On the Mechanism of Iodination. The Addition of Iodine to 9,10-Dihydro-9,10-ethenoanthracene

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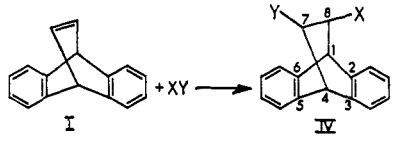
Abstract: The addition of iodine to 9,10-dihydro-9,10-ethenoanthracene (I) in nonpolar solvents proceeds by an ionic mechanism yielding as the sole product *endo*-4-*syn*-8-diiododibenzobicyclo[3.2.1]octadiene (II). The rearranged diiodide II slowly isomerizes at room temperature to an equilibrium mixture of the starting materials, *exo*-4-*anti*-8-diiododibenzobicyclo[3.2.1]octadiene (VI), and its thermodynamically more stable isomer, *trans*-7,8-diiododibenzobicyclo[2.2.2]octadiene (III). Irradiation of a solution of iodine and I at low temperature (−22°) produced exclusively the product of free-radical addition, *trans*-7,8-diiododibenzobicyclo[2.2.2]-octadiene.

The mechanism of the addition of halogen to unsaturated hydrocarbons has received the attention of numerous workers. Attempts to establish a consistent mechanism for the halogenation of olefins in nonpolar media have only served to demonstrate the complexity of the reaction.[1–3] Recently, Poutsma[4] has demonstrated that at ambient temperatures, in the absence of molecular oxygen, carbon tetrachloride solutions of cyclohexene are chlorinated by mechanisms involving ionic and/or free-radical pathways. Our attempts to investigate this duality of mechanisms in iodine addition reactions has not met with great success, but in the course of these investigations, both the ionic and free-radical addition reactions of iodine to 9,10-dihydro-9,10-ethenoanthracene (I) have been observed and a mechanistic distinction between the two reaction pathways can clearly be made in this system.

Discussion and Results

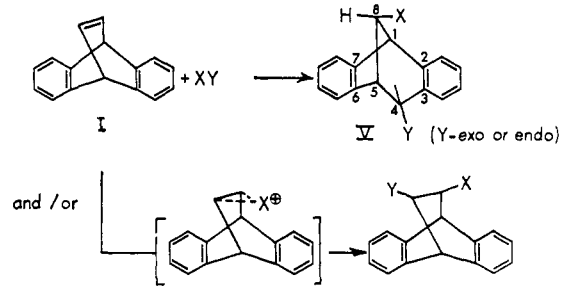
The reactions of 9,10-dihydro-9,10-ethenoanthracene (I) have been investigated extensively by Cristol and co-workers[5–7] and on the basis of these studies, both the products of ionic and free-radical addition can be predicted. Radical addition would lead one to expect 7,8-disubstituted dibenzobicyclo[2.2.2]octadiene (IV), the unrearranged addition product (Scheme I). Ionic

Scheme I. Radical Addition



addition would yield rearranged 4,8-disubstituted dibenzobicyclo[3.2.1]octadiene (V), or possibly unrearranged products if the effects of neighboring group participation were to predominate (Scheme II).[7,8]

Scheme II. Ionic Addition



Since the mechanism clearly defines the products in this system, the mode of addition of iodine to this olefin could be investigated profitably.

Nuclear magnetic resonance correlations have been published on the dibenzobicyclo[3.2.1]octadiene system[9] and these correlations provided a sensitive tool for both structural assignment and quantitative analysis. The assignments made by Cristol, Mohrig, and Plorde of both proton chemical shifts and coupling constants for a variety of substituents having all four of the possible combinations of stereochemistry for the 4,8-disubstituted dibenzobicyclo[3.2.1]octadienes enabled us to follow the course of the reaction using nmr spectroscopy. Both rearranged (V) and unrearranged (IV) ring systems have easily differentiable nmr spectra,[10] and mixtures of the two systems could be detected with better than 2% accuracy by the Varian HR 100 spectrometer.

