Table XIX. Rate Data for (**8** + **15**) $\rightleftharpoons$ **16** Interconversion

temp, °C	10^5k_{-E}	10^7k_{obsd}	K^a	$10^7k_E{}^b$
219.0	0.883 ± 0.007	0.462 ± 0.004	0.0065	0.0465 ± 0.004
257.25	14.9 ± 0.1	16.7 ± 0.1	0.0119	16.9 ± 0.1
269.0	35.9 ± 0.2	49.8 ± 0.3	0.0141	50.5 ± 0.3
283.75	91.5 ± 0.3	163.8 ± 0.5	0.0173	166.6 ± 0.5
288.25	124.3 ± 0.5	239.9 ± 0.9	0.0183	244.3 ± 0.9
293.25	164.7 ± 0.5	345.2 ± 1.0	0.0195	352. ± 1.0

[a] K = **15**/**8**. [b] $k_E = k_{obsd}(1 + K)$.

Table XX. Equilibrium Ratios for the Perfluoro-1,3-pentadiene System

temp, °C	**8**	**15**	**16**
200.1	294.2	1.38	1
209.6	235.7	1.31	1
219.5	188.9	1.25	1
228.4	156.0	1.20	1
257.25	88.0	1.05	1
269.0	71.0	1.00	1
283.75	54.9	0.95	1
288.25	51.0	0.93	1
293.25	46.9	0.91	1

3387E potentiometer. The thermocouple was immersed in a well which was placed midway between the center of the two pyrolysis vessels. The temperature of the bath was controlled by using a Hallikainen (now Totco Instrument). Thermocontrol Proportional Controller with a platinum resistance probe. For low-temperature runs (below 160 °C), a similar apparatus was used: the pyrolysis vessels were immersed in silicon oil bath, with the Omega Proportioning Thermocontroller Model 49 with platinum resistance probe. The temperature was constant to 0.1 °C. Thermocouple-derived temperatures were calibrated with thermometers (Brooklyn Thermometer Co.). The thermocouple and thermometers temperatures were found to be close enough that any possible systematic error in the precision in reading of the temperature was found to contribute a smaller error than the standard deviation in the activation parameters.

The starting materials (perfluorodienes or/and perfluorocyclobutenes) were introduced into the pyrolysis vessels by expansion from the contiguous vacuum line. Initial pressure of kinetic runs varied between 4 and 12 mmHg of a starting material. The test runs at higher pressure of a starting material (25–30 mmHg) did not show any significant differences in obtained kinetic parameters.

Each kinetic pyrolysis run was sampled at least 6–8 times by removing a small fraction of the pyrolysis mixture by expansion into a small section of the vacuum line into a vessel, diluting with argon (total pressure ~400–500 mmHg), and removing to make multiple GLPC injections via a gas sampling valve. As indicated above, a Hewlett-Packard 5710A gas chromatograph in conjunction with a Hewlett-Packard 3380S integrator was used for all these analyses. Base-line resolution of peaks was observed under all GLPC quantitative studies. Each point in a rate constant is an average of at least three GLPC runs. Each rate constant plot contains at least six points, while all reported rate constants and activation parameters were derived by a linear least-square analysis of the experimental data, with each such analysis yielding a correlation coefficient of at least 0.999. Rate constants for the 2,4-hexadiene system are given in Tables XI–XIII, the 3,5-octadiene system in Tables XV and XVI, and the 1,3-pentadiene system in Tables XVIII and XIX. To determine the thermodynamic parameters, the thermal equilibria of investigated systems have been studied. The starting material was introduced to the reaction vessel and pyrolyzed for at least 10 half-lives, and then at least 3 independent samples of reaction mixture (within next 2 half-lives) were taken and analyzed. The equilibrium data were found to be identical despite the starting materials which have been used (perfluorodienes and appropriate perfluorocyclobutene). To determine the thermodynamic parameters for the above-described systems, the data at at least six different temperatures have been taken into consideration and derived by a linear least-squares analysis, yielding a correlation coefficient of at least 0.997. Equilibrium data for the three systems are provided in Tables XIV, XVII, and XX.

