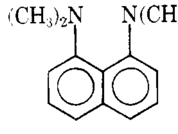
hydroxyl oxygen to serve as an effective nucleophile toward triethyloxonium ion.

Attempts to form methyl ethers through use of amine **3** and trimethyloxonium tetrafluoroborate (**2**) were unsuccessful as the amine proved more nucleophilic toward trimethyloxonium ion than did the alcohol. Thus, when **2** (1 equiv)[15] was suspended in a dichloromethane solution of **3** (1.5 equiv) and 2-methyl-1-butanol and stirred for 1 week, a white precipitate of diisopropylethylmethylammonium tetrafluoroborate was obtained. The unreacted alcohol was recovered.

The sterically more hindered, less nucleophilic base 1,8-bis(dimethylamino)naphthalene (**4**)[16,17] did prove effective



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in the methylation of alcohols with **2**. In the presence of this amine, the methyl ethers of both (*S*)-(−)-2-methyl-1-butanol and (*R*)-(+)-1-phenylethanol were obtained in good synthetic yields and with excellent optical purities (Table I). Although no 2-*tert*-butyl-2-methoxyadamantane was obtained by the addition of **2** and **4** to 2-*tert*-butyl-2-adamantanol, over a period of several weeks the alcohol slowly disappeared and was replaced by the methyl-shifted elimination product 2-methyl-2-(2′-propenyl)adamantane. This suggests that, unlike the case with **1**, this alcohol may slowly attack the less hindered trimethyloxonium ion to yield an intermediate secondary oxonium ion (protonated ether) which then loses methanol to form products of diminished internal steric strain.[14,18]

The number of alcohols studied to date has not been great and the yields of products have not been optimized, but it would appear that the use of trialkyloxonium salts in conjunction with nonnucleophilic amine bases to effect alkylation of labile alcohols is an attractive, general synthetic route to ethers which may be difficult to obtain by other means.

Experimental Section

General. NMR spectra were obtained on a Varian T-60A instrument using tetramethylsilane as an internal standard. Optical rotations were measured on neat samples using a Rudolph Model 26202 automatic digital polarimeter. VPC analyses were performed on a Varian Aerograph 90-P chromatograph using 0.25-in. columns. All glassware was oven dried and assembled while hot.

Materials. Reagent grade dichloromethane was dried over Linde 4A molecular sieves prior to use. Triethyloxonium tetrafluoroborate and trimethyloxonium tetrafluoroborate were prepared according to previously reported procedures[10,15] and were washed several times with anhydrous diethyl ether just prior to use.

General Alkylation Procedures. (*S*)-(+)-1-Ethoxy-2-methylbutane. The preparation of this compound is representative of all successful ethylations. Into a 100-mL, round-bottomed flask fitted with a condenser, drying tube, and magnetic stirring bar were placed 20.0 g (0.16 mol) of *N*,*N*-diisopropylethylamine (Aldrich), 25.2 g (0.13 mol) of triethyloxonium tetrafluoroborate, 40 mL of dichloromethane, and 14.0 mL (0.13 mol) of (*S*)-(−)-2-methyl-1-butanol [Eastman, $[\alpha]^{23}_{\mathrm{D}}$ −5.69° (neat), optical purity 96.8%[19]]. The resulting solution was stirred at room temperature for 7 days before it was quenched with ice water and extracted with two 50-mL portions of diethyl ether. The combined ether extracts were washed twice with 5% aqueous sodium bicarbonate solution and once with water prior to drying ($MgSO_4$). Distillation produced 13.3 g (89%) of colorless product which was pure by VPC (20-ft Carbowax 20M, 140 °C), NMR, and IR analyses: bp 105–106.5 °C; $[\alpha]^{24}_{\mathrm{D}}$ +0.92° (neat) [lit.[19] bp 109–110 °C; $[\alpha]^{20}_{\mathrm{D}}$ +0.89° (neat)].

