in maintaining saturation of the solution with oxygen leads to the formation of increasing proportions of both α-methylstyrene oxide and distillation residue and less acetophenone. Slowing the oxidation (and presumably increasing the oxygen concentration) by dilution with o-dichlorobenzene increases the yield of acetophenone at the expense of epoxide and residue. Residues are associated with epoxide formation and the formation of ether links, reactions 4 and 6. Residues made at low oxygen concentrations have H:C ratios that seem also to require incorporation of $-OCH_2O-$ groups,[1] particularly in residues that have not been strongly heated. At higher conversions, residues also contain condensation products of acetophenone, formaldehyde, and α-methylstyrene oxide, the major primary products of oxidation.

Detailed investigations of some residues confirm the presence of ether groups and $-OCH_2O-$ units but they bring out the great complexity of the residue and, with the exception of 6% of α-methylstyrene glycol, the absence of important proportions of any single component. This work shows that the hydrocarbon units between the ether links contain seven, eight, and ten carbon atoms as well as two kinds of C_9 units. Some of the cuts in this investigation contained many more than 50 individual components.

This work is consistent with, and extends, our findings that oxidations of isobutylene[4,5] and cyclopentene[5,6] also give high-boiling residues. Those residues also consist of monomer units, or fragments of them, joined together with ether links (and some peroxide links in oxidations below 100°), some with additional oxygen-containing groups on the chains.

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Registry No.—α-Methylstyrene, 98-83-9.

Supplementary Material Available. Details of investigations of residues 18, 39, 45, and 53 will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-889.

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α-Methylenelactam Rearrangement

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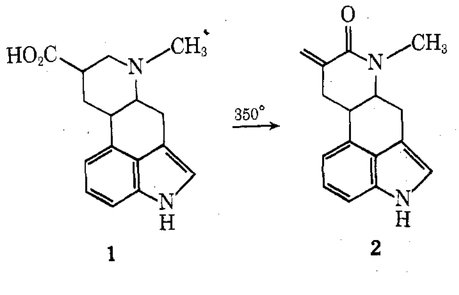
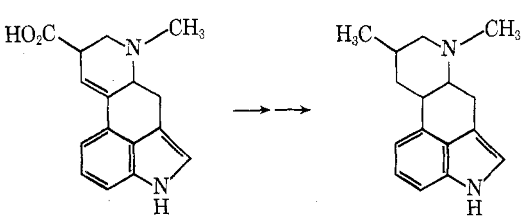
The acetic anhydride promoted rearrangement of cyclic β-amino acids to α-methylenelactams has been investigated. In particular, the effect of ring size, N substitution, and α substitution on the yield of the rearranged product was determined. When applicable, the stereochemistry of the rearrangement was also examined. These observations have led to elucidation of the mechanism of the α-methylenelactam rearrangement which is initiated by a cyclic β-amino acid reacting in its zwitterionic form with acetic anhydride to yield the protonated amino mixed anhydride. β elimination then readily occurs, and recyclization takes place by nucleophilic attack of the amino group on the mixed anhydride function.

The rearrangement of a cyclic β-amino acid to an α-methylenelactam was first observed[1] in an attempt to purify dihydrolysergic acid (1). Sublimation of acid 1 led to a substantial portion of rearranged product, dihydrolysergic lactam (2). Subsequently, this rearrangement was utilized in the transformation of lysergic acid (3) to 6,8-dimethylergoline (4).[2]



1 2



3 4

In addition to the above pyrolytic route, the rearrangement of cyclic β-amino acids to α-methylenelactams has been effected through the use of acetic anhydride. In seeking to racemize the C-8 asymmetric center of lysergic acid (3), it was treated[3] with acetic anhydride in the expectation of preparing lysergic acetic anhydride. The product obtained was lactam 5. Similarly, the rearrangement of