phorane (0.01 mol) in dioxane (50 ml) was refluxed for 17 hr The dioxane was evaporated under reduced pressure. The residue was recrystallized from ethyl acetate–methylene chloride to give analytically pure material.

Attempted Reaction of Phosphonium Ylides (3a, 3c, and 5b) with Aldehydes.—The reaction of **3a**, **3c**, and **5b** with benzaldehyde, *p*-nitrobenzaldehyde, and *p*-chlorobenzaldehyde was investigated in dioxane and benzene at reflux temperatures and room temperature for periods as long as 24 hr. In all cases the starting material was recovered. Extensive decomposition of the ylide took place when the reaction was run in DMF at 130°.

Registry No.—**1**, 1099-45-2; **2a** (R = Ph), 102-96-5; **2b** (R = *p*-F–Ph), 706,08-1; **2c** (R = 1-naphthyl), 4735-49-3; **2d** (R = 2-thienyl), 874-84-0; **3a** (R = Ph), 37709-90-3; **3b** (R = *p*-F–Ph), 37709-91-4; **3c** (R = 1-naphthyl), 37709-92-5; **3d** (R = 2-thienyl), 37709-93-6; **4a** (R = H), 118-48-9; **4b** (R = Me), 10328-92-4; **5a** (R = H), 37709-95-8; **5b** (R = Me), 37709-96-9.

Planarity of the Carbon Skeleton in Various Alkylated Olefins

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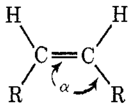
The planarity and extent of bond angle deformation in an alkene is of increasing interest to both the theoretical and the experimental chemist. In principle, a carbon–carbon double bond may experience both inplane nonbonded repulsions, **1**, and out-of-plane "torsional strain,"[1] **2**, as a result of steric interactions. The strain in an alkene has traditionally been estimated experimentally from thermochemical data.[1,2] More recently, the force field method of calculation has been found to give reliable estimates of the strain energy and the structure of a variety of alkenes.[3]



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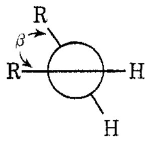

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Though the quantitative interpretation of photoelectron spectra almost always follows from a previous knowledge of the molecular geometry, in specific cases this can be reversed,[4] and we here offer several examples of this approach to the determination of certain gross geometric features of various alkylated olefins. Very briefly, the basic idea behind our work is that the π ionization potential of an olefin (or polyene) will depend strongly on the coplanarity of the $2p\pi$ AO's, and that twists in the π system of a particular molecule can be revealed by comparing its π-electron ionization potentials with that of a related standard molecule known to be planar. A semiquantitative estimate of the twist angle can be obtained if we then apply the theoretically determined curve of ionization potential *vs.* twist angle derived for ethylene.[5] According to this theoretical curve, the ionization potential of planar ethylene decreases by 3.24 eV on going to the form twisted by 90°.[6]

Recently, Harvey and Nelson[7] showed that the Raman spectrum of perfluoropropene was characteristic of a molecule having a plane of symmetry, in contrast to the report of Bauer and Chang,[8] who studied this molecule by electron diffraction and concluded that it is twisted by 40° about the C=C bond. Several other molecules of this sort were also reported to be twisted according to the diffraction study; the largest twist was reported for *cis*-perfluorobutene-2, 60 ± 2°. We can test this claim by comparing the ionization potentials of a series of cis and trans alkenes, which then leads indirectly to the degree of out-of-plane deformation of the double bond in the crowded isomer.

The photoelectron spectra of *cis*- and *trans*-butene-2 (Figure 1) understandably look very much alike since both molecules are planar[3,9] and differ only in the relative orientation of the ends, which are noninteracting. Note especially that the π ionization potentials at 9.29 and 9.32 eV (vertical) are very nearly equal. Extrapolating to the perfluorobutenes, the spectra will again resemble one another closely for the two planar isomers, but, at intermediate angles of twist about the central bond, the π-bond order is reduced, and the π ionization potential will decrease. According to the curves of Merer and Mulliken,[5] a twist of 60° will reduce the π ionization potential by 1.5 eV. In the same twisted olefin, the $\pi \rightarrow \pi^*$ interval in the optical spectrum will also decrease greatly over that in the planar configurations.

