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Selective, High-Yield, Linear Dimerization of 1,3-Butadiene Catalyzed by $(PPh_3)_2NiBr_2$ and $NaBH_4$ and Its Polymer-Bound Ni(0) Analog

Charles U. Pittman, Jr.,* and Larry R. Smith

Contribution from the Department of Chemistry, University of Alabama, University, Alabama 35486. *Received May 4, 1974*

Abstract: The tendency of nickel to cyclodimerize butadiene has been overcome with the catalytic system $(Ph_3P_2)NiBr_2$ + $NaBH_4$ in THF–ethanol or benzene–ethanol. The reaction gives, in high yield (95%), one specific linear product, (*E,E*)-1,3,6-octatriene. $(Ph_3P)_2NiCl_2$ gives the same product though in only 81% yield. The polymer-bound analog (**2**) also gives the same product in good yield (91%). This polymer-bound system has the advantages of both homogeneous catalysis, plus the ease of catalyst recovery of heterogeneous catalysis. Attempts to dimerize isoprene with this catalytic system were unsuccessful, as were attempts to codimerize isoprene and butadiene. In equimolar amounts, isoprene also inhibited the self-dimerization of butadiene.

Cyclic oligomerization of acetylenes[1-4] and butadiene[2-5] by Ni(0) catalysts is well known. Linear oligomerization of butadiene by Ni(0) catalysts is less common, but it has been accomplished using nickel carbonyl phosphites and phosphines, as well as bisacrylonitrile nickel and phosphites in the presence of alcohols,[6] to give 1,3,6-, 1,3,7-, and 2,4,6-octatrienes. In the presence of dialkylamines (*i.e.*, morpholine) and a nickel(0) triethylphosphite, butadiene was converted to (*E,E*)- and (*Z,E*)-1,3,6-octatriene.[7] The linear dimerization of butadiene[8] has also been catalyzed with both salts and zero valent complexes of Co and Fe to give product mixtures where 3-methyl-1,4,6-heptatriene predominates,[8] by $RhCl_3$ and particularly $(Ph_3P)_2Pd$(maleic anhydride)$_2$ to give 1,3,7-octatriene.[9,10]

Because the linear dimerization of butadiene is of commercial interest,[11] the discovery of butadiene to a single linear dimer in high yield is an important goal. Furthermore, selective catalysts which are easy to handle, readily recycled, and inexpensive are needed. Thus, research on butadiene oligomerization continues to appear. Bis(triphenylphosphine)(*p*-benzoquinone)palladium, for example, produces linear dimers with 4-vinylcyclohexene as a by-product.[12] High yields of octatrienes were also obtained from butadiene over $(PPh_3)_3Pt$ under 400 psi of carbon dioxide, but in the absence of carbon dioxide, 4-vinylcyclohexene was formed in 90–97%.[12] Similar results were obtained with $(PPh_3)_4Pd$.[13,14] With bis(π-allyl)palladium, linear trimers (*n*-dodecatetraene) and higher oligomers are formed, while bis(π-allyl)nickel converts butadiene to cyclododecatriene, and bis(π-allyl)platinum gives trimer and tetramer mixtures at higher temperatures.[15] When triphenylphosphine is added to π-allylpalladium acetate, linear dimerization predominates.[16] Gardner and Wright[17] have reported that an 80% yield of octa-1,7-diene can be obtained when platinum salts, such as $LiPtCl_4$, were used in formic acid–dimethylformamide.

Features common to most catalytic systems capable of butadiene oligomerization are (1) their dependence on solvent and (2) their tendency to give product mixtures. Recently, Beger, *et al.*,[18] showed that the oligomerization of butadiene over nickel chloride or nickel acetylacetonate, in the presence of butyllithium and PL_3 (L = NMe_2, *n*-Bu, Ph, or *n*-BuO), gave complex mixtures of octatrienes and both monomeric and dimeric ethers when ethanol was present. Similarly, a bis(triphenylphosphine)nickel catalyst, produced *in situ* by the reduction of $(Ph_3P)_2NiBr_2$ with $NaBH_4$ in ethanol, catalyzed dimerization of butadiene to a mixture of linear and cyclic products.[19] When the $NaBH_4$/Ni ratio was 1 or less, the main product was 2-methylenevinylcyclopentane. When this ratio exceeded 1, linear dim-

Table I. Results of Linear Dimerization of 1,3-Butadiene by Homogeneous and Polymer-Bound $(Ph_3P)_2NiBr_2$[a]

