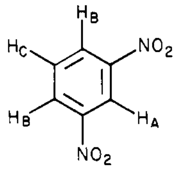
product 3 increased with time. By NMR studies it was possible to show that the exchange was occurring at H_A and not at a H_B, the site vacated by the diazonium group.



3

For authentic *m*-dinitrobenzene: ^{1}H NMR δ 9.1 (1 H, H_A, t, J_{AB} = 2 Hz (meta)), 8.7 (2 H, H_B, dd, J_{BC} = 8 Hz (ortho), J_{AB} = 2 Hz (meta)), 7.95 (1 H, H_C, t, J_{BC} = 8 Hz (ortho)). After 10 min in the presence of 0.5 M EtO$^-$/EtOD, the integral for H_A had decreased by 50%, and if left overnight, the signal due to H_A disappeared completely. No change in the relative intensity of the signals due to H_B and H_C was observed. Thus H/D exchange occurs at H_A (the hydrogen on carbon 3 of the original diazonium salt). No deuterium incorporation at H_B could be detected. GC/MS confirmed the incorporation of 50% of one D in the product from **1m** after 10 min in 0.5 M EtO$^-$/EtOD.

Acknowledgment. We are pleased to acknowledge the assistance of Mr. J. F. Smith with the GC/MS analyses and Mr. J. Hall with the carbon-13 NMR spectra.

Registry No. (*Z*)-**1a** (R = Et), 71099-75-7; (*Z*)-**1b** (R = Et), 71099-76-8; (*Z*)-**1c** (R = Et), 71099-77-9; (*Z*)-**1d** (R = Et), 62375-92-2; (*Z*)-**1d** (R = Me), 62375-91-1; (*Z*)-**1e** (R = Et), 71099-79-1; (*Z*)-**1e** (R = Me), 81536-33-6; (*Z*)-**1f** (R = Et), 71099-80-4; (*Z*)-**1f** (R = Me), 81536-34-7; (*Z*)-**1g** (R = Me), 81536-35-8; (*Z*)-**1h** (R = Et), 71099-81-5; (*Z*)-**1h** (R = Me), 81536-36-9; (*E*)-**1h** (R = Me), 81536-37-0; (*Z*)-**1j** (R = Et), 81536-38-1; (*Z*)-**1j** (R = Me), 81536-39-2; (*E*)-**1j** (R = Me), 81536-40-5; (*Z*)-**1k** (R = Et), 81536-41-6; (*Z*)-**1l** (R = Et), 81536-42-7; (*Z*)-**1l** (R = Me), 81536-43-8; (*Z*)-**1m** (R = Et), 81536-44-9; (*Z*)-**1m** (R = Me), 81536-45-0; 2-nitro-4-(trifluoromethyl)benzenediazonium ion, 81536-46-1.

Lithium Perchlorate as a Reagent for Synthesis of Covalently Bonded Organic Perchlorates via Electrophilic Additions of Halogens and Nitronium Tetrafluoroborate to Olefins

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The reaction of a series of olefins with chlorine and bromine in the presence of a large excess of lithium perchlorate in ether gave 1,2-halo perchlorates together with the corresponding 1,2-dihalides. Analogous reactions of NO_2BF_4 in the presence of $LiClO_4$ in methylene chloride or ethyl acetate with monoolefins gave 1,2-nitro perchlorates. Norbornadiene reacted with a $NO_2BF_4/LiClO_4$ system to give two isomeric nitro perchlorates of nortricyclenic structure. Several synthetic and mechanistic aspects of this new reaction of electrophilic perchloration of olefins are discussed.

The influence of added salts on the rates and even the modes of organic reactions is of both fundamental and applied interest.[1,2] For example, salt effects can provide valuable information about the mechanism because rate changes can be used to determine the charge distribution in the transition state.[1] If the added salt should not interfere in the reaction by capturing any intermediates, the salts of perchloric acid usually can be used to meet this requirement due to the very weak nucleophilicity of perchlorate ions. For example, the addition of perchlorates to reaction media is commonly used to maintain a constant ionic strength in buffer-catalysis studies. Anodic oxidation is often performed in the presence of the salts of perchloric acid.[3] The addition of perchlorates produces a rate acceleration, and the rate constant is directly proportional to the salt concentration (normal salt effect).[4]

However, the additon of perchlorates, e.g., $LiClO_4$, sometimes induces a number of interesting chemical effects.[5,6] Studies of salt effects due to the addition of $LiClO_4$ have proved to be extremely successful in investigations of ion-pair phenomena in solvolysis.[6] A special salt effect characterized by Winstein et al.[5] led to the proposal that at least two types of ion pairs were present in many solvolyses. Anhydrous solutions of $LiClO_4$ in solvents of low ionizing capacity exhibit a significant acceleration of processes which proceed via carbocationic-like intermediates.[7,8] For example, epoxides undergo facile rearrangements when perchlorate salts are present.[7] This promotion appears to be due to electrostatic effects.[7c] Catalysis by ionic aggregates of $LiClO_4$ in diethyl ether is also clearly documented.[8]

The rates of electrophilic addition reactions often have been measured in the presence of added lithium per-

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chlorate.[9-12] For example, the striking catalytic effect of $LiClO_4$ has been observed in addition of various hydrohalic acids to olefins.[11] Yates et al. were the first to find that the product composition may be significantly affected by the addition of $LiClO_4$.[12] For example, the bromination[12a] (but not the chlorination[12b]) of styrenes shows a marked increase in solvent-incorporated (AcOH) product even at low concentration of perchlorate added.