Nmr Studies of Radical Addition. When an oxygen-free $CDCl_3$ solution 0.4 *M* in both iodine and I was kept in the dark at −47°, no trace (<2%) of either free-radical or ionic addition products could be detected after 14 hr. When the solution was warmed to −22°, the appearance of the spectrum of the rearranged diiodide II could be observed. Equimolar carbon tetrachloride solutions of iodine and I (0.4 *M*) at −22° in the absence of light could be observed to undergo a very slow ionic addition reaction to form II (a maximum value of its assumed bimolecular rate constant is 10^{-6} l./mole sec, $t_{1/2}$ = 695 hr). The nmr spectrum taken periodically showed the gradual appearance of II (15% in 72 hr) while no detectable amount (<2%) of

(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.
(2) P. B. D. de la Mare, *Quart. Rev.* (London), 3, 126 (1949).
(3) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959.
(4) M. L. Poutsma, *J. Am. Chem. Soc.*, 87, 2161 (1965).
(5) S. J. Cristol and R. K. Bly, *ibid.*, 82, 6155 (1960).
(6) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, 28, 1374 (1963).
(7) S. J. Cristol, F. P. Parungo, and D. E. Plorde, *J. Am. Chem. Soc.*, 87, 2870 (1965).
(8) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *ibid.*, 87, 2870 (1965).
(9) S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, 30, 1956 (1965).
(10) Private communications of unpublished works from Dr. Cristol's laboratory on the nmr spectra of the rearranged and unrearranged ring systems.

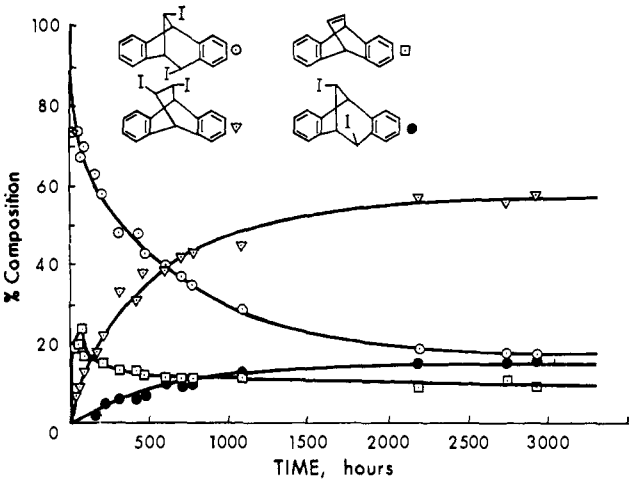


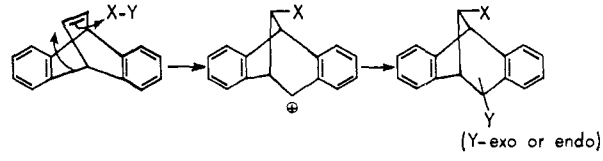
Figure 1.

the unrearranged diiodide III could be observed. Irradiation of a degassed sample at −22° for several hours produced as the sole detectable product *trans*-7,8-diiododibenzobicyclo[2.2.2]octadiene (III).

Under our conditions, −22°, equimolar concentrations of iodine and I (0.4 *M*) and in the absence of oxygen, we could observe no detectable "spontaneous" radical addition of iodine, while under similar conditions "spontaneous" halogenation reactions for *t*-butyl hypochlorite[11] and for chlorine[4] are observed.

