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Density Functional Theory Investigation of the Reaction of Isodiiodomethane with Acetylene: Potential Utility of Isodiiodomethane for Cyclopropenation Reactions

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Abstract: We present density functional theory calculations for the reactions of CH_2I-I and CH_2I with acetylene ($HC\equiv CH$) to form a cyclopropene product. CH_2I-I readily reacts with $HC\equiv CH$ to form a cyclopropene product and an I_2 leaving group via a rate-determining step barrier of ∼3.9 kcal/mol (B3LYP/Sadlej-pVTZ). Calculations indicated that the CH_2I radical reacts to form an iodopropenyl radical, which can close to a cyclopropene only with difficulty. Our results indicate that CH_2I-I may act as an effective carbenoid to produce cyclopropenated products from alkynes.

Polyhalomethanes have a rich history of being used for addition reactions[1−3] and for cyclopropanation reactions[4−21] with olefins. Ultraviolet photolysis of diiodomethane (CH_2I_2) in the presence of olefins gives rise to formation of cyclopropanated products with reasonable yield and high stereospecificity.[6,13,15,16] The lack of noticeable C−H insertion reaction as well as the high stereospecificity of the diiodomethane photocyclopropanation reaction indicate that the carbenoid species is not a free carbene.

We have recently employed time-resolved resonance Raman spectroscopy experiments to directly examine the identity and structure of chemical intermediates formed after photolysis of diiodomethane in room-temperature solutions and observed appreciable formation of isodiiodomethane (CH_2I-I) photoproduct.[22,23] Density functional theory (DFT) calculations were done to investigate the chemical reactivity of CH_2I-I, the CH_2I radical, and the CH_2I^+ cation species toward olefins (using ethylene as an example).[24] These calculations found that CH_2I-I readily reacted with ethylene to form a cyclopropane product and an iodine molecule leaving group via a one-step reaction with a low barrier of about 2.9 kcal/mol.[24] However, the CH_2I radical and CH_2I^+ cation species reacted with ethylene via a two-step reaction to produce a cyclopropane product with the rate-determining step having much larger barriers to reaction than that found for the CH_2I-I reaction.[24] A time-resolved resonance Raman investigation of the ultraviolet photolysis of CH_2I_2 in cyclohexene solution observed that CH_2I-I is produced and then reacts with cyclohexene on the 5−10 ns time scale to almost immediately form a I_2:cyclohexene complex from the I_2 leaving group of the reaction of CH_2I-I with cyclohexene.[25] These results combined with those from the DFT calculations point to CH_2I-I being the methylene transfer agent species mostly responsible for the photocyclopropanation of olefins using ultraviolet photolysis of diiodomethane. We proposed a reaction mechanism for the photocyclopropanation that is consistent with both experimental and theoretical results for the reaction intermediates and products made following ultraviolet photolysis of solution phase diiodomethane in the presence of olefins.[24,25] We compared the structures and properties of the CH_2I-I species with the closely related ICH_2ZnI Simmons-Smith carbenoid and found that their different structural features and the mode of activation of the methylene moiety could explain their similarities and differences in chemical reactivity toward olefins.[26]

Some catalysts used for cyclopropanation of olefins have also been observed to form cyclopropenation products from reactions with alkynes. For example, the homoscorpionate complex $Tp^*Cu(C_2H_4)$ where Tp^* = hydrotris(3,5-dimethylpyrazol-1-yl)-borate and Tp^*Cu complex can be used to form some cyclopropenated products from reactions with some alkynes.[27,28] These Cu catalysts can also form cyclopropanated products from olefins.[29] Recent work using Cu(I) catalysts containing trispyrazolylborate ligands found improved procedures

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capable of obtaining high yields of cyclopropenes.[30,31] One interesting study found a $CH_2I_2-Et_3Al$ reagent useful for some cyclopropanation reactions with alkynes.[32]