(*S*)-(+)-1-Methoxy-2-methylbutane. Procedures for methylation were essentially the same as those used in ethylation except that the reduced solubility of trimethyloxonium tetrafluoroborate in dichloromethane resulted in a suspension rather than a solution of reactants. After 3 days of stirring, workup of a mixture of 7.0 mL (0.06 mol) of (*S*)-(−)-2-methyl-1-butanol, 9.5 g (0.06 mol) of trimethyloxonium tetrafluoroborate, and 15.0 g (0.07 mol) of 1,8-bis(dimethylamino)naphthalene[17] in 20 mL of dichloromethane yielded 3.5 g (57%) of pure product: bp 89.5–90.5 °C; $[\alpha]^{25}_{\mathrm{D}}$ +0.57° (neat) [lit.[19] bp 90 °C; $[\alpha]^{20}_{\mathrm{D}}$ +0.61° (neat)].

In a similar experiment using *N*,*N*-diisopropylethylamine instead of 1,8-bis(dimethylamino)naphthalene, workup yielded only unreacted alcohol together with a white, crystalline precipitate which could be recrystallized from hot water. This material had microanalytical and spectral properties consistent with diisopropylethylmethylammonium tetrafluoroborate: NMR (CD_3CN) δ 3.60 (2 H, septet), 3.05 (2 H, q), 2.50 (3 H, s), and 1.10 (15 H, m). Careful examination of the upfield multiplet region showed it to consist of a 12-proton doublet (J = 6.7 Hz), each line of which was split into a triplet of equal intensity (J = 1.7 Hz), which partially overlapped a three-proton doublet (J = 7.5 Hz), each line of which was further split into a triplet of equal intensity (J = 1.8 Hz). This pattern is consistent with three-bond coupling between nitrogen and the isopropyl group methyl protons with J_{NH} equal to 1.7 Hz and with the ethyl group methyl protons with J_{NH} equal to 1.8 Hz. These values compare closely with analogous couplings reported in the cases of other tetraalkylammonium salts.[20]

Acknowledgment. We thank the National Science Foundation for support of this work.

Registry No.—**1**, 368-39-8; **2**, 420-37-1; **3**, 7087-68-5; **4**, 20734-58-1.

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Unsaturated Carbenes from Primary Vinyl Triflates. 6. Competitive Addition of Isopropylidene Carbene to Olefins[1]

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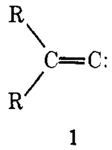
Unsaturated carbenes[2], **1**, have been shown to be singlets,[3] electrophilic,[4] and at least in the case of the vinyl triflate, **2**, derived species,[5] free rather than carbenoid.[4a] In order to as-



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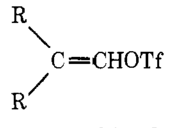

2, OTf = OSO_2CF_3

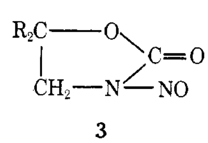

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Table I. Relative Reactivity of Triflate Derived $(CH_3)_2C{=}C{:}$ with Various Olefins at −20 °C

Registry no.	Substrate	Rel reactivity[a]
109-92-2	Ethyl vinyl ether	2.53
110-83-8	Cyclohexene	1.00
590-18-1	*cis*-2-Butene	0.96
931-88-4	Cyclooctene	0.88
498-66-8	Norbornylene	0.54
513-35-9	2-Methyl-2-butene	0.30
106-99-0	1,3-Butadiene	0.30
111-66-0	1-Octene	0.22
624-64-6	*trans*-2-Butene	0.18
106-98-9	1-Butene	0.17
115-11-7	Isobutylene	0.11
563-79-1	2,3-Dimethyl-2-butene	0.027

[a] Relative to cyclohexene, estimated error ±5–10%.

sess further the nature of these intermediates, we have investigated and wish to report the selectivity of isopropylidene carbene (**1**, R = CH_3) toward a series of olefins. Relative reactivity studies have proven to be of considerable value and interest in gaining insight into the electronic as well as steric factors operative in the addition of carbenes to alkenes.[6] Such a study has already been carried out by Newman and Patrick[4c] for the *N*-nitrosooxazolidone, **3**, derived unsaturated carbene, **1**, but we felt that there was merit in extending it to the triflate derived species as well as extending the scope of olefinic substrates.

