In the determination of free-radical efficiencies with such scavengers as stable free radicals oxygen, or iodine, the reaction is (or is assumed to be) zero order with respect to scavenger. The Tobolsky dead-end polymerization technique is an interesting contrast in that excess vinyl monomer is used as the "scavenger," and the rate of polymerization is first order in monomer.[11]

The mechanism of the scavenger action is as follows.

$$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_1} \mathrm{M}\cdot$$

$$\mathrm{M}\cdot + \mathrm{M} \xrightarrow{k_\mathrm{p}} \mathrm{M}\cdot$$

$$2\mathrm{M}\cdot \xrightarrow{k_\mathrm{t}} \text{polymer}$$

Assuming the initiator decomposes by the first mechanism given and neglecting the volume change due to contraction, the differential rate expression becomes eq. 23 which when integrated becomes eq. 24 and 25.

$$-\mathrm{d(M)}/\mathrm{d}t = k_\mathrm{p}/k_\mathrm{t}^{1/2}[k_\mathrm{d} f(\mathrm{In})_0 \exp(-k_\mathrm{d}t)]^{1/2}(\mathrm{M}) \qquad (23)$$

$$\ln\left[\frac{\ln(\mathrm{M}/\mathrm{M}_\infty)}{\ln(\mathrm{M}_0/\mathrm{M}_\infty)}\right] = -k_\mathrm{d}t/2 \qquad (24)$$

$$\ln\ (\mathrm{M})_0/(\mathrm{M})_\infty = 2k_\mathrm{p}/k_\mathrm{t}^{1/2}[f(\mathrm{In})_0/k_\mathrm{d}]^{1/2} \qquad (25)$$

Therefore if $k_\mathrm{p}/k_\mathrm{t}^{1/2}$ is known (and truly constant) for the polymerization used, then both k_d and f may be determined in the same experiment. More complex equations result in case volume contraction due to polymerization is important.[12]

Finally, we mention the case in which excess stable radical is used when an initiator is decomposed in vinyl monomer. In case concentrations of the initiator and stable radical are both dilute, there is a chance that the free radicals formed in the decomposition of the initiator will add to vinyl monomer before reacting with the stable radical. Should the stable radical subsequently scavenge all the growing polymer radicals, this will not alter the kinetics of disappearance of stable radical, *i.e.*, eq. 1, 2, and 3 still hold. However, this amounts to changing the mechanism of termination of polymerization to

$$\mathrm{M}\cdot + \mathrm{Z} \xrightarrow{k_\mathrm{t}'} \mathrm{M{-}Z}$$

and the rate of disappearance of monomer becomes eq. 26. Dividing eq. 26 by eq. 1 and integrating, one obtains eq. 27. Thus, if one can measure the degree of polymerization in a stable free radical inhibited polymerization, the selectively $k_\mathrm{p}/k_\mathrm{t}'$ can be determined.

$$-\mathrm{d(M)}/\mathrm{d}t = k_\mathrm{p}(\mathrm{M}\cdot)(\mathrm{M}) = \frac{2k_\mathrm{a}f(\mathrm{In})}{k_\mathrm{t}'(\mathrm{Z})}k_\mathrm{p}(\mathrm{M}) \qquad (26)$$

$$\ln(\mathrm{M}_0/\mathrm{M}) = k_\mathrm{p}/k_\mathrm{t}' \ln(\mathrm{Z}_0/\mathrm{Z}) \qquad (27)$$

Experimental

The BDPA used in this work was prepared by the method of Koelsch.[7a] Simpler syntheses have recently been described by Kuhn and Neugebauer.[7d] The synthesis of γ-benzylidenebutyryl peroxide has been described.[4] The method by which the kinetics runs were performed has also been described in detail.[5]

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research (AF-AFOSR-62-53) for support. We are also indebted to Dr. Francis J. Johnston for helpful discussions.

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[11] A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 5927 (1958).

[12] A. V. Tobolsky, C. E. Rogers, and R. D. Brickman, *ibid.*, **82**, 1277 (1960).