The gas sampling technique utilized in all of the above-described studies introduced multiple pressure variations per run. The fact that good unimolecular behavior was nevertheless always observed for over 5 half-lives indicates clearly the lack of significant surface effect problems. The kinetic apparatus as well as a technique utilized in determining rate constants is modeled after the apparatus and technique of Dr. H. M. Frey, University of Reading, England.

Acknowledgment. We gratefully acknowledge financial support of this research in part by the National Science Foundation (W.R.D., D.J.B.), the Air Force Office of Scientific Research, (D.J.B.), and the Petroleum Research Fund, administered by the American Chemical Society, (W.R.D.).

Registry No. 6, 89031-88-9; **7**, 105311-62-4; **8**, 105311-66-8; **9**, 83168-67-6; **10**, 83168-65-4; **11**, 83168-66-5; **12**, 105311-63-5; **13**, 105311-61-3; **14**, 105311-64-6; **15**, 105311-65-7; **16**, 105311-67-9; **17**, 89031-87-8; $F_2C{=}CFI$, 359-37-5; (*E*)-$F_3CCF{=}CFI$, 102682-82-6; (*Z*)-$F_3CCF{=}CFI$, 102682-81-5.

Anti, Vicinal Hydrogen–Hydrogen Interactions. A Fundamental Shift Effect in ^{13}C NMR Spectroscopy

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Abstract: The spatial disposition of two vicinal hydrogens in an anti stereochemical relationship contributes to a downfield shift for each of the carbon atoms involved. Applications of this shift effect to both configurational and conformational stereochemical analyses are discussed.

The dependence of ^{13}C NMR spectral shifts on the spatial position of γ substituents (the γ effect) represents one of the most powerful features of carbon NMR spectroscopy. Following the lead of key researchers in this area,[1–3] we have recently correlated in a highly precise fashion stereochemical and conformational properties of molecules with ^{13}C spectral data.[4,5] These results

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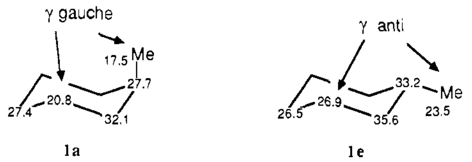
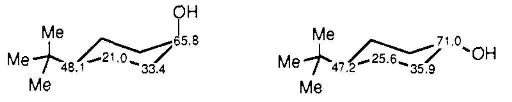
(1) Smith, D. H.; Jurs, P. C. *J. Am. Chem. Soc.* **1978**, *100*, 3316.



1a 1e

Figure 1.



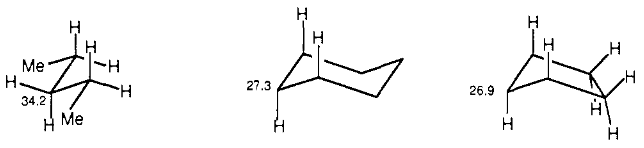
2 3

Figure 2.

in total represented precise predictions of carbon spectral data with a low overall average error (based upon known stereochemistry and either assumed or calculated conformational populations). However, predictions for a few examples fell out of line with observed spectral information. We have found that by taking into account a carbon shift effect due to the presence or absence of anti-related, vicinal hydrogens we can significantly improve our predictions and, as well, account for many otherwise unexplained phenomena observed in spectral differences between stereoisomers.

