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Photolysis of Methylene Iodide in the Presence of Olefins

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The photolysis of methylene iodide in olefins gives cyclopropanes and carbon–hydrogen insertion products. Cyclopropane formation occurs with high stereospecificity with *cis-* and *trans*-2-butene and *cis-* and *trans*-3-hexene. In auxiliary experiments, the intermediacy of iodomethyl radicals was shown to be unlikely. These observations have been interpreted in terms of the occurrence of both free methylene and an excited methylene iodide molecule.

Alkyl iodides show maximum continuous absorption in the region 2500–2600 Å., and the chemical consequence of such absorption has long been known to be homolytic fission of the carbon–iodine bond.[1] Methyl iodide has a distinct maximum at 2575 Å. (ϵ 378) in hexane solution,[2] and the quantum yield for dissociation is 0.05 at 2610 Å. and 0.008 at 3130 Å. in this solvent.[3]

$$CH_3I \xrightarrow[\text{hexane}]{h\nu} CH_3\cdot + I\cdot$$

Less is known concerning the photochemistry of aliphatic geminal diiodides. Methylene iodide has a rich spectrum with bands at 2120 (ϵ 1580), 2400 (ϵ 600), and 2900 Å. (ϵ 1300)[2]; the last consists of two overlapping bands. Previous studies have suggested that two processes (A and B) follow photon absorption. Gibson and Iredale found the quantum yield for the production of iodine atoms at 3130 Å. to be 0.55 in hexane[4] and assumed B as the initial mode of dissociation. Gregory and Style showed the quantum yield to increase to 1.45 in the presence of oxygen in the vapor phase at 3100 Å.,[5] and from product and kinetic studies they concluded that A is the important initial process.

$$CH_2I_2 \xrightarrow{h\nu} CH_2\colon + I_2 \qquad (A)$$

$$CH_2I_2 \xrightarrow{h\nu} CH_2I\cdot + I\cdot \qquad (B)$$

In later work, Style and co-workers[6,7] studied the fluorescence emission when methylene iodide is irradiated in the gas phase with light of 1250–2000-Å. wave length. They observed the spectrum of excited molecular iodine and showed that this was not due to combination of iodine atoms followed by secondary absorption. Their work supports process A*, which is expected to be favored thermochemically with light of about 1750 Å. or shorter wave length.

$$CH_2I_2 \xrightarrow{h\nu} CH_2\colon + I_2^* \qquad (A^*)$$

From these studies it can be concluded that absorption of photons with energies of 1200–3100 Å. gives excited methylene iodide molecules that dissociate primarily by path A and A*. If this is so, it might be expected that irradiation of methylene iodide in the presence of olefins would reveal the presence of free methylene *via* cyclopropane formation and/or insertion into carbon–hydrogen bonds.

Results and Discussion

When a 0.4 *M* solution of methylene iodide in diethyl ether was irradiated at 35° with a low-pressure mercury coil, 24% of the iodide disappeared in 22 hr. No gases were evolved, and iodine and hydriodic acid were detected in the solution. Vapor phase chromatography (v.p.c.) showed several products in individual low yields; three of these were identified as ethyl *n*-propyl ether, ethyl isopropyl ether, and methyl iodide in the ratio 1:2.7:8.3. When this experiment was repeated in two-phase systems containing sodium thiosulfate solution or tin metal to remove iodine and acid, the results were unchanged.

When a 2 *M* solution of methylene iodide in cyclohexene was irradiated at 35° with a low-pressure mercury coil, 19% of the methylene iodide was consumed after 44 hr. V.p.c. analysis showed a 3% yield

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(1) See review by E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I and II, Reinhold Publishing Corp., New York, N. Y., 1954.

(2) K. Kimura and S. Nagakura, *Spectrochim. Acta*, **17**, 166 (1961).

(3) N. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

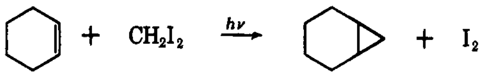
(4) K. E. Gibson and T. Iredale, *ibid.*, **32**, 571 (1936).

(5) R. A. Gregory and D. W. G. Style, *ibid.*, **32**, 724 (1936).

(6) P. J. Dyne and D. W. G. Style, *J. Chem. Soc.*, 2122 (1952).