We have previously shown that the addition of massive amounts of $LiClO_4$ to the addition reactions of arenesulfenyl chlorides (ArSCl) to olefins exhibits the "doping" effect which consists of a drastic increase in the effective electrophilicity of the reagent.[13-20] Exploration of this doping-addition principle in ArSCl additions permitted us to obtain the products of simple skeletal rearrangement,[14,17] of a series of skeletal rearrangements,[16-18] of hydride shifts,[15,19] and of new types of 1,2-additions.[20] In summary, it is clear that certain unique additions occur only in the presence of added $LiClO_4$.[18,21]

The influence of added electrolytes usually has been explained in terms of ion-pair mechanisms.[5,6] It is generally assumed that the exchange reaction between the ion pairs of type $R^+||X^-$ and $Li^+||ClO_4^-$ leads to the formation of the perchlorate ion pair, $R^+||ClO_4^-$, which (i) reduces the ion-pair return to RX and (ii) does not collapse to a covalent perchlorate ester but breaks down to product owing to the very weak nucleophilicity of the perchlorate ion. Thus a number of ionization-like processes presumably can be catalyzed by $LiClO_4$ without the risk of contamination by additional covalent products (e.g., of the type $ROClO_3$). Although some kinetic data seem to indicate a carbenium–perchlorate ion-pair return,[22] there still exists doubt as to whether the components of the carbenium–perchlorate ion pair ever interact to the point of giving covalent perchlorate. For example, the existence of a carbocationic intermediate encumbered with two perchlorate counterions has been accepted for the reaction of tetramethylethylene oxide in the media containing $HClO_4$ and $NaClO_4$.[7c]

In the course of our investigation of the "doped" addition of ArSCl to olefins in the tricyclo[4.2.2.0^{2,5}]decane series it was surprisingly found that lithium perchlorate is not a chemically inert media but can supply the nucleophilic species, namely, ClO_4^-, in the final step of these electrophilic additions with the formation of covalent perchlorates.[17,18] Their formation has unequivocably been proven by their isolation in pure form[18] and by X-ray diffraction studies.[24] Moreover, some of these results have been additionally supported by the study of Garratt et al.[25] The most amazing point of these results was that ClO_4^- ion can successfully compete with such nucleophilic species as Cl^- and AcO^- in attack on carbocationic-like centers.

Later we were also able to demonstrate that the formation of covalent perchlorates is a general phenomenon for a number of electrophilic addition reactions (including halogenation) for these tricyclic olefins.[26] The purpose of the present paper is to apply the reaction of electrophilic perchloration to a number of aliphatic, monocyclic, and bicyclic olefins and hence to attach the status of a new general reaction to this process (for preliminary reports see ref 27 and 28).

Results and Discussion

We have studied the involvement of $LiClO_4$ as a reagent in the addition of halogens and of NO_2BF_4 to olefins. Lithium perchlorate was used in a large excess. Halogenation reactions were performed in diethyl ether due to its capacity to dissolve $LiClO_4$.[29] Good results in the reaction of NO_2BF_4 were also achieved by using either ethyl acetate or CH_2Cl_2 as the solvent.[30] Preparative isolations of products have been accomplished by using TLC on silica gel. The perchlorates are conveniently identified by heating the TLC plate to induce a characteristic decomposition with formation of a black spot.

We examined the reactivity of a variety of olefins in these reactions. Some of them, especially those bearing electron-withdrawing groups (e.g., stilbenes, esters of fumaric, maleic acids, etc.) gave invariably only the corresponding products of the usual addition (without formation of products of ClO_4^- participation). In contrast, in many cases we only established the formation of perchlorates by their characteristic TLC behavior but failed to isolate them in a pure form by preparative TLC. This is especially true for the tertiary perchlorates (those from isobutylene, methylenecyclobutane, etc.). Nevertheless, we could definitely obtain a number of perchlorates for some aliphatic (ethylene, 1-heptene), cyclic (cyclohexene), and bicyclic (norbornadiene) olefins: the perchlorates were isolated and purified by chromatography and identified by their IR (1200–1300-cm^{-1} region) and especially their ^1H NMR spectra. The most successful results are summarized in Table I. Below we discuss these data in detail.