The archetypical example that illustrates the influence of the normal γ effect as well as anti, vicinal hydrogen interactions is the observed differences between the equatorial and axial conformational isomers of methylcyclohexane. In Figure 1 we have provided the spectral data for these isomers obtained at -90 °C (see Experimental Section). It can be seen that the chemical shift for both the methyl group and the ring carbons 3 and 5 are shifted dramatically upfield in the axial isomer as compared with the equatorial isomer. Further, there is also a large effect (in the same direction) on the absorptions for carbons 1, 2, and 6. It has been rationalized in the past that the carbon atoms that constitute γ-related termini of a gauche butane system are shifted upfield by a van der Waals repulsive interaction of the hydrogen atoms on these terminal carbons.[3] While the origin of this phenomenon has often been questioned, the semiempirical calculations carried out by Grant[6] come very close in predicting the magnitude of this shift when proper account is taken of the relative conformational populations of the gauche and anti forms of butane in solution.[7] Extensive applications in the past have made use of the γ effect to assign stereochemistry: in general, carbons that are sterically congested will be observed at higher field than those experiencing fewer such van der Waals interactions.

On the other hand, we are unaware of any explanation in the literature for the observed upfield shift of carbons 1, 2, and 6 in the axial conformer. In particular, it should be noted that the spatial relationships of the methyl groups and carbons 1 and 2 (and 6) in both conformers are precisely the same assuming bond lengths and bond angles are not dramatically different between the isomers. Thus, the upfield shifts noted cannot be due to the spatial relationships of the carbon atoms involved. On the other hand, the spatial relationships of hydrogens are different in the two conformers. In the equatorial isomer the sole hydrogen on carbon 1 is anti to hydrogens on both carbon 2 and carbon 6 (as well as one on the methyl group[8]), while in the axial conformer only one of the methyl group hydrogens is anti to the C-1 hydrogen. From a correlation of the chemical shift differences with the change in the number of anti hydrogen interactions, it would appear that each such interaction contributes approximately +3δ to the shift of each of the carbons bearing the hydrogen atoms involved.[9] In the case of the methylcyclohexane isomers, carbon 1 gains two such anti hydrogen–hydrogen (H–H) interactions in the progression from the axial to the equatorial isomer and is shifted downfield by 5.6. Only one additional anti hydrogen–hydrogen interaction is added for carbon 2 (as well as carbon 6) in the equatorial isomer, and thus this carbon is shifted downfield by only 2.8.

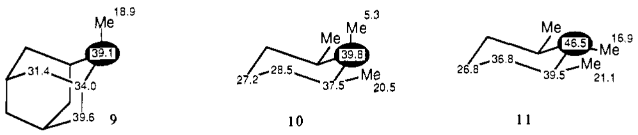


4 5 6

Figure 3.

7 8

Figure 4.



9 10 11

Figure 5.

The effect of H–H interactions on carbon chemical shift is apparent even when the substituents are not all carbon. Thus, the differences between the chemical shifts of the cis (**2**) and trans (**3**) isomers of 4-*tert*-butylcyclohexanol[10] for carbons 1 and 2 (4.2 and 2.5, Figure 2) correspond qualitatively with those noted above for the methylcyclohexane conformers. However, while the methyl group has 3-fold symmetry, the hydroxyl group does not, and the contributions to the chemical shift of carbon 1 from an anti H–H interaction need not be the same in **2** and **3**.

There are numerous other examples of the effect of anti hydrogens on carbon shifts. For example, the observed difference between the absorption of the central carbon of pentane (**4**, 34.2)[11] which bears two α- and two β-carbon substituents and each carbon of cyclohexane (**5**, 27.3)[11] which are similarly substituted has heretofore been unexplained (Figure 3). In the extended conformation of pentane, the two hydrogens on the central carbon are each anti to two other hydrogens (on carbons 2 and 4), while in chair cyclohexane each carbon bears only one hydrogen which is anti to two others on the neighboring carbon atoms. The loss of two anti hydrogen–hydrogen (H–H) interactions would be anticipated to lead to an approximately 6δ upfield shift, in reasonable agreement with the observed spectral difference of 6.9.

