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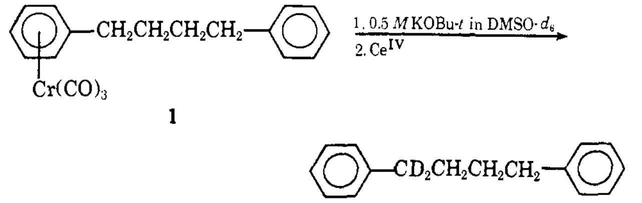
Arene–Metal Complexes. IV. Base-Catalyzed Stereoselective Hydrogen–Deuterium Exchange of Benzylic Protons of Tricarbonylchromium(0)-Complexed Alkylbenzenes[1]

Sir:

We have found that benzylic protons of tricarbonylchromium(0)-complexed alkylbenzenes undergo base-catalyzed hydrogen–deuterium exchange fairly rapidly. For example, the monotricarbonylchromium complex of 1,4-diphenylbutane (**1**) was prepared from 1,4-diphenylbutane and hexacarbonylchromium: mp 44.5–45.0°; nmr (CCl_4) δ 7.16 (m, 5), 5.10 (m, 5), 2.9–2.2 (m, 4), and 1.66 (m, 4).[2] Treatment of **1** with 0.5 *M* potassium *tert*-butoxide in dimethyl-d_6 sulfoxide (DMSO-d_6) followed by decomplexation of the arene by oxidation with ceric ammonium nitrate (CAN) gave a 70% yield of 1,1-dideuterio-1,4-diphenylbutane (**2**).

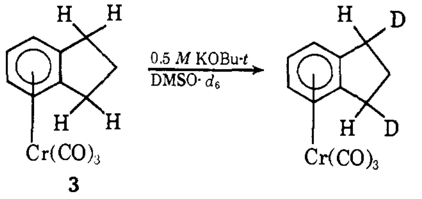


1

(70%)
2

The nmr spectrum of **2** was very similar to that of 1,4-diphenylbutane except that the intensity of the downfield methylene absorption was decreased: nmr (CCl_4) δ 7.1 (s, 10), 2.6 (m, 2), and 1.65 (m, 4). The mass spectrum of **2** contained peaks at *m/e* 212 (molecular weight for **2**), 211, and 210 in ratios of 100:02:02 and peaks at *m/e* 93 and 91 in a ratio of 97:100. Thus, **2** was obtained in ≥96% isotopic purity.

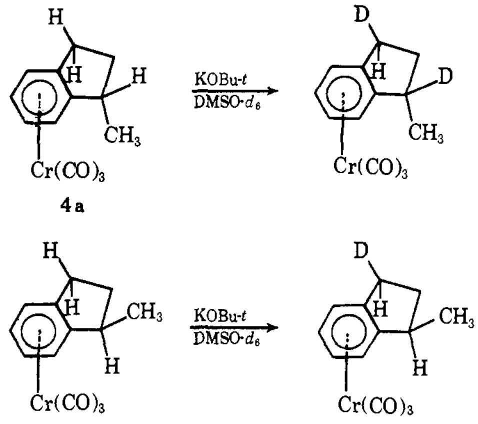
(Indan)tricarbonylchromium[2,3] (**3**) exchanged only two of its benzylic protons when placed in a 0.5 *M* potassium *tert*-butoxide–DMSO-d_6 solution. Both protons were shown to exchange within 15 min and no further exchange occurred when the complex was left in the basic solution for as long as 4 hr. The exchange was followed by observing the decrease of the nmr signal[4] of the benzylic protons which is a multiplet centered at δ 2.8. This signal decreased from a relative area of 4 to 2 while the relative areas for the signals of the complexed aromatic protons at δ 5.2 and the nonbenzylic methylene at δ 2.1 remained 4 and 2, respectively. The half-life for exchange of the two benzylic protons in a 0.013 *M* potassium *tert*-butoxide–DMSO-d_6 solution at 25° was determined to be *ca.* 15 min.



3

These results from the indan complex indicate that the base-catalyzed hydrogen–deuterium exchange is stereoselective. The results from a mixture of *ca.* 45:55 *syn-* and *anti-*(1-methylindan)tricarbonylchromium isomers indicate that only the benzylic protons which are anti to the tricarbonylchromium moiety undergo exchange.

