Table VII. Irradiation of Diiodide 31[a]

	yield,[b] %					
solvent	31	32	(*Z*)-33	(*E*)-33	34	35
$(C_2H_5)_2O$	19	12	14	26	20	6
$(CH_2Cl)_2$	19	3	14	28	22	8

[a] Irradiations were conducted for 2 h as described in the Experimental Section. [b] Determined by gas chromatographic analysis relative to a hydrocarbon standard.

(84), 79 (35), 77 (20), 69 (83), 68 (24), 67 (54), 55 (99). Anal. Calcd for $C_{10}H_{18}I_2$: C, 30.64; H, 4.63; I, 64.74. Found: C, 30.72; H, 4.58; I, 64.34.

(B) Photoproducts. The following were isolated by preparative gas chromatography from the irradiations described in Table VII.

2,6-Dimethyl-8-iodo-2-octene (citronellyl iodide) (32) had spectral properties in agreement with those previously published.[14]

***cis*-3,7-Dimethyl-1-iodo-1,6-octadiene (33c)** was obtained as a colorless liquid: IR ν_{max} 3063, 2962, 2923, 2864, 2845, 1610, 1452, 1377, 1338, 1312, 1292, 1271, 703 cm^{-1}; ^{1}H NMR δ 6.14 (d, 1, J = 7.4 Hz, CH-1), 5.94 (dd, 1, J = 7.4, 8.4 Hz, CH-2), 1.66 (br s, 3, CH_3), 1.56 (s, 3, CH_3), 0.96 (d, 3, J = 6.8 Hz, CH_3-3); mass spectrum, *m/e* (relative intensity) 264.0375 (calcd for $C_{10}H_{17}I$, *m/e* 264.0377), 264 (1), 262 (22), 194 (52), 181 (25), 137 (100), 119 (57), 107 (27), 95 (99), 93 (47), 91 (44), 81 (93), 69 (84), 67 (98).

***trans*-3,7-Dimethyl-1-iodo-1,6-octadiene (33t)** was isolated as a clear oil: IR ν_{max} 3044, 2964, 2923, 2918, 2871, 2855, 1608, 1454, 1441, 1378, 1196, 949 cm^{-1}; ^{1}H NMR δ 6.42 (dd, 1, J = 14.4, 8.0 Hz, CH-2), 5.96 (dd, 1, J = 14.4, 1.0 Hz, CH-1), 5.02 (m, 1, CH-6), 1.65 (br s, 3, CH_3), 1.56 (s, 3, CH_3), 0.96 (d, 3, J = 6.6 Hz, CH_3-3); mass spectrum, *m/e* (relative intensity) 264.0375 (calcd for $C_{10}H_{17}I$, *m/e* 264.0377), 264 (1), 262 (23), 194 (54), 181 (29), 137 (100), 119 (55), 107 (27), 95 (99), 93 (45), 91 (40), 81 (98), 69 (84), 67 (39).

1-Iodo-2-(2-propenyl)-5-methylcyclohexane (isopulegyl iodide, 34) was obtained as a colorless oil: IR ν_{max} 3079, 2958, 2925, 2871, 1651, 1458, 1449, 1379, 1154, 1090, 939, 896 cm^{-1}; ^{1}H NMR 4.78 (m, 2, $C{=}CH_2$), 4.11 (ddd, 1, J = 11.8, 11.5, 4.1 Hz, CHI), 1.66 (br s, 3, $CH_3C{=}C$), and 0.92 (d, 3, J = 6.0 Hz, CH_3); mass spectrum, *m/e* (relative intensity) 264.0375 (calcd for $C_{10}H_{17}I$, *m/e* 264.0377), 264 (1), 262 (14), 194 (33), 181 (16), 161 (8), 137 (100), 119 (34), 95 (60), 93 (26), 91 (24), 81 (84), 79 (27), 77 (18), 69 (96), 67 (57), 55 (99).

A mixture of *cis*- and *trans*-carane (35) had spectral properties consistent with those expected from the pure cis[31] and trans[32] isomers.