Reactions of Olefins with Halogens and $LiClO_4$. First we have found that for all olefins used, the iodo-

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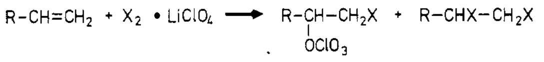
[30] We have found that nitronium fluoroborate reacted rapidly with diethyl ether even at 0 °C with the formation of ethyl nitrate, and hence we have not used this solvent for reactions of NO_2BF_4 with olefins.

perchloration reactions (cf. data of ref 26) gave, at best, only traces of extremely unstable perchlorates, and we concentrated our effort on the chloroperchloration and bromoperchloration reactions. Second, we achieved our goal in the reactions with ethylene, 1-heptene, and cyclohexene (see table I).

The reactions of ethylene with Cl_2 in presence of $LiClO_4$ in ether proceed smoothly at room temperature to give a mixture (1:1) of 1,2-dichloroethane and the desired 2-chloroethyl perchlorate (1) which has been obtained in a



$$R\text{-}CH{=}CH_2 + X_2 \cdot LiClO_4 \longrightarrow R\text{-}\underset{OClO_3}{\underset{|}{CH}}\text{-}CH_2X + R\text{-}CHX\text{-}CH_2X$$

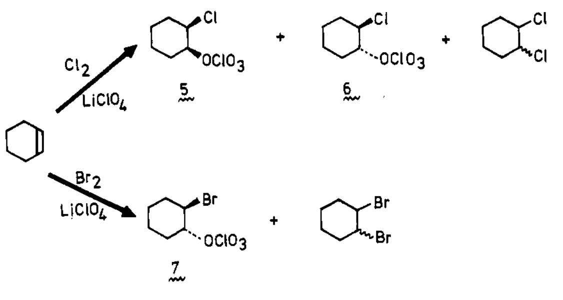
1–4

1 R=H, X=Cl ; 2 R=H, X=Br ; 3 R=n-C_5H_{11}, X=Cl ; 4 R=n-C_5H_{11}, X=Br

pure state by evaporation of the volatile compounds by a stream of dry nitrogen. Careful heating of 1 in an open capillary tube permitted one to obtain its boiling point (~125–130 °C) with a subsequent (after 150 °C) explosion. The analogous bromination reaction proceeds to give predominantly 1,2-dibromoethane with the perchlorate 2 as a minor product (10%). Nevertheless, perchlorate 2 has been isolated by chromatography as an oil, which decomposed near 125 °C without reaching its boiling point. The mass spectrum for $C_2H_4ClBrO_4$ (mol wt 206) was obtained, and peaks at m/e 206, 208, and 210 were observed. Both perchlorates 1 and 2 exhibit a number of bands in their IR spectra in the region 1200–1300 cm^{-1}.[31] ^1H NMR spectra of perchlorates 1 and 2 exhibit the typical AA′XX′ system with triplets at δ 4.7–4.8 ($HCOClO_3$) and 3.5–3.9 (HCHal) with J = 6–7 Hz.

Reactions of 1-heptene with Cl_2 and Br_2 in the presence of $LiClO_4$ in ether proceed extremely rapidly at −78 °C and also give mixtures of the corresponding 1,2-dihalides together with perchlorates 3 (27% yield) and 4 (10% yield). The perchlorates 3 and 4 are relatively stable at room temperature but explode when heated to 150 °C. The ^1H NMR spectra support their structures and confirm that the additions followed Markovnikov's rule.

Addition of Cl_2 and $LiClO_4$ to cyclohexene in ether proceeds rapidly at −78 °C to give a mixture of three perchlorates (TLC data). We could not identify the minor (less than 5%) perchlorate, but we have been able to separate and isolate the two major perchlorate products and to identify them as the *cis*- (5, 13% yield) and *trans*- (6, 41% yield) 2-chlorocyclohexyl perchlorates. The configurational assignment was performed by using the widths of the low-field signals over the outermost peaks (W parameter; cf. data of ref 32). The magnitude of W is about 18 Hz for the trans isomer 6 and about 14 Hz for the cis isomer 5. Both isomers are stable at room temperature over several weeks but decompose readily upon heating to at least 100 °C. Bromoperchloration of cyclohexene produced only a single *trans*-perchlorate, 7 (15% yield), which is less stable than the analogous chloro derivative 6.

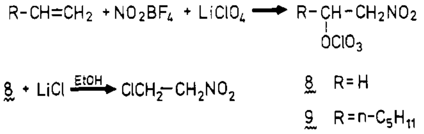


The results obtained reveal a general regularity: chloroperchloration reactions give higher yields of perchlorate esters in respect to the dihalides as compared with bromoperchloration reactions. This circumstance is easily understood since Br^- is more nucleophilic than Cl^-.[49] The surprising point is that perchlorate ion can even compete with the bromide anion which is regarded as a powerful nucleophile.

