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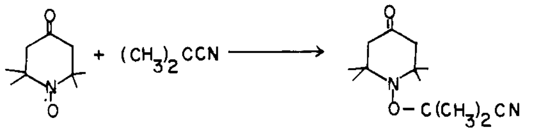

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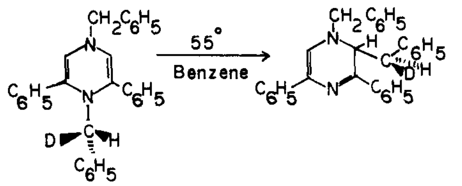

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Reaction of Chemically Generated Carbon Atoms with Propane[1]

Philip B. Shevlin* and Seetha Kammula

Contribution from the Department of Chemistry, Auburn University,
Auburn, Alabama 36830.

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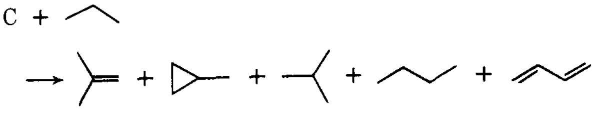
Abstract: The reaction of atomic carbon, generated by the thermolysis of 5-tetrazoyldiazonium chloride (**1**), with propane has been studied. The products are isobutylene (**5**), 1-butene (**4**), *cis*- and *trans*-2-butene, methylcyclopropane (**6**), propylene (**8**), methane, and acetylene. Examination of the yields of C_4 products indicates that carbon attacks preferentially at the secondary C–H bond. Competitive experiments demonstrate that propane is a least five times as reactive as cyclopropane in generating C_4 products, indicating preferential attack on the weaker C–H bonds of propane. MINDO/3 calculations suggest that the C–H insertion proceeds via initial transfer of hydrogen followed by carbon-carbon bond formation. Studies with ^{14}C atoms reveal that **8** contains no ^{14}C, implying that it is formed by abstraction of two hydrogens from propane.

There have been a number of studies of the reactions of atomic carbon with saturated hydrocarbons.[2] Both arc-generated atomic carbon[3] and nucleogenic carbon-11 atoms[4] have been postulated to react via an initial C–H insertion to produce a carbene which reacts further to give products.

$$C + H\text{-}R \rightarrow H\text{-}\ddot{C}\text{-}R \qquad (1)$$

However, a comparison of the reactions of ^{11}C with those of arc-generated carbon reveals substantial differences in product distributions. For example, Skell and Engel[5] report that reaction of arc-generated carbon with propane gives the products shown in eq. 2. By contrast, the reaction of carbon-11 with

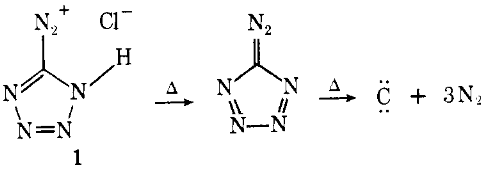


(2)

propane generates relatively small amounts of C_4 products with fragmentation predominating.[6] The fact that reactions of arc-generated carbon are studied at 77 K, while nucleogenic carbon is generally reacted under more energetic conditions undoubtedly accounts for some of the differences in product distribution.

An additional point of much interest concerns the selectivity of C-H insertion by atomic carbon. The fact that no 1-butene is reported in the reaction of arc-generated carbon with propane implies a striking preference for insertion into secondary over primary C-H bonds.