Acknowledgment. Generous financial support by the National Science Foundation and the University Research Council of the University of North Carolina is gratefully acknowledged.

Registry No. **1b**, 2443-89-2; **3b**, 15501-33-4; **7**, 65826-85-9; **7**-*d*, 85390-83-6; **9**, 5469-33-0; **11**, 65826-86-0; **13**, 23904-33-8; **14**, 18231-08-8; **17**, 52470-92-5; **22**, 85390-84-7; **27**, 85390-85-8; **30**, 62617-39-4; **31**, 85390-86-9; **33c**, 85390-87-0; **33t**, 85390-88-1; **34**, 85390-89-2; cyclohexanecarboxaldehyde, 2043-61-0; cyclohexanecarboxaldehyde hydrazone, 85390-90-5; 1-deuteriocyclohexanecarboxaldehyde, 85390-91-6.

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Notes

Photochemistry of Organic Geminal Diiodides

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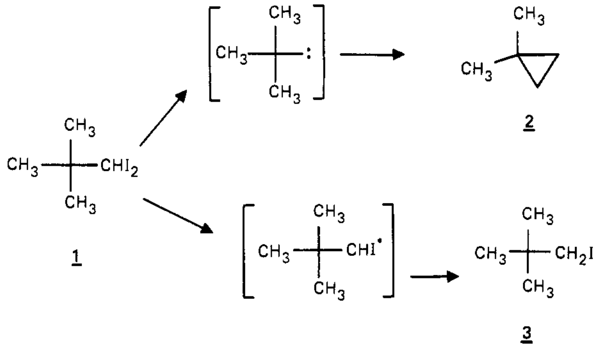
It has been previously reported that irradiation of methylene iodide in the presence of olefins results in cyclopropane products leading to speculations of a carbene or carbenoid intermediate in this photochemistry.[2,3] However, other geminal diiodes when irradiated in the presence of olefins have not yielded cyclopropanes but rather have exhibited chemistry which is dependent upon both their structure and the solvent in which they were irradiated.[3,4] In the present study, we undertook to clarify under what conditions, if any, a carbene is formed.

After the initial reports of cyclopropanation of olefins by photolysis of methylene iodide,[2] Neuman and Wolcott examined the photolysis of 2,2-dimethyl-1,1-diiodopropane (1) in nonpolar solvents such as cyclohexane and cyclohexene.[4] They did not observe formation of 1,1-dimethylcyclopropane (2), which had been shown in previous studies to be the major product from neopentylcarbene.[5] Instead, the appearance of the monoiodo product 3 as the major product provided evidence for a predominant radical pathway (Scheme I).

Scheme I



Subsequently, Kropp and co-workers examined the photochemistry of methylene iodide and 1,1-diiodomethylcyclohexane (4) in more polar media and suggested that a carbene or carbenoid intermediate could be consistent with their observations, i.e., cyclopropane products from CH_2I_2 and insertion products from 4.[3] They proposed that the formation of a carbene(oid) is preceded by initial

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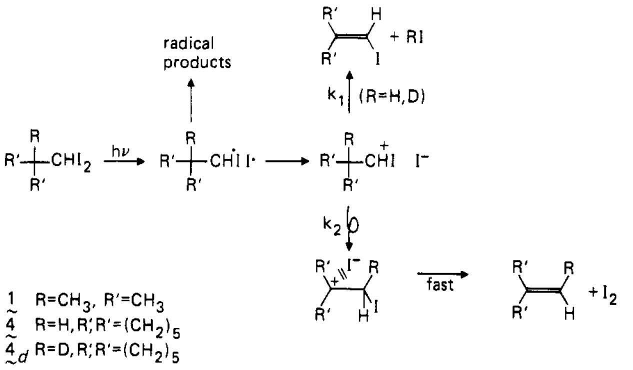
Table I. Irradiation of 1,1-Diiodo-2,2-dimethylpropane

	product yield,[a] %	
solvent	2-methyl-2-butene	1-iodo-2,2-dimethylpropane
cyclohexane[4]	trace	100
cyclohexene[4]	10	20
1,2-dichloroethane	65	trace

[a] No 1,1-dimethylcyclopropane was detected in all cases.