The slight upfield shift (26.9)[11] of cyclopentane relative to cyclohexane can be readily accounted for. Over the full energy surface for this molecule (envelope and half-chair), each of the carbons will spend some significant portion of time where at least

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(2) Beierbeck, H.; Saunders, J. K. *Can. J. Chem.* **1980**, *58*, 1258.

(3) Crandell, C. W.; Gray, N. A. B.; Smith, D. H. *J. Chem. Inf. Comput. Sci.* **1982**, *22*, 48. Shelley, C. A.; Munk, M. E. *Anal. Chem.* **1982**, *54*, 516. van de Ven, L. J. M., de Haan, J. W. *J. Phys. Chem.* **1982**, *86*, 2516. Gray, N. A. B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1982**, *15*, 201. Wiberg, K. B.; Pratt, W. E.; Bailey, W. F. *J. Org. Chem.* **1980**, *45*, 4936. Grant, D. M.; Dalling, D. K. *J. Am. Chem. Soc.* **1972**, *94*, 5318. Sergeev, N. M.; Subbotin, O. A. *Russ. Chem. Rev. (Engl. Transl.)* **1978**, *47*, 265. Booth, H.; Everett, J. R.; Fleming, R. A. *Org. Magn. Reson.* **1979**, *12*, 63.

(4) Whitesell, J. K.; Hildebrandt, B. *J. Org. Chem.* **1985**, *50*, 4975.

(5) Whitesell, J. K.; Lacour, T.; Lovell, R. L.; Pojman, P.; Ryan, P.; Yamada-Nosaka, A., submitted for publication in *J. Am. Chem. Soc.*

(6) Grant, D. M.; Cheney, B. V. *J. Am. Chem. Soc.* **1967**, *89*, 5315.

(7) Rosenthal, L.; Rabolt, J. F.; Hummel, J. *J. Chem. Phys.* **1982**, *76*(2), 817.

(8) The addition of an α substituent will generally add an additional anti H–H interaction. The effect of this interaction is of course accounted for in the normal, α substituent effect.

(9) While it is tempting to speculate on the physical significance of this spectral phenomenon in terms of actual orbital interactions, doing so would only divert attention from the very significant use of these observations in configurational and conformational analysis.

(10) Schneider, H.-J.; Hoppen, V. *J. Org. Chem.* **1978**, *43*, 3866.

(11) *Sadtler Standard Carbon-13 NMR Spectra*; Sadtler Research Laboratories: Philadelphia, Pa. 1976–1982.

Table I.

conformer	temp, °C	Me	C-1	C-2,6	C-3,5	C-4
av.	+24	23.0_7	33.3_5	36.0_1	26.9_8	26.8_7
av. (calcd[16])	+29	22.9_4	32.9_7	35.6_3	26.6_0	26.6_2
eq.	−70	23.4_8	33.2_9	35.7_2	26.9_3	26.5_7
eq.	−90	23.5_0	33.2_4	35.6_2	26.8_6	26.5_2
eq. (calcd[16])	+29	23.2_0	33.2_4	35.8_0	26.9_0	26.5_8
ax.	−90	17.4_6	27.6_8	32.0_7	20.8_4	27.3_6
ax. (calcd[16])	+29	17.5_3	27.8_1	32.4_0	20.8_2	27.3_6

one of the adjacent carbons is in an eclipsed conformational arrangement with no anti hydrogen interactions possible. In certain conformationally fixed and rigid arrays, adjacent carbons are locked into eclipsed arrangements where no such interactions are present. For example, in norbornane (**8**, Figure 4), the bond between carbons 2 and 3 (and 5 and 6) is eclipsed and there are no anti H–H interactions for either of these carbons. Thus, the shift of these carbons at 29.6[12] is found significantly upfield from an appropriate carbon of a similarly substituted five-membered ring compound (carbon 2, methylcyclopentane, 35.1[11]). There would be two anti H–H interactions for carbon 2 of methylcyclopentane, whereas there were none in norbornane, and the loss of two such interactions should contribute 6δ to an upfield shift of the latter, a prediction quite close to the observed difference of 5.5.