For the past several years, we have been studying the reactions of atomic carbon generated in the thermolysis of 5-tetrazoyldiazonium chloride (**1**).[7] Since this method provides interesting comparisons with other methods of generating carbon atoms, we now report the results of a study of the reactions of chemically-generated carbon with propane.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Experimental Section

5-Tetrazoyldiazonium Chloride (1). 5-Aminotetrazole (1 g, 0.98 mmol) was dissolved in 20 mL of tetrahydrofuran and 6 mL of concentrated HCl. The flask containing the above was cooled in an ice bath. The mixture was stirred magnetically behind a safety shield and 2 mL of isoamyl nitrite was added dropwise. After 5 min, 20 mL of ether was added and the mixture stirred for an additional 5 min. At this time the mixture was poured into a 100-mL graduated cylinder kept immersed in an ice bath. Two layers separated. A 2-mL aliquot of the yellow ether layer was pipetted into a 500-mL round-bottomed flask. Keeping the flask at 0 °C, the ether was removed on a rotary evaporator first under aspirator pressure and then with high vacuum. The diazonium chloride appeared as a film of white crystals along the sides of the flask. The flask was attached to a vacuum line with an adapter and evacuated.

It should be emphasized that **1** is an extremely explosive compound and should be handled with extreme care. The crystalline diazonium salt will detonate at the touch of a spatula. An ethereal solution of **1** has exploded violently after 1 h at −78 °C, presumably as a result of precipitation of the salt.

5-Tetrazoyldiazonium-^{14}*C* Chloride.[7c] This labeled compound was prepared by diazotization of 5-aminotetrazole-^{14}*C* by the procedure described above. The carbon-14 labeled tetrazole was conveniently synthesized by the reaction of cyanamide-^{14}*C* with hydrazoic acid according to the procedure described by Satzinger.[8] A specific activity of $(2.6 \pm 0.1) \times 10^7$ dpm/mmol for the tetrazole was determined by combustion followed by radiochemical assay. This analysis was performed by Drs. A. P. Wolf and D. R. Christman of Brookhaven National Laboratory.

Reaction of Chemically-Generated Carbon Atoms with Propane. After evacuating the flask containing crystals of **1**, 200 mm of propane was introduced and the vacuum stopcock to the flask closed. Using a safety shield, **1** was decomposed by immersing the flask in a 110 °C oil bath for 5 min. The flask was then opened to the vacuum line and the contents analyzed.

The C_4 products were separated from the propane by pumping the reaction mixture through traps at −78 and −115 °C into a trap at −196 °C. Analysis of the contents of the −78 °C trap for 1,5-hexadiene by GC-mass spectroscopy showed less than 8×10^{-6} mmol of this compound. An IR analysis of the contents of the −115 °C trap revealed the presence of all the C_4 hydrocarbons shown in Table I. Quantitative analysis of the mixture of C_4 products was accomplished by gas chromatography on a 20-ft 20% dimethylsulfolane (DMS) on 40/60 firebrick column. The column separated all the reported C_4 products except 1-butene and isobutylene, which were determined by trapping from the DMS column and analysis on an 8-ft 10% $AgNO_3$/ethylene glycol column.[9] The products from the reaction of ^{14}C atoms with propane were analyzed by trapping from the DMS column into a liquid scintillation cocktail. Activities were then measured on a Beckman β-Mate scintillation counter. An analysis of the contents of the −196 °C trap for ethylene and ethane by GC on the DMS column was negative.

Table I. Products in the Reaction of Chemically-Generated Carbon Atoms with Propane

Product	Yield, mmol × 10^3	^{14}C specific activity,[a] dpm/mmol × 10^{-7}
 (5)	1.14	2.0 ± 0.4[b]
 (4)	0.38	
	0.38	2.6
	0.30	2.3
 (6)	0.45	3.1
 (8)	1.9	>0.1
CH_4	1.3	
C_2H_2	3.35	1.2

[a] The activity of starting 5-aminotetrazole was 2.6×10^7 dpm/mmol. [b] This quantity is the total specific activity in 4 and 5 which was not separated by GC under the conditions of the analysis for radioactivity.

Detection of propylene in this reaction was complicated by the great difficulty in separating it from large quantities of propane. This separation was accomplished by passing the entire reaction mixture through a 600 × 5 mm Pyrex U-tube containing 10% $AgNO_3$/ethylene glycol on 40/60 firebrick cooled to −78 °C under vacuum. It was found that pumping on the U-tube for 1 h removed the propane, leaving the alkenes behind. Alkenes were then collected by pumping them from the U-tube at 0 °C. The resultant mixture of propylene and C_4 alkenes was analyzed by IR, GC, and scintillation counting as described above.