Scheme II



homolytic cleavage of the carbon–iodine bond followed by electron transfer to form a carbonium ion/iodide ion pair. Subsequent loss of iodine leads to carbene(oid). The intermediacy of the carbonium ion was demonstrated by trapping experiments. Failure to form the carbonium ion (in nonpolar solvents) would presumably prevent the subsequent steps leading to carbene. Thus, upon irradiation of the diiodide 1 in cyclohexane, 2 would not be expected and was not observed. However, by the above mechanism, 2 might be produced by irradiation of 1 in a more polar solvent.

We have examined the photolysis of 1 in 1,2-dichloroethane and compared the observed behavior with Neuman and Wolcott's data for irradiation in nonpolar solvents.[4] The results are shown in Table I. Analysis indicates that photolysis of 1 in 1,2-dichloroethane results in a unique product distribution, suggesting that neither a carbenoid pathway, such as for diazoneopentane,[5] nor a radical pathway, as for 1 in nonpolar solvents, is operative. The observed rearrangement of the neopentane skeleton to that of isobutylene strongly suggests the initial intermediacy of a neopentyl cation which was expected but apparently did not lead to carbene. Rearrangement of the primary cation can also explain Kropp's observation of methylenecyclohexane from 4.[3]

The deuterium labeling results from deuterated 4 (4-*d*) would be the same from a carbonium ion rearrangement or carbene insertion, i.e., for 4-*d*, deuterium would end up in the terminal methylene position as is observed.[6] However, the major product from the photolysis of 4 is not methylenecyclohexane but rather 1-iodo-methylenecyclohexane. This product, if it arises from the same rearranged intermediate, should contain approximately 50% deuterium, but recent results show that it contains none.[6] Both these observations can be explained by the mechanism proposed in Scheme II. After initial light-induced homolytic cleavage, a carbonium ion/iodide ion pair is formed. This species can undergo competing loss of a proton, k_1 (if R = H), leading to complete loss of deuterium (when R = D) or rearrangement, k_2, to a tertiary carbonium ion. From this latter species, elimination of I^+ must be fast, leading to retention of deuterium in the product. The effect of a more polar solvent, then, would be to enhance k_2. For R = H (4), this still must compete with k_1. For R = CH$_3$ (1), k_2 is the exclusive pathway.

Table II. Irradiation of α,α-Diiodotoluene

	product yield,[c] %		
solvent	stilbene	$PhCH_2I$	PhCHO/ PhCH(OMe)$_2$
methylene chloride[a]	46	trace	<2
methylene chloride/ methanol[b]	15	8	60
cyclohexene[a]	44	4	trace
cyclohexene/ methanol[b]	4	17	50
cyclohexane	38	8	trace
cyclohexane/ methanol[b]	35	7	trace

[a] Two milliliters of aqueous 10% sodium bisulfite + 10% sodium bicarbonate. [b] 95/5 volume ratio. [c] No 7-phenylnorcarane was detected in all cases.

In both the above cases, competing rearrangements precluded α elimination to generate a carbene. This is a complication not possible for methylene iodide for which cyclopropanation products are observed and the question of carbene intermediacy still exists. Thus, we chose to study the photolysis of (diiodomethyl)benzene (α,α-diiodotoluene, 5) where these alternative rearrangement pathways are prevented.

Table II lists the results for the photolysis of 5 under a variety of conditions. The data indicate that irradiation of 5 in the presence of cyclohexene in no case gave a detectable yield of 7-phenylbicyclo[4.1.0]heptane, the product of cyclopropanation. For comparison, irradiation of diazotoluene in the presence of a variety of olefins resulted in good yields of cyclopropane products.[7] The principal product from 5 was stilbene (cis and trans) except under conditions where the nucleophilic trapping agent methanol was employed. In this case, benzaldehyde and benzaldehyde dimethyl acetal were produced at the expense of stilbene. Stilbene could arise in one of several ways, perhaps by dimerization of the initially formed radical with subsequent loss of I_2. It does not appear likely that it arises by carbene dimerization since that same carbene arising by another route adds to cyclohexene.