In this paper, we report DFT calculations that explore the chemical reactivity of the isodiiodomethane (CH_2I-I) molecule and the CH_2I radical toward acetylene to form a cyclopropene product. We find that CH_2I-I can react fairly easily with acetylene to produce a cyclopropene product via a rate-determining barrier of about 3.9 kcal/mol at the B3LYP/Sadlej-pVTZ level of theory. However, the CH_2I radical reacted with ethylene via a multistep reaction to produce a cyclopropene product with the rate-determining step having a much larger barrier to reaction of about 21−29 kcal/mol. Our results suggest that CH_2I-I can act as a reasonable carbenoid to form cyclopropenated products from alkynes. We compare the carbenoid behavior of CH_2I-I toward alkenes and alkynes and discuss the similarities and differences observed in the cyclopropanation and cyclopropenation reactions.

Computational Details

Density functional theory (DFT) calculations employing the Gaussian 98W program suite[33] were used to investigate the potential energy surfaces for the reactions of the CH_2I-I molecule and the CH_2I radical with acetylene. The stationary structures on the surfaces were fully optimized at the B3LYP or UB3LYP level of theory[34−38] using C_1 symmetry and the 6-311G** basis set. Analytical frequency calculations were done to confirm that the optimized structure found was a minimum or first-order saddle point. These frequency calculations were also used to estimate the zero-point energy correction. Intrinsic reaction coordinate (IRC) calculations[39] were done to confirm that the transition states found from the optimization calculations connected the related reactants and products. To obtain more accurate energies, single-point calculations were performed with the Sadlej-pVTZ basis set on the 6-311G** optimized geometries. The Sadlej-pVTZ basis set was contracted as (6s4p//3s2p),[40] (10s6p4d//5s3p2d),[41] and (19s15p12d4f//11s9p6d2f)[42] for the H, C, and I atoms, respectively, with 290 basis functions contracted from 996 Gaussian functions. Previous calculations for the related reactions of CH_2I-I and the CH_2I radical with ethylene showed only modest differences between the optimized structures obtained with 6-311G** and Sadlej-pVTZ basis sets.[24] Thus, we expect that there will be little dependence on the basis set size for the optimized structures for the corresponding reactions with acetylene reported here.

A. Reaction of CH_2I-I with Acetylene. Figure 1 displays the optimized geometry obtained from the B3LYP/6−311-G** calculations for selected reactants, transition state(s), intermediates, and products for the reactions of the CH_2I-I molecule and the CH_2I radical with acetylene to form a cyclopropene product. The CH_2I-I molecule approaches $HC\equiv CH$ in an asymmetric manner and preferentially attacks one of the CH groups (similar to the reaction of CH_2I-I with ethylene in ref 30). A transition state (TS1) was found on the way to a cyclopropene product and an I_2 leaving group. Inspection of the optimized geometry structural parameters for TS1 shown in Figure 1 shows that the $C\equiv C$ and C−I bonds lengthen by 0.031 and 0.189 Å, respectively, compared to the reactant molecules. The C−I−I angle changes from 123.3° in CH_2I-I to about 146.6° in TS1. These structural changes in TS1 relative to the reactants are consistent with the C−C bond formation in TS1 between one carbon atom of acetylene and the carbon atom of CH_2I-I, which leads to weaker intramolecular $C\equiv C$ and C−I bonds. Frequency calculations for TS1 showed one imaginary vibration 341.4i cm^{-1} with an eigenvector of $-0.19\ R_{C-I} + 0.65\ R_{C1-C2} + 0.38\ R_{C1-C3} - 0.31\ A(C_3-C_2-H_3)$. This indicates that the internal coordinate reaction vector is mostly composed of changes in the C_1-C_2, C_1-C_3, and C_1-I bond lengths as well as the $C_3-C_2-H_3$ bond angle. IRC calculations showed that TS1 connects the reactants to an intermediate X. Further IRC calculations for X showed that it connected TS1 to a cyclopropene product and an I_2 leaving group. There was no barrier found for X to proceed to the cyclopropene product. The potential surface appears to be relatively flat in the region of X, and this probably made it difficult for the IRC calculations to directly converge to connect TS1 with the cyclopropene product. The optimized geometry of X shows that the C−I bond increases by ∼0.238 Å, the C_1-C_2 bond decreased by ∼0.402 Å, and the $C_1-C_2-C_3$ angle decreased by about 3° relative to that in TS1. This is consistent with X being on the way to a cyclopropene product and an I_2 leaving group. Our B3LYP density functional calculations indicate that CH_2I-I reacts fairly easily (barrier to reaction of ∼6.7 kcal/mol for the 6-311G** basis set and 3.9 kcal/mol for the Sadlej-pVTZ basis set) with acetylene to produce cyclopropene and I_2 via the transition state (TS1) located in the entrance channel.

