[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVESRSITY]

Iodine and Styrene. II.[1a] The Kinetics and Mechanism of the Formation of Styrene Diiodide

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RECEIVED APRIL 14, 1959

In carbon tetrachloride at 25° the formation of styrene diiodide from iodine and excess styrene is an equilibrium reaction. Carefully degassed, the reactants (0.17 *M* styrene and 0.01 *M* iodine) approach equilibrium with a half-time of less than two minutes. Oxygen in saturated solution or 2,2-diphenyl-1-picrylhydrazyl (DPPH) at 2×10^{-4} *M*, reduces the rate by more than a hundredfold to the same reproducible value in both cases. In the latter case, however, iodine is still disappearing 15 times as fast as DPPH. These facts are interpreted as indicating the existence of both a radical–chain mechanism which can be inhibited by efficient radical-capturing reagents and a non-radical reaction which cannot be so inhibited. The experiments with DPPH show a rate of generation of radicals expressible as 1.2×10^{-8} *M* sec.$^{-1}$, much faster than the thermal dissociation of iodine molecules in the gas phase. The kinetics of the uninhibited reaction, followed with a recording spectrophotometer, indicates an over-all first-order dependence of the rate on iodine concentration and a 3/2-order dependence on styrene concentration. This is consistent with a chain mechanism of the type proposed by Schumacher and Polissar for ethylene diiodide, but with an initiating step involving one iodine and two styrene molecules. The kinetics of the inhibited reaction is also consistent with this sequence of steps. Pure benzoquinone and bromanil occupy a peculiar place as inhibitors in that they produce a constant retardation to a rate about ten times that allowed by oxygen or DPPH. A possible interpretation of these results is discussed. In strong light iodine is consumed from the equilibrium mixture of styrene, iodine and styrene diiodide. One product was identified by synthesis as 1,4-diiodo-2,3-diphenylbutane; evidence from spectra, chemical behavior and molecular weight indicates that the principal product has the composition of a tristyrene diiodide; it may reasonably be 1,6-diiodo-1,2,5-triphenylhexane.

Introduction

The introduction of iodine into a system undergoing change by free radical paths provides a simple means for identifying the intermediates and measuring their rates of formation. This method[2–6] has found extensive and successful application and iodine appears to be one of the most efficient radical scavengers known.

Thus iodine inhibits the radical polymerization of vinyl acetate,[7] allyl acetate,[8] styrene and methyl methacrylate.[9] Concentrations of iodine as low as 10^{-5} *M* in styrene and vinyl acetate at 25° were found to inhibit polymerization for months at a time.

Consideration of the mode and nature of primary processes in thermal polymerization[10–12] and of the possibility of iodine interference with initiation has prompted investigation of the styrene–iodine system under a variety of conditions.

Among the several reactions[13,14] between iodine and styrene the rapid reversible addition to yield styrene diiodide is a simple appearing process for which many analogies exist. Bromination of the double bond is known to proceed, depending upon the environment and structure of the olefin, by way of an ionic mechanism or by a free radical chain.[15]

In view of the powerful inhibition by iodine of free radical polymerization, one might at first suppose that iodine atoms were incapable of attacking the double bond. The present investigation has shown that such a surmise is incorrect; more than 99% of the rapid addition of iodine to styrene at room temperature occurs by a chain mechanism.

The work described here deals with the kinetic aspects of styrene diiodide formation together with some studies on the photochemical reaction between iodine and styrene.

Results

The Action of Inhibitors.—The formation of styrene diiodide from styrene and iodine in carbon tetrachloride was followed by observing the consumption of iodine spectrophotometrically. In order to learn something about the general character of the mechanism the reaction was studied in the presence of oxygen, quinones and 2,2-diphenyl-1-picrylhydrazyl (DPPH) (see Table I).

TABLE I

THE REACTION OF STYRENE (0.1736 *M*) WITH IODINE (0.0107 *M*) IN CARBON TETRACHLORIDE

Run	*T*, °C.	Added substance	$\left(\frac{-d(I_2)}{dt}\right)_i \times 10^7$ m./l. sec.
17	25	O_2[a]	1.64
30	25	Quinone,[b] 0.0902 *M*	1.50
31	25	DPPH,[c] 0.000202 *M*	1.63
38	25	Quinone,[d] 0.0914 *M*	19.8
28	25	Bromanil, 0.005 *M*	15.9
53	22	None	200

[a] Saturated solution in CCl_4. [b] Impure. [c] $d(DPPH)/dt = 1.15 \times 10^{-8}$ m./l.sec. [d] Highly purified.

All these added materials behave as retarders (*cf.* run 53) and since they are all free radical scavengers the radical–chain nature of styrene diiodide formation is strongly indicated.

The Uninhibited Reaction.—With such information in mind, it was not suprising that only under the most rigorous conditions of reactant purity, deoxygenation and absence of stopcock grease was

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(1) (a) Part I, D. S. Trifan and P. D. Bartlett, THIS JOURNAL, **81**, 5573 (1959). (b) From a thesis submitted for the Ph.D. degree by Gideon Fraenkel, Harvard University, January, 1957.

(2) E. Gorin, *Acta Physiochim., U.R.S.S.*, **8**, 513 (1938).

(3) E. Gorin, *ibid.*, **9**, 681 (1938).

(4) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

(5) A. Feldman, unpublished work.

(6) G. S. Hammond, THIS JOURNAL, **72**, 3737 (1950).