Results and Discussion

Relative reactivities were determined by interacting the triflate, $(CH_3)_2C{=}CHOTf$, and *t*-BuOK with a large excess of a known mixture of cyclohexene and a second olefin at −20 °C. The reaction mixture was analyzed directly for product adducts by gas chromatography. Authentic adducts were obtained by preparative GC and, where not previously known, characterized by spectral means as given in the Experimental Section. Relative reactivities were calculated by means of the well-known relationship developed by Skell and Doering.[7] Reactions were carried out in duplicate or triplicate and the results are given in Table I. To assess the internal consistency and accuracy of these relative reactivities cross-check experiments were performed. The direct experimental relative reactivity of *cis*-2-butene to *trans*-2-butene was found to be 4.6 while their calculated relative reactivity is 5.3, for butadiene/isobutylene the observed value was 2.3 and the predicted value 2.7, and for 1-butene/isobutylene the direct experimental value was 1.46 and the calculated value 1.55. Within the limits of this technique these values are in good agreement.

Scrutiny of the data in Table I reveals a number of interesting facts and trends. First of all, there is very good agreement between our data and Newman's[4c] values for cyclooctene, 1-octene, and 2,3-dimethyl-2-butene. The agreement is particularly good if one considers the differences in the two methods of generating the carbene and the differences in temperature of the two determinations. This would suggest that the carbenes derived from the *N*-nitrosooxazolidone, **3**, and the primary vinyl triflate, **2**, are very similar if not identical, at least in their behavior toward certain olefins.

It is also obvious from the data in Table I that a combination of electronic and steric factors is operative in the addition of isopropylidene carbene to olefins. Electron-rich olefins such as ethyl vinyl ether react very much faster than normal olefins, a result generally in agreement with the behavior of saturated carbenes.[6,8] On the other hand, tetramethylethylene, an electron-rich but sterically hindered olefin, reacts very much slower than cyclohexene toward isopropylidenecarbene (**1**, R = CH_3) contrary to the behavior[6] of normal carbenes. Such steric effects are understandable in terms of the nature of unsaturated carbenes and their mode of interaction with olefins. Alkylidene carbenes have been shown both to be electrophilic[4] and to have a singlet ground state, with an empty p orbital.[3,9] Hence, the initial approach and interaction of the carbene with the olefinic π system occurs via this empty p orbital which is constrained to lie in the same place as the β-alkyl substituents thereby causing steric congestion with the substituents on the olefin.

Vicinally disubstituted olefins generally react faster than either monosubstituted olefins or geminally disubstituted olefins further confirming the opposing nature of electronic and steric factors in the behavior of unsaturated carbenes toward alkenes.

Interestingly, but for reasons not quite clear to us, cis alkenes react considerably faster than their trans counterparts with a relative reactivity for 2-butene of $k_{\text{cis}}/k_{\text{trans}} = 5.3$ and *cis*-4-methyl-2-pentene/*trans*-4-methyl-2-pentene of about 7.[4c] Such factors as dispersion forces or secondary electrostatic interactions[10] and/or steric attraction[11] have been suggested as being responsible for such contrathermodynamic behavior.

Finally, the relative reactivity of 0.30 for 1,3-butadiene is quite instructive. As expected reaction results in a 1,2 addition rather than a 1,4 addition.[12] The slower reactivity of the diene compared to a monoene clearly suggests a singlet for 1 for a triplet should react faster with a diene than a simple olefin. This result confirms our previous conclusions on the spin multiplicity of such unsaturated carbenes.[3]

Experimental Section

General. All boiling points are uncorrected. NMR spectra were recorded on a Varian Associates A-60 or EM-360 spectrometer and data are given in δ (ppm) relative to tetramethylsilane (Me_4Si, δ 0). All IR spectra were recorded neat between NaCl plates on a Beckman IR-5A and are reported in wavenumbers (cm^{-1}) calibrated to the 1602-cm^{-1} line of polystyrene. Mass spectra were recorded on a AE-1-MS-30 spectrometer. Analytical GC analysis was performed on a Hewlett-Packard 700 chromatograph with a flame ionization detector coupled to a Hewlett-Packard 3370B electronic integrator. All analyses were performed on a 6 ft × 0.125 in. 10% UC-W98 column. Preparative GC was performed either on a Varian Aerograph 90P or 920 chromatograph using the following aluminum columns: (A) 0.25 in. × 5 ft 10% SF-96 on 60–80 Chromosorb W; (B) 0.375 in. × 15 ft 15% Apiezon on 45–60 Chromosorb W; (C) 0.375 in. × 15 ft 15% Carbowax 20M on 45–60 Chromosorb W.