In the analysis carried out above, it was assumed that the differences between the spectral shifts for axial and equatorial methylcyclohexane were not due to changes in either bond lengths or bond angles. While such changes might indeed be expected to go hand in hand with the steric interactions, appropriate comparisons rule out these factors as being responsible for the spectral differences noted above. For example, compare the indicated carbons for 2-methyladamantane (**9**) and all *cis*-1,2,3-trimethylcyclohexane (**10**) (Figure 5). In each compound the carbon has the same number of α (two) and β (two) substituent carbon atoms as well as anti hydrogen interactions (none). However, in the former, the methyl group experiences two gauche-butane-like interactions, while the methyl group on the indicated carbon in the latter has four. Thus, while the steric congestion is obviously much greater in the latter compound, as is evident in the chemical shift difference between the methyl groups (18.9[13] vs. 5.3[14]), the shifts for the carbons *bearing* the methyl groups are essentially identical (39.1 vs. 39.8). By contrast, the indicated carbon of the diastereomer **11** is substituted similarly to carbon 2 in 2-methyladamantane, *and* the methyl group experiences the same number of gauche interactions (two). Nonetheless, the spectral shift[14] for **11** is 7.4δ downfield from that for **9** due to the presence of two anti H–H interactions present in **11** that are absent in **9**.

Parameters that have been developed in the past to account for varying effects of substituents may be in fact the result of the effect that added groups have on the number of anti H–H interactions. For example, most systems for predicting carbon-13 spectral shifts incorporate an upfield correction for adjacent, highly substituted carbons, an effect rationalized on the basis of steric interactions. However, increased substitution, by default, decreases the number of adjacent hydrogens and thus the number of H–H interactions. In the progression from methylcyclohexane to *tert*-butylcyclohexane (**12**–**15**) by successive additions of three methyl groups, the effects of each additional methyl on carbon 1 are +6.8, +4.6, and +4.2.[11] The addition of the first methyl group (forming ethylcyclohexane) has little effect on the number of anti H–H interactions for C-1 since the conformation for ethylcyclohexane (A) that retains an anti H–H interaction is favored 8:1 over the mirror symmetric arrangement (B) by both enthalpy (0.84 kcal/mol, MM-2) and entropy of mixing (Figure 6). Thus, the 6.8δ shift-of-shift represents solely the effect of one additional β substituent for a tertiary carbon. On the other hand, the conformers C and D for isopropylcyclohexane do not differ in enthalpy, and thus C would be approximately twice as populated as D (favored again by entropy). Thus, the addition of the methyl group to ethylcyclohexane reduces the downfield effect on C-1 from anti H–H interactions, resulting in a smaller net effect for the additional β substituent (+4.6). The addition of the last methyl group to form *tert*-butylcyclohexane removes all of the remaining anti H–H interaction of C-1, with the side chain resulting in a further diminished β effect (+4.2).

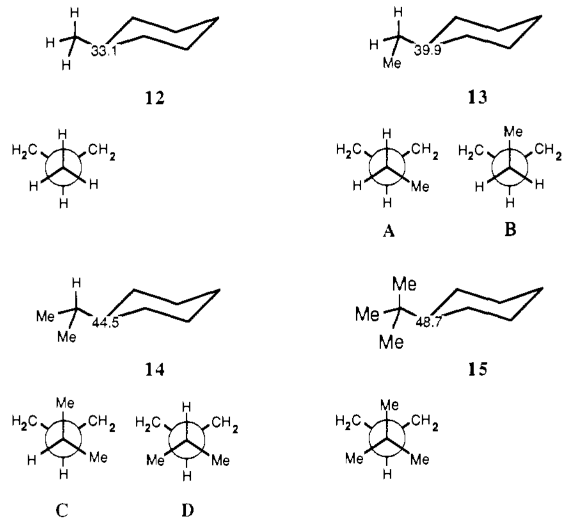

Figure 6.