In Figure 1, we also show the photoelectron spectra of *cis*- and *trans*-perfluorobutene-2 and notice immediately that the two vertical π ionization potentials are again virtually identical at 11.46 and 11.55 eV, respectively. We take this result to show that both molecules are planar, or very nearly so (±10°). The optical spectra of the two isomers show $\pi \rightarrow \pi^*$ absorption maxima at 1640 (trans) and 1650 Å (cis) again indicating that the π-bonding strength is very nearly equal in the two systems. The π ionization potentials in the perfluoromethyl series seem to vary in a regular way, without any suggestion of nonplanarity in the carbon skeleton. Thus, the vertical π ionization potentials of perfluorotetramethylethylene, *cis*- and *trans*-perfluorobutene-2,

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(1) For a general review of strained alkenes, see N. S. Zefirov and V. I. Sokolov, *Russ. Chem. Rev.*, **36**, 87 (1967).

(2) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, Elmsford, N. Y., 1962.

(3) N. A. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, **94**, 5734 (1972).

(4) See, for example, C. R. Brundle and M. B. Robin, *ibid.*, **92**, 5550 (1970).

(5) A. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

(6) Actually, the Mulliken–Roothaan diagram relates the total energy to the angle of twist, always at the ground state C–C distance. The molecule, of course, will increase this distance in the excited ionic state, but, by the usual line of reasoning, the energy which most closely represents the transition in the fixed geometry of the ground state will have the maximum Franck–Condon factor, *i.e.*, the vertical ionization potential.

(7) A. B. Harvey and L. Y. Nelson, *J. Chem. Phys.*, **55**, 4145 (1971).

(8) S. H. Bauer and C. H. Chang, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Paper Phys. 14.

(9) A. Almenningen, I. M. Anfinsen, and A. Haaland, *Acta Chem. Scand.*, **24**, 43 (1970).