A Solvent Effect in the Reaction of Benzaldesoxybenzoin with Phosphorus Pentachloride[1]

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Received March 2, 1965

Reaction of benzaldesoxybenzoin (I) with phosphorus pentachloride in methylene chloride led to a mixture of products from which 1-chloro-2,3-diphenylindene (V) was obtained in 30% yield. In a similar reaction in carbon tetrachloride a different mixture of products was obtained from which 3,3-dichloro-1,2,3-triphenylpropene (VII) was isolated in 47% yield. These results are discussed in the light of the fact that phosphorus pentachloride is monomeric in methylene chloride and dimeric in carbon tetrachloride.

In a discussion of possible mechanisms for the reaction of ketones with phosphorus pentachloride, the hypothesis was made that chlorocarbonium ions were involved.[3] As a result of studies on 4-phenyl-2-butanone and 5-phenyl-2-pentanone, the conclusion was reached that chlorocarbonium ions were not involved because no products resulting from cyclization were obtained.[4] In the present work, the behavior of benzaldesoxybenzoin (I) with phosphorus pentachloride has been studied.

Treatment of I with 1 equiv. of phosphorus pentachloride *in methylene chloride* at room temperature for 2 hr. (the same result after 20 hr.) yielded about 30% of 1-chloro-2,3-diphenylindene (V). The oily residue contained other products which were not studied in detail because of their instability. However, when a mixture of these products in carbon disulfide was treated with a catalytic amount of aluminum chloride, hydro-

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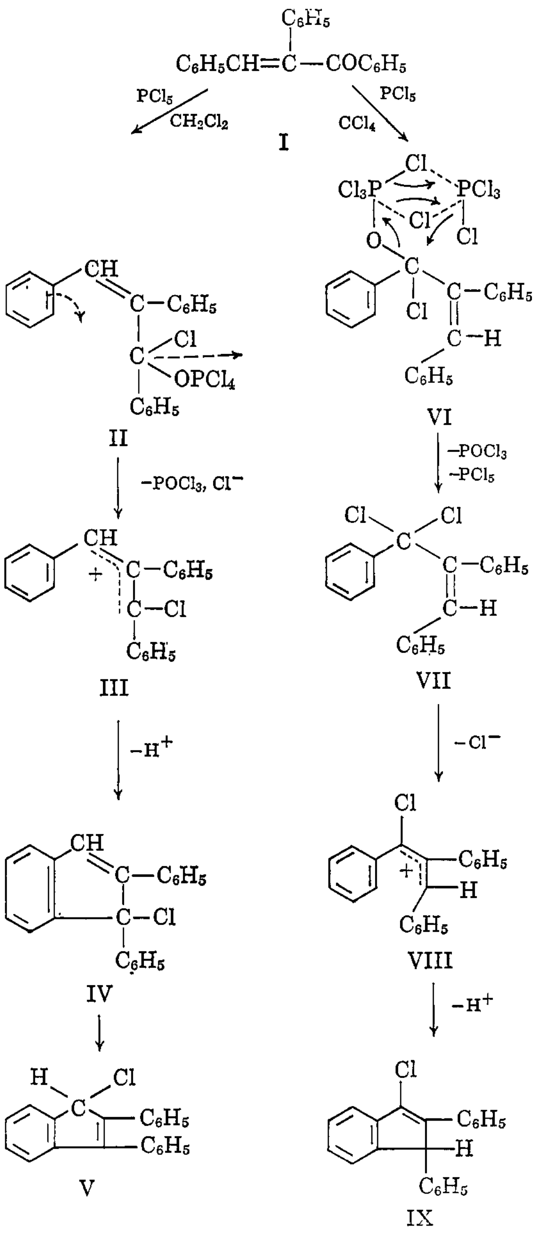
[1] The material in this paper was taken from the Ph.D. thesis presented by G. K. to the Ohio State University, 1964. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant No. AF-AFOSR-569-64.