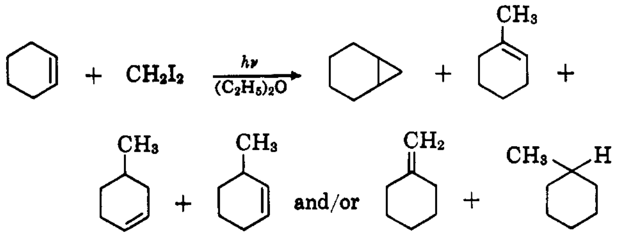
(7) D. W. G. Style and J. C. Ward, *ibid.*, 2125 (1952).

of norcarane and only a trace of other C_7 hydrocarbons.[8] Of the methylene iodide that was consumed, 14% was converted to norcarane. Irradiation with an AH-6 high-pressure mercury lamp or a GE sunlamp gave 7 and 4% yields of norcarane, respectively. In all cases an iodine color developed rapidly so that the solutions transmitted little light after about 6 hr. Experiments carried out for 4–6 hr. indicated qualitatively that the initial rate of norcarane formation is similar to that of the disappearance of methylene iodide, so that an early primary reaction is



although the fate of all the methylene iodide over long irradiation times was not accounted for. Irradiation of a mixture of cyclohexene and methylene iodide with a low-pressure mercury lamp in a quartz vessel in the vapor phase (1–25 mm.) produced no norcarane and only traces of methylcyclohexenes.

When the photolysis was carried out in a dilute ether solution of cyclohexene with a low-pressure mercury lamp until 50% of the iodide was consumed, ethylene (2%) and methane (2%) were evolved, and the solution contained norcarane (10%), 1-methylcyclohexene (1%), 3-methylcyclohexene and/or methylenecyclohexane (1%),[9] 4-methylcyclohexene (0.5%), and methylcyclohexane (0.1%; yields based on methylene iodide consumed). It was further shown that formation of norcarane and the methylcyclohexenes was a consequence of absorption of light near 2900 Å. by methylene iodide. When the irradiation was carried out using an acetone filter so that only a small region (<5%) on the low energy side of the long-wave-length band of methylene iodide was available for absorption, norcarane formation was detected at once and could be followed by v.p.c. After *ca.* 2% norcarane was formed, an iodine color developed and the initial rate (qualitative) became erratic.



In other solvent studies using the AH-6 lamp, irradiation in tetrahydrofuran, methanol, and benzene for 6.5 hr. gave 4, 3, and 11% yields of norcarane, respectively, based on methylene iodide charged.

From these observations, three intermediates were considered as possible precursors to norcarane, methylcyclohexenes, and/or ether insertion products: (1) iodomethyl radical, (2) methylene, and (3) an electronically excited methylene iodide molecule.

Iodomethyl Radical.—Although the carbon–iodine bond energy in $ICH_2\cdot$ is not known with certainty, it has been pointed out[5] that vibrationally excited $ICH_2\cdot$ would be expected to lose an iodine atom very rapidly. In the ground state, the electron density on carbon may not be so strongly reduced owing to overlap of a p-orbital on carbon with several iodine orbitals

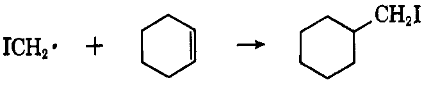
$$I{-}\dot{C}H_2 \longleftrightarrow \dot{I}{=}CH_2$$

as it is in the case of chlorine and bromine because of the diffuseness of the large iodine orbitals. If this is so, $ICH_2\cdot$ may show considerable reactivity in addition and abstraction reactions.

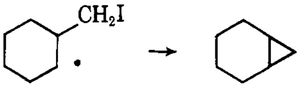
A possible mechanism for the formation of norcarane from cyclohexene and $ICH_2\cdot$ is shown by eq. 1–4 where

$$CH_2I_2 \xrightarrow{h\nu} ICH_2\cdot^* + I\cdot \qquad (1)$$

$$ICH_2\cdot^* + S \xrightarrow[\text{fast}]{} ICH_2\cdot + S^* \qquad (2)$$



(3)



(4)

eq. 2 represents relaxation in the solvent S. Only a few examples of additions involving $ICH_2\cdot$ (eq. 3) are recorded, although other halomethyl radicals are well known to add to unactivated double bonds.[10] Benzoyl peroxide has been reported to catalyze the addition of methylene iodide to ethylene to give 1,3-diiodopropane.[11] The most unlikely step is 4, since radical displacements on carbon of this type are believed to be uncommon.

Examples of processes that involve a radical displacement on carbon are the reactions of cyclopropane with iodine atoms[12] (which may also involve a displacement on carbon by a carbon radical) and spiropentane with chlorine atoms.[13] In our work, some experiments were carried out to try to demonstrate a carbon–carbon radical displacement by generating 3-iodopropyl radicals by other means.

4-Iodobutyryl peroxide was prepared from 4-iodobutyryl chloride and 30% hydrogen peroxide in ether. Pyrolysis of the peroxide in the vapor phase under reduced pressure occurred at a significant rate at 225° and was surprisingly clean. 1,3-Diiodopropane and γ-butyrolactone were isolated in 66% yield in exactly a 1:1 ratio, and the gaseous products were carbon dioxide (92%) and cyclopropane (2–3%). Although this result afforded no support for eq. 4, it was sufficiently interesting to pursue briefly. Since it is known[12] that 1,3-diiodopropane produces significant amounts of cyclopropane under these conditions, the low yield of cyclopropane probably arose in this man-

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[8] V.p.c. analysis and isolation techniques for the compounds discussed in this paper are described by E. P. Blanchard and H. E. Simmons [*J. Am. Chem. Soc.*, **86**, 1337 (1964)].