B. Reaction of CH_2I Radical with Ethylene. The CH_2I radical reacts with acetylene by preferentially attacking one of the CH groups of acetylene similar to the CH_2I-I molecule. The reaction has a multistep mechanism with formation of an iodopropylene radical intermediate that has a large barrier (about 21.0 kcal/mol for B3LYP/6-311G** and 29.0 kcal/mol for B3LYP/Sadlej-pVTZ) to the formation of a cyclopropene product and an I atom leaving group. The addition of the CH_2I radical to $HC\equiv CH$ in the first step occurs relatively easily (with barriers to reaction of ∼8.5 kcal/mol for B3LYP/6-311G** or ∼5.2 kcal/mol for B3LYP/Sadlej-pVTZ) with a transition state TS2 shown in Figure 1. The C−C bond between the CH_2I radical and $HC\equiv CH$ is partially formed in TS2 with a separation of 2.252 Å at the B3LYP/6-311G** level of theory. Frequency analysis of TS2 found one imaginary frequency at 458.8i cm^{-1} with a reaction vector of $0.72\ R_{C1-C3} + 0.31\ R_{C3-C4} - 0.46\ A(C_4-C_3-H_8)$ indicating changes in the C_1-C_3 and C_3-C_4 bond lengths as well as the $C_4-C_3-H_8$ angle. The $C_1-C_3-C_4$ angle is 112.1° in TS2, and this suggests that it is not likely to form cyclopropene directly. An IRC computation indicates that TS2 connects to an intersection point RS1, which is a transition state between intermediates IM1 and P. Intermediate IM1 can change via TS3 to from another intermediate IM2, which in turn, via RS2, can form intermediate IM3 that can form intermediate P via TS5. The structures of these intermediates and intersection points are shown in Figure 1, and Figure 2 shows their relative energies. Inspection of Figure 2 shows that the intermediates IM1, IM2, IM3, and P have similar energies, with the transition states connecting them being several kcal/mol higher in energy than the intermediates.

