Anal. Calcd for $C_{20}H_{35}NO_4$: C, 68.00; H, 9.92; N, 3.96. Found: C, 67.76; H, 9.57; N, 3.94.

Rearrangement of Benzyltrimethylammonium *p*-(*t*-Butyl)-phenoxide.—The product yields are summarized in Table I. The details of a characteristic reaction and product identification procedures are described here. The quaternary salt (3.0 g, 8.6 mmoles) was placed in 100 ml of anhydrous ethyl ether and cooled to 10°.[10] *n*-Butyllithium in hexane (1.5 *N*;[11] 50 ml, 75 mmoles) was mixed with 50 ml of anhydrous ethyl ether and cooled to the same temperature as the previous mixture. The *n*-butyllithium solution was then quickly added to the salt without cooling. The temperature rapidly rose to 30–35°; the new temperature was maintained by a water bath during the remainder of the reaction.

The progress of the reaction was monitored by removing 1-ml samples at intervals, quenching with ice, adding a standard (N,N-dimethyl-*o*-toluidine), and gas chromatographic (gc) analysis of 100 μl of the organic phase. Gc analyses were made with an F & M Model 700 using a 0.25 in. × 16 ft column of 27% Apiezon L and 6% KOH on 40–60 mesh Chromosorb P. Separation characteristics and calculations for quantitative yields were comparable to those previously described.[5]

Product identification was definitive for *o*,N,N-trimethylbenzylamine; all other assignments were compatible by peak enhancement only. Compound II was confirmed by collecting the material separated by gc directly in an NMR Specialites 25-μl spherical cavity microtube, diluting with 1% TMS in CCl_4, and immediate measurement of the pmr spectrum. The spectrum was identical with that of II under similar conditions and showed no evidence of trace impurities.

Registry No.—I′, 13427-01-5; II, 4525-48-8; III, 2449-49-2; *n*-butyllthium, 109-72-8.

[10] Reactions were not performed under nitrogen but care was taken to exclude moisture and reactive amines or alcohols from reagents and equipment.

[11] The concentration of active carbanion was determined by the double titration method: H. Gilman and A. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944); H. Gilman and F. H. Cartledge, *J. Organometal. Chem.*, **2**, 447 (1965).

Ozonide Stability during Gas Phase Chromatography

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There is renewed interest in olefin ozonolysis[2–10] concerned with evaluating the "zwitterion" mechanism proposed by Criegee.[11,12] The experiments carried out for this purpose rely mostly upon product analysis wherein the amount of ozonides formed from the *cis* and *trans* olefins is determined using gas chromatography (gc).[2–7,9,10] Ozonides have been gas chromatographed by several workers on various substrates at temperatures between 40 and 100°.[2–4] More recent articles on this subject do not list column temperatures.[5–7,9] Since ozonides are unstable, existing data suggest that ozonide stabilities during gas chromatography should be investigated.

Results

Tables I and II summarize the gc analysis of *cis*- and *trans*-3-hexene ozonides. Separation of the *cis* and *trans* isomers was achieved on column A, but not on column B.

TABLE I

DECOMPOSITION STUDY OF 3-HEXENE OZONIDES (COLUMN A)

Run	Sample size, μl	Column temp, °C	Detector temp, °C	Injector temp, °C	Decomposition ratio $\times 10^2$
1	1	65	100	90	No decomposition observed
2	1	81	98	88	8.0
3	4	81	97	91	1.25
4	1	85	118	108	3.7
5	4	90	101	98	4.2
6	4	90	125	100	4.1
7	4	95	125	105	8.2
8	5	100	125	110	5.5
9	5	105	126	113	7.3
10	4	110	126	118	13.5
11	4	115	147	123	41.6
12	4	120	146	125	71.5
13	4	125	147	125	No ozonide peak observed

TABLE II

DECOMPOSITION STUDY OF 3-HEXENE OZONIDES (COLUMN B)

Run	Sample size, μl	Column temp, °C	Detector temp, °C	Injector temp, °C	Decomposition ratio $\times 10^2$
14	1	65	98	90	No decomposition observed
15	1	85	118	108	0.535
16	5	88	101	99	No decomposition observed
17	4	90	125	101	No decomposition observed
18	4	110	125	120	2.27
19	4	110	145	125	2.32
20	4	124	147	128	9.66