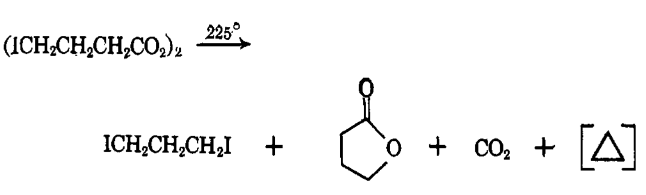
[9] On the v.p.c. columns employed[8] it was not possible to separate 3-methylcyclohexene and methylenecyclohexane. In these studies, synthetic mixtures of all of the pertinent C_7 hydrocarbons were available for comparison.

(10) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 6.

(11) J. Harmon, T. A. Ford, W. E. Hanford, and R. M. Joyce, *J. Am. Chem. Soc.*, **72**, 2213 (1950).

(12) R. A. Ogg, Jr., and W. J. Priest, *J. Chem. Phys.*, **7**, 736 (1939); S. W. Benson, *ibid.*, **34**, 521 (1961).

(13) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Am. Chem. Soc.*, **82**, 2368 (1960).

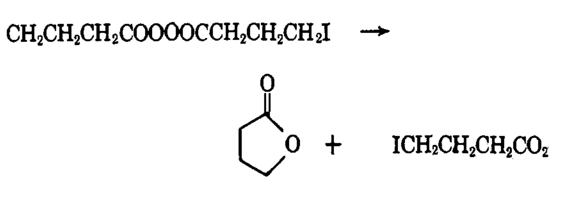


ner. The mechanism of formation of the primary products is not known but may involve a long, but clean, radical-chain process.

$$(ICH_2CH_2CH_2CO_2)_2 \longrightarrow 2ICH_2CH_2CH_2CO_2\cdot \quad (5)$$

$$ICH_2CH_2CH_2CO_2\cdot \longrightarrow ICH_2CH_2CH_2\cdot + CO_2 \quad (6)$$

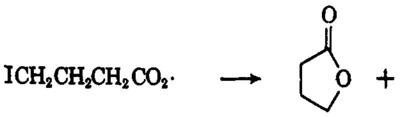
$$ICH_2CH_2CH_2\cdot + (ICH_2CH_2CH_2CO_2)_2 \longrightarrow ICH_2CH_2CH_2I + \cdot CH_2CH_2CH_2COOOOCCH_2CH_2CH_2I \quad (7)$$



(8)

Step 8 is an intramolecular example of the well-known induced decomposition of diacyl peroxides.[14] Some evidence for this scheme was obtained by carrying out the vapor phase pyrolysis in the presence of iodine, where a negligible quantity of γ-butyrolactone was formed and the product was almost exclusively 1,3-diiodopropane. This may indicate that iodine acts as a chain terminator by scavenging $ICH_2CH_2CH_2\cdot$ and/or $ICH_2CH_2CH_2CO_2\cdot$ provided that it is not consumed solely in inducing peroxide decomposition. 4-Bromobutyryl peroxide was prepared and pyrolyzed under the same conditions as the iodo compound. The only products observed were γ-butyrolactone and 1,3-dibromopropane.

A referee has pointed out that the pyrolysis of 4-iodobutyryl peroxide might better be interpreted in terms of eq. 5, 6′, and 7′. His argument is that, since

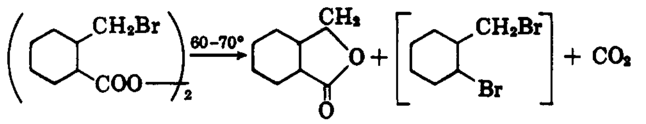


(6′)

$$I\cdot + (ICH_2CH_2CH_2CO_2)_2 \longrightarrow ICH_2CH_2CH_2I + CO_2 + ICH_2CH_2CH_2CO_2\cdot \quad (7')$$

step 7 is essentially thermoneutral, hydrogen abstraction to produce secondary radicals ought to be competitive and important, and further that a reaction similar to 6′ would explain the decomposition of 2-bromomethylcyclohexanecarbonyl peroxide (see below). The results from the iodine-trapping experiment can also be explained *via* this alternative scheme. This suggestion certainly merits consideration, although a displacement reaction such as 7′ perhaps is no more likely than 7. Unfortunately, no experimental evidence has been obtained to favor either alternative.