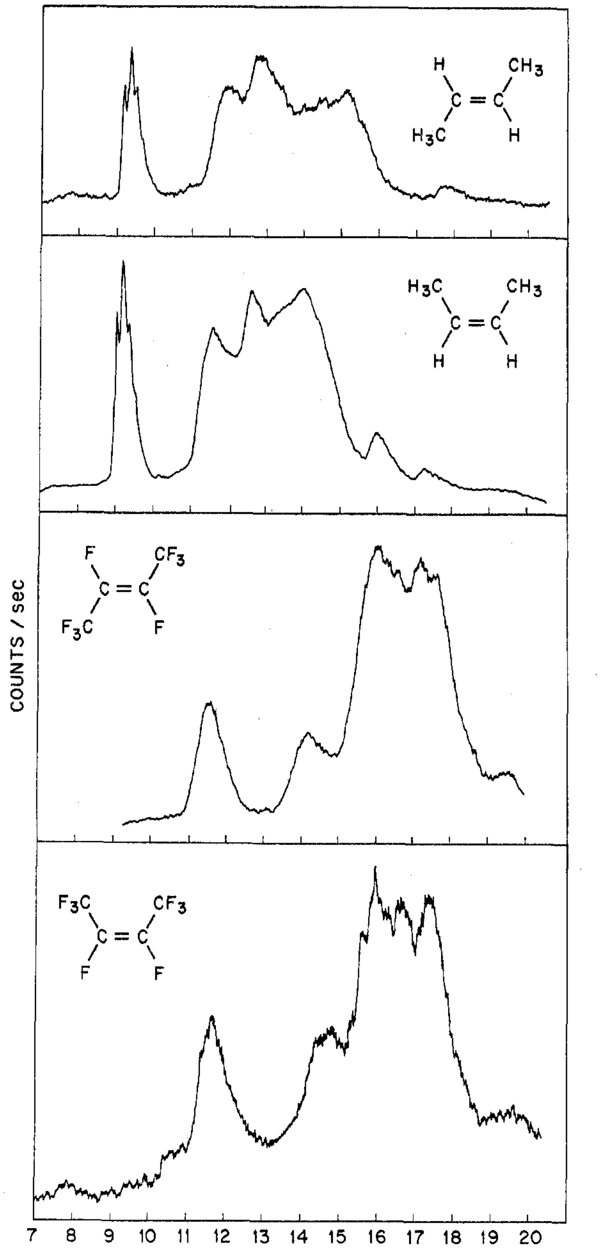

Figure 1.—Comparison of the He(I) photoelectron spectra of *cis*- and *trans*-butene-2 and their perfluoro derivatives.

and tetrafluoroethylene are 12.61, 11.46, 11.55, and 10.52 eV, respectively.

A second pair of molecules amenable to this type of study are *cis*- and *trans*-1,2-di-*tert*-butylethylene, the photoelectron spectra of which are shown in Figure 2. Offhand, we would expect the cis molecule to be sterically hindered and therefore twisted about the C=C double bond, whereas the trans isomer is expected to be planar. In fact, Demeo and El-Sayed[10] have already studied the photoionization thresholds of these molecules and having found that of the cis isomer to be 0.05 eV below that of the trans isomer concluded that the cis isomer was nonplanar. Our photoelectron spectra show the energetics of the ionization process more clearly (Figure 2, insert), from which it is seen that the vertical ionization potentials of the two isomers are essentially identical (8.95 eV, cis; 8.89 eV, trans), with that of cis actually somewhat higher than that of trans. It is also of interest that the $\pi \rightarrow \pi^*$ vertical excitation wavelengths are virtually identical in the two isomers of di-*tert*-butylethylene (1830 Å; cis; 1840 Å, trans).[11] We conclude that the strain in the cis molecule is not manifested as an appreciable twist (torsional strain) about the C=C double bond, but rather in the form of in-plane distortions. In support of this suggestion two calculations on the geometry of *cis*-1,2-di-*tert*-butylethylene have appeared[1,12] that agree on a value of 136° for the C=C—R bond angle (α in **1**). More recent force field calculations[3] also suggest that *cis*-1,2-di-*tert*-butylethylene is almost planar with the allylic carbon atoms being only 0.03 Å above and below the nodal plane of the π orbital.