Our work supports Kropp's recent conclusions that the intermediacy of a carbene from a geminal diiode is highly unlikely[6,8] and that the observed chemistry is completely consistent with radical and ionic pathways.

Experimental Section

Gas chromatographic analyses were performed on a Hewlett-Packard 5830A instrument by using 6 ft × $^1/_8$ in. (analytical) and $^1/_2$ in. (preparation) stainless steel columns packed with 10% OV-1 on 80–100-mesh Chromosorb. Proton NMR spectra were obtained on chloroform-*d* solutions with a Varian T 60 or EM 390 spectrometer. The diiodides were prepared by standard procedures. The irradiations were performed under a nitrogen atmosphere through Pyrex with a Hanovia medium-pressure mercury lamp. Reagent grade solvents were degassed by a stream of nitrogen prior to use. The products of the irradiations were identified by comparison with authentic samples by both gas chromatography

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(peak enhancement) and proton magnetic resonance (on preparative gas chromatography samples).

1,1-Diiodo-2,2-dimethylpropane (1.61 g, 4.98 mmol) in 1,2-dichloroethane (35 mL) was stirred with an aqueous solution of 10% sodium thiosulfate and 10% sodium bicarbonate (10 mL) and irradiated for 31 h. A sample of the organic layer was analyzed by gas chromatography with cyclopentane as an internal standard. Yields are as indicated in Table I. The identity of the major product was confirmed by a proton magnetic resonance spectrum obtained for the first fraction of the distillate of the dried (potassium carbonate) organic layer.

Diiodomethylbenzene (1.72 g, 5 mmol) in solvent (35 mL) as indicated in Table II was irradiated for 20 h. For the cases where no aqueous layer was used during the irradiation, it was added with stirring prior to the analysis. Fluorene (ca. 30 mg) was then added as an internal standard, and the organic layer was analyzed by gas chromatography.

Acknowledgment. We thank Professor Kropp for kindly sharing with us his results and comments during the preparation of this manuscript.

Registry No. 1,1-Diiodo-2,2-dimethylpropane, 2443-89-2; α,α-diiodotoluene, 28000-59-1; 2-methyl-2-butene, 513-35-9; 1-iodo-2,2-dimethylpropane, 15501-33-4; stilbene, 588-59-0; benzyl iodide, 620-05-3; benzaldehyde, 100-52-7.

Reaction of 4-(Iodomethyl)azetidin-2-ones with Tetracarbonylferrate(−II)

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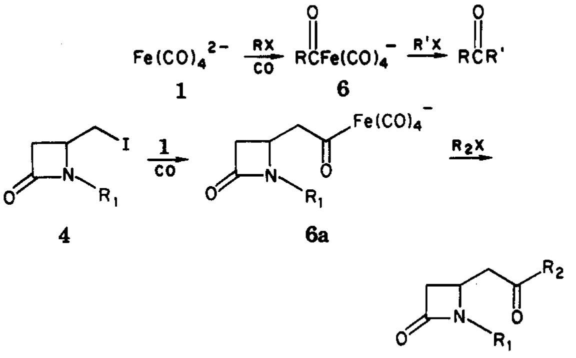
Collman and co-workers have recently introduced the use of disodium tetracarbonylferrate(−II) as a reagent for the preparation of unsymmetrical ketones according to eq 1.[1] The tetracarbonyl ferrate dianion, an excellent nucleophile, is first reacted with an alkyl halide to form the acyliron intermediate **6**, the result of initial formation of a carbon–iron bond followed by CO insertion. The intermediate **6** can also be prepared directly from **1** upon reaction with acid halides. It is less reactive than **1** and is alkylated only by the very reactice primary alkyl iodides. The reagent **1** was shown to react cleanly with primary bromides and tosylates without interference from groups such as esters and nitriles.[1] We therefore felt that it should be possible to displace iodide from the 4-(iodomethyl)azetidin-2-ones while retaining the β-lactam ring. The expected intermediates **6a** should have been further alkylated to the desired intermediates **2**[2] and **3**[3] upon treatment with the appropriate alkyl iodides.