Methane was analyzed by first trapping it at −196 °C in a U-tube containing activated charcoal followed by gas chromatography on a 12-ft 16X molecular sieves column. Methane was not analyzed for ^{14}C activity. Acetylene was quantitated by IR and GC and analyzed for activity by trapping from the DMS column.

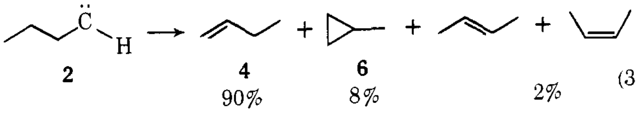
Yields and carbon-14 activities in the reaction of carbon with propane are shown in Table I.

Results and Discussion

Products in the Reaction of Carbon with Propane. Table I shows the products resulting from the reaction of chemically-generated carbon atoms with propane. This table also shows the distribution of radioactivity of these products when ^{14}C atoms, produced by the thermolysis of 5-tetrazoyldiazonium-^{14}*C* chloride,[7c] were used. A comparison of the specific activity of the starting tetrazole with that of the C_4 products reveals that the latter are formed from the reaction of a single ^{14}C atom with propane as expected. In these studies, it was observed that the addition of up to 10% oxygen to the propane had no effect on the yield of the C_4 products. Since oxygen is known to be an effective scavenger of $C(^3P)$,[10] we conclude that a singlet carbon atom is the precursor to the C_4 products.

In this investigation, as in other studies of atomic carbon, high yields of acetylene are observed. Much elegant experimental work has been directed toward determination of the mechanism of acetylene formation in the reactions of atomic carbon.[6b,11] While this mechanism has not been completely elucidated, results point strongly toward multiple pathways. Recent experimental evidence implicates a partial intermolecular pathway for acetylene formation in the reaction of nucleogenic carbon with propane.[11a] However, there is no direct evidence that acetylene produced in the reactions of carbon with propane results from fragmentation of either the *n*-propylcarbene (**2**) or the isopropylcarbene (**3**). In fact, no acetylene is formed when either **2** or **3** is produced photolytically in gas phase.[12,13] In the following discussion we shall direct our attention toward the mechanism of formation of C_4 products and assume that carbenes **2** and **3** are precursors of these compounds. The mechanism of acetylene formation in this system is unclear at this time and its elucidation must await further labeling experiments.

In order to consider the intermediacy of the *n*-propylcarbene (**2**) and isopropylcarbene (**3**) in this system, we must first examine the reactions of these carbenes when generated by other methods. Equations 3 and 4 summarize the products that have been reported when **2**[12] and **3**[13] are generated in the gas phase by photolysis of the corresponding diazo compounds. A comparison of these products with the C_4 products in Table I reveals that, if **2** and **3** are intermediates in the reaction of carbon with propane, **3** must predominate. This is so, as the major product expected from **2** is 1-butene (**4**) while a 3:1 ratio of isobutylene (**5**) to methylcyclopropane (**6**) should result from **3**. The ratio of (**5** + **6**):**4** of 4.1 from Table I allows us to estimate that the formation of carbene **3** is favored over that of **2** by approximately 6:1.



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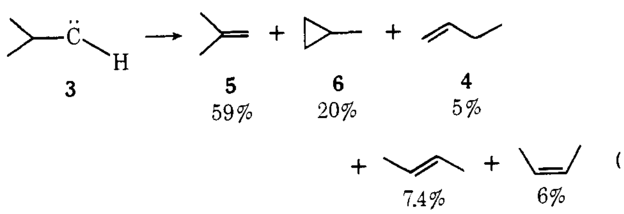

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The above arguments lead to the conclusion that, if carbon reacts by C–H insertion, it is a highly selective insertion preferring the secondary C–H bond over the primary by a factor of 6. This selectivity is in qualitative agreement with that deduced from the distribution of products in the reactions of arc-generated carbon with propane (eq 2).[5] However, such selectivity in a species as energetic as atomic carbon seems unusual and deserves further investigation.