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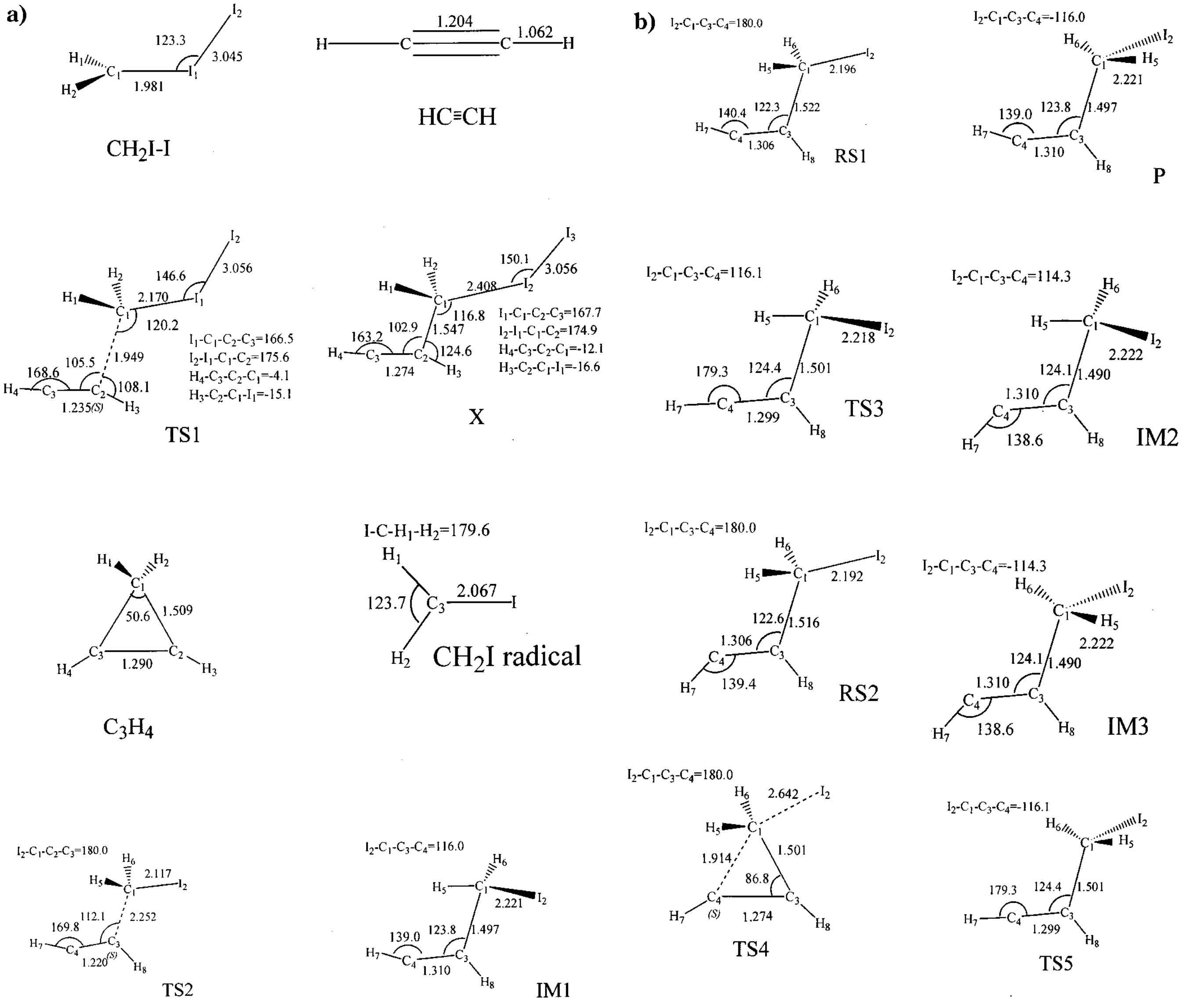

Figure 1. Schematic diagram showing the optimized geometry for selected reactants, transition state(s), intermediates, and reaction products for the reactions of CH_2I-I and the CH_2I radical with acetylene to form a cyclopropene product. The numbers present selected key structural parameters from B3LYP/6-311G** calculations (bond lengths in Å and bond angles in degrees) for the species shown (CH_2I-I, $HC\equiv CH$, TS1, X, cyclopropene, CH_2I radical, TS2, IM1, RS1, P, TS3, IM2, RS2, IM3, TS4 and TS5).

Intermediate IM2 has two reaction channels to form products from intersection RS2: one to form intermediate IM3 and a second to form cyclopropene via TS4. TS4 has one imaginary frequency, 643.3i cm^{-1}, with a reaction vector of $-0.40\ R_{C1-I2} + 0.10\ R_{C3-C4} + 0.83\ A_{C1-C3-C4}$ composed of changes in the C_1-I_2 and C_1-C_3 bond lengths and the $C_1-C_3-C_4$ bond angle. IRC calculations from TS4 show that it can form cyclopropene and an I atom directly. TS4 has C_s symmetry, although the initial guess geometry used C_1 symmetry. Further IRC calculations indicate that TS4 connects to RS2 that in turn leads to IM3. It appears important for the C–I bond to be in the plane of the C4–C3 bond for the cyclopropenation reaction to take place as well as the H_7 atom to be on the other side of the C_4-C_3 bond as the C_1 atom. This and the large barrier to reaction of 21–29 kcal/mol (from RS2 to TS4) indicate that little cyclopropenation will occur from addition of the CH_2I radical to the C≡C. It is likely that the intermediates from CH_2I radical addition to acetylene will react with other species (like iodine atom, the CH_2I radical, or CH_2I-I) to form products other than cyclopropene.