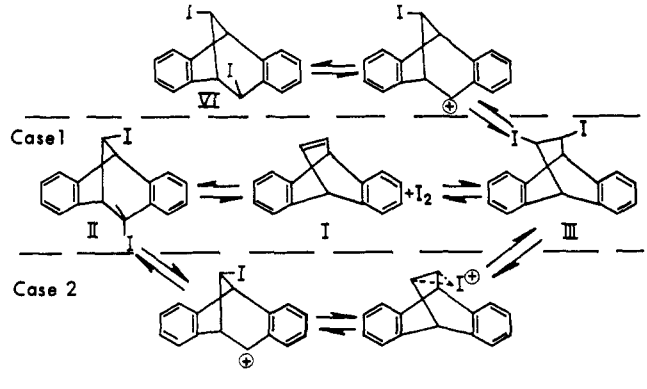
Nmr Studies of Ionic Addition, Rearrangement, and Equilibration. The addition of iodine to I leads exclusively to the rearranged diiodide II by a stereospecific addition–rearrangement similar to that found with chlorine.[6] In carbon tetrachloride, as well as in chloroform, the reaction is exothermic and proceeds extremely rapidly. In both solvents the only product which is detectable by nmr was II. More than 2% of the unrearranged or of the other rearranged isomeric diiodides would have been observed. When a $CDCl_3$ solution of pure II remained, in the absence of light, at room temperature for extended periods of time a gradual change in its nmr spectrum was observed. The disappearance of the spectrum of II and the appearance of the spectra of I and III, as well as that of a third product (VI), could be followed by periodically taking the nmr spectrum of the solution, which was always kept in complete darkness. If one of the samples was looked at in the light, the strong color of iodine confirmed the existence of the starting materials in the equilibrium mixture. A plot of per cent concentration of the equilibrium products *vs.* time (Figure 1) indicates the approximate concentration of the five components in the equilibrium mixture. Isolation of the equilibrium product having the spectrum of the [2.2.2]diiodide (III) and the comparison of its melting point and mixture melting point confirmed its identity to be the same as the product formed by photoaddition. The diiodide VI we have assigned as having the *anti*-8-*exo*-4-diiodibenzobicyclo[3.2.1]octadiene structure on the basis of its nmr spectrum (see Table II). Efforts to isolate this product have so far been unsuccessful. As a check on the equilibrium values, a $CDCl_3$ solution of pure III was allowed to remain at room temperature in the absence of light, in a degassed nmr tube for a similar length of time to the solution of II. The spectrum of the solution of III underwent an extremely slow change (approximately 6–10% in 3×10^3 hr) to give an identical spectrum (exclusive of quantity, since equilibrium was not reached) which was obtained during the equilibration of II.

Stereospecific addition–rearrangement of I to give the *syn–endo* and *exo* epimeric pair of rearranged isomers without the formation of any nonstereospecific rearrangement products has been firmly established.[6,7]



It has been argued[6] that as X and Y increased in size the steric interaction between the *syn–exo* diaxial substituents would favor the formation of the *syn–endo* product, which although the thermodynamically more stable of the two is not the product of kinetic preference. The observation, that the addition of the sterically large iodine molecule to I produces only the single predicted diiodinated isomer, II, seems to substantiate both the stereospecificity of the reaction and the steric requirements of the substituents. The kinetic behavior of II in its rearrangement back to starting materials, III and VI, Figure 1, is that of a typical four-component equilibrium. Two questions pose themselves upon examining this equilibrium: first, does the rearrangement of II to III proceed through olefin (see Chart I), as in case 1, or can II directly rearrange to

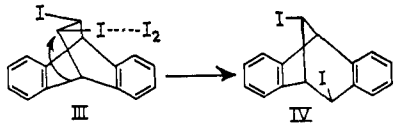
Chart I



III *via* carbonium ion intermediates, as in case 2, or possibly a combination of the two; and, second, is the very slow addition of iodine to I in case 1 the thermodynamically favored ionic addition, or, in fact, the extremely slow "spontaneous" radical addition? The complete solution to these problems is not available at this time, but some evidence does exist that the rearrangement of II to III proceeds through the intermediacy of ions similar to those depicted in case 2. The stereospecific rearrangement of *syn*-8-iododibenzobicyclo[3.2.1]octadien-*exo*-2-ol acetate with perchloric acid in acetic acid (equilibrium conditions) to yield *trans*-3-iododibenzobicyclo[2.2.2]octadien-2-ol acetate has been explained by Cristol[8] as proceeding by a series of ions which are equivalent to those in case 2. In this reaction as well as in ours, if this path for rearrangement is invoked, neighboring group participation of iodine is