In other experiments, we attempted to prepare a radical more structurally similar to that which might be involved in the methylene iodide photolysis studies. The reaction of silver bromoacetyl peroxide and *t*-butyl bromoperacetate in cyclohexene gave complex mixtures in which no norcarane was detected. An attempt was made to prepare the 2-bromomethylcyclohexyl radical directly. 2-Bromomethylcyclohexanecarbonyl peroxide was synthesized from the corresponding acid chloride and aqueous alkaline hydrogen peroxide. The peroxide was decomposed in monoglyme at 60–70°, and the only product identified in the complex mixture was hexahydrophthalide. A small amount of a liquid bromide, presumed to be 2-bromomethylcyclohexyl bromide, was also detected. Although carbon dioxide was evolved, no trace of norcarane was found.

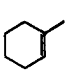
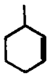
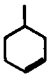


From these observations we cannot rule out the intermediacy of $ICH_2\cdot$ in the formation of norcarane during photolysis of methylene iodide in cyclohexene. In our opinion, however, it is more reasonable to consider the following alternatives.

Methylene.—The occurrence of norcarane and the methylcyclohexenes among the products in the reaction under question could be explained by the intermediacy of free methylene. The photolyses of diazomethane in cyclohexene[15] and in cyclohexene containing the photosensitizer benzophenone[16] produce predominantly singlet and triplet methylene, respectively. The product distribution in these reactions is given in Table I.

Table I

Product Distribution from Reaction of Methylene with Cyclohexene

Source[a]				
Photolysis of CH_2N_2 (singlet)[b]	1	0.25	0.63	0.63
Photolysis of CH_2N_2 with benzophenone (triplet)[c]	1	Trace	0.42[d]	
Photolysis of CH_2I_2	1	~0.1		~0.05

[a] All photolyses were carried out in diethyl ether. [b] See ref. 15. [c] See ref. 16. [d] Combined yield of 3-methyl- and 4-methylcyclohexene.

The result from the photolysis of methylene iodide is not quite comparable to either of those involving diazomethane. This is probably not due to the heavy-atom effect of having methylene iodide and iodine in the medium which could disturb the normal rate of spin relaxation, since the photolysis of diazomethane in the presence of methyl iodide[16] gave the same results as shown in the first row of Table I. Our results could be interpreted in terms of the occurrence of both singlet and triplet methylene in roughly comparable quantities, except that less carbon–hydrogen insertion occurs at the allylic and aliphatic positions.

In general, singlet methylene reacts with olefins stereospecifically to produce cyclopropanes with considerable concurrent carbon–hydrogen insertion, while

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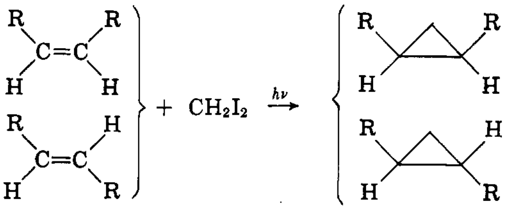
[14] Also see P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1864 (1963).

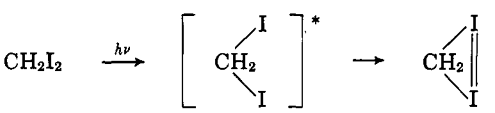
[15] W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

[16] K. R. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **84**, 1015 (1962).

triplet methylene favors nonstereospecific cyclopropane formation and reduced insertion.[17] The criterion of stereospecificity was tested by photolyzing methylene iodide in benzene solutions of *cis*- and *trans*-2-butene and in *cis*- and *trans*-3-hexene with the olefin as solvent. The irradiations were carried out until *ca.* 2% of the cyclopropane had formed, and the additions were found to be stereospecific. In each case, none of the isomeric cyclopropane was detected; however, the limit of detection would not preclude the presence of up to 5% of the other isomer. Pure samples of the four product cyclopropanes were prepared by the addition of iodomethylzinc iodide to the corresponding olefins.[18] The insertion products were formed in yields too low to isolate or measure. The high stereospecificity of these additions suggests that the reacting system is rich in singlet methylene. This result is not readily reconciled, however, with the low degree of insertion observed in these studies and those with neat cyclohexene.

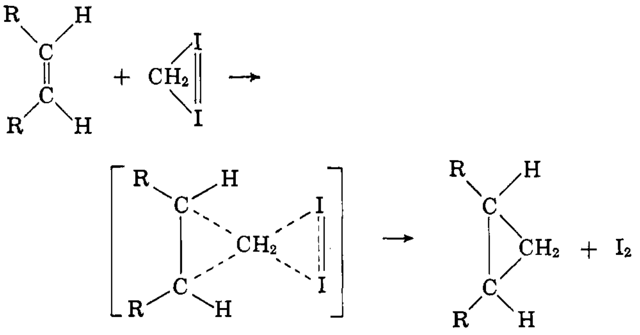


Excited Methylene Iodide.—Another possibility is that an electronically excited methylene iodide (I) or a valence tautomer (II) is an important intermediate. It is interesting to note that theoretical interpretation of the methylene iodide spectrum suggests that the lowest excited state involves considerable iodine–iodine interaction,[2,19] so that decay of I to II may be favorable. The experiments with filtered light showed that this state (corresponding to absorption at 2900 Å.) produced the species ultimately giving cyclopropanes. This state is presumably a singlet[2]; however, intersystem crossing could produce the corresponding triplet.