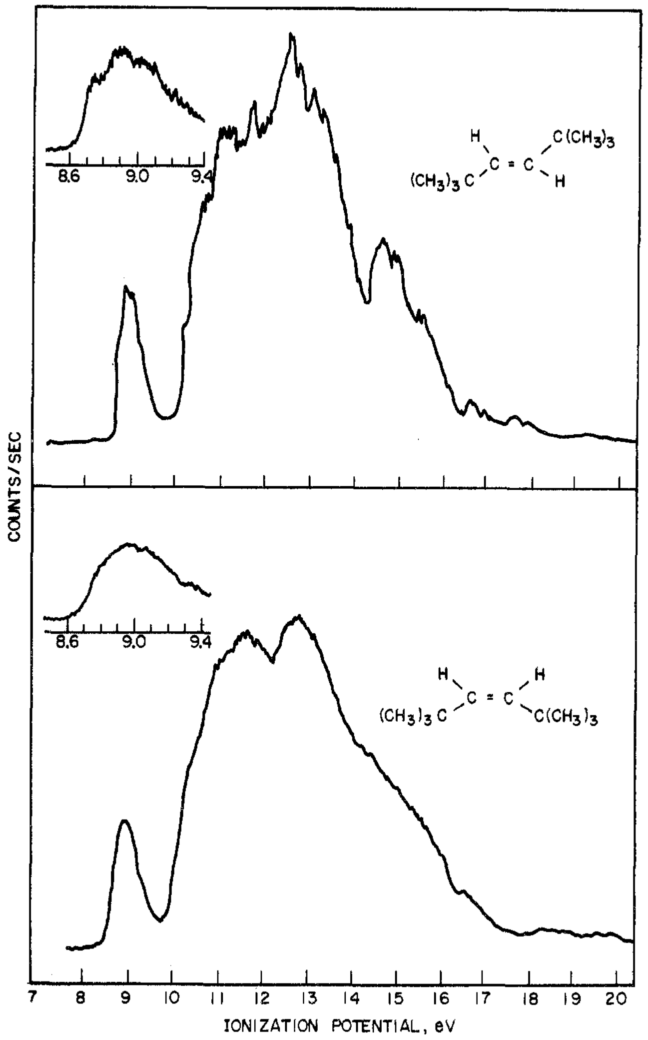

Figure 2.—He(I) photoelectron spectra of *cis*- and *trans*-di-*tert*-butylethylene.

Numerous earlier optical studies on *trans*-cyclooctene have been based on the assumption that the double bond is an inherently dissymmetric chromophore, the twist (β in **2**) typically being assumed to be in the range of 5–20°.[13] As a test of this idea, we have recorded the photoelectron spectra of *cis*- and *trans*-cyclooctene (Figure 3). The π ionizations in each of the isomers is a broad band, but with a clearly defined (0,0) spike

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[10] D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970).

[11] G. J. Abruscato, R. G. Binder, and T. T. Tidwell, *J. Org. Chem.*, **37**, 1787 (1972).

[12] E. H. Wiebenga and E. Bouwhuis, *Tetrahedron*, **25**, 453 (1969).

[13] C. C. Levin and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 3446 (1972).

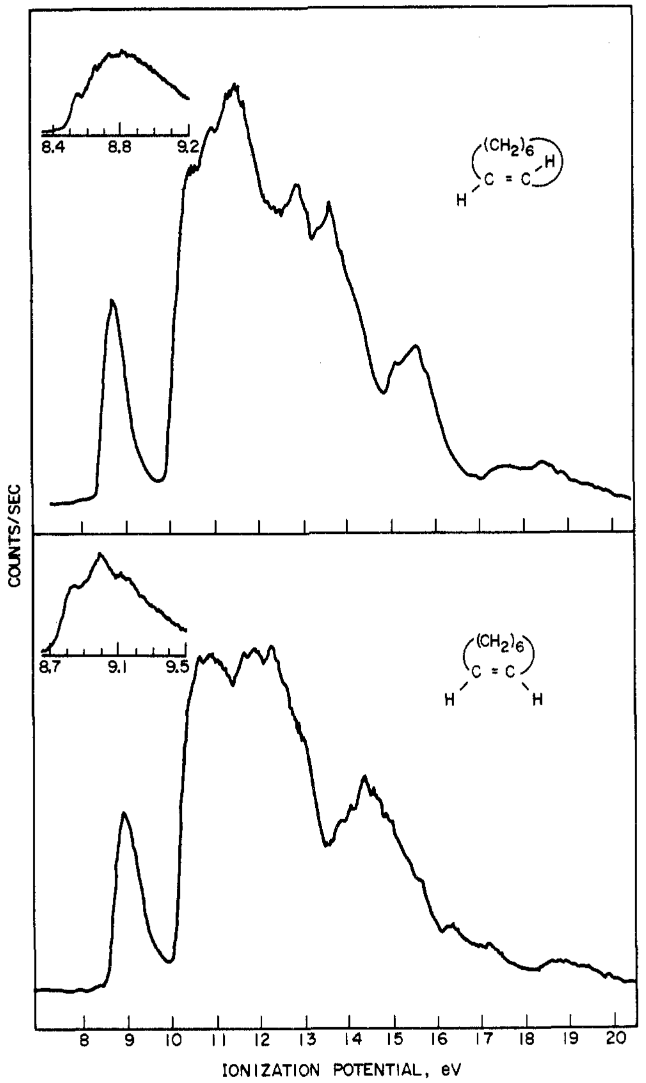

Figure 3.—He(I) photoelectron spectra of *cis*- and *trans*-cyclooctene.