[2] Upjohn Fellow, 1960–1961; Lubrizol Fellow, 1962–1963.

[3] M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 4300 (1959).

[4] M. S. Newman, G. Fraenkel, and W. N. Kirn, *J. Org. Chem.*, **28**, 1851 (1963).

SCHEME I



gen chloride was evolved and an additional 28% of V was produced.

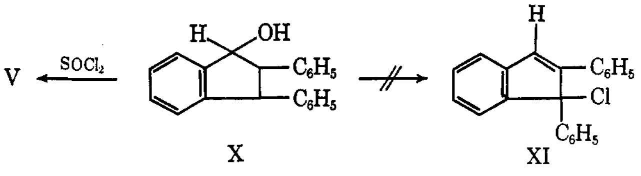
Treatment of I with an equivalent of phosphorus pentachloride *in carbon tetrachloride* at reflux for 90 min. or at room temperature for 24 hr. afforded a mixture of products which was quite different from that obtained in the methylene chloride experiments. On recrystallization from pentane, 47–54% yields of 3,3-dichloro-1,2,3-triphenylpropene (VII) were obtained. This dichloride was unstable as it lost hydrogen chloride slowly even when analytically pure. On standing at room temperature for about 6 months, VII was converted into 3-chloro-1,2-diphenylindene (IX). When a solution of VII in methylene chloride containing phosphorus pentachloride and phosphorus oxychloride was allowed to stand for 2 hr. at room temperature, VII was recovered unchanged almost quantitatively. This proves that in methylene chloride solution VII is not formed first and then rearranged into V.

The chief point in discussing the reactions of I in the solvents mentioned is that phosphorus pentachloride is *monomeric in methylene chloride but dimeric in carbon tetrachloride*.[5] Thus, in methylene chloride we believe that the carbonyl oxygen of I makes a nucleophilic attack on the phosphorus in PCl_5 monomer and that the chloride ion thus produced adds to the carbonyl carbon to produce the intermediate II. Further reaction of II may involve elimination of chloride ion and phosphorus oxychloride from II to form the chlorocarbonium ion III, which, in turn, cyclizes as shown in Scheme I to yield IV. Conversion of IV to V is an allylic rearrangement, although we would not have predicted that V would prove to be more stable than IV. An alternate explanation involves conversion of II directly to IV by having the phenyl group in which cyclization occurs participate in the cleavage of the carbon–oxygen bond as indicated by the dotted arrows in II.

In carbon tetrachloride the carbonyl oxygen of I makes a nucleophilic attack on the phosphorus in PCl_5 dimer to yield the intermediate VI which collapses to VII by a cyclic path as shown. On standing, ionization of VII occurs to yield an allylic chlorocarbonium ion VIII, which cyclizes to IX.

Actually, III and VIII represent the same carbonium ion and one might wonder why entirely different products are formed from each. The explanation may be that the cyclization reactions occur under different conditions: in the methylene chloride reaction, cyclization occurs in solution with phosphorus oxychloride present, whereas VII reacts neat over a much longer period of time. The formation of V from II may involve a tight ion pair so that cyclization to V occurs before much delocalization of charge. Participation of the phenyl ring is pictured by the dotted arrows in formula II. The cyclization of VII may involve a much freer carbonium ion so that cyclization involves the phenyl ring attached to the same carbon to which the chlorine atom was attached; *e.g.*, VII → VIII → IX. Other explanations involving stereochemical differences might also be advanced. However, in view of the experimental difficulties in handling the reaction products, no further work was done in order to cast further light on the processes involved. The salient fact remains that on treatment with phosphorus pentachloride I yields 1-chloro-2,3-diphenylindene (V) in methylene chloride and 3,3-dichloro-1,2,3-triphenylpropene (VII) in carbon tetrachloride.[6]

The structure of V was established by synthesis and n.m.r. analysis. The known[7] 2,3-diphenylindenol X was converted into V in 79% yield on treatment with thionyl chloride. The alternate structure, 1-chloro-



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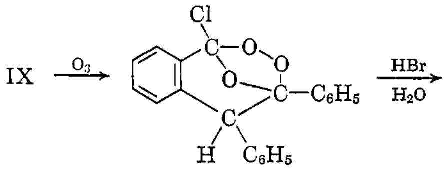
(5) In a private communication, Professor Sheldon Shore and Dr. V. Petro of this department informed us of these facts. In dilute carbon tetrachloride solution, monomer and dimer are in equilibrium. However, all of our experiments were carried out in concentrated solutions.