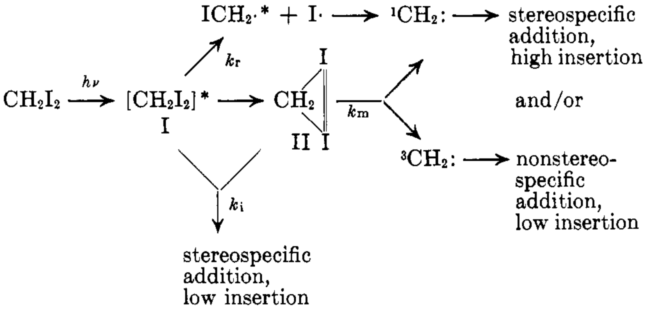


I II

It seems reasonable on energy grounds that either I or II might collide with a double bond to transfer the methylene group to form a cyclopropane stereospecifically, especially if they are considered to be in singlet states. Such a process is analogous to methylene-transfer reactions previously postulated for iodomethylzinc iodide and similar reagents.[18,20] It is also expected that I or II, like other methylene-transfer reagents, will show only low reactivity in carbon–hydrogen insertions.



The photolysis of methylene iodide in the presence of olefins can be interpreted then in terms of the intermediacy of I or II, methylene, and iodomethyl radical. In particular, the occurrence of I or II could account for the large amount of (stereospecific) cyclopropane formation relative to carbon–hydrogen insertion under certain conditions. Excited methylene iodide (I) presumably is the precursor of iodomethyl radical and methylene. It is unlikely that iodomethyl radical gives methylene under these conditions (irradiation at >3000 Å.).[6,7] Such a scheme is also in accord with the observation that much less carbon–hydrogen insertion occurred in neat cyclohexene than in ether solution. This would be reasonable if the excited methylene iodide has an appreciable lifetime with respect to dissociation to $ICH_2\cdot(k_r)$ or to methylene (k_m). The reaction of the excited intermediate with an olefin is a bimolecular process (k_i) whose rate will depend on the olefin concentration. Therefore, it is only necessary that $k_i > k_m$, k_r to have agreement with observation. As the concentration of double bonds is lowered by replacement of olefin by saturated solvents, the rate of the bimolecular process is depressed compared with the unimolecular dissociation which produces methylene. Apparently, $k_i > k_r > k_m$, since in the absence of olefin the major product produced is methyl iodide when the irradiation is carried out in diethyl ether, a solvent whose α hydrogens are prone to radical abstraction. It is also conceivable that II can react with ether to produce methyl iodide directly; however, we have no evidence yet on the fate of the ether fragment. Our results suggest, then, that cyclopropanes formed during photolysis of methylene iodide in olefins are produced primarily by reaction of I or II with the double bond in a methylene-transfer process.



Experimental

Melting points are corrected and boiling points are uncorrected. The v.p.c. columns and spectrometers used in this study have been described in ref. 8, 18, and 20.

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[17] For vapor phase results, see H. M. Frey, *Proc. Roy. Soc.* (London), **A250**, 409 (1959); **A251**, 575 (1959); F. A. L. Anet, R. F. W. Bader, and A.-M. Van der Auwera, *J. Am. Chem. Soc.*, **82**, 3217 (1960); H. M. Frey, *ibid.*, **82**, 5947 (1960). For reactions in solution, see P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956); ref. 16.

[18] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

[19] R. S. Mulliken, *Phys. Rev.*, **47**, 413 (1935); *J. Chem. Phys.*, **8**, 382 (1940); **8**, 234 (1940).

[20] E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964); H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

Irradiation of Methylene Iodide in Ether.—Methylene iodide (10.72 g., 0.040 mole) in diethyl ether (100 ml.) was irradiated at 35° for 22 hr. in a quartz tube under nitrogen with a low-pressure mercury coil. No gas was evolved during the irradiation period, at the end of which 76% of the methylene iodide was recovered. The ether solution was washed with sodium thiosulfate and sodium bicarbonate solutions to remove iodine and hydriodic acid. V.p.c. on previously described columns[8] showed the presence of a large number of minor products. Three major products were proved to be ethyl isopropyl ether, ethyl *n*-propyl ether, and methyl iodide by comparison with authentic samples. The combined yield was low and was not accurately determined; however, the ratio of these products was 8:3:25, respectively.

When this experiment was repeated in the presence of a stirred aqueous phase containing sodium thiosulfate, 35% of the methylene iodide was consumed after 67 hr. Titration showed that 43% of the sodium thiosulfate had been destroyed. The yields of methyl iodide and propyl ethers were not significantly different from previous experiment yields. In another experiment, tin powder was added to the ether solution before irradiation but again the results were essentially unchanged.