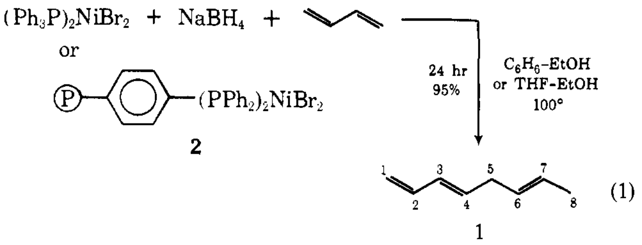
Run	Catalyst	Catalyst, mmol	$NaBH_4$, mmol	Solvent (mmol)	Isoprene, mmol	% 1,3,6-octatriene	Products incorp. isoprene
1	$(Ph_3P)_2NiBr_2$	0.203	0.42	C_6H_6-EtOH 74		99.6	
2	$(Ph_3P)_2NiCl_2$	0.200	0.41	C_6H_6-EtOH 74		81.0	
3	$(Ph_3P)_2NiBr_2$	0.201	0.43	THF-EtOH 90		98.9	
4	SX1-$NiBr_2$	0.105	0.21	C_6H_6-EtOH 74		5.0	
5	SX1-$NiBr_2$	0.105	0.21	THF-EtOH 74		91.2	
6	SX2-$NiBr_2$	0.090	0.18	THF-EtOH 74		90.8	
7	$(Ph_3P)_2NiBr_2$	0.203	0.42	C_6H_6-EtOH	20.0		0.0
8	$(Ph_3P)_2NiBr_2$	0.203	0.42	C_6H_6-EtOH 35.2	35.2	0.0	0.0
9	$(Ph_3P)_2NiBr_2$	0.203	0.42	THF-EtOH 35.2	35.2	0.0	0.0
10	$(Ph_3P)_2NiBr_2$	0.203	0.42	THF-EtOH 100.0	10.0	76.0	0.0
11	SX1-$NiBr_2$	0.105	0.21	THF-EtOH 185.0		85.1	
12	$(Ph_3P)_2NiBr_2$	0.200	0.41	THF-EtOH 74		99.4	

[a] Reactions at 100°, 24 hr, $NaBH_4$ to Ni ratio 2:1, total volume of solvents, 20 ml.

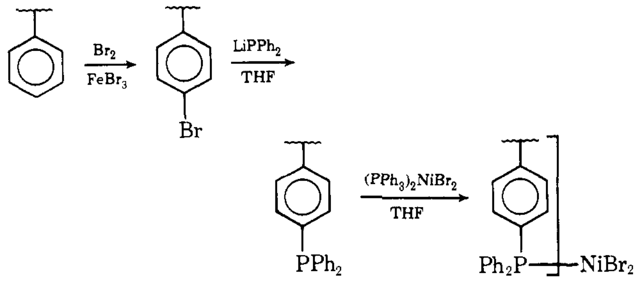
erization increased giving mainly 1,3,6-, 2,4,6-, and 1,3,7-octatriene and less cyclic product. However this method had the disadvantage of producing a complex mixture of the cyclic and various linear products.

Results and Discussion

We have now achieved the selective linear dimerization of butadiene in high yield. Using THF-ethanol (50/50 to 90/10) at 100° and a $NaBH_4$ to $(Ph_3P)_2NiBr_2$ ratio of 2:1, butadiene was selectively dimerized to (*E,E*)-1,3,6-octatriene (**1**) in 95% or greater yield and in greater than 99% selectivity. In benzene-ethanol (50/50 to 90/10) the reaction was very slow (5% yield, 24 hr) but still very selective. Furthermore, $(Ph_3P)_2NiBr_2$ was also anchored to swollen styrene-divinylbenzene resins, *via* bound phosphine ligands, and then reduced by $NaBH_4$, providing an anchored, fixed-bed, "homogeneous" catalyst **2**.[20,21] Similar yields (>90%) and selectivities were obtained with this anchored catalyst. Using the same reaction conditions, $(PPh_3)_2NiCl_2$ gives the same product in slightly lower yield (81%).