Reactions of Olefins with Nitronium Tetrafluoroborate and LiClO. Nitronium tetrafluoroborate is a typical strong electrophile (definition; see ref 33), and its reactions with olefins often proceed to give products of skeletal rearrangements,[34] elimination,[35] and hydride shifts,[34] together with the products of incorporation of other nucleophilic species (mainly nucleophilic solvent, e.g., AcOH[36]). It is worth emphasizing that BF_4^- ions can also play the role of a nucleophilic species in the final step of some carbocationic-like processes,[37] including additions,[18] since it is a source of a fluoride ion.

We have studied the reactions of NO_2BF_4 with olefins in the presence of $LiClO_4$. The possible success of these attempts to obtain products of incorporation of ClO_4^-, namely, nitroperchlorates, might also be affected by competition between ClO_4^- and BF_4^- ions. The results of these experiments are present in Table I.

The reaction of ethylene with NO_2BF_4, performed in CH_2Cl_2 in the presence of a two-fold excess of $LiClO_4$, gave nitroperchlorate 8, which can be isolated even as a pure liquid. The ^1H NMR spectrum of 8 shows only one singlet signal at δ 4.8. The treatment of a sample of 8 with LiCl in ethyl alcohol leads to the substitution of the $OClO_3$ group by chlorine[38] and hence to the appearance of two triplets of an AA′BB′ system (δ 4.72 and 4.05) in the ^1H NMR spectrum of 1-chloro-2-nitroethane.



$$R\text{-}CH{=}CH_2 + NO_2BF_4 + LiClO_4 \longrightarrow R\text{-}\underset{OClO_3}{\underset{|}{CH}}\text{-}CH_2NO_2$$

$$\mathbf{8} + LiCl \xrightarrow{EtOH} ClCH_2\text{-}CH_2NO_2$$

8 R=H
9 R=n-C_5H_{11}

Reaction of 1-heptene with the NO_2BF_4 and $LiClO_4$ system in CH_2Cl_2 proceeds smoothly at −78 °C to give at least five perchlorates (TLC data). However, this reaction in ethyl acetate at −20 °C gave a single perchlorate, 9 (17%), which could be isolated in a pure form. ^1H NMR data shows that the addition reaction also obeys Markovnikov's rule.

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[38] In our recent work[39] we have shown that all caged covalently bonded perchlorates obtained previously[26] interact with LiCl, LiBr, or $LiONs$ in acetone to give the products of nucleophilic substitution with inversion of configuration. The perchlorates prepared in this work also undergo substitution of the perchloryloxy group in acetone and in some other solvents by these nucleophilic agents. A study of the kinetic and synthetic implications of these processes is now under investigation.

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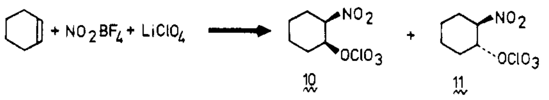
Table I. Reactions of Halogens and Nitronium Tetrafluoroborate with Olefins in the Presence of $LiClO_4$

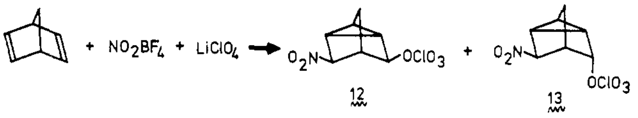
				reaction product yield, %	
olefin	electrophilic agent	solvent	temp, °C	perchlorates (no.)	1,2-dihalides
ethylene	Cl_2 [a]	ether	25	50 (**1**) [b]	50 [b]
1-heptene		ether	−78	27 (**3**)	44
cyclohexene		ether	−78	13 (**5**), 41 (**6**)	39
ethylene	Br_2 [a]	ether	25	9 (**2**) [b]	90 [b]
1-heptene		ether	−78	10 (**4**)	50
cyclohexene		ether	−78	15 (**7**)	58
ethylene	NO_2BF_4 [a]	CH_2Cl_2 [d]	25	70 (**8**)	
1-heptene		AcOEt	−20	17 (**9**)	
cyclohexene		AcOEt	−78	75 (**10** + **11**)	
norbornadiene		AcOEt [c]	−50	43 (**12**), 29 (**13**)	

[a] With 4 molar equiv of $LiClO_4$. [b] The yield was established on the basis of ^{1}H NMR. [c] With 10 molar equiv of $LiClO_4$. [d] The $NO_2BF_4/LiClO_4$ ratio was 1:2.

Addition of the NO_2BF_4 and $LiClO_4$ system to cyclohexene proceeds to give a 1:1 mixture of the cis (**10**) and trans (**11**) stereoisomeric 2-nitrocyclohexyl perchlorates (75% yield) together with a small amount (~10%) of a mixture of the 3- and 4-nitrocyclohexenes.