Jackson and coworkers have shown that treatment of 1-methylindan with hexacarbonylchromium gives rise to approximately equal amounts of the syn and anti isomers.[5] These workers have separated and rigorously characterized both isomers, including their stereochemistry.[5] They report that the syn isomer has its methyl nmr absorption (δ 1.28) at lower field than the anti isomer (δ 1.16).[3] Thus, an nmr spectrum of a mixture of the two isomers shows two clearly separated methyl doublets at δ 1.28 (J = 3 Hz) and 1.16 (J = 4 Hz). A mixture of *ca.* 45:55 *syn-* (**4a**) and *anti-* (**4b**) (1-methylindan)tricarbonylchromium was submitted to conditions similar to those used to bring about hydrogen–deuterium exchange of the indan complex **3**. The nmr spectrum of the product mixture showed that the downfield methyl doublet collapsed into a broad singlet while the upfield methyl doublet remained unchanged. These results clearly demand that only the benzylic protons which are anti to the metal atom of both the *syn*-methyl (**4a**) and the *anti*-methyl (**4b**) isomers undergo exchange.



4a

4b

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[1] (a) Part III: D. K. Wells and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, **92**, 7461 (1970). (b) Based on work by R. J. C. in partial fulfillment of the requirements for the M. S. degree at Iowa State University. (c) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research by Grant No. 5261-AC.

[2] Acceptable elemental analyses were obtained for these complexes by Spang Microanalytical Laboratory, Ann Arbor, Mich., or Chemalytics, Inc., Tempe, Ariz.

[3] D. E. F. Gracey, W. R. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *J. Chem. Soc. B*, 1210 (1969).

[4] Water was added to the basic solution and the complex was extracted with ether. The yellow ethereal solution was washed with water and dried ($MgSO_4$), and the solvent was removed. The residue was dissolved in carbon tetrachloride and an nmr spectrum of the solution was taken.

[5] D. E. F. Gracey, W. R. Jackson, C. H. McMullen and N. Thompson, *J. Chem. Soc. B*, 1197 (1969).

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.

(6) T. J. Katz and M. Rosenberger, *J. Amer. Chem. Soc.*, **85**, 2030 (1963).

(7) J. W. Kang and P. M. Maitlis, *J. Organometal. Chem.*, **30**, 127 (1971).

(8) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

(9) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 3444 (1966).

(10) (a) R. E. Davis and R. Pettit, *ibid.*, **92**, 716 (1970); (b) R. Victor, R. Ben-shoshan, and S. Sarel, *Tetrahedron Lett.*, 4257 (1970).

(11) Alfred P. Sloan Research Fellow, 1970–1972.

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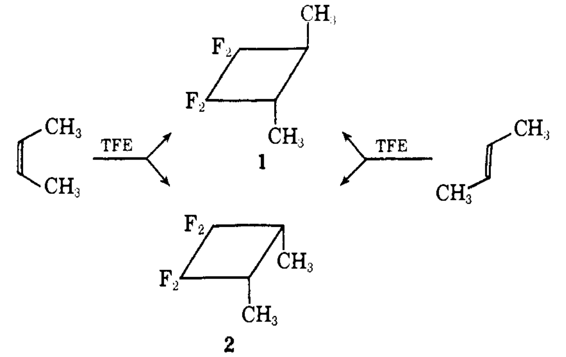
Cycloaddition of Tetrafluoroethylene to *cis*- and *trans*-2-Butenes

Sir:

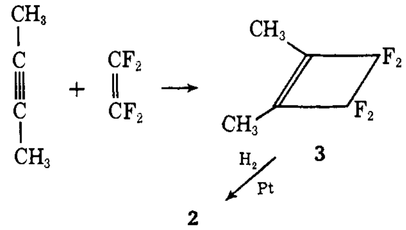
Comparison of 2-butene with ethylene[1] in cycloaddition affords an informative calibration point for the initiation and stereochemical course of a simple biradical mechanism.

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.



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.



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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(1) P. D. Bartlett, G. M. Cohen, S. P. Elliott, K. Hummel, R. A. Minns, C. M. Sharts, and J. Y. Fukunaga, *J. Amer. Chem. Soc.*, **94**, 2899 (1972).