C. Comparison of Reactions of the CH_2I-I Molecule and the CH_2I Radical with Acetylene and Ethylene. The reactions of CH_2I-I with ethylene to form cyclopropane[30] and with acetylene to form cyclopropene (this work) are similar to one another reaction. The B3LYP/6-311G** transition states for both reactions (see values in parentheses for TS1 in Figure 1 of ref 24 for reaction with ethylene and those for TS1 in Figure 1 of this paper) show that the C–C bond formation is somewhat stronger (1.949 Å compared to 2.266 Å), the C–I bond is weaker (2.170 Å compared to 2.097 Å), and the C–C–C angle is larger (105.5° compared to 95.7°) for the cyclopropenation reaction relative to the cyclopropanation reaction. This suggests that CH_2I-I interacts more strongly with the more electron-rich C≡C bond than the C=C bond, and this is consistent with the CH_2I^+ cationlike character of the CH_2I moiety in the CH_2I-I species.[24,26] The bond lengths for both the C≡C and C=C bonds as well as the C–I bond in the transition states are close to those of the reactants, and the barriers for both the cyclopropenation and cyclopropanation reactions are in the entrance channel. The barrier for the cyclopropenation reaction (~3.9 kcal/mol) is moderately larger than that for the cyclopropanation reaction (~2.9 kcal/mol) at the B3LYP/Sadlej-pVTZ level of theory. Both the CH_2I-I cyclopropenation and cyclopropanation reactions occur easily with low barriers to reaction. There is one interesting difference in the two reactions. Cyclclopropenation appears to have a somewhat flat potential surface on the way from TS1 to the cyclopropene product, and this leads the TS1 IRC calculation to converge to an intermediate X, which does not happen in the analogous cyclopropanation reaction. Comparison

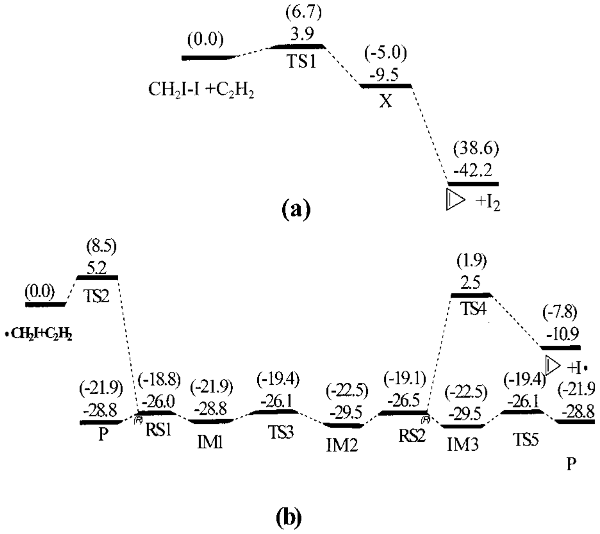

Figure 2. Schematic diagram showing the computed relative energies (in kcal/mol) for reactants, transition state(s), intermediate, and reaction products for the reactions of CH_2I-I (a) and CH_2I with acetylene (b) to form a cyclopropene product. See text for more details.

of the structure of X for the cyclopropenation to TS1 for the cyclopropanation reaction reveals that the C−I bond increases (2.408 Å for X; 2.097 Å for TS1) and the C_1-C_2 bond decreases (1.547 Å for X; 2.266 Å for TS1). Meanwhile, the $C_1-C_2-C_3$ bond angle is noticeably larger in X (102.9°) compared to that in TS1 (95.7°). X is further along the reaction path with the C−I bond cleavage and C1−C2 bond formation nearing completion and the $C_1-C_2-C_3$ angle of ~102.9° still moving toward formation of the cyclopropene product but still larger than the $C_1-C_2-C_3$ angle of ~95.7° found for TS1 of the cyclopropanation reaction. This suggests that it is important for the C−I bond cleavage, C_1-C_2 bond formation, and change in the $C_1-C_2-C_3$ bond angle accompanied by C_1-C_3 bond formation to be reasonably concerted for efficient formation of the three-membered ring product. While both the CH_2I-I cyclopropanation and cyclopropenation reactions with C═C and C≡C bonds, respectively, are concerted reactions, it appears that the formation of the three-membered cyclic ring occurs more easily for the cyclopropanation reaction.