Irradiation of Methylene Iodide in Cyclohexene.—Methylene iodide (55 g., 0.21 mole) in cyclohexene (83 ml.) was irradiated at 35° in a quartz tube with a low-pressure mercury coil. After 44 hr., 81% of the methylene iodide remained, and analysis by v.p.c. showed that 14% of the methylene iodide consumed was converted to norcarane. The other C_7 hydrocarbons were formed in no more than trace amounts.

In a similar experiment, methylene iodide (5.5 g., 0.021 mole) in cyclohexene (8.1 ml.) was irradiated at 35° with an AH-6 high-pressure mercury lamp. After 6.5 hr. the norcarane yield was 7% based on the iodide charged. In another run, the solution was degassed by freezing and thawing *in vacuo*, sealed, and irradiated 4.75 hr. after which time the norcarane yield was 4%. In still another run, benzophenone (0.18 g.) was added after 3 hr. of irradiation at which time the rate of norcarane formation determined by v.p.c. was constant. After the photosensitizer was added, the rate tripled initially but slowed after 3 hr. of further irradiation.

When methylene iodide (13.3 g., 0.05 mole) in cyclohexene (20 ml.) was irradiated with a GE sunlamp at 35° for 37 hr., the yield of norcarane was 4% based on methylene iodide charged.

Irradiation of Methylene Iodide in Cyclohexene (Acetone Filter).—Two quartz tubes were charged with methylene iodide (2.0 g., 0.0075 mole) and cyclohexene (5.0 g., 0.061 mole), and one tube was surrounded with an acetone filter whose absorbance was >2 at 3240 Å. Both tubes were irradiated simultaneously with a low-pressure mercury lamp for 60 hr. Norcarane formation could be detected in both tubes by v.p.c. after a few minutes of irradiation, and an iodine color was detected only after several hours. Norcarane was formed to the extent of *ca.* 5% in both tubes, the yield in the tube surrounded by the filter being 75% of that in the unfiltered run.

This experiment was repeated using a polystyrene filter which admitted *ca.* 10% of the light with a wave length of 2750 Å. The results were practically the same as in the former experiment.

Irradiation of Methylene Iodide and Cyclohexene in Ether.—A solution of methylene iodide (5.36 g., 0.020 mole) in diethyl ether (40 ml.) was added over 22 hr. to a solution of cyclohexene (11 g., 0.13 mole) in diethyl ether (100 ml.) heated at reflux and contained in a quartz flask that was continuously irradiated with a low-pressure mercury lamp. During this period a gas was evolved which was shown by v.p.c. to consist of methane and ethylene, each formed in 2% yield. V.p.c. analysis[8] of the reaction mixture showed it to contain norcarane (10%), 1-methylcyclohexene (1%), 3-methylcyclohexene and/or methylenecyclohexane (1%), 4-methylcyclohexene (0.5%), and methylcyclohexane (0.1%). The indicated yields are based on methylene iodide consumed in the reaction. Unchanged methylene iodide (50%) was recovered from the reaction mixture.

In other experiments, methylene iodide (1.66 g., 0.0062 mole) and cyclohexene (2.4 g., 0.029 mole) were irradiated in various solvents at 35° for 6.5 hr. with an AH-6 mercury lamp. In separate runs, 10 ml. of tetrahydrofuran, methanol, and benzene were employed as solvents, and the yields of norcarane based on methylene iodide charged were 4, 3, and 11%, respectively. The other products were not accurately determined.

Irradiation of Methylene Iodide with *cis*- and *trans*-3-Hexene.—In separate experiments, *cis*- and *trans*-3-hexene (1.0 g., 0.012 mole) and methylene iodide (3.0 g., 0.011 mole) were placed in a quartz tube equipped with a magnetic stirrer. The iodide is only partially soluble in the olefin and the mixture was stirred vigorously during reaction. The mixture was irradiated under nitrogen with a low-pressure mercury coil. After 18 hr. the mixture was diluted with 5 ml. of ether, and the ether solution was washed successively with sodium thiosulfate solution and water and was dried over sodium sulfate. The reaction mixture from *cis*-3-hexene contained only one major product in addition to recovered olefin as shown by v.p.c., which was shown to be *cis*-1,2-diethylcyclopropane by direct comparison with an authentic sample.[18] Other products were detected only in trace amounts, and the maximum yield of *trans*-1,2-diethylcyclopropane, if present, could have been no more than 5%. The product from the reaction of *trans*-3-hexene was similarly shown to be *trans*-1,2-diethylcyclopropane[18] with the same limit of contamination by the *cis* isomer.