(11) C. Walling, L. Heaton, and D. D. Tanner, *J. Am. Chem. Soc.*, 87, 1715 (1965).

necessary to explain the formation of *trans* product. *cis* isomers have been established to be the sole products formed in these [3.2.1] to [2.2.2] rearrangements, unless neighboring group participation has dictated otherwise.[8] In the presence of appreciable amounts of iodine it is not surprising to find a lack of complete stereochemical control by the bridged iodonium ion, since one would expect iodine-assisted solvolysis leading to the *anti*-8-[3.2.1]system to be a favorable process.[8,12]



Structural Assignments. The structures of the rearranged and unrearranged diiodides and their derivatives can be assigned on the basis of their nmr spectra. The empirical correlations (Table I) presented by Cristol, *et al.*, are consistent with our assumptions and with the independent chemical evidence throughout our work.

Table I[a]. Average Values for Coupling Constants for 4- and 8-Substituted Dibenzobicyclo[3.2.1]octadiene[b]

	Spin–spin coupling constants, J (cps)
exo-4-Substituted (*endo*-4 proton)	$J_{45} = 1.8 \mp 0.5$
endo-4-Substituted (*exo*-4 proton)	$J_{45} = 5.1 \mp 0.5$
syn-8-Substituted (*anti*-8 proton)	$J_{18} = J_{58} = 4.2 \mp 1.0$
anti-8-Substituted (*syn*-8 proton)	$J_{18} = J_{58} = <1$

[a] See ref 9. [b] Limits of error are standard deviations.

endo-4-*syn*-8-Diiododibenzobicyclo[3.2.1]octadiene (II). Compound II showed nmr absorption at τ (4 H) 3.52, (8 H) 5.32, (5 H) 6.31, and (1 H) 6.09, with $J_{45} = 5.1$ cps and $J_{18} = 4.7$ cps,[13] and on this basis was assigned the *syn–endo* structure (II). In order to confirm this structural assignment the acetolysis of II was carried out. Heating a glacial acetic acid solution of II to 60° produced iodine and therefore it was necessary to use silver acetate to assist in the solvolysis. The silver-catalyzed acetolysis of II produced two isomeric iodoacetates, VII (25%) and VIII (75%). The structure of VII and VIII could be assigned by nmr. The nmr spectrum and the melting point of VII established its identity as that of the known *syn–exo* iodoacetate.[7,9]

exo-4-*anti*-8-Diiododibenzobicyclo[3.2.1]octadiene (VI). The structure of VI was assigned purely on the basis of its nmr spectrum. The bands at τ 4.43 and 4.68 have been assigned to the *endo*-4 and the *syn*-8 protons of VI, respectively. The 5 proton absorbed at τ 5.76 and spin-decoupling experiments showed it to be coupled to the 4 H at τ 4.42. The 1 H can be assumed to be hidden under the peaks of the 7,8 protons of III. This assumption is confirmed by the difference in integration areas between the 1,4 and 7,8 protons of III. The spin–spin coupling constants for VI, $J_{45} = 2.3$ cps and $J_{18} = <1$ cps, are consistent with an *anti*-8-*exo*-4-diiodide.

trans-7,8-Diiododibenzobicyclo[2.2.2]octadiene (III). Diiodide III showed the easily distinguishable twin, two-proton multiplets characteristic of the 7,8-disubstituted dibenzobicyclo[2.2.2]octadiene ring system.[10] Since the photoinitiated product and the disubstituted [2.2.2] product obtained from equilibrations were identical, it was reasonable to assign to III the *trans* configuration. In order to substantiate this assignment the silver-assisted solvolysis of III in acetic acid was carried out. It has been shown that the solvolysis of *cis*-7,8-disubstituted dibenzobicyclo[2.2.2]octadienes leads exclusively to *syn–exo* and *syn–endo* products while the solvolysis of the *trans* isomers leads exclusively to *anti–endo* and *anti–exo* products.[8] The silver-assisted acetolysis of III leads to a mixture of *anti*-8-iododibenzobicyclo[3.2.1]octadien-*exo*-2-ol acetate (IX, 63%) and *anti*-8-iododibenzobicyclo[3.2.1]octadien-*endo*-2-ol acetate (X, 37%). The structural assignments of IX and X can be made on the basis of their nmr absorptions (see Table II).