In order to further elaborate this unusual selectivity, we have investigated the energetics of the reaction of carbon with propane using the MINDO/3 semiempirical molecular orbital method developed by Dewar and coworkers.[14] Dewar, Haselbach, and Shanshal[15] have used MINDO/2 to study the reaction coordinate for the addition of atomic carbon to ethylene. We have recently used MINDO/3 to investigate the pathway for deoxygenation of ethylene oxide by atomic carbon.[16] The agreement between MINDO/3 calculations and experimental results in the deoxygenation reaction encouraged us to extend the method to the study of carbon and propane.

In these calculations, we have attempted to get an idea of the energetics by using the distance between the attacking carbon atom and propane as the reaction coordinate. Calculations were started with the carbon atom 2 Å from either C-1 or C-2 in an H–C–H plane and bisecting the H–C–H angle. Calculation was carried out allowing all geometric parameters to optimize except the attacking carbon–C-1 (or C-2) distance, which was systematically varied to generate the reaction coordinate.

The calculations were carried out for attack at C-1 and C-2 along both open and closed-shell singlet energy surfaces. The results of these four calculations are shown in Figure 1 as plots of calculated energy vs. atomic carbon–propane distance.

An inspection of the actual geometries generated by this method reveals a significant difference between the closed- and open-shell energy surfaces. Figures 2 and 3 contrast several geometries along closed- and open-shell energy surfaces for

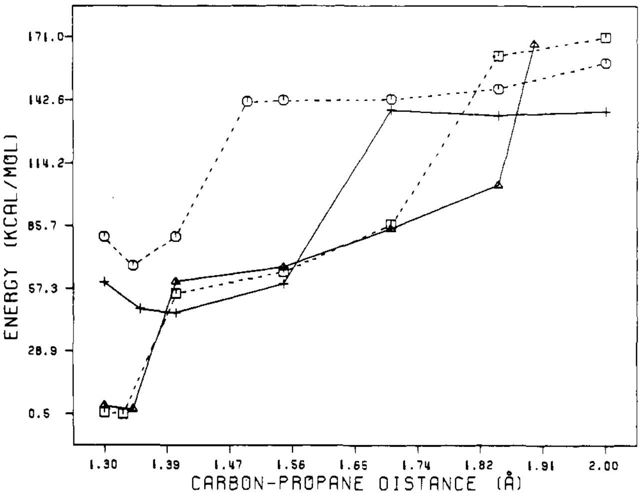


Figure 1. Plot of energy, calculated by MINDO/3, as a function of carbon–propane distance for attack of atomic carbon on propane: open-shell attack at C_2, +—+; open-shell attack at C_1, - -○- - - - ○ - -; closed-shell attack at C_2, —▲—▲—; closed-shell attack at C_1, - - □- - - - □ - -.