The resin-bound catalyst was prepared as shown below. Polystyrene-1% divinylbenzene was brominated, then treated with lithium (or sodium) diphenylphosphide to give diphenylphosphinated resin **3**. Phosphine exchange with $(PPh_3)_2NiBr_2$ gave **2**. Two moles of PPh_3 was displaced for



every mole of nickel anchored. This was shown by analysis of the resulting resins and recovery of the PPh_3 displaced. Similar procedures have recently been used for immobilizing $(Ph_3P)_3Rh(H)(CO)$,[22] $(Ph_3P)_2RhCl$,[23] $(Ph_3P)_2Ni(CO)_2$,[21] $Co_2(CO)_4$,[21] and $Rh_6(CO)_{16}$[24] on swellable styrene polymers.

Butadiene was then dimerized in the presence of **2** and $NaBH_4$ in 91% after 24 hr at 110-115° according to eq 1. THF-ethanol or benzene-ethanol solvent mixtures were used in order to maintain a swollen polymer matrix. In pure ethanol, the reaction failed, presumably due to failure of the resin to swell. In benzene-ethanol, as in THF-ethanol, the only product was **1**. About 1500 mol of butadiene was converted to product in batch reactions before both the homogeneous and polymer-bound catalysts were deactivated in THF-ethanol, but this conversion limit was higher (over 8000) for continuous fixed-bed operation. Using $(PPh_3)_2NiBr_2$ and $NaBH_4$ in absolute ethanol gave the complex product mixture that had been reported by Kiji, *et al.*[19]

$(Ph_3P)_2NiBr_2$ was dissolved in the mixed solvents to give a green solution. Upon addition of $NaBH_4$, evolution of HBr began, and the color of the solution changed to yellow and then slowly to dark brown. The brown color persisted throughout the remainder of the reaction. Butadiene was condensed into the reaction mixture at −78°, and the reaction was then heated to 110°. After 24 hr, analytical glc of the reaction solution showed only one product (**1**) in contrast to the mixture of 2-methylenevinylcyclopentane and 1,3,6-, 2,4,6-, and 1,3,7-octatrienes reported by Kiji.[19] After concentrating the solution, only traces of any other product could be found.

The product **1,** purified by preparative glc, was found to be (*E,E*)-1,3,6-octatriene. A parent ion at *m/e* 108 showed it to be a dimer of 1,3-butadiene. A single uv absorption at 228 nm was indicative of two conjugated double bonds. The infrared spectrum showed absorptions of a single terminal methyl group at 1380 cm^{-1} as well as a strong absorption at 965 cm^{-1} indicating trans double bonds. The complete absence of an ir absorption in the region of 705 cm^{-1} showed that no trace of a cis double bond was present. The uv and ir spectra were identical with those reported[25] for (*E,E*)-1,3,6-octatriene. The published nmr spectrum[25] was of very poor resolution. Thus a higher resolution spectrum (100 MHz) was obtained to reveal greater detail. It exhibited a three-proton doublet of doublets at δ 1.66, a two-proton doublet of triplets at δ 2.78, and a very complex pattern from δ 4.88 to 6.78 resulting from the seven olefinic protons. Further homoallylic coupling could be seen on an expanded scale spectrum.

Table I gives the results of some representative reactions carried out at 100° where the $NaBH_4$ to Ni ratio was held constant at 2:1. Reactions 1 and 2 show that $(Ph_2P)_2NiBr_2$ was more reactive than $(Ph_3P)_2NiCl_2$, and that in homogeneous solution the reaction of 1,3-butadiene with

$(Ph_3P)_2NiBr_2$ was essentially quantitative. In benzene-ethanol solvent, the bound catalyst (run 4) promoted the reaction very slowly, presumably because of failure of the polymer to swell. In THF-ethanol, the reaction gave better than 90% yield of (*E,E*)-1,3,6-octatriene (reaction 5). Comparing reactions 5 and 6 revealed that no difference exists between the catalyst bound to 1 or 2% divinylbenzene-crosslinked resin beads.

Attempts to linearly dimerize isoprene (run 7) failed, even when heated as high as 150°. Attempts to codimerize 1,3-butadiene and isoprene in equimolar amounts (runs 7 and 8) also failed. Surprisingly, isoprene also inhibited the self-dimerization of 1,3-butadiene. [Attempts to codimerize equimolar amounts of isoprene and butadiene were also unsuccessful (runs 8 and 9)]. Using a 10:1 excess of 1,3-butadiene to isoprene (run 9), no codimerization products were found, isoprene was recovered unchanged, and 1,3-butadiene self-dimerized in 76% yield to (*E,E*)-1,3,6-octatriene at 100° in 24 hr.