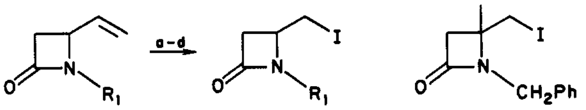


$$\mathrm{Fe(CO)_4^{2-}} \xrightarrow[\mathrm{CO}]{\mathrm{RX}} \mathrm{R\overset{O}{\overset{\|}{C}}Fe(CO)_4^-} \xrightarrow{\mathrm{R'X}} \mathrm{R\overset{O}{\overset{\|}{C}}R'}$$

2, R_2 = alkyl, H
3, R_2 = $CH_2CO_2PNB_2$

Results and Discussion

The β-lactams **4** required for this study were prepared by ozonolysis of the corresponding 4-vinylazetidin-2-ones followed by reduction of the intermediate aldehyde with sodium borohydride, tosylation and subsequent treatment with sodium iodide in acetone (eq 2). 1-Benzyl-4-(iodomethyl)-4-methylazetidinone (**5**) was obtained from 4-(chloromethyl)-4-methylazetidin-2-one via N-benzylation[4] and treatment with sodium iodide in DMF.

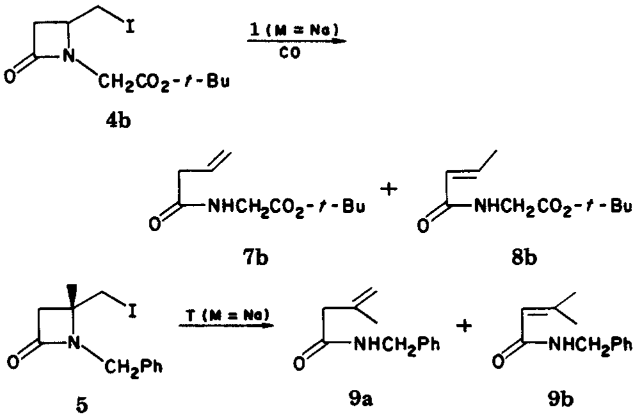


4a, R_1 = CH_2Ph
b, R_1 = CH_2CO_2-*t*-Bu
c, R_1 = $SiMe_2$-*t*-Bu
d, R_1 = *n*-Bu

5

Reagents: a, O_3; b, $NaBH_4$; c, TsCl/pyridine; d, NaI

Reaction of **4b** with the potassium salt of **1** in dry THF–10% *N*-methylpyrrolidone at 65 °C for 45 min afforded after chromatography on silica gel a roughly 2:1 mixture of the unsaturated amides **7b** and **8b** in 64% yield; there was no evidence of any of the desired β-lactam-containing product. The yield of **7** + **8** was increased to 98% when the same reaction was carried out at room temperature for 60 h. The structures of **7b** and **8b** followed readily from the NMR spectra which showed the vinylic methyl group of **8b** as a doublets (J = 6 and 2 Hz) at δ 1.13 and the $C(O)CH_2$ group of **7b** as a doublet (J = 7 Hz) at δ 3.02. Furthermore, in the series **4a** → **7a** + **8a**, the product **8a** was synthetized by reaction of methyl crotonate with benzylamine. The ratio of **7**/**8** varied somewhat with the reaction time and temperature, the amount of excess of **1**, and the workup and isolation procedure, since **7** and **8** are readily interconverted by the action of base. Similar results were obtained when **4b** was reacted with Li-*n*-BuC(O)Fe(CO)$_4$, prepared from Fe(CO)$_5$ and *n*-BuLi.[5] Finally, the tosylate corresponding to **4b** and the sodium salt of **1**, as the dioxane complex,[6] gave the above amides



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