Materials. 2-Methylpropenyl triflate and *t*-BuOK were prepared as previously reported.[5] Commercially available olefins were fractionally distilled and a narrow center cut was used in the preparation of the olefin mixtures. Matheson or Phillips research grade 1,3-butadiene, *cis*- and *trans*-2-butene, isobutylene, and 1-butene were used without further purification.

General Procedure for Relative Reactivity Studies. Stock solutions of a known binary mixture of cyclohexene and an additional olefin were prepared by accurately weighing each component on an analytical Mettler balance. Gaseous olefins were condensed at dry ice–acetone temperature, then weighed and mixed with a known amount of cold cyclohexene. To each of two 15-mL round-bottom flasks equipped with a magnetic stirring bar and stopper or wired-on serum cap were added 158 mg (1.4 mmol) of *t*-BuOK and 10 mL of the desired olefin mixture. The entire solution was equilibrated at −20 °C, then 160 μL (1.0 mmol) of 2-methylpropenyl triflate was added all at once by means of a syringe. The solutions were allowed to stir at −20 °C for 24 h and then were analyzed by direct injection into a flame ionization GC. The products consisted of the respective adducts and various amounts of *tert*-butyl vinyl ether, $(CH_3)_2C{=}CH[OC(CH_3)_3]$, all identified by coinjection with the authentic compounds. Analysis of each sample was carried out in triplicate and if the duplicate runs did not agree to within 10%, an additional set of duplicate determinations was carried out and the three best runs averaged. Calibrations were carried out on two of the olefin runs and on the ethyl vinyl ether run. In the olefin runs calibrated and uncalibrated determinations agreed to within the experimental error of ±10%, hence no further calibrations were carried out on the remaining olefins. Calibrations made a significant difference in the ethyl vinyl ether run and the value in Table I is the corrected calibrated value. Relative rates were calculated by means of the given equation[7] and are reported in Table I.

Preparation and Identification of Authentic Adducts. All authentic adducts were prepared by reaction of 1.0–2.0 g (5–10 mmol) of the triflate and 0.8–1.7 g (7–15 mmol) of *t*-BuOK with the appropriate pure olefin at −20 °C for 24–48 h. The reaction mixtures were taken up in pentane, washed once with water, and dried over anhydrous $MgSO_4$, the solvent was distilled off, and the product was collected from the residue by preparative GC and identified by spectral means. Adducts with ethyl vinyl ether, cyclohexene, *cis*- and *trans*-2-butene, cyclooctene, 1-octene, and 2,3-dimethyl-2-butene have been previously prepared and reported.[3-5] The remaining adducts were obtained and characterized as follows.

Norbornylene Adduct. *exo*-3-Isopropylidenetricyclo[3.2.1.0^{2,4}]octane was collected on column A at 75 °C: mass spectrum *m/e* 148 (M^+, 18), 105 (100); IR 1772 cm^{-1} (C=C); NMR (CCl_4) δ 0.77 (m, 2 H, cyclopropyl), 1.12 (bs, 2 H, CH_2), 1.39 (m, 4 H, 2 CH_2), 1.69 (m, 6 H, 2 CH_3), 2.30 (bs, 2 H, 2 CH).

2-Methyl-2-butene Adduct. 2-Isopropylidene-1,1,3-trimethylcyclopropane was collected on column C at 45 °C: mass spectrum *m/e* 124 (M^+, 47), 67 (100); IR 1775 cm^{-1} (C=C); NMR (CCl_4) δ 1.08 (s, 6 H, 2 CH_3), 1.12 (d, J = 5.2 Hz, 3 H, CH_3), 1.13 (m, 1 H), 1.74 (s, 6 H, 2 CH_3C=C).

1,3-Butadiene Adduct. 1-Isopropylidene-2-vinylcyclopropane was collected on column A at 50 °C: mass spectrum *m/e* 108 (M^+, 42), 93 (100); IR 1785 cm^{-1} (C=C); NMR (CCl_4) δ 1.17 (m, 2 H, cyclopropyl), 1.76 (m, 6 H, 2 CH_3), 2.41 (m, 1 H, cyclopropyl), 5.42 (m, 3 H, 3 HC=C).