Overall, we feel that interpretation of stereochemical factors on carbon chemical shifts can now be made with much greater precision based on the application of this newly uncovered phenomenon of H–H interactions in combination with the established, γ-gauche interaction.

Experimental Section

Observation of Axial and Equatorial Methylcyclohexane. Samples of methylcyclohexane and dichloromethane-d_2 were obtained from two sources. MCB practical grade methylcyclohexane was washed with sulfuric acid, neutralized with sodium carbonate, filtered through alumina, and doubly distilled through a spiral wire column, a center cut being used. An 80% v/v solution of this material in KOR Isotopes CD_2Cl_2 containing tetramethylsilane was examined by using a 10-mm NMR tube. The second sample was Aldrich Gold Label methylcyclohexane, used as received. This was diluted to an 80% v/v solution in Aldrich CD_2Cl_2 containing tetramethylsilane and examined in a 5-mm NMR tube. Spectra were recorded on a General Electric GN-500 instrument at 125 MHz using 32K data points and a sweep width of ±7576 Hz. Temperature measurement was calibrated by using the methanol chemical shift thermometer[15] down to −60 °C and extrapolated to lower temperatures.

The ^{13}C NMR spectrum of methylcyclohexane in CD_2Cl_2 is noticeably broad at −45 °C. At −70 °C a new set of sharp resonances for the equatorial conformer has appeared, accompanied by another set of very low-intensity, still broad peaks. Not until −90 °C do these weak lines become completely sharp. The chemical shifts observed at various temperatures are given in Table I. The set of minor resonances agrees very well with the values calculated for axial methylcyclohexane, when long-

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(12) Stothers, J. B.; Tan, C. T. *Can. J. Chem.* **1973**, *51*, 2893.

(13) Duddeck, H.; Hollowood, F.; Karim, A.; McKervey, M. A. *J. Chem. Soc., Perkin Trans. 2* **1979**, 360.

(14) Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 5318. Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 6612.

(15) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227.

range effects and the difference in temperature and solvent are taken into account.[16-18] These peaks are not likely due to impurities, satellites, or spinning side bands since they are not present in the room-temperature spectrum run under identical conditions. From the Lorentzian heights of corresponding peaks for the two conformers, the amount of axial present at −90 °C was calculated to be 0.45–0.50%, in excellent agreement with previous results.[19] The small temperature effects observed for equatorial methylcyclohexane between −70 and −90 °C are also in agreement with results for similar systems.[17]

The excellent agreement between these directly observed shifts for the axial conformer and those predicted from spectral data for dimethylcyclohexanes[16] firmly establishes the use of ^{13}C NMR for the study of conformational behavior of cyclic systems.

Acknowledgment. We thank B. A. Shoulders for helpful discussions and S. Sorey for running the spectra. Financial support of this research by grants from the National Institute of Health (GM-31750), the Robert A. Welch Foundation (F-626), and the National Science Foundation Instrumentation Program is gratefully acknowledged.

Registry No. 19, 108-87-2; **2**, 937-05-3; **3**, 21862-63-5; **4**, 109-66-0; **5**, 110-82-7; **6**, 287-92-3; **7**, 96-37-7; **8**, 279-23-2; **9**, 700-56-1; **10**, 1839-88-9; **11**, 1678-81-5; **13**, 1678-91-7; **14**, 696-29-7; **15**, 3178-22-1.

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[16] Vierhapper, F. W.; Willer, R. L. *Org. Magn. Reson.* **1977**, *9*, 13.

[17] Schneider, H.-J.; Freitag, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 478.

[18] van de Ven, L. J. M.; de Haan, J. W. *J. Phys. Chem.* **1982**, *86*, 2516, and references cited therein. Especially: Tiffon, B.; Doucet, J.-P. *Can. J. Chem.* **1976**, *54*, 2045.