The nitroperchloration reaction of norbornadiene gave two nitroperchlorates (**12** and **13**; 72%, 3:2) which have been separated by chromatography. The ^{1}H NMR data for **12** and **13** support the nortricyclenic structures. Hence,



the addition proceeds with the participation of a second double bond in accordance with literature data concerning norbornadiene reactions with strong electrophiles.[15,34,40]

The assignment of configuration was made by using the chemical shift data of the low-field signals in the ^{1}H NMR spectra. Usually, the configurations of the substituents at C3 and C5 of the nortricyclene moiety have been assigned on the basis of ^{1}H NMR spectra.[41] The main criterion is a low-field shift of the signal for the endo proton (e.g., H3) due to the influence of the endo substituent at C5 and the absence of such a shift in the case of the exo configuration of the C5 substituent. In exo–exo isomer **12** both signals have a normal chemical shift at δ 4.6 (H–C-NO_2) and 5.0 (H–$COClO_3$), while for the exo–endo isomer **13**, the signal of the H–CNO_2 proton is shifted downfield to 5.3 ppm, while the second signal keeps its position at 5.1 ppm.

Conclusion

In conclusion, we summarize the main results of the present and our previous[27,28] studies as follows. First of all, these data revealed the pronounced nucleophilic character of ClO_4^- in electrophilic addition reactions. In other words, lithium perchlorate is not just an "inert" addendum for studies of carbocationic-like processes but should be regarded as a reagent which is capable of intercepting the cationoid intermediates. In turn, this discovery raises a question of the role of perchlorate salts for the other carbocationic reactions.

Second, we have shown that electrophilic perchloration may be performed for (i) a variety of electrophilic agents (halogens, ArSCl, NO_2BF_4) and (ii) various olefins. Clearly the possibility of isolation of perchlorates depends strongly on their stability, the technique used for purification, etc. However, the successful results we have obtained permit the statement that *electrophilic perchloration of olefins is a new reaction of general character.* In turn, this statement raises another question as to the extent that this process may be involved with other electrophiles as well as other unsaturated compounds (other olefins, dienes, allenes, acetylenes, cyclopropanes, etc.).

Third, this reaction is of potential synthetic utility because it allows access to new types of 1,2-disubstituted ethane systems and represents a new convenient method for the synthesis of esters of perchloric acid. This procedure undoubtedly will compete with existing synthetic methods (for short reviews see ref 42). Moreover, taking into account the ability of perchlorates to undergo nucleophilic substitution (e.g., see result with perchlorate **8** as well as ref 39 and 43) and the possibility of using the perchlorates without isolation, one may expect that future studies will reveal the appreciable synthetic potential of this reaction.

Finally, we reemphasize the amazing ability of ClO_4^- (which is regarded to be a superweak nucleophile[49]) to compete successfully with anionic species of higher nucleophilicity such as Hal^- or AcO^-, even though the concentration of perchlorate is only slightly higher than the other nucleophiles (see Table I). That means that the theory of nucleophilicity orders[44,49] does not apply in this

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case. At present we have no sufficient explanation for that apparent discrepancy. It is well-known that nucleophilicity orders often change with solvent changes, especially if one goes from protic to aprotic solvents. In other words, in all nucleophilic reactions, desolvation of the anions is an important factor. At present, one may just speculate that "naked" perchlorate ion in aprotic solvents will be a significantly better nucleophile than solvated perchlorate ion. If so, our data can be regarded as a promising way to involve the other superweak nucleophilic ions (e.g., $CF_3SO_3^-$ or FSO_3^-[50]) in synthetically useful addition reactions. Additional experimental data on the mechanism of this reaction should be useful in examining subtle aspects of nucleophilicity.

Experimental Section

The NMR spectra were obtained in the indicated solvents by using Varian ST-60 or JEOL XL-100 spectrometers. Tetramethylsilane was used as an internal standard, and the chemical shifts are presented in δ values. The IR spectra were taken with an UR-10 infrared spectrophotometer. Analytical and preparative thin-layer chromatography were carried out by using silica gel 40/100 or 5/40 on 18 × 24 cm plates.

Caution: The following small-scale procedures have proved innocuous, but caution is still strongly advised.

Reactions of Ethylene in the Presence of LiClO. (A) With Chlorine. A solution of 2.14 g of $LiClO_4$ in 10 mL of ether was saturated with ethylene (0.5 L) and with excess chlorine. The solution was washed with water and dried with sodium sulfate. Evaporation of the solvent gave 0.3 g of a volatile colorless oil [1:1 mixture of 1,2-dichloroethane and 2-chloroethyl perchlorate (**1**) according to the ^1H NMR spectrum]. Blowing dry nitrogen through the mixture evaporated the dichloroethane and left the perchlorate **1**: R_f 0.14 (hexane); bp 125–130 °C (in an open capillary tube, without decomposition); IR 1280, 1250, 1230 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 4.85 (t, 2H, J = 6 Hz), 3.90 (t, 2 H, J = 6 Hz).

(B) With Bromine. A solution of 1 g of bromine and 4.28 g of $LiClO_4$ in 20 mL of ether was saturated with ethylene at ambient temperature up to decoloration. The workup as described in part A gave an oil, which was a 1:10 mixture of 2-bromoethyl perchlorate (**2**) and 1,2-dibromethane according to ^1H NMR data. The yield of perchlorate **2** was about 10°. Column chromatography (hexane) gave pure perchlorate **2**: R_f 0.23; decomposition near 125 °C, bp 35–40 °C (15 mm); IR 1283, 1275, 1270, 1255, 1240 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 4.75 (t, 2 H, J = 7 Hz), 3.55 (t, 2 H, J = 7 Hz); mass spectrum, m/e 206 (M^+), 208, 210.