Table II. Proton Chemical Shifts and Spin–Spin Coupling Constants for the Disubstituted Dibenzobicyclo[3.2.1]octadiene in $CDCl_3$

Compd	Chemical shift, τ (ppm) 4 H	8 H	5 H	1 H	J, cps[a]
II	3.52	5.32	6.31	6.09	$J_{45} = 5.1$ $J_{18} = 4.7$
VI	4.42	4.65	5.76	Masked	$J_{45} = 2.3$ $J_{18} = <1$
VII	3.51	5.01	6.05	5.87	$J_{45} = 1.0$ $J_{18} = 3.5$
VIII	4.23	5.16	6.27	5.92	$J_{45} = 5.4$ $J_{18} = 4.4$
IX	4.17	4.87	6.16	5.72	$J_{45} = 2.1$ $J_{18} = <1$
X	3.75	5.19	5.78	5.86	$J_{45} = 5.0$ $J_{18} = <1$

[a] J values obtained from first-order analysis.

Experimental Section

Nmr Studies. The nmr spectra, where high accuracy of integration ($\lesssim 2\%$) is indicated or where variable temperature or spin-decoupling experiments are indicated, were obtained using the Varian HR100 spectrometer. The relative areas of the absorption bands were obtained using a Varian V-3521 integrator. The proton chemical shifts are relative to tetramethylsilane and were assigned from the A-60 spectrum of the pure compounds. Routine nmr spectra were obtained using the Varian A-60 spectrometer. The reactions followed in the nmr were run in degassed Pyrex nmr tubes and were obtained oxygen free by the freeze–thaw method and then were sealed. The solutions always were kept at the indicated temperature during these operations. Irradiation of the samples was carried out using a 200-w tungsten bulb. The samples were irradiated through an unsilvered Pyrex dewar containing the sample and the appropriate cooling bath.

endo-4-*syn*-8-Diiododibenzobicyclo[3.2.1]octadiene (II). A carbon tetrachloride solution of I, 0.40 g (0.653 *M*), and 0.50 g (0.656 *M*) in iodine, was stirred at room temperature in the absence of light until the first solid material crystallized (about 15 min). Stirring was continued for 1 additional hr, while 6 ml of petroleum ether (bp 60–70°) was added slowly. The reaction mixture was cooled in an ice bath and the solid material was collected and washed with a 2:1 mixture of cold petroleum ether–carbon tetrachloride. The crude product, 0.60 g (67%), melted at 108–109°. Recrystallization from petroleum ether–carbon tetrachloride gave an analytical sample of II, mp 110.5–111°. The nmr spectrum of II was consistent with its assigned structure (see Table II).

(12) F. R. Jensen and W. E. Coleman, *J. Org. Chem.*, **23**, 809 (1958).
(13) J values reported in this paper were obtained by first-order analysis of the spectra.

Anal. Calcd for $C_{16}H_{12}I_2$: C, 41.95; H, 2.64. Found: C, 41.65; H, 2.54.

***trans*-7,8-Diiododibenzobicyclo[2.2.2]octadiene (III).** A 20-ml carbon tetrachloride solution of 0.4 g of I and 0.51 g of iodine was irradiated for 2 hr at reflux. The contents of the Pyrex reaction vessel was warmed by the heat of the two 200-w tungsten lamps by which it was irradiated. The solvent was removed and the oily product was washed with petroleum ether. The pink crystals were collected and the material was recrystallized from a 1:1 mixture of carbon tetrachloride and petroleum ether. The yield was 300 mg (33%) of a white crystalline product, mp 146.5–147°. The nmr spectrum showed it to be the unrearranged diiodide III. Compound III had nmr absorption bands centered τ 2.67 (eight protons), 5.50 (two protons), and 5.72 (two protons).