These experiments were repeated with *cis*- and *trans*-2-butene under the same conditions except that benzene was used as a solvent. The products were compared by v.p.c. with authentic *cis*- and *trans*-1,2-dimethylcyclopropane prepared from the olefins and iodomethylzinc iodide.[18] In each case the irradiation reactions were 95–100% stereospecific. No carbon–hydrogen insertion products were detected under these conditions.

4-Iodobutyryl Peroxide.—4-Iodobutyric acid was prepared from γ-butyrolactone and hydrogen iodide according to the procedure of Oelschlaeger, Schmersahl, and Toporski.[21] The acid (11.0 g., 0.051 mole) was dissolved in thionyl chloride (10 ml.) and the mixture was allowed to stand at 25° for 2 hr. The mixture was heated for 15 min. on the steam bath and then distilled directly under reduced pressure. **4-Iodobutyryl chloride** was obtained in 80% yield as a colorless oil, b.p. 65–70° (0.6 mm.).

Anal. Calcd. for C_4H_6ClIO: C, 20.66; H, 2.60. Found: C, 21.18; H, 2.82.

The peroxide was prepared following the general procedure of Criegee.[22] 4-Iodobutyryl chloride (1.6 g., 0.0069 mole) was dissolved in ether (50 ml.), and the solution was stirred and cooled to −5°. Hydrogen peroxide (30%, 3.80 ml.) was added dropwise over 3 min. followed by the dropwise addition over 20 min. of a solution of sodium hydroxide (3.0 g.) in water (15 ml.). During the additions the temperature was maintained at −10 to −5°. Stirring was continued for 15 min., the ether layer was decanted and dried over sodium sulfate, and the ether was removed under vacuum in an ice bath. The residue was crystallized from ether–petroleum ether at −40°. Colorless crystals (1.15 g., 78%) of **4-iodobutyryl peroxide**, m.p. 30–31°, were obtained.

Anal. Calcd. for $C_8H_{12}I_2O_4$: C, 22.56; H, 2.84. Found: C, 22.61; H, 3.13.

The infrared spectrum showed the characteristic peroxide doublet at 5.52 and 5.63 μ.

Pyrolysis of 4-Iodobutyryl Peroxide.—4-Iodobutyryl peroxide (1.30 g., 0.00305 mole) was placed in a small flask connected to a vertical pyrolysis tube packed with quartz rings. The top exit of the tube was attached to a trap cooled in liquid nitrogen. The apparatus was evacuated to 0.002-mm. pressure, and the pyrolysis tube was heated by an electrical furnace to 225° (inside thermocouple). The flask containing the peroxide was heated slowly to 85° by an oil bath, and the peroxide sublimed almost completely over 5 hr. The volatile products collected in the trap were analyzed by mass spectroscopy. The gas was principally carbon dioxide (92.2 mole %) and cyclopropane (2–3 mole %).

The nonvolatile liquid in the trap consisted of two components formed in almost exactly a 1:1 ratio as shown by v.p.c. Comparison of the chromatogram with those of authentic samples showed the products to be γ-butyrolactone and 1,3-iodopropane. The mixture was dissolved in ether, washed with sodium thiosulfate solution and with water, and dried over sodium sulfate. Distillation gave 600 mg. (66%) of 1,3-diiodopropane whose infrared spectrum was identical with that of an authentic sample.

The above experiment was repeated in an apparatus modified by the attachment of a second flask *via* a side arm to the pyrolysis tube. An excess of iodine was placed in the second flask, and the peroxide and iodine were sublimed concurrently into the pyrolysis zone. The products were worked up as before, and no γ-

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(21) H. Oelschlaeger, P. Schmersahl, and W. Toporski, *Arch. Pharm.*, **294**, 488 (1961).

(22) R. Criegee in Houben-Weyl, "Methoden der Organischen Chemie," Vol. III, Georg Thieme Verlag, Stuttgart, 1952, p. 81.

butyrolactone could be detected. The only product identified was 1,3-diiodopropane which was formed in good yield. It was further shown that γ-butyrolactone was stable under the conditions of the experiments.

Preparation and Pyrolysis of 4-Bromobutyryl Peroxide.—**4-Bromobutyryl chloride** was prepared according to a general literature procedure[21] and was obtained as a colorless oil, b.p. 40° (0.6 mm.).

Anal. Calcd. for C_4H_6BrClO: C, 25.90; H, 3.26. Found: C, 26.38; H, 3.49.

The chloride was converted to the peroxide by a procedure similar to that described for the iodo derivative. 4-Bromobutyryl peroxide was obtained as a colorless oil that could not be induced to crystallize. Attempts at purification led to much decomposition; however, the infrared spectrum was very similar to that of the iodo peroxide and revealed only small impurities. The sample was used directly in pyrolysis experiments.

The vapor phase decomposition of the bromo peroxide was carried out analogously to that of the iodo compound. No cyclopropane was detected, and the only products that were identified by v.p.c. were γ-butyrolactone and 1,3-dibromopropane.