This catalytic system has the unique advantage of giving, in almost quantitative yield, one specific linear dimer. Thus, purification problems are drastically reduced. Operation of this reaction with the polymer-bound catalyst permits the application of continuous, *vs.* batch, operation and easy recovery of catalyst by filtration in batch runs. $(PPh_3)_2NiBr_2$ + $NaBH_4$ (and the polymer catalyst) are not sensitive to moisture in contrast to alkyl aluminum promoted catalysts. The reaction was easily carried out in the presence of 1% water. Further, the catalyst precursor is easily made from $NiBr_2 \cdot 6H_2O$ (or $NiCl_2 \cdot 6H_2O$) and PPh_3, in butanol in an open beaker. Even after addition of $NaBH_4$ this catalyst system is cheap, safe, and easy to handle. The polymer-anchored system can be exposed to air for short periods without losing its activity.[26]

Experimental Section

Benzene, THF, and toluene were dried over CaH_2 for at least 24 hr and then distilled under nitrogen. Similar care was taken to dry all solvents. Nitrogen, carbon monoxide, hydrogen, and 1,3-butadiene (instrumental grade) were obtained commercially (99+%) and used as received. Glc separations were done on a Varian Model 90-P gas chromatograph. The ir, ^1H nmr, uv, and mass spectra were obtained on a Beckman Ir-33, Perkin-Elmer R20B or Varian HA-100, Cary 14, and a Perkin-Elmer Hitachi RMU-6M, respectively.

Bromination of Styrene-Divinylbenzene Resin Beads. In a typical bromination, resin beads (15 g, Bio Beads, Bio Rad Labs, either SX-1, 1% divinylbenzene, 14,000 mol wt exclusion limit, or SX-2, 2% divinylbenzene, 2700 mol wt exclusion limit), iron powder (2.0 g, 35.7 mmol), and CCl_4 (150 ml) were cooled to 0°. In the dark a solution of Br_2 (3.5 g, 2.19 mmol) in CCl_4, was added dropwise over a period of 1 hr. Stirring was continued 20 hr, and the HBr gas generated was allowed to escape into an aqueous $AgNO_3$ solution. Solvent was then removed by filtration and the excess iron powder removed with a magnet. The resin beads were then washed (by stirring 4-6 hr) successively in 700 ml each of 5% aqueous $Na_2S_2O_3$, 5% aqueous Na_2CO_3, water-acetone, benzene, and methanol and dried [25° (0.05 Torr)]. Analysis showed 9.25% Br which corresponds to bromination of 13% of the phenyl rings. Degrees of bromination varying from 7 to 40% of the rings were accomplished. Generally, bromine incorporation was lower in the more crosslinked, SX-2 beads.

Reaction of Brominated Styrene-Divinylbenzene Resin with Lithium Diphenylphosphide. A dry THF solution (75 ml, nitrogen saturated) containing chlorodiphenylphosphine (40 g, 0.233 mol) was added slowly to a suspension of lithium metal (5 g, 0.72 mol) in dry THF (100 ml) under nitrogen. A bright red color confirmed the formation of lithium diphenylphosphide. Stirring was continued 20 hr at 21°. Unreacted lithium was then removed and the solution transferred under nitrogen to a rapidly stirred THF slurry of the brominated (9.25% Br, 13% rings brominated) styrene-divinylbenzene resin beads (15.0 g, 1.16 mmol bromine g^{-1}). This mixture was stirred under nitrogen for 24 hr; unreacted lithium diphenylphosphide was then hydrolyzed in a nitrogen purged acetone-water (3:1, 700 ml) solution for 1 hr. The resin beads were then washed successively in 700 ml each of the following nitrogenated solvents: acetone-water, benzene, and methanol. The beads were dried [25° (0.05 Torr)]. Analysis found 2.61% P which corresponded to 10.4% of the phenyl rings containing a bound PPh_2 group. Residual Br (0.23%) corresponded to 0.35% of the rings still containing a bromine.