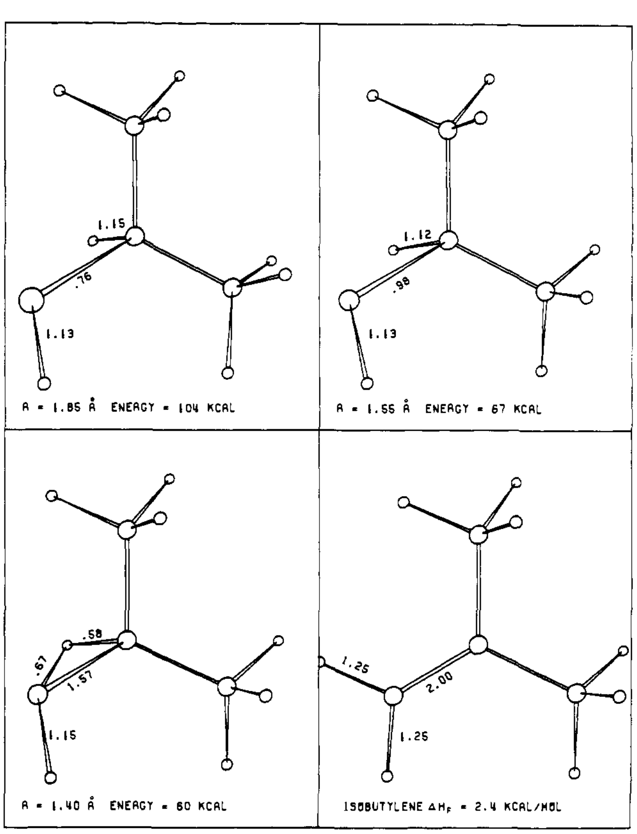


Figure 2. Several geometries along a closed-shell energy surface for attack of atomic carbon at C-2 of propane. Energies are heats of formation calculated by MINDO/3. Relevant Mulliken overlap populations are shown on the figure.

attack at C-2. Exactly analogous geometries are generated by attack at C-1, but are not shown due to space limitations.

Figure 2 shows several geometries and energies for attack at C-2 along a closed-shell energy surface. This reaction is calculated to proceed via a structure whose geometry is close to that of carbene **3**, but which spontaneously rearranges to **5**. The fact that **3** is not calculated to lie at an energy minimum is not surprising as there is much experimental[17] and theoretical[18] evidence to indicate that intramolecular reactions of alkylcarbenes require little activation energy. In this system

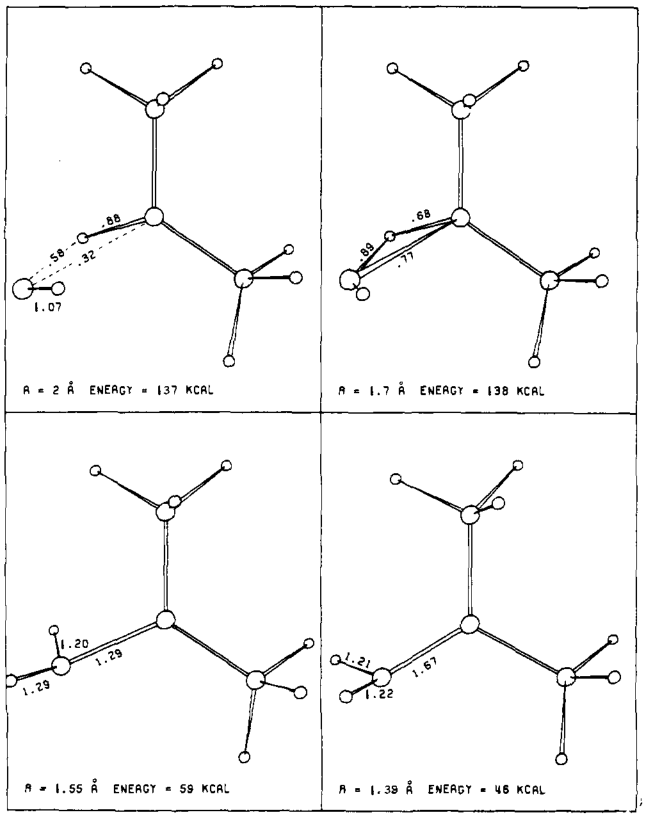


Figure 3. Several geometries along an open-shell energy surface for attack of atomic carbon at C-2 of propane. Energies are heats of formation calculated by MINDO/3. Relevent Mulliken overlap populations are shown on the figure.