1-Butene Adduct. 1-Ethyl-2-isopropylidenecyclopropane was collected on column C at 45 °C: mass spectrum *m/e* 110 (M^+, 13), 67 (100); IR 1782 cm^{-1} (C=C); NMR (CCl_4) δ 0.33–1.58 (m, 8 H, 3 cyclopropyl H, CH_3CH_2), 1.76 (bs, 6 H, 2 CH_3C=C).

Isobutylene Adduct. 1,1-Dimethyl-2-isopropylidenecyclopropane was collected on column A at 40 °C: mass spectrum *m/e* 110 (M^+, 58), 67 (100); IR 1788 cm^{-1} (C=C); NMR (CCl_4) δ 0.80 (m, 2 H), 1.13 (s, 6 H, 2 CH_3), 1.73 (m, 6 H, 2 CH_3C=C).

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Registry No.—1, 26265-75-8; *exo*-3-isopropylidenetricyclo[3.2.1.0^{2,4}]octane, 61558-31-4; 2-isopropylidene-1,1,3-trimethylcyclopropane, 61558-32-5; 1-isopropylidene-2-vinylcyclopropane, 35234-77-6; 1-ethyl-2-isopropylidenecyclopropane, 61558-33-6; 1,1-dimethyl-2-isopropylidenecyclopropane, 1121-36-4.

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Preparation of Allenyl Esters

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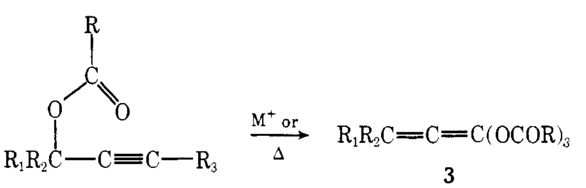
The formation of allenyl acetates and substituted benzoates by symmetry-allowed thermal rearrangement and by metal-catalyzed rearrangement is well documented.[2] The formation of allenyl[3] phosphonates, phosphinates, and phosphine oxides from thermal rearrangement of the corresponding propargyl phosphites, phosphonites, and phosphinites, respectively, is also well known.[4a-c] We wish to report the extension of these reactions to the preparation of the hitherto unknown allenyl dialkylphosphates, **1**,

$$R_1R_2C{=}C{=}C(R_3)OP(O)(OR)_2$$

1

as well as to describe our procedure for the preparation by silver-catalyzed rearrangement of these and other allenyl esters. This procedure affords yields comparable to those reported earlier while providing greater convenience. In addition we have prepared a number of new allenyl esters by thermal rearrangement of the isomeric propargyl compounds.

A variety of methods has been utilized to effect the silver ion catalyzed rearrangement of tertiary propargyl acetates[2,5a-c] and substituted nitrobenzoates,[2,5a] **2** → **3**. Reported



2 **3**

yields vary from 40 to 65% depending upon the degree of substitution and the steric nature of the substituent groups, R_1, R_2, and R_3. Terminal alkynes generally give better yields than internal alkynes. Tertiary esters generally rearrange with higher yields and shorter reaction times than secondary esters. And, in our experience, the rearrangement will not tolerate the presence of an aromatic substituent at R_1, R_2, or R_3. Mixtures of **2** and **3** are often obtained. The reported procedures normally employ chlorobenzene or aqueous dioxane as the solvent and utilize up to 10 mol % amounts of $AgNO_3$, Ag_2CO_3, $AgClO_4$, $AgBF_4$, or AgOAc as the catalyst.

We required a number of allenyl esters in connection with a study of the acid- and base-catalyzed hydrolysis of allenyl-X substrates. Three disadvantages to earlier procedures became apparent in our first attempts to prepare several known allenyl acetates. It seemed to us that the choice of chlorobenzene or aqueous dioxane as a solvent did not facilitate the workup because of their relatively low volatility. Chlorobenzene was particularly troublesome in this respect. We preferred a solvent of high volatility but noted that the use of acetone by Benn[6] to effect the rearrangement of steroidal tertiary alkynyl acetates required reaction times of 96 h to acquire high yields. Secondly, the use of large quantities of Ag^+ salts very often resulted in the precipitation of silver acetylides during the reaction and workup, thus necessitating several tedious filtrations or extractions with CN^- to redissolve the propargyl ester and allow a reasonably clean purification procedure. Finally, the material thus obtained required lengthy purification by column chromatography with subsequent distillation or recrystallization.

We chose to perform the reaction in dichloromethane because of its high volatility and the similarity of its dielectric