The initial reactions of the CH_2I radical with ethylene and acetylene to form an intermediate species are similar with barriers of reaction of about 5.2 kcal/mol for both ethylene and acetylene at the B3LYP/Sadlej-pVTZ level of theory. The transition states for the CH_2I addition to ethylene (see values in parentheses for TS2 in Figure 1 of ref 24) and acetylene (see TS2 of Figure 1) at the B3LYP/6-311G** level of theory indicate that the C−C bond formation is somewhat stronger (2.252 Å compared to 2.308 Å), the C−I bond is the same (2.117 Å), and the C−C−C angle is larger (112.1° compared to 106.9°) for the acetylene (ethyne) reaction relative to the ethylene reaction. While the initial addition of the CH_2I radical is very similar for the C═C and C≡C bonds, they form distinctly different intermediates. The CH_2I radical addition to ethylene produces a relatively stable iodopropyl radical with a C−C−C angle of about 109.6° (see IM in Figure 1 of ref 24). However, the CH_2I radical addition to acetylene results in formation of a somewhat more stable intermediate iodopropylene radical that easily interconverts between several conformational forms (IM1, IM2, IM3, and P) which have different orientations of the C_4-H_7 and C−I bonds relative to the C_4-C_3 bond (see Figure 1). These iodopropylene radical intermediates have a greater C−C−C bond angle in the 122−125° range compared to the 109.6° found for the iodopropyl radical intermediate in the ethylene reaction. The presence of a C═C bond in the iodopropylene radical appears to lead to some interaction between the C−I bond and the C_4-H_7 moiety, which in turn leads to several conformations depending on the orientation of the C−I and C_4-H_7 bonds relative to one another. If the C−I bond comes close to the same plane as the C_4-C_3 bond and the orientation of the C_4-H_7 bond is away from the C_1 atom (leaving an open site to attack on C_4), then there is the possibility for the iodopropylene radical to form a cyclopropylene product and an I atom leaving group via TS4. However, the barrier to reaction is large (~21−29 kcal/mol) and not likely to be overcome.

Ultraviolet photolysis of diiodomethane in the presence of olefins has long been known to produce reasonable yields of cyclopropanated products in room-temperature solutions,[6,15,16] but we are not aware of corresponding work done with alkynes. Part of the reason for this may be because the popular and closely related Simmons−Smith cyclopropanation carbenoid reagents formed products of CH_2 introduction on the terminal C−H bond of terminal acetylenes and disubsituted acetylenes gave similar rearrangement products.[43−45] This failure of the Simmons−Smith-type reagents to give cyclopropanated or cyclopropenated products with alkynes likely led researchers not to consider using the ultraviolet photolysis of diiodomethane method. Some of the more reactive halogen-lithium carbenoids could react with cyclooctyne to produce cyclopropene products.[45] However, subsequent modifications of the Simmons−Smith reaction using organolithium reagents for cyclopropanation of olefins have not had their reactions with alkynes explored very much.[46] Our present results indicate that CH_2I-I produced from ultraviolet photolysis of diiodomethane in the condensed phase can probably be used to react with alkynes to produce appreciable amounts of cyclopropenated product. We plan to perform experimental work to examine if this is indeed the case. We hope to explore the chemical reactivity of these cyclopropenation reactions with alkynes versus cyclopropanation reactions with alkenes, and the experimental results will be reported in due course.

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Supporting Information Available: Selected output from density functional theory computations for reactions of CH_2I-I and CH_2I radicals with acetylene. This material is available free of charge via the Internet at http://pubs.acs.org.

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