The last column in Tables I and II gives the relative amount of decomposition undergone by the samples. The origin and significance of these numbers may be seen by reference to Figures 1 and 2. Figure 1 shows a typical gc analysis of hexene 3-ozonides carried out at low temperatures on column A. The region between the aldehyde and ozonide peaks shows no appreciable recorder deflection. Figure 2 shows the same sample analyzed on column A at an elevated temperature. In the higher temperature run a considerable recorder deflection can be seen in the region between the aldehyde peak and the ozonide peaks. This deflection is caused by decomposition of the ozonides to propionaldehyde during the gc analysis. The decomposition ratio was calculated by comparing the average peak height of the propionaldehyde between point 1 and point 2 (see Figure 2) with that of the first ozonide peak. While this comparison is not usually so valid as a comparison of the relative peak areas, comparison of peak heights or peak areas gave the same relative de-

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(1) This work was carried out under the support of Academic Year Extension Grant GY-414 from the National Science Foundation.

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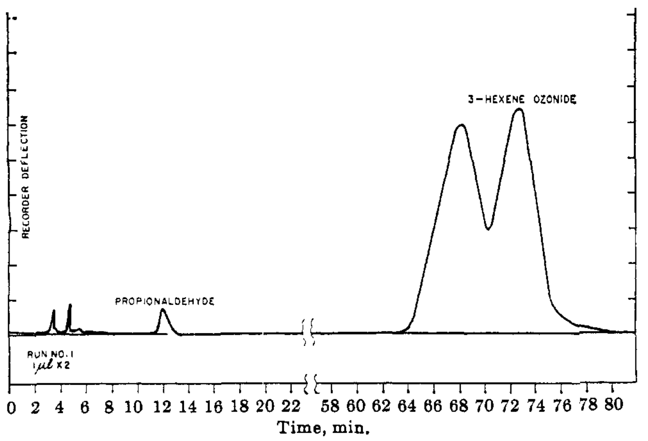

Figure 1.—Chromatogram of 3-hexene ozonide from run 1, column temperature 65°.

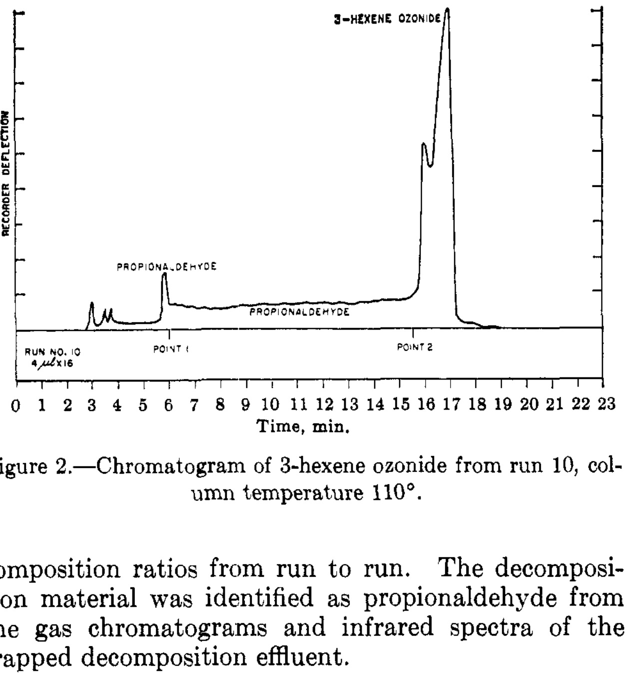

Figure 2.—Chromatogram of 3-hexene ozonide from run 10, column temperature 110°.

composition ratios from run to run. The decomposition material was identified as propionaldehyde from the gas chromatograms and infrared spectra of the trapped decomposition effluent.

Table III summarizes experiments designed to determine whether any significant *cis–trans* isomer interconversion (or ratio change) occurs during the course of gc analysis. Column six of Table III gives the ratio of ozonide peak 1 to peak 2[13] after passage of the sample over the chromatographic column.