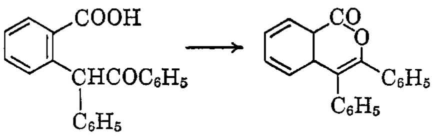
(6) In another forthcoming publication, the formation of different products on treatment of certain cyclopropyl ketones with phosphorus pentachloride in methylene chloride and carbon tetrachloride will be described.

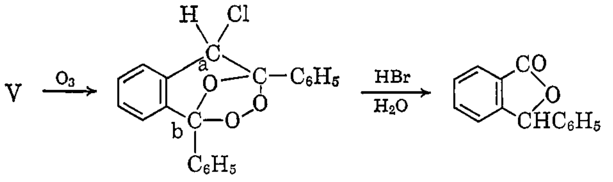
(7) A. Garcia-Banus and E. de Salas, *Anales real soc. espan. fis. quim.* (Madrid), **33**, 53 (1935); *Chem. Abstr.*, **29**, 4020 (1935).

1,2-diphenylindene (XI) was ruled out by the fact that a singlet at τ 4.38 was observed whereas the vinyl hydrogen in XI would be expected to be hidden in the aromatic region.

The structure of IX was established by the fact that a singlet at τ 5.12 was observed.[8] Also on ozonization, a stable ozonide[9] XII was obtained which, on treatment with hydrobromic acid in acetic acid, afforded 3,4-diphenylisocoumarin (XIV) in 90% yield. This result would be expected from XII as hydrolysis should lead to the keto acid XIII, which is known[10] to yield XIV. A stable ozonide[9] XV was also obtained from V. On similar treatment with hydrobromic acid, 54% yields of benzoic acid and phenylphthalide (XVI) were obtained. This decomposition is difficult to explain as the carbon atom in position a of the ozonide XV has been oxidized while carbon atom b has been reduced.


XII


XIII XIV


XV XVI

Experimental[11]

Benzaldesoxybenzoin (I), m.p. 101.5–102.5°, was prepared in 78% yield by condensation of benzaldehyde with desoxybenzoin in the presence of piperidine and benzoic acid.[12]

1-Chloro-2,3-diphenylindene (V). Method A.—A mixture of 11.0 g. of phosphorus pentachloride and 14.2 g. of I in 50 ml. of methylene chloride was allowed to stir at room temperature for 20 hr. (When the original reaction time was 2 hr., approximately the same results were obtained.) The homogeneous solution was poured on ice. The methylene chloride layer was evaporated under reduced pressure and the residue was taken up in ether-benzene (1:1). After washing with dilute sodium carbonate and saturated sodium chloride solutions, the solution was filtered through anhydrous magnesium sulfate.[13] The solvent was largely removed and petroleum ether (b.p. 30–60°) was added. Crystallization afforded 4.6 g. (31%) of V, m.p. 156–158°. Recrystallization from benzene–Skellysolve B (petroleum ether, b.p. 65–70°) yielded the analytical sample, m.p. 160–161°, with little loss. The n.m.r. spectrum showed a signal at τ 4.38 (0.9H) and 2.92–2.73 (14H). Distinctive strong infrared bands appeared at 11.5, 12.6, and 13.8 μ.

Anal. Calcd. for $C_{21}H_{15}Cl$: C, 83.3; H, 5.0; Cl, 11.7. Found: C, 83.2; H, 5.0; Cl, 12.0.