Table II. A Comparison of the Reaction of Chemically-Generated Carbon Atoms with Propane and Cyclopropane

Reactant	% yield of C_4 products	Activity in products, dpm C_4H_8 products	 C_4H_6 products
200 mm propane	0.310	61 689	
200 mm cyclopropane	0.030		6589
150 mm propane + 150 mm cyclopropane		7 043	664

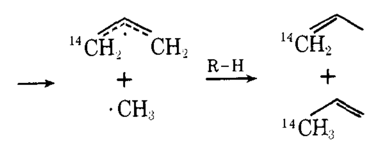
3 never reaches its ground-state geometry and consequently rearranges directly to **5**.

The geometries shown in Figure 3 for the open-shell attack at C-2 reveal that an alternate pathway for reaction of carbon with propane proceeds directly to electronically excited **5**. At large interatomic distances, attack of carbon on a secondary C–H bond along an open-shell energy surface appears to be the most favorable mode of reaction. If we assume that the reaction proceeds initially along an open shell energy surface, the calculations are in qualitative agreement with the observed preference for secondary C–H insertion over primary insertion. An examination of the degree of bonding between relevant atoms as the reactions proceed provides a rationale for the observed selectivity. In all systems the calculated Mulliken overlap populations[19] (MOPs) were used as a measure of the degree of bonding between the various atoms.

Figures 2 and 3 show relevant MOPs along the reaction coordinate for attack at C-2. In all cases, attack of carbon atoms on propane was calculated to proceed via initial strong bonding of the attacking carbon to one of the hydrogens. This stage of the reaction was followed by formation of the carbon–carbon bond. Thus, attack of atomic carbon on a C–H bond is calculated to proceed via a species which resembles a complex between methyne and a radical. Collapse of this biradical species subsequently yields products. Since reaction initially involves cleavage of a C–H bond, the observed selectivity results from the fact that the primary C–H bond in propane is stronger than the secondary C–H bond.

Competitive Reactions of Atomic Carbon with Propane and Cyclopropane. In order to assess the effect of bond strengths on the selectivity of C–H insertion, we have measured the relative reactivities of carbon with propane and cyclopropane. Inasmuch as the C–H bond strengths in cyclopropane (101 kcal) are stronger than those of the secondary (94 kcal) and primary (97 kcal) C–H bonds of propane, atomic carbon is expected to attack propane more readily than cyclopropane. The products in the reaction of chemically-generated carbon atoms with cyclopropane have been reported previously.[7c] Table II compares the yields of C_4 products obtained in the present study with those reported for the reaction of carbon with cyclopropane. In addition to these separate reactions of carbon with propane and cyclopropane, ^{14}C atoms were allowed to react with a mixture containing equal pressures of propane and cyclopropane and the total counts in the C_4H_8 and C_4H_6 products measured. Table II shows that, in both competitions, propane was more reactive than cyclopropane to yield C_4 products by a factor of approximately 10. However, initial C–H insertion on cyclopropane produced the cyclopropylcarbene (**7**) which, in the gas phase, undergoes 50% fragmentation to ethylene and acetylene.[20] Similar fragmentations have not been observed for carbenes **2** and **3**. If it is assumed that **7** produced by C–H insertion of carbon on cyclopropane also gives 50% fragmentation, propane is calculated to be five times more reactive toward C–H insertion than cyclopropane. Although there may be more fragmentation when **7** is generated in the carbon atom system than when it is produced by other methods, these experiments support the conclusion that the selectivity observed in the reaction of carbon with propane is a result of preferential attack by carbon at the weakest C–H bond.