[19] Subbotin, O. A.; Sergeyev, N. M.; Chlopkov, V. N.; Nikishova, N. G.; Bundel', Y. G. *Org. Magn. Reson.* **1980**, *13*, 259.

Acetylenic Esters. Preparation and Mechanism of Formation of Alkynyl Tosylates and Mesylates via Tricoordinate Iodonium Species

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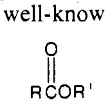
Abstract: The preparation and characterization of the first acetylenic esters of any kind (alkynyl tosylates, RC≡COTs, and mesylates, RC≡COMs) is reported. A simple, two-step procedure, starting from commercially available iodosobenzene diacetate, was employed in the synthesis. The final step involved ligand–ligand coupling in a tricoordinate iodonium species, $C_6H_5I(OTs)C{\equiv}CR$, via metal complexing. X-ray data indicate an ionic structure for the precursor alkynylphenyliodonium tosylate, $C_6H_5I^+C{\equiv}CC_6H_5{\cdot}{}^-OTs$. A metal assisted nucleophilic acetylenic displacement, via an addition–elimination process, is suggested as the most likely mechanism for this novel main group ligand–ligand coupling reaction.

Esters of all types, carboxylate **1**, sulfonate **2**, and phosphate **3**, are ubiquitous and play a key role in organic as well as biochemistry.[1] Likewise, their unsaturated counterparts, enol esters **4–6**, are well-known, important, and widely used in synthetic as well as mechanistic organic chemistry and biochemistry. Surprisingly, despite the importance and wide uses of esters, simple acetylenic esters of any kind, carboxylate **7**, sulfonate **8**, or phosphate **9**, are, to our knowledge, unknown. This is all the more puzzling, since a wide variety of functionalized acetylenes **10** with diverse substituents are well-known and generally stable.[2]

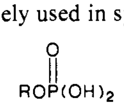


$RC(=O)OR'$

1

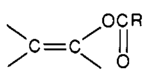
$ROSO_2Ar$

2



$ROP(=O)(OH)_2$

3



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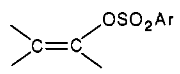

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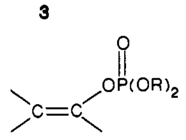

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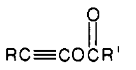
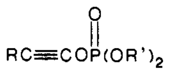


$RC{\equiv}COC(=O)R'$

7

$RC{\equiv}COSO_2Ar$

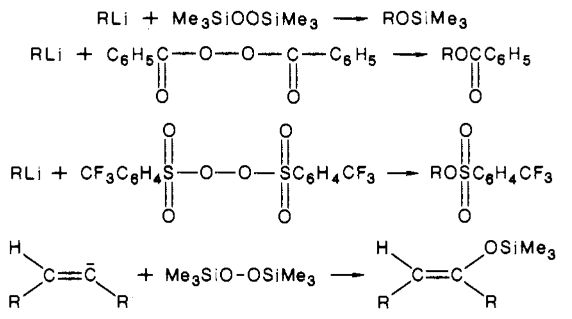
8



$RC{\equiv}COP(=O)(OR')_2$

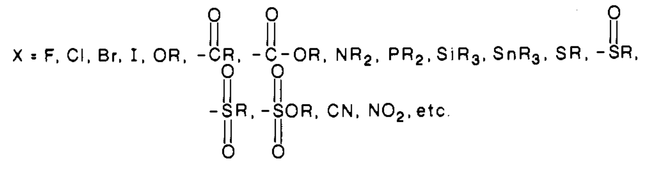
9

Scheme I



$R{-}C{\equiv}C{-}X$

10



$X = F, Cl, Br, I, OR, -C(=O)R, -C(=O)-OR, NR_2, PR_2, SiR_3, SnR_3, SR, -S(=O)R, -S(=O)_2R, -S(=O)_2OR, CN, NO_2,$ etc.

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