2-Bromomethylcyclohexanecarboxylic Acid Chloride.—Hexahydrophthalide (12.0 g., 0.086 mole) and anhydrous hydrogen bromide (27.0 g., 0.34 mole) were heated in a sealed tube for 1 hr. at 100°. The tube was cooled, and the excess hydrogen bromide was removed under reduced pressure. The residue was dissolved in thionyl chloride (30 ml.) and the solution was heated for 1 hr. on a steam bath. Distillation gave 18.4 g. (90%) of **2-bromomethylcyclohexanecarboxylic acid chloride**, b.p. 90–100° (0.5 mm.).

Anal. Calcd. for $C_8H_{12}BrClO$: C, 40.12; H, 5.05. Found: C, 40.30; H, 4.87.

The infrared spectrum showed a carbonyl stretching vibration at 5.60 μ.

Preliminary experiments showed that the acid chloride reacted very slowly with alkaline hydrogen peroxide. The acid chloride (4.78 g., 0.020 mole) in ether (15 ml.) was treated with 30% hydrogen peroxide (1.44 ml.) and sodium hydroxide (1.2 g.) in water (10 ml.). The mixture was stirred for 24 hr. at −5° and was then worked up as previously described for 4-iodobutyryl peroxide. 2-Bromomethylcyclohexanecarbonyl peroxide (0.50 g.) was obtained as a crystalline white solid at −70° from ether–petroleum ether. The peroxide was very sensitive to losses during purification, and acceptable analyses could not be obtained although the products had a clean infrared spectrum. On heating it decomposed violently at 65°. The recrystallized product was used in the pyrolysis experiments.

A solution of the peroxide (0.32 g., 0.00073 mole) in monoglyme (1 ml.) was heated at 60–70° until gas evolution ceased. No norcarane was detected in the residue by a v.p.c. technique sufficiently sensitive to detect 0.2%. Hexahydrophthalide (0.12 g.), identical with an authentic sample, and a liquid believed to be 2-bromomethylcyclohexyl bromide (*ca.* 0.05 g.) were also isolated. The former was determined by direct v.p.c. calibration, but the small amount of the bromide was only estimated.

Excited State p*K* Values. III. The Application of the Hammett Equation

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The possibility of application of the Hammett equation to the acid–base equilibrium constants in excited states of aromatic acids and bases was investigated. The excited state p*K* values are obtained by use of the Förster cycle, and the assumptions and approximations involved in its use are reviewed and carefully examined. The most important conclusion is that excited-state p*K* values conform, at least roughly to linear free-energy relations with ground-state parameters (σ). Universally, exalted substituent constants are required, probably because of the highly polar nature of excited states. The data presented suggest that *meta-* and *para-*substituted compounds may require different reaction constants (ρ). An attempt is made to interpret magnitudes of reaction constants for the p*K* values of different excited states in various reaction series.

The chemistry of excited states has recently become a focal point of wide interest. On the one hand, a large number of investigators are delving deeply into the mechanisms of reactions occurring in excited states. On the other hand, the pioneering work of Förster,[2] Weller,[3] and Porter[4] has paved the way to the measurement of chemical equilibria between molecules in their excited states; in particular, of acid–base equilibria.

Since acid–base equilibria have been one of the original and most fruitful areas for the application of linear free-energy relations, the question arises naturally whether such relations will be equally applicable to electronically excited states. The only attempt to provide an answer to this question is contained in the investigations of Bartok and co-workers.[5] Before we deal with these papers, we must briefly discuss the experimental techniques used to obtain excited-state equilibrium data.

The determination of the p*K* of a compound in the electronic ground state is readily achieved if it is possible to estimate the ratio of the concentrations of a conjugate acid–base pair as a function of pH. An analogous procedure is, of course, applicable to excited states. The entire field of excited-state equilibrium measurements was therefore opened when Förster showed that the fluorescence spectra of a few acids depended on pH. When it was shown that this pH dependence of fluorescence in the excited state was vastly different from the pH dependence of the absorption of the ground-state species, it was demonstrated that equilibrium had been established in the excited state. Careful fluorescence measurements in buffered solutions then permit determination of the p*K* in the excited singlet state (p*K**). This technique, however, is extremely exacting, very time consuming, and applicable only to compounds in which at least one of the pair of conjugate acid–base fluoresces. The last factor produces some extreme limitations.

The measurement of the p*K* values of the lowest triplet state is achieved by a method of Porter.[4] It involves excitation of the substrate in buffered solution to the triplet state by flash photolysis, followed by triplet–triplet absorption measurements, which are

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[1] Procter and Gamble Fellow, 1963–1964.

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[5] (a) W. Bartok, P. J. Lucchesi, and N. S. Snider, *J. Am. Chem. Soc.*, **84**, 1842 (1962); (b) W. Bartok, P. J. Lucchesi, and R. B. Hartman, *ibid.*, in press.