Formation of Propylene in the Reaction of Carbon with Propane. Table I shows that propylene (**8**), a product also reported in the reaction of ^{11}C with propane,[6a] is formed in the present study. A possible mechanism for propylene formation involves fragmentation of energetic 1-butene to allyl radicals, which subsequently abstract hydrogen (eq. 5). If this is the case, reaction of ^{14}C atoms should yield propylene-*1*-^{14}C and propylene-*3*-^{14}C (eq 5). However, when ^{14}C atoms are reacted with propane, **8** is formed without appreciable activity. Thus, the mechanism shown in eq 5 is ruled out. Fragmentation of energetic 1-butene, produced by rearrangement of carbene **2**, has been reported by Figuera, Perez, and Wolf.[12] However, the extent of this fragmentation was pressure dependent and would not have been an important process at the pressures used in the current investigation. If reaction of carbon with propane produced appreciable quantities of allyl radicals, dimerization should produce 1,5-hexadiene.[12] However, analysis of reaction mixtures failed to reveal significant amounts of 1,5-hexadiene.



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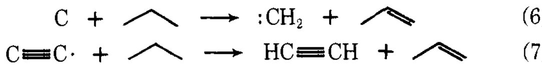
The lack of activity in **8** formed by reaction of ^{14}C with propane implies that it is produced by some type of hydrogen abstraction mechanism. Possibilities include abstraction of two hydrogens by C to produce CH_2 and **8** (eq 6) or abstraction by C_2 to produce acetylene and **8** (eq 7).[21]



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A Comparison of C–H Insertion by Atomic Carbon with that by Methylene. Studies of the reactions of methylene with hydrocarbons have demonstrated that this species is completely nonselective in its C–H insertions.[22] Molecular orbital calculations of the energetics of the reaction of methylene with methane[23,24] indicate that the insertion proceeds by initial transfer of hydrogen to the methylene in much the same manner as that postulated here for carbon atom insertion. However the results of this investigation indicate that atomic carbon is considerably more selective in its C–H insertions than methylene. A consideration of the thermodynamics of the extreme case of complete hydrogen transfer in each reaction may provide a clue to the reason for the observed selectivity:[25]

$$C(^1D) + CH_4 \rightarrow H{-}\dot{C}{:}\ (^2\Sigma) + \cdot CH_3 \quad \Delta H = -5 \text{ kcal/mol}$$

$$CH_2(^1A_1) + CH_4 \rightarrow H_3C\cdot + \cdot CH_3 \quad \Delta H = -15 \text{ kcal/mol}$$

Thus heats of reaction indicate that the initial hydrogen transfer is more favorable in methylene insertion than in insertion by atomic carbon.

Conclusion

Experimental evidence indicates that C–H insertion by atomic carbon occurs by preferential attack at the weakest carbon–hydrogen bond. MINDO/3 calculations suggest that this preference is the result of an initial transfer of hydrogen from propane to the attacking carbon. The energetics of this hydrogen transfer dictate a preferential reaction at the secondary C–H bond in propane.

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Cyclopropanes. 39. The Configurational Stability of the 1-Isocyano-2,2-diphenylcyclopropyl Anion[1]

M. P. Periasamy and H. M. Walborsky*

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306. *Received October 18, 1976*

Abstract: In contrast to the 1-cyano-2,2-diphenylcyclopropyl anion, in ether solvents, the 1-isocyano-2,2-diphenylcyclopropyl anion was found to be configurationally stable at −72 °C. The stability was not affected by changing the gegenion from lithium to sodium to potassium. Nor was it affected by change in solvent or by the addition of coordinating agents such as crown ethers, triglyme, and hexamethylphosphoramide (HMPA). The stabilizing effect of the isocyano substituent is discussed.

The chemistry of carbanions has been the subject of extensive investigation.[2-4] The results from these studies have shown that carbanions exist in solution in equilibrium with different types of ion pairs. Spectroscopic studies of alkali metal salts

$$A^-M^+ \rightleftharpoons A^-/S/M^+ \rightleftharpoons A^- + M^+$$

of resonance stabilized carbanions have revealed that such equilibria are affected not only by the structure of the carbanion but also by the gegenion, the solvent polarity, temperature, and the presence of gegenion-coordinating additives.[2b] It has been concluded from these studies that the less associated solvent separated ion pairs ($A^-/S/M^+$) and the free ions are