(C) With Nitronium Tetrafluoroborate. Caution: *The nitroethyl perchlorate 8 is sufficiently stable for several months at room temperature in the presence of a small amount of solvent. However, pure samples exhibited a highly explosive property.* A mixture of 0.21 g of NO_2BF_4 and 0.32 g of $LiClO_4$ in 10 mL of methylene chloride was saturated with ethylene during 3 h under vigorous stirring. The workup as described in part A gave a solution which contained exclusively the single product **8** according to TLC and ^1H NMR data. Blowing dry nitrogen through 1 mL of the solution gave 0.02 g (70%) of pure 2-nitroethyl perchlorate (**8**): R_f 0.6 (chloroform); decomposition near 150 °C; IR 1540, 1360, 1280, 1250 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 4.8 (s).

A sample of 2-nitroethyl perchlorate (**8**, 150 mg) was treated with a solution of LiCl (100 mg) in ethanol (2 mL). The mixture was kept for 10 h and then poured into water, extracted with carbon tetrachloride, and dried with sodium sulfate. Removal of the solvent gave 1-chloro-2-nitroethane: bp 173 °C[45];^1H NMR (60 MHz, CCl_4) 4.72 (t, 2 H, J = 6 Hz, CH_2NO_2), 4.05 (t, 2 H, J = 6 Hz, CH_2Cl).

Reactions of 1-Heptene in the Presence of $LiClO_4$. (A) With Chlorine. A solution of 0.39 g of 1-heptene and 1.71 g of $LiClO_4$ in 10 mL of ether was saturated with excess chlorine. The solution was washed with water and dried with sodium sulfate. the solvent was removed by evaporation, and the oily residue was chromatographed on a silica gel column. Elution with hexane gave 0.3 g (44%) of 1,2-dichloroheptane (R_f 0.82; bp 191 °C; $n^{20}{}_D$ 1.4440)[46] and 0.25 g (27%) of 1-chloro-2-(perchloryloxy)heptane (**3**): R_f 0.55, decomposition near 120 °C; IR 1275, 1245, 1225 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 5.05 (1 H, m, $HCOClO_3$), 3.90 (2 H, d, J = 5 Hz, CHCl), 2.2–0.9 (11 H, m, C_5H_{11}); ^{17}O NMR (in δ from D_2O) broad multiplet centered at 270.8 (cf. ref 47).

(B) With Bromine. Bromine (0.8 g) was added dropwise to a stirred solution of 1-heptene (0.49 g) and $LiClO_4$ (2.14 g) in 10 mL of ether at −78 °C. A workup as described in past A gave a residue which contained 15–20% of perchlorate **4** (^1H NMR data). Column chromatography (hexane) gave 0.65 g (50%) of 1,2-dibromoheptane (R_f 0.77; bp 227 °C; $n^{20}{}_D$ 1.4990)[46] and 0.14 g (10%) of 1-bromo-2-perchloryloxyheptane (**4**): R_f 0.5; decomposition at 100–105 °C; IR 1275, 1268, 1245, 1230 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 5.1 (1 H, m, $HCOClO_3$), 3.9 (2 H, d, J = 5 Hz, CH_2Br), 2.2–0.9 (11 H, m, C_5H_11).

(C) With Nitronium Tetrafluoroborate. The NO_2BF_4 (0.8 g) was added in small portions to a stirred solution of 1-heptene (0.49 g) and $LiClO_4$ (2.14 g) in 10 mL of ethyl acetate at −20 °C. The solution was poured into water (50 mL) and extracted with chloroform (2 × 15 mL). The organic solvent was removed by evaporation, and an oily residue was chromatographed on a silica gel column. Elution with 1:4 mixture of ethyl acetate–hexane gave 0.21 g (17%) of 1-nitro-2-(perchloryloxy)heptane (**9**): R_f 0.6; decomposition at 105–110 °C; IR 1540, 1360, 1280, 1250 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 5.0 (3 H, overlaping signals of CH_2NO_2 and $HCOClO_3$), 2.2–0.9 (11 H, m, C_5H_{11}).