After further attempts to isolate crystalline material from the mother liquor had failed, a solution of the products in 50 ml. of carbon disulfide was treated with 1 g. of aluminum chloride in four portions. When evolution of hydrogen chloride stopped, the solvent was distilled on the steam bath and the residue was treated with ice. After the usual work-up an additional 4.2 g. (28%) of V, m.p. 158–161°, was isolated by crystallization as above.

Method B.—To a solution of 3.8 g. of lithium aluminum hydride in 500 ml. of dry ether was added 42.4 g. of 2,3-diphenylindenone[14] by Soxhlet extraction during 5 hr. Excess hydride was decomposed with ethyl acetate and then dilute hydrochloric acid was added. After the usual work-up, the product was crystallized from benzene–Skellysolve B to yield 30.1 g. (71%) of 2,3-diphenylindenol,[7] m.p. 84–85 and 132–135°. The same polymorphic forms were previously encountered.[7] The ultraviolet spectrum in 95% alcohol had maxima at 246 mμ (ϵ 18,000) and 310–325 mμ (ϵ 11,000). In the n.m.r. spectrum the benzylic hydrogen peak was at τ 4.65.

To 12.0 g. of 2,3-diphenylindenol was added 25 ml. of pure thionyl chloride with cooling. After 15 min. at room temperature the mixture was refluxed for 30 min. After removal of excess thionyl chloride under reduced pressure, the residue was crystallized from benzene–Skellysolve B to yield 10.1 g. (79%) of pure V, m.p. and m.m.p. (with the material described above) 159–161°. The infrared spectra were identical.

3,3-Dichloro-1,2,3-triphenylpropene (VII).—After refluxing a mixture of 45.8 g. of phosphorus pentachloride, 56.9 g. of I, and 350 ml. of carbon tetrachloride for 1.5 hr., the solvent was removed under reduced pressure. The residue was treated with ice and the products taken into ether–benzene. After the usual work-up the product was crystallized from pentane to yield 32.1 g. (47%) of VII, m.p. 76–79°. After two crystallizations from Skellysolve B, pure VII, m.p. 80–82°, was obtained with little loss. The n.m.r. spectrum showed no hydrogen out of the aromatic region.

Anal. Calcd. for $C_{21}H_{16}Cl_2$: C, 74.3; H, 4.8; Cl, 20.9. Found: C, 74.6; H, 5.0; Cl, 20.4.

Similar results were obtained when the reaction of I with phosphorus pentachloride was carried out in carbon tetrachloride at room temperature for 2 and 24 hr. Small amounts (<5%) of V were present in the products from the 24-hr. run but almost none from the 2-hr. one.[15] No IX was present as judged by the absence of absorption at 10.3 and 12.8 μ (see below).

Compound VII was unstable, even when pure, as after a few hours traces of hydrogen chloride were found.

When a solution of 2.0 g. of VII, 0.62 g. of phosphorus pentachloride, and 0.46 g. of phosphorus oxychloride in 10 ml. of methylene chloride (the solution turned yellow immediately) was allowed to stand at room temperature for 2 hr., a conventional work-up afforded 1.33 g. (67%) of VII. The infrared spectrum of the entire filtrate showed that mainly VII was present. No peaks corresponding to the characteristic ones for V or IX were present.[15]

3-Chloro-1,2-diphenylindene (IX).—After the above pure sample of VII had been allowed to stand for about 6 months, it was apparent that a different compound had been formed. Additional quantities of this were obtained from the original mother liquors, which had stood for the same period. In all, a total of 37.3 g. (62%) of IX, m.p. 85–87°, was obtained. After recrystallization from Skellysolve B, pure IX, m.p. 86–87°, distinctive bands at 10.3 and 12.8 μ, was obtained.

Anal. Calcd. for $C_{21}H_{15}Cl$: C, 83.3; H, 5.0; Cl, 11.7. Found: C, 83.5; H, 5.0; Cl, 11.7.