(Figure 3, insert). The ionization potential of the trans isomer is 0.29 eV lower than that of the cis as measured by the positions of the (0,0) bands, and *ca.* 0.2 eV lower as measured by the approximate positions of the band maxima. Using the Mulliken diagram for ethylene and assuming that the 0.29 eV lowering of the trans ionization potential is due solely to twisting, we get a twist angle of 20 ± 3°, which is within the range of previous estimates for this quantity. This result is also in good agreement with the results of a force field calculation[3] in which the angle β between the π atomic orbitals is calculated to be 16.3°.

The present study demonstrates that the strain energies of *cis*-di-*tert*-butylethylene (10.5 kcal/mol)[14] and of *trans*-cyclooctene (9.2 kcal/mol)[15] are not necessarily indicators of the nonplanarity of these olefins. Consequently, any such structural assignments based solely on strain energies are suspect. The conclusions derived from these simple experiments must now be confirmed by more sophisticated measurements. If they are confirmed, and we think they will be, then medium resolution photoelectron spectroscopy will have been shown to be of unsuspected value in the gas phase structure determination of sterically crowded molecules such as olefins, dienes, biphenyls, etc.[16]

Registry No.—*trans*-2-Butene, 624-64-6; *cis*-2-butene, 590-18-1; *trans*-perfluorobutene-2, 1516-64-9; *cis*-perfluorobutene-2, 1516-65-0; *trans*-di-*tert*-butylethylene, 692-48-8; *cis*-di-*tert*-butylethylene, 692-47-7; *trans*-cyclooctene, 22770-27-0; *cis*-cyclooctene, 931-87-3.

Acknowledgment.—It is a pleasure to thank Professors S. H. Bauer, T. T. Tidwell, and L. S. Bartell for several of the samples used in this study.

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(14) J. D. Rockenfeller and F. D. Rossini, *J. Phys. Chem.*, **65**, 267 (1961).

(15) R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, **79**, 4133 (1957).

(16) Note Added in Proof.—Professor Bauer has recently informed us that the electron diffraction work of his group on the fluorinated olefins in many cases yielded incorrect structures due to convergence to false minima. In *cis*-perfluorobutene-2, the revised dihedral angle is now quoted as equal to or less than 6°, in agreement with the photoelectron spectra. (S. H. Bauer Third Biannual Conference on Molecular Structure, Austin, Tex., Feb 1972).

2-Imino-4-methyleneoxazolidines from the Reaction of Propargyl Alcohols and Carbodiimides

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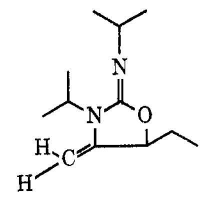
The formation of pseudoureas from the reaction of alcohols and carbodiimides, catalyzed by cuprous or cupric chloride, is well known.[1] Allyl alcohol and diisopropylcarbodiimide give *O*-allyl-*N*,*N'*-diisopropylpseudourea;[2] an analogous reaction of propargyl alcohol has not been reported. In the course of some earlier studies of propargyl alcohols, we investigated their reaction with carbodiimides.

The reaction of ethylethinylcarbinol with diisopropylcarbodiimide in the presence of cuprous chloride was slightly exothermic. Distillation gave a product which could be assigned structure **1** based on the spectral data. The presence of a terminal methylene group in the nmr spectrum (see Table I) and lack of an NH or C≡CH moiety in infrared or nmr spectra excludes several possible structures which could be written *a priori* except **1** and **2**. The intense uv absorption maximum at 238 mμ, a pK_a of 9.4, and the ability to form salts lend support to structure **1**, 2-isopropylimino-3-isopropyl-4-methylene-5-ethyloxazolidine.



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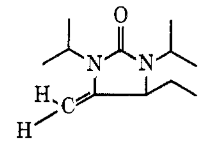

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This facile reaction had thus provided a new entry into the iminooxazolidine class of compounds. Previous syntheses of iminooxazolidines and their deriva-

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(1) F. Kurzer and K. Douraghi-Zadeh, *Chem. Rev.*, **67**, 107 (1967).

(2) E. Schmidt, E. Däbritz, K. Thulke, and E. Grassmann, *Justus Liebigs Ann. Chem.*, **686**, 161 (1965).