Reaction of 1,3-Butadiene with Homogeneous and Polymer-Bound $(Ph_3P)_2NiBr_2$ and $NaBH_4$ in THF-Ethanol or Benzene-Ethanol. Bis(triphenylphosphine)nickel dibromide (0.150 g, 0.203 mmol), $NaBH_4$ (0.016 g, 0.42 mmol), and a magnetic stirring bar were added to a thick-walled Pyrex tube. After a nitrogen purge, 20 ml of dry THF-ethanol or dry benzene-ethanol (50/50 to 90/10 and nitrogen saturated) was added and the tube sealed. Gas evolution began immediately, and the solution changed from green to yellow to dark brown. Butadiene (4.0 g, 74 mmol) was condensed in at −78°. The tube was then warmed to 25°, placed in an oil bath at 100-105°, and stirred for 24 hr. After cooling to 25°, the tube was vented to a −78° trap, but no unreacted 1,3-butadiene was recovered. Analytical glc of the reaction mixture showed only a trace of unreacted 1,3-butadiene and also only one product in 99+% yield, which was identified as (*E,E*)-1,3,6-octatriene. To be certain that only one isomer of 1,3,6-octatriene was obtained, glc separations were attempted on several different columns including Carbowax 20-M, SE-30, OV-17, and Apiezon-L, all 15% on NAW 100-120 Chromosorb P, in columns 6 ft × 0.25 in. Also isothermal and programmed temperature methods were employed.

Samples were collected by preparative glc for: mass spec (70 eV) *m/e* 108, 93, 67, 53; uv λ_{max} (EtOH) 228 nm (ϵ 2.35×10^4) [lit.[25] λ_{max} (cyclohexane) 228 nm (ϵ 3.7×10^4)]; ir (neat) 3062 (m), 3000 (s), 2900 (bs), 1651 (m), 1605 (m), 1380 (m), 1000 (s), 965 (s), 895 (s), identical with literature value;[25] nmr ($CDCl_3$) (lit.[25]) δ 1.66 (doublet of doublets, 3 H, $J_{7-8} = 5.3$, $J_{6-8} = 1.4$ Hz, $C^8H_3C^7H{=}C^6H-$), 2.78 (triplet of doublets, 2 H, $J_{4-5} = J_{6-5} = 5.1$, $J_{7-5} = 1.2$ Hz, ${=}C^4HC^5H_2C^6H{=}C^7H-$), and 4.88-6.78 (7 H, olefinic protons). Indications of homoallylic coupling are also present.

Analogous reactions with $(Ph_3P)_2NiCl_2$ gave the same one product, (*E,E*)-1,3,6-octatriene, though in only 81% yield.

Reactions using polymer-bound bis(triphenylphosphine)nickel dibromide (0.50 g, 0.09 mmol of Ni) and $NaBH_4$ (0.0068 g, 0.18 mmol) also gave as the only product (*E,E*)-1,3,6-octatriene in 91% yield.

Attempted Oligomerization of Isoprene with Homogeneous and Polymer-Bound $(Ph_3P)_2Ni(CO)_2$ or $(Ph_3P)_2NiBr_2$. Bis(triphenylphosphine)nickel dicarbonyl (0.15 g, 0.235 mmol), isoprene (1.36 g, 20 mmol), dry benzene (15 ml, nitrogen saturated), and a magnetic stirring bar were placed in a thick-walled Pyrex tube under nitrogen. The tube was sealed, heated to 80°, and stirred for 24 hr. The tube was then cooled to 25°. Analytical glc of the reaction mixture showed no trace of products, only unreacted isoprene. Similar reactions were heated as high as 160° with no results. Analogous reactions using bis(triphenylphosphine)nickel dibromide (0.15 g, 0.203 mmol) and $NaBH_4$ (0.006 g, 0.42 mmol) in ethanol with isoprene gave equally unsuccessful results. Oligomerization attempts made using polymer-bound catalysts were also unsuccessful.

Attempted Co-oligomerization of Butadiene and Isoprene by Homogeneous and Polymer-Bound $(Ph_3P)_2NiBr_2$. Bis(triphenylphosphine)nickel dibromide (0.15 g, 0.2 mmol), $NaBH_4$ (0.016 g, 0.41 mmol), butadiene (1.9 g, 35.2 mmol), isoprene (2.4 g, 35.2 mmol), dry ethanol (15 ml, nitrogen saturated), and a magnetic stirring bar were placed in a thick-walled Pyrex tube under nitrogen. The tube was then sealed and heated at 100° for 24 hr. After being cooled to 25°, the tube was vented to a −78° trap where butadiene (1.8 g) was recovered. Analytical glc of the reaction mixture showed unreacted butadiene and isoprene but no oligomerization products. Identical reactions heated as high as 150° also gave no results. A similar reaction using an excess of butadiene (10.0 g, 185 mmol) over isoprene (1.26 g, 18.5 mmol) at 100° did result in oligomerization of butadiene. Isoprene was unchanged, and butadiene (2.4 g) was recovered. The product (76%) was identified as (*E,E*)-1,3,6-octatriene. The polymer-bound catalyst also failed to oligomerize butadiene and isoprene when present in equimolar quantities. With 9:1 butadiene–isoprene, butadiene dimerization also gave (*E*,*E*)-1,3,6-octatriene (71%) as the only product.