The n.m.r. spectrum showed a singlet at τ 5.12 (1H) and a multiplet near τ 2.99 (14H). The ultraviolet spectrum in 95% alcohol had a maximum at 304 mμ (ϵ 20,200).

Ozonization of V and IX.—A solution of 1.0 g. of V in 15 ml. of methylene chloride cooled by a Dry Ice–acetone bath was

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[8] This agrees well with the singlet at τ 5.08 observed for 1,2-diphenylindene for the benzhydryl-type hydrogen.

[9] R. Criegee, A. Kerckow, and H. Zincke [*Ber.*, **88**, 1878 (1955)] list a number of stable ozonides. In most a strong band appears at 9.4–9.6 μ which is attributed to the C–O stretching frequency.

[10] C. F. Koelsch and S. D. LeClaire, *J. Am. Chem. Soc.*, **65**, 754 (1943).

[11] All microanalyses were by Galbraith Laboratories, Knoxville, Tenn. All n.m.r. determinations were recorded on a Varian A-60 instrument. Carbon tetrachloride solutions were used unless otherwise noted. All melting points were taken with calibrated thermometers but were uncorrected.

[12] Compare A. Dornow and G. Wiehler [*Ann.*, **578**, 101 (1952)] who obtained a 61% yield with piperidine only.

[13] This type of work-up will be referred to as "usual."

[14] C. F. H. Allem, J. W. Gates, Jr., and J. A. VanAllan, "Organic Synthesis," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 353.

[15] We thank Mr. Bernard Ream for performing these experiments.

ozonized (0.055 mole of O_3/hr.) for 15 min. The solution was poured into water and the mixture was warmed on the steam bath for 30 min. After the usual work-up, the solution was concentrated and diluted with petroleum ether (b.p. 30–60°). The stable ozonide XV, m.p. 129–131°, was obtained in 83% yield (0.96 g.). The analytical sample, m.p. 130–131.5°, was obtained by recrystallization from benzene–petroleum ether.

Anal. Calcd. for $C_{21}H_{15}ClO_3$: C, 71.9; H, 4.2; Cl, 10.1. Found: C, 71.9; H, 4.3; Cl, 10.2.

There was no hydroxyl or carbonyl band in the infrared spectrum. The n.m.r. spectrum had a singlet at τ 4.73 (1H) and a multiplet with the largest peak at τ 2.56 (14H).

A solution of 4.0 g. of XV in 50 ml. of acetic acid containing 10 ml. of 48% hydrobromic acid was heated on a steam bath for 1 hr. The solvent was then removed on a rotary evaporator and the products were separated into acid and neutral fractions as usual. From the acid fraction 0.75 g. (54%) of benzoic acid was isolated. From the neutral fraction 1.3 g. (54%) of phenylphthalide, m.p. 115–117°, was obtained. Both products had infrared spectra identical with authentic spectra.

A solution of 10.0 g. of IX in 100 ml. of methylene chloride was ozonized (0.030 mole of O_3/hr.) for 4 hr. at Dry Ice–acetone temperature. The solvent was removed and the residue was crystallized from benzene–Skellysolve B to yield 8.9 g. (77%) of the ozonide XII, m.p. 138–140°. After two recrystallizations from benzene–Skellysolve B, the analytical sample, m.p. 138–140°, was obtained.

Anal. Calcd. for $C_{21}H_{15}ClO_3$: C, 71.9; H, 4.2; Cl, 10.1. Found: C, 71.8; H, 4.3; Cl, 9.9.

A solution of 1.75 g. of XII in 50 ml. of acetic acid was treated exactly as in the case of XV to yield 1.35 g. (91%) of 3,4-diphenylisocoumarin (XIV), m.p. 169–171°.