Anal. Calcd for $C_{16}H_{12}I_2$: C, 41.95; H, 2.64. Found: C, 41.79; H, 2.87.

A solution of 64 mg of I and 52 mg of iodine in 0.3 ml of CCl_4 was irradiated at −22° as was the above mixture. The nmr spectrum indicated the formation of III. The solvent was evaporated and the product was washed with cold methanol. It gave white crystals, mp 146.5–147.5°, which did not depress the melting point of the irradiation product from the photoaddition at reflux temperatures.

Acetolysis of II. To a stirred 10-ml solution of dry acetic acid containing 413 mg (0.902 mmole) of II was added 149 mg (0.892 mmole) of silver acetate. The mixture was stirred for 30 min and the yellow precipitate of silver iodide was filtered and washed with additional acetic acid. The acetic acid was removed from the filtrate and an nmr spectrum in $CDCl_3$ of the residual oil (373 mg) was taken. The spectrum showed absorption bands consistent with a mixture of *syn*-8-iododibenzobicyclo[3.2.1]octadien-*exo*-2-ol acetate (VII, 25%) and its epimeric isomer the *syn*-8-iodo-*endo*-2-acetate (VIII, 75%). The mixture was subjected to alumina chromatography on a column made of 25 g of Woelm neutral alumina packed with petroleum ether. The column was eluted with progressive mixtures of petroleum ether, carbon tetrachloride, chloroform, and ethyl acetate. Fractions eluted with chloroform and carbon tetrachloride mixtures yielded two products whose nmr spectra were those of VII and VIII. Compound VII had the nmr spectrum of the authentic *syn*-8-iodo-*exo*-2-acetate and the same melting point (144–145°) as this previously reported compound. Compound VIII, mp 165–167°, had an nmr spectrum consistent with the *syn*-8-iodo-*endo*-2-acetate (see Table II).

An analytical sample of VIII was obtained by sublimation and recrystallization from ethanol.

Anal. Calcd for $C_{18}H_{15}IO_2$: C, 55.40; H, 3.87. Found: C, 55.45; H, 3.76.

Acetolysis of III. A 10-ml solution of 420 mg (0.916 mmole) of III and 119 mg (0.713 mmole) of silver acetate in glacial acetic acid was stirred for 1 hr. The yellow silver iodide precipitate was filtered and the residue was washed with glacial acetic acid. The filtrate was evaporated by rotary evaporation leaving 483 mg of residual oil. An nmr spectrum of the crude mixture indicated the presence of the two isomeric iodoacetates IX and X in the ratio of 63:37, respectively. The mixture was subjected to alumina chromatography on a column packed with 25 g of Woelm neutral alumina in carbon tetrachloride. The column was eluted with carbon tetrachloride and carbon tetrachloride solutions of chloroform. The fractions eluted with pure carbon tetrachloride contained 57 mg (0.124 mmole) of unreacted starting material, as determined by melting point, mixture melting point, and nmr spectra. The fractions eluted with pure chloroform contained 296 mg (83%) of a 63:37 mixture of the compounds assigned the structures IX and X. The mixture was a white crystalline product, mp 128–142°. By the use of integration and spin-decouplinge xperiments the structures of IX and X could be assigned from the nmr spectra of the mixture (see Table II). Analysis of a mixture of the two epimeric iodoacetates agreed with the structural assignments.

Anal. Calcd for $C_{18}H_{15}IO_2$: C, 55.40; H, 3.87. Found: C, 55.31; H, 3.88.

Acknowledgment. The authors are indebted to Dr. S. J. Cristol for his kindness in supplying the details of his then unpublished nmr work and for his helpful discussion concerning the rearrangement reactions.