(7) P. D. Bartlett and H. Kwart, *ibid.*, **72**, 1051 (1950).

(8) G. S. Hammond, Thesis, Harvard University, 1947, p. 73.

(9) R. H. Jones, Thesis, Harvard University, 1952.

(10) (a) F. R. Mayo, THIS JOURNAL, **75**, 6133 (1953); (b) R. R. Hiatt and P. D. Bartlett, *ibid.*, **81**, in press (1959).

(11) G. M. Burnett and L. D. Loan, *Trans. Faraday Soc.*, **51**, 219 (1955).

(12) K. E. Russell and A. V. Tobolsky, THIS JOURNAL, **75**, 5052 (1953).

(13) (a) D. S. Trifan, Thesis, Harvard University, 1948; (b) Part I of this series, THIS JOURNAL, **81**, 5573 (1959).

(14) P. D. Bartlett, *Angew. Chem.*, **67**, 51 (1955).

(15) P. B. D. de la Mare, *Quart. Revs.* (*London*), **3**, 126 (1949).

it possible to obtain reproducible results for the uninhibited reaction (see Table II). At 22° the reactants approach equilibrium with a half-time of less than two minutes.

TABLE II
THE UNINHIBITED REACTION OF STYRENE WITH IODINE IN CARBON TETRACHLORIDE

Run	T, °C.	k^a × 10^8	$(S)_0{}^d$, m./l.	$(I_2)_0$, m./l.	$\left(\frac{-d(I_2)}{dt}\right)_i$ × 10^5 m./l. sec.^{c}
52	22	7.9	0.1736	0.00955	1.90
53	22	7.8	.1736	.0102	1.98
54	8	..	.1736	.0090	1.17
55	8	..	.1736	.0095	1.20
56	22	..	.1736	.0108	1.90^b
58	22	9.0	.1736	.02032	4.00
61	22	7.7	.3441	.01016	6.42
62	22	9.6	.3441	.00530	3.40
64	22	23.4	.3472	.02032	12.9
66	22	10.4	.2604	.01050	3.40
68	22	6.7	.3472	.000530	0.15
72	22	7.6	.3472	.00405	2.56
73	22	5.0	.3472	.000203	0.107

[a] Uncorrected pseudo first-order rate constants, sec.$^{-1}$. [b] Initial rate after induction period. [c] Initial rates of reaction. [d] Zero subscripts indicate initial concentrations.

An induction period was observed only in run 56 where the degassed styrene solution in the cell had been stored about two hours at room temperature.

Comparison of the initial rates in runs 52, 53, 54 and 55 yields an apparent activation energy of 6 ± 1 kcal.

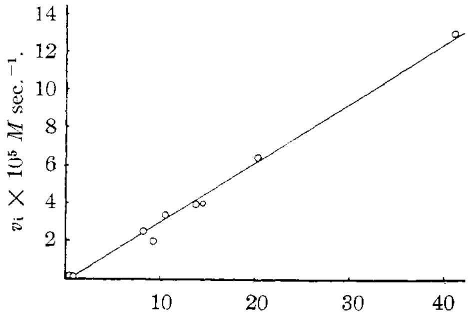

Fig. 1.—Linear variation of initial rate of iodine disappearance (v_i) with $(I_2)(S)^{3/2}$ in nine runs.

The initial rate of reaction is three-halves order in styrene and first order in iodine (equation 1), as shown by Fig. 1 and from the slope of Fig. 1, k' = 3.2×10^{-2} $M^{-3/2}$sec.$^{-1}$. The styrene was present

$$\left[\frac{-d(I_2)}{dt}\right]_i = k'(S)^{3/2}(I_2) \qquad (1)$$

in an excess of eight- to over a thousand-fold; the variation of iodine concentration with time could be expressed by two relationships, (2) and (3), as illustrated by Figs. 2 and 3. The constants

$$\log((I_2) - (I_{2\infty})) = -kt + c_1 \qquad (2)$$

$$\log\frac{(I_2)^{1/2} - (I_{2\infty})^{1/2}}{(I_2)^{1/2} + (I_{2\infty})^{1/2}} = -k''t + c_2 \qquad (3)$$

in (2) and (3) are characteristic only for particular runs; $(I_{2\infty})$ is the equilibrium concentration of iodine.

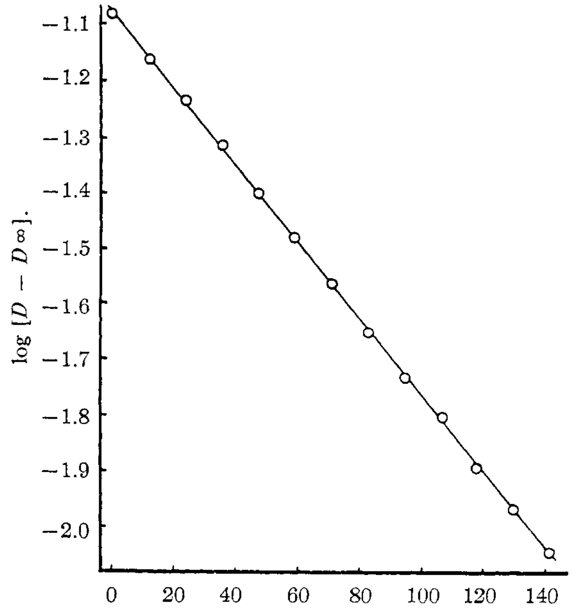

Fig. 2.—Decrease in iodine concentration, plotted according to equation 2.

