The increased acidity of protons on carbon atoms which are attached to a tricarbonylchromium-complexed benzene ring is analogous to the increased acidity of protons on carbon atoms which are attached to ferrocene systems[6] or rhodium-complexed cyclopentadienides.[7] The intermediate tricarbonylchromium-complexed benzyl anion could involve the interaction of all 8π electrons with the tricarbonylchromium moiety, but the chromium atom would not have an inert gas electronic configuration. Alternatively, fluxional isomers[8] of the intermediate anion, which would use only 6π electrons of the benzyl group, could be involved. The neutral tricarbonylchromium complex of cyclooctatetraene has been shown to consist of fluxional isomers which bind only 6π electrons to the metal.[9] Moreover, several complexes of benzene are known in which only part of the π electrons of the benzene ring are united with the metal. For example, tricarbonyliron complexes of vinylarenes have the isolated double bond and only one pair of π electrons from the benzene ring complexed with the iron.[10]

We feel that the *anti*-benzylic protons of the tricarbonylchromium-complexed indan system are preferentially removed because the back lobes of the sp^3 orbitals of the benzylic carbon atoms which form the bonds to the anti protons are closer to the chromium atom than are the front lobes of the sp^3 orbitals which form the bonds to the syn protons, and thus participation of the chromium moiety should be easier when an anti proton is removed instead of a syn proton.

Alternatively, an adverse steric effect between the tricarbonylchromium group and the base could account for the exclusive exchange of the anti protons.

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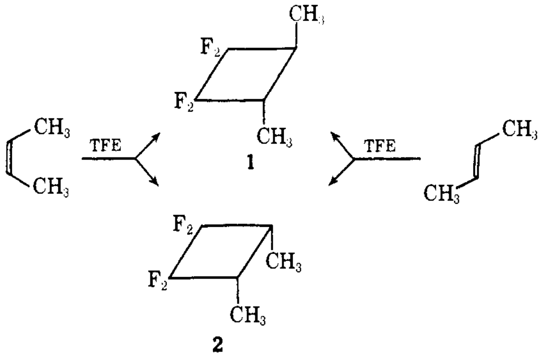
Cycloaddition of Tetrafluoroethylene to *cis*- and *trans*-2-Butenes

Sir:

Comparison of 2-butene with ethylene[1] in cycloaddition affords an informative calibration point for the initiation and stereochemical course of a simple biradical mechanism.

Tetrafluoroethylene (50 g), *cis*-2-butene (125 g), and a small amount of hydroquinone were heated, after degassing, to 175° for 14 hr in a 540-ml steel bomb under autogenous pressure. The product was separated by distillation from about 0.8 g of high-boiling liquid and distilled through a short Vigreux column. The product, boiling at 86°, was obtained in a yield of 8 g (10% based on TFE). From a similar preparation with *trans*-2-butene the yield, same boiling point, was 12 g (15%). Vapor-phase chromatography at 100° on a 20-ft column of tricresyl phosphate showed only two components in each product, in the ratio 58.2:41.8 from the *cis*- and 72.0:28.0 from the *trans*-2-butene. The isomers of the product were separated by preparative glpc at 80° on a 13.5-ft column of 20% Carbowax 20M. The trans isomer **1**, of shorter retention time and 3.5° lower boiling point, showed a multiplet in the nmr centered at τ 7.78 (2 H) and a finely split doublet at 8.83 (J = 6 Hz, 6 H); ir peaks at 3146 (m), 1445 (m), 1374 (s), 1312 (m), 1245 (m), 1194 (s), 1154 (s), 1126 (sh), 1090 (m), 1044 (sh), 1023–1017 (s), 978 (m), 920 (s), 748 (w), 691 (w) cm^{-1}. The cis cycloadduct **2** had an nmr spectrum with a multiplet centered at τ 7.23 (2 H) and a finely split doublet at τ 8.95 (J = 6 Hz, 6 H); ir 2977 (w), 1454 (m), 1387 (s), 1365 (s), 1297 (m), 1275 (m), 1224–1211 (s), 1168 (s), 1135–1126 (s), 1040 (m), 1004 (sh), 985 (sh), 980 (s), 918 (m), 774 (w), 696 (w) cm^{-1}. Both isomers of the cycloadduct had identical mass spectra, with very weak parent peaks.

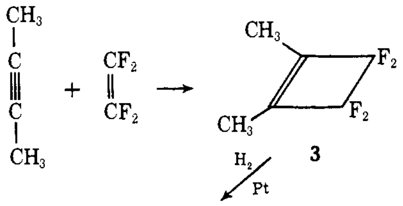


1

2

During the reaction of *cis*-2-butene, the trans isomer, initially 0.3%, increased to 5.9% in the recovered olefin. During reaction of the *trans*-2-butene the cis isomer, originally 0.1%, increased in the recovered olefin to 3.1%. *cis*-2-Butene, heated for 14 hr under the conditions of the cycloadditions, underwent no isomerization.

1,2-Dimethyl-3,3,4,4-tetrafluorocyclobutene (**3**) was prepared in 5% yield by the cycloaddition of 2-butyne to tetrafluoroethylene, heated in the bomb for 18 hr at 200°; bp 103°. A glpc-purified sample gave an nmr spectrum consisting of a single finely split singlet at τ 8.17. Catalytic hydrogenation with platinum oxide in acetic acid followed by preparative chromatography on Carbowax 20M yielded a product identical with **2** by nmr, ir, and glpc retention time.