Ozonolysis. VII. Factors Controlling the Stability of *cis*- and *trans*-Molozonides of Straight-Chain Alkenes. Role of Nucleophilic Solvents in Alkene–Ozone Reactions

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Received March 29, 1965

Ozonation of *cis*- and *trans*-2-butene, 1-butene, and ethylene in ether solution at −110° followed by treatment with isopropyl Grignard reagent at this temperature gave propene, propane, and 2-propanol as reaction products. In addition, *cis*-2-butene gave 3-methyl-2-butanol, *trans*-2-butene gave 3-methyl-2-butanol and *dl*-butane-2,3-diol, 1-butene gave isobutyl alcohol, 2-methyl-3-pentanol, and butane-1,2-diol, and ethylene gave isobutyl alcohol. The data indicate that both a steric factor and a solvent effect are involved in the stability of the molozonide. One role a nucleophilic solvent may serve in ozonation reactions is to facilitate the rearrangement of the molozonide to the ozonide.

Previously,[1] it has been reported that ozonation of *trans*-3-hexene in ether solution at −110° and subsequent treatment of the ozonation mixture at −110° with isopropyl Grignard reagent gave rise to *dl*-hexane-3,4-diol. Similar treatment of *trans*-2-pentene and of 1-pentene produced *threo-dl*-pentane-2,3-diol and pentane-1,2-diol, respectively. From *cis*-3-hexene and *cis*-2-pentene no α-diol was obtained; the products in these instances were carbinols which would result from reaction of the Grignard reagent with the cleavage products of the ozonide of the alkene. Such carbinols also were found in minor amount in the reactions with the *trans*-alkenes and the 1-alkene. These facts were interpreted to indicate that the initial alkene–ozone adduct, the molozonide,[2] was stable in the case of a *trans*- or 1-alkene but not stable for steric reasons in the case of a *cis*-alkene. The various carbinols were attributed to reaction of the Grignard reagent with ozonide present in the ozonation mixture.

These studies have been extended to lower alkenes, and the reaction pattern follows the picture outlined above. *trans*-2-Butene gave rise to *dl*-butane-2,3-diol, methylisopropylcarbinol, isopropyl alcohol, propane, and propene. By vapor phase chromatography (v.p.c.) it was shown that if the diol contained any of the *meso* isomer, it contained something less than 10% of this isomer. The evidence would support the belief that the addition of ozone to *trans*-2-butene was a stereospecific process, as it was with *trans*-3-hexene and *trans*-2-pentene. With *cis*-2-butene no trace of an α-diol could be found; the crude reaction products remaining after the removal of solvent gave a negative test for α-diol with periodic acid. The reaction products in this instance were methylisopropylcarbinol, isopropyl alcohol, propane, and propene. A reaction with 1-butene gave as products butane-1,2-diol, ethylisopropylcarbinol, isopropylcarbinol, isopropyl alcohol, propane, and propene. The α-diols are presumed to have arisen from the reaction of the Grignard reagent with the molozonide. It has been established[3] that the various carbinols arose from interaction of the Grignard reagent with the ozonide.

There were some disturbing data among those reported above and in the earlier paper.[1] If steric factors only were involved in the stability of the molozonide, then one should expect the molozonide from an 1-alkene to be at least as stable, if not more so, than the molozonide from a *trans*-alkene. Yet, the facts were that 1-pentene and 1-butene gave considerably less α-diol than did the *trans*-alkenes. The ultimate experiment would be one using ethylene, for here we should obtain the parent molozonide, and steric factors should be at a minimum. Surprisingly, when this experiment was carried out, no trace of ethylene glycol could be detected in the reaction products; the identifiable products were isobutyl alcohol, isopropyl alcohol, propane, and propene. Clearly, factors other than steric must be involved in the stability of the molozonide. It would appear that a solvent effect is also involved.

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[1] F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964).

[2] (a) H. Staudinger, *Ber.*, **58**, 1088 (1925). Direct evidence on the structure of the molozonide has yet to be obtained. (b) Like R. Criegee and G. Schröder [*Chem. Ber.*, **93**, 689 (1960)], we assign a 1,2,3-trioxolane structure to the molozonide.

[3] F. L. Greenwood and B. J. Haske, *J. Org. Chem.*, **30**, 1276 (1965).