Reactions of Cyclohexene in the Presence of $LiClO_4$. (A) With Chlorine. A solution of 0.2 g of cyclohexene and 1.07 g of $LiClO_4$ in 5 mL of ether was saturated with excess chlorine. The solution was washed with water and dried with sodium sulfate. The solvent was removed, and an oily residue was chromatographed on a silica gel column. Elution with a 1:4 mixture of ethyl acetate–hexane gave 0.15 g (39%) of 1,2-dichlorocyclohexane [R_f 0.69 (identified by ^1H NMR)], 0.22 g (41%) of *trans*-2-chlorocyclohexyl perchlorate [**6**: R_f 0.55; decomposition near 120 °C; IR 1290, 1275, 1250, 1235, 1210 cm^{-1}; ^1H NMR (100 MHz, CCl_4) 4.9 (1 H, m, $W_{1/2}$ = 17.5 Hz, $HCOClO_3$), 4.05 (1 H, m, $W_{1/2}$ = 18 Hz, CHCl), 2.6–1.2 (8 H, m)], and 0.07 g (13%) *cis*-2-chlorocyclohexyl perchlorate (**5**): R_f 0.43; decomposition near 140 °C; IR 1275, 1260, 1243, 1235, 1210 cm^{-1}; ^1H NMR (100 MHz, CCl_4) 5.25 (1 H, m, $W_{1/2}$ = 14 Hz, $HCOClO_3$), 4.35 (1 H, m, $W_{1/2}$ = 13 Hz, CHCl), 2.8–1.2 (8 H, m).

(B) With Bromine. Bromine (0.8 g) was added dropwise to a stirred solution of cyclohexene (0.41 g) and $LiClO_4$ (2.14 g) in 10 mL of ether at −78 °C. A usual workup as described in part A gave an oil which was chromatographed on a silica gel column. Elution with a 1:6 mixture ethyl acetate–hexane gave 0.7 g (58%) of 1,2-dibromocyclohexane [R_f 0.62 (identified by ^1H NMR)] and 0.19 g (15%) of *trans*-2-bromocyclohexyl perchlorate (**7**): R_f 0.44; decomposition near 115 °C; IR 1290, 1278, 1264, 1205 cm^{-1}; ^1H NMR (60 MHz, CCl_4) 5.1 (1 H, m, $W_{1/2}$ = 19 Hz, $HCOClO_3$), 4.0 (1 H, m, $W_{1/2}$ = 20 Hz, CHBr), 2.6–1.2 (8 H, m).

(C) With Nitronium Tetrafluoroborate. The NO_2BF_4 (1.46 g) was added in small portions to a stirred solution of cyclohexene (0.82 g) and $LiClO_4$ (4.28 g) in 20 mL of ethyl acetate at −78 °C. The mixture was allowed to warm to 0 °C and was poured into an ice–water mixture (70 mL). Extraction with methylene chloride (2 × 20 mL) and a subsequent workup gave an unstable oil. According to TLC and ^1H NMR data this oil contained ~10% of a mixture of the 3- and 4-nitrocyclohexenes (R_f 0.58, identical with available samples[48]) and 75% of a 1:1 mixture of the *cis*- (**10**) and *trans*-2-nitrocyclohexyl perchlorates (**11**): R_f 0.5; decomposition at 60–70 °C. For the cis isomer **10**: ^1H NMR (60 MHz, CCl_4) 5.6 (1 H, m, $W_{1/2}$ = 13 Hz, $HCOClO_3$), 4.55 (1 H, m, $CHNO_2$), 2.8–1.0 (8 H, m). For the trans isomer **11**: ^1H NMR (60 MHz, CCl_4) 5.0 (1 H, m, $W_{1/2}$ = 20 Hz, $HCOClO_3$), 4.55 (1 H, m, $CHNO_2$), 2.8–1.0 (8 H, m).

Reaction of Norbornadiene with NO_2BR_4 and $LiClO_4$. The nitronium tetrafluoroborate (0.67 g) was added in small portions to a stirred solution of norbornadiene (0.46 g) and $LiClO_4$ (5.35 g) in 25 mL of ethyl acetate at −50 °C. The reaction mixture was stirred for 30 min and poured into an ice–water mixture (50 mL).

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[50] We have found that $CF_3SO_3^-$ and FSO_3^- ions may also compete successfully with some other nucleophilic species at the final step of the addition reaction of some different electrophilic agents to olefins. These results will be published.

Extraction with chloroform (2 × 15 mL) and the usual workup gave 0.86 g (72%) of a 3:2 mixture (by ^{1}H NMR) of 3-*exo*-nitro-5-*exo*-(perchloryloxy)nortricyclene (**12**) and 3-*exo*-nitro-5-*endo*-(perchloryloxy)nortricyclene (**13**). Silica gel column chromatography (elution with 1:3 mixture ethyl acetate–hexane) gave pure 5-exo isomer **12** [R_f 0.4; decomposition at 100 °C; IR 1550, 1370, 1275, 1250, 840 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) 5.02 (1 H, s, $HCOClO_3$), 4.58 (1 H, s, $CHNO_2$), 2.98 (2 H, m), 2.2–1.7 (10 H, m)] and pure 5-endo isomer **13**: R_f 0.3; decomposition at 90 °C; IR 1550, 1375, 1275, 1245, 840, 800 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) 5.37 (1 H, m, $CHNO_2$), 5.15 (1 H, m, $HCOClO_3$), 2.98 (2 H, m), 2.2–1.7 (10 H, m).