3

2

In a competition experiment 2.74 g of ethylene, 9.96 g of tetrafluoroethylene, and 11.64 g of *cis*-2-butene were condensed into a 215-ml high-pressure reaction vessel,

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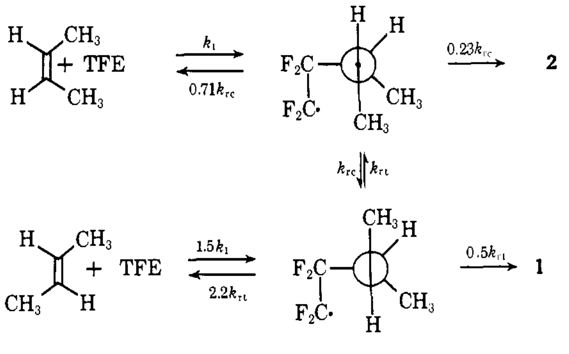
which was held at 150° for 8.5 hr. After the reaction was over, glpc analysis of the cycloadducts showed that the ratio $k_{\text{ethylene}}/k_{\text{butene}}$ was 10.2 ± 0.3.

The cycloaddition of 2-butene and tetrafluoroethylene shows two features characteristic of stepwise reactions with biradical intermediates: partial loss of configuration in the products,[2a] and geometrical isomerization of a reactant during, and only during, cycloaddition.[3,4] The formulation of this cycloaddition involves eight rate constants (Scheme I). The information reported here allows us to express these in terms of the three constants k_1, k_{rc}, and k_{rt}. By methods previously described,[2ab] the retention ratios $p = 41.8/58.2 = 0.72$, $q = 72/28 = 2.57$, and $pq = 1.85$ lead to $0.23k_{\text{rc}}$ as the rate constant for ring closure to **2** and $0.5k_{\text{rt}}$ the rate constant for ring closure to **1**. In view of the low conversion to product and small fraction of isomerization we neglect the "recycle" effect of product formation from preisomerized olefin, and note that *cis*-2-butene gave 0.129 mol of trans olefin and 0.0298 mol of **1**, indicating that the rate constant for cleavage that competes with closure to **1** is equal to $(0.129/0.0298)0.5k_{\text{rt}} = 2.2k_{\text{rt}}$. Since *trans*-2-butene gave 0.0667 mol of *cis*-2-butene and 0.0125 mol of **2**, the cleavage that competes with closure to **2** has a rate constant of $(0.0667/0.0215)\cdot 0.23k_{\text{rc}} = 0.71k_{\text{rc}}$, as shown in Scheme I.

Scheme I



The competition between ethylene and 2-butene is analogous to that between butadiene and 2,4-hexadiene, previously investigated[5] at 80°. The relative rates of addition of 1,1-dichloro-2,2-difluoroethylene ("1122") to one double bond of butadiene, *trans*-piperylene, and *trans,trans*-2,4-hexadiene are 1.0, 1.65, and 0.046. The enhancement due to the methyl group on the allylic system in the biradical is much less than the hindrance imposed by the methyl group at the site of the first bond formation. The overall factor of 10 between ethylene and 2-butene at 175° seems quite in accord with the factor of 22 at 80° between butadiene and 2,4-hexadiene. By contrast, in the concerted Diels–Alder reaction, methyl substitution at the ends of the conjugated system brings about an *increase* in reaction rate (12-fold toward maleic anhydride at 175°[6]).

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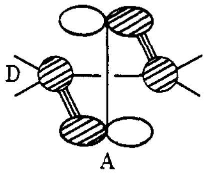
Nonstereospecific Cycloaddition of Tetrafluoroethylene to Ethylene-*1,2*-d_2

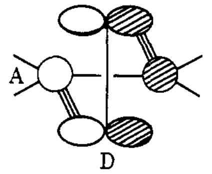
Sir:

Concerted (2 + 2) cycloaddition of alkenes from the ground state is required by the orbital symmetry rules to be suprafacial, retaining configuration, in one component and antarafacial, inverting configuration, in the other $(2_s + 2_a)$.[1] Although molecular rearrangements have been observed with inversion of the migrating group,[2] the only examples of the $(2_s + 2_a)$ cycloaddition mechanism observed to date have involved antarafacial components of special character, *i.e.*, ketenes or allenes, linear systems in which one carbon atom has no protruding substituents to hinder close approach to its reaction partner. The evidence for the mechanism[3] is so convincing as to pose the intriguing question whether any alkene pair exists with low enough barriers to approach and twisting to yield a concerted cycloaddition with inversion at one member of the pair. The most unhindered alkene would appear to be ethylene itself, and the question of what happens to the configuration of *cis*- or *trans*-1,2-dideuterioethylene (**2**) during cycloaddition deserves examination.

Theory affords an imperfect guide to the choice of a reaction partner most likely to make ethylene add antarafacially. In terms of the usual correlation diagrams, two interactions are equally important: **1a**, in which the π orbital of the suprafacial component and π^* of the antarafacial component interact to yield the new orbital combination $\sigma_1 + \sigma_2$, and **1b**, in which π^* of the suprafacial component and π of the antarafacial component interact to yield the combination $\sigma_1 - \sigma_2$. However, the most rapid cycloadditions are not those between identical reactants where the donor tendencies are exactly balanced, allowing **1a** and **1b** to contribute equally to the transition state; it is well known that concerted reactions proceed favorably through unsymmetrical transition states in which one bond for-



1a



1b

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