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The Characterization of Carbene Selectivity. Applications to Difluorocarbene

Robert A. Moss*[1] **and Charles B. Mallon**[2]

Contribution from the Wright and Rieman Laboratories, School of Chemistry, Rutgers University, The State University of New Jersey, New Brunswick, New Jersey 08903.

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Abstract: By means of the dual substituent parameter equation, $m_{\mathrm{CXY}} = -0.94\ \Sigma_{\mathrm{X,Y}}\ \sigma_R^+ + 0.69\ \Sigma_{\mathrm{X,Y}}\ \sigma_I - 0.27$ in which m_{CXY} is the least-squares slope of log $(k_i/k_{\mathrm{isobutene}})$ for CXY *vs.* log $(k_i/k_{\mathrm{isobutene}})$ for CCl_2, the olefinic selectivity of six carbenes could be mutually correlated. Included was CF_2, $m = 1.48$. A Hammett correlation of the relative rates of addition of CF_2 to substituted styrenes (benzene, 80°) gave $\rho = -0.57$. The significance of these correlations is discussed.

Two quantitative treatments of the selectivity of carbenes toward olefins are currently in use. (1) A carbene is allowed to discriminate between variously substituted styrenes; relative reactivities are calculated, and a Hammett analysis then affords a ρ value for the carbene–olefin addition reaction. (2) Relative reactivities are determined for the addition of a carbene to each of a set of alkenes (which differ in degree or pattern of alkylation at the olefinic carbon atoms). The ability of the carbene to discriminate between the alkenes is then quantitatively compared with that of a "standard carbene" (or other electrophilic reagent) over the same set of alkenes. We have reviewed applications of these methods through 1972.[3] More recent noteworthy examples include Schöllkopf's study of carboethoxycarbene and bromocarboethoxycarbene,[4] and Kostikov's work with CCl_2.[5]

Interpretation of the resulting carbenic "selectivities" is difficult. Much attention has been given to the role of the structure of the olefinic substrate in the carbene addition reaction.[3] A crucial problem, however, is the correlation of carbenic selectivity with carbenic *identity; i.e.*, how does the selectivity of CXY vary with X and Y? Qualitative discussions abound in the literature,[3] but *quantitative* treatments are essentially nonexistent. The problem could be solved if either of the above measures of carbenic selectivity could be quantitatively related to electronic parameters characteristic of X and Y.

Initially, we employed a standard set of olefinic substrates[6] and defined a carbene selectivity index, m_{CXY}, as the least-squares slope of log $(k_i/k_{\mathrm{isobutene}})$ for CXY *vs.* log $(k_i/k_{\mathrm{isobutene}})$ for CCl_2.[3,7] The concept of a carbene selectivity index was not new; similar descriptors had previously been employed.[3,7,8] However, we pointed out the existence of a "fair linearity" between the *m* values of four chlorocarbenes, CXCl, and σ_R^+ of X. We suggested that, within this limited set of carbenes, selectivity toward alkenes was governed by the ability of X to donate electrons by resonance to the (singlet) carbene's vacant p orbital.[7]

Subsequent attempts to extend this treatment to include the selectivity of CF_2 failed.[9] Strongly curved correlations were obtained, with CF_2 at the apogee. CF_2 seemed to be *less* selective than expected, based on the behavior of the other, less resonance-stabilized carbenes.

This latter observation was interesting, in view of Jefford's report of apparent [2 + 2 + 2] cycloadditions of CF_2 and CFCl to norbornadiene.[10] It was suggested that these reactions might represent "engagement of the sp^2 orbital (nucleophilic attack)" of the carbenes.[10] We considered this possibility unlikely, because, although the selectivities of CF_2[11] and CFCl[12] toward olefins had not been as extensively studied as had that of CCl_2,[3,13] there was evidence of their electrophilic behavior toward simple alkenes.[3,11,12]

Our active interest in the analysis of carbenic selectivity, our concern with the selectivity of CF_2,[14] and the publication of Jefford's reports[10] all combined to lend a sense of ur-