Registry No. **1**, 81971-79-1; **2**, 81971-80-4; **3**, 81971-81-5; **4**, 81971-82-6; **5**, 81971-83-7; **6**, 81971-84-8; **7**, 81971-85-9; **8**, 78053-17-5; **9**, 78053-18-6; **10**, 81971-86-0; **11**, 81971-87-1; **12**, 78053-20-0; **13**, 78088-38-7; $LiClO_4$, 7791-03-9; ethylene, 74-85-1; 1,2-dichloroethane, 107-06-2; 1,2-dibromoethane, 106-93-4; 1-chloro-2-nitroethane, 625-47-8; 1-heptene, 592-76-7; 1,2-dichloroheptane, 10575-87-8; 1,2-dibromoheptane, 42474-21-5; cyclohexene, 110-83-8; 1,2-dichlorocyclohexane, 1121-21-7; 1,2-dibromocyclohexane, 5401-62-7; 3-nitrocyclohexene, 6925-08-2; 4-nitrocyclohexene, 4883-68-5; norbornadiene, 121-46-0.

Photochemical Beckmann Rearrangements. Correspondence between Substituent Effects in Oximes and Oxaziridines[1]

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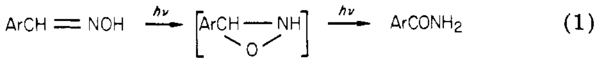
The relative migratory tendencies of hydrogen and aryl groups in the photochemical Beckmann rearrangement of benzaldoximes **2a–c** were compared with those in the photochemical rearrangement of 2-alkyl-3-aryloxaziridines **3a–f**. The migratory tendencies depended on the nature of the aryl substituent and were similar in **2a–c** and **3a–c**, implying that the photochemical Beckmann rearrangement proceeds through an oxaziridine intermediate. A similar order of migratory tendencies was not found in the *tert*-butyloxaziridines **3d–f**, presumably because of steric effects.

The photochemical rearrangement of oximes to amides, or the photochemical Beckmann rearrangement,[2–6] has been shown to proceed by intramolecular oxygen transfer through studies of ^{18}O-labeled oximes.[2b] Accordingly, it has been postulated that the rearrangement goes through an intermediate oxaziridine, 1 (eq 1). Evidence for this type of intermediate is provided by the low-temperature photolysis of *p*-anisaldoxime, which gave an unstable material containing activie oxygen and with a UV absorption maximum near 235 nm. These properties suggest an oxaziridine, although the material was not thoroughly characterized.[2b]



(1)

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The rearrangement of aryl aldoximes can lead to aryl carboxamides or to *N*-arylformamides, depending on whether the migration involves hydrogen or the aryl group, respectively (eq 2). If the photochemical Beckmann rearrangement proceeds through an oxaziridine intermediate, then these relative migration tendencies should parallel those in similar oxaziridines. Since oxaziridines of the type 1 are too unstable to isolate, we have prepared and studied the photolysis of several 2-methyl- and 2-*tert*-butyl-3-aryloxaziridines (**3a–f**) to compare the migratory tendency of the aryl group with that of aryl aldoximes with the same aryl substituents.

$$HCONHAr \xleftarrow{Ar\sim} ArCH{=}NOH \xrightarrow{H\sim} ArCONH_2 \qquad (2)$$

Table I. Photolysis of Oximes ArCH=NOH

compd	Ar	irrad time, h	% yield of products ArCONH₂	% yield of products ArNH₂
2a	C_6H_5	3.5	21	
2b	p-$CH_3OC_6H_4$	25	34	4.1
2c	p-ClC_6H_4	4	25,[a] 40	

[a] $C_6H_5CONH_2$.

Results and Discussion

Photolysis of Aryl Aldoximes. Ethanol solutions of aryl aldoximes **2a–c** were irradiated with UV light through quartz, with the results shown in Table I. Benzaldoxime (**2a**) and *p*-chlorobenzaldoxime (**2c**) gave only amides via hydrogen migration. In the latter case, the product was a mixture of *p*-chalorobenzamide and benzamide, the latter arising from photochemical dechlorination of *p*-chlorobenzamide, as was shown by an independent photolysis of *p*-chlorobenzamide under the same conditions. Photolysis of *p*-anisaldoxime (**2b**) gave *p*-anisamide and *p*-anisidine in a ratio of 8.3:1. Since independent photolysis showed that *N*-formyl-*p*-anisidine was converted into *p*-anisidine about 10 times as efficiently as was **2b**, we conclude that the formamide was formed initially in the oxime rearrangement and then photolyzed to *p*-anisidine. It appears that the ratio of hydrogen to aryl group migration in this rearrangement is about 8:1. Although our analysis of the product from photolysis of **2b** did not reveal any *N*-formyl-*p*-anisidine, its presence has been reported.[2]

Photolysis of 2-Alkyl-3-aryloxaziridines. Oxaziridines **3a–f** were irradiated under nitrogen in the same way

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[1] Contribution No. 291.

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