Table III

Stability Study of 3-Hexene Ozonides (Column A)

Run	Column temp, °C	Detector temp, °C	Injector temp, °C	Number[a] of passes	Ratio × 10²	Reference[b] peak ratio × 10²
21[c]	64	100	85	2	109	83
22	64	144	130	2	79	75
23	84	101	96	2	90	82
24	85	110	100	2	91	89
24′	85	110	100		74	
25	100	112	107	2	88	87
26	110	120	120	2	97	84
27	115	122	122	2	89	89
28	120	132	128[d]	1[d]	90	94
29	130	143	140[d]	1[d]		

[a] Number of passes through chromatograph before final analysis. [b] Fresh sample of ozonide. [c] All runs except 21 and 22 showed decomposition. [d] Because of the extensive decomposition only one pass was possible before analysis.

Conclusions

A comparison of the data of Tables I and II indicates that the decomposition of the ozonide depends on the type of column used. It is also apparent that the sample size has an effect upon the relative amount of decomposition undergone by the ozonide as is seen by comparing runs 2 with 3 or 15 with 16. The larger the sample injected at any given temperature (without flooding the column), the less will be the relative amount of decomposition of the ozonide during the course of gc analysis. By comparing runs 5 with 6 and 18 with 19 it can be seen that a moderate change of detector or injector temperature has little effect upon the decomposition of the sample.[14] We conclude, therefore, that decomposition of the ozonide takes place on the column itself.

The stability study data of Table III indicate that two passes of the ozonides over the column at a given temperature does not drastically change the ratio of *cis* and *trans* ozonide.[15] An interesting observation can be made with reference to run 24′. This experiment indicates that the ozonide ratio changes if the sample is allowed to stand at room temperature for a prolonged period of time after it is passed over the gc column. This observation is particularly interesting since untreated samples of ozonide which are left at room temperature for longer periods do not change their peak ratio. Run 24′ does not in itself show whether *cis–trans* interconversion is taking place[7] or whether one of the isomeric ozonides is relatively less stable than the other.[16]

Experimental Section

Preparation of *cis*- and *trans*-3-Hexane Ozonide.[17]—A solution of 3.26 g (38.7 mmoles) of American Petroleum Institute standard sample of *cis*-3-hexene in 200 ml of ozone-purified *n*-pentane was cooled to −63° and treated with 36.8 mmoles of ozone during a period of 2.53 hr. After the ozonation the solvent was removed at −50° on a rotary evaporator. The ozonide was then collected with the reaction flask being allowed to warm to room temperature. The ozonide was vacuum distilled giving 3.85 g (79.2% yield) of material of bp 43.7–44.0° (20 mm). A second similar preparation gave 4.02 g (81.7% yield) of material of bp 43.3–43.9° (20 mm).

Gas Chromatography.—An F & M Model 720 dual column programmed temperature gas chromatograph was used. The injector inlet was enlarged and fitted with a Pyrex tube insert in order to minimize artifacts. All columns were 20 ft × 0.25 in. stainless steel. The support was Diatoport S. Diethylene glycol succinate (10%, LAC-728) was the substrate for column A; 10% silicone DC-710 was the substrate for column B. Helium flow throughout this study was 10 ml per 10.5 sec. All samples were injected neat.

Stability Study.—Effluents were trapped in a 3-mm-o.d. spiral glass column attached to the exit port and immersed in a Dry Ice–acetone bath.

Registry No.—*cis*-3-Hexene ozonide, 6822-01-1; *trans*-3-hexene ozonide, 1696-23-7.

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(13) Absolute identification of these peaks as *cis* or *trans* has not been made in this study. See ref 9 and 10 for pertinent discussions.

(14) Slightly larger injector temperature differences were also investigated and the results of these experiments confirm that these temperature differences (*ca.* 20°) have *little* effect on decomposition.

(15) Run 21 seems to be an exception to this and cannot be properly accounted for at this time.

(16) It has been suggested by one of the referees that contamination of the sample by esters bleeding from the column can also account for these observations.

(17) The author is indebted to Dr. Fred Greenwood of Tufts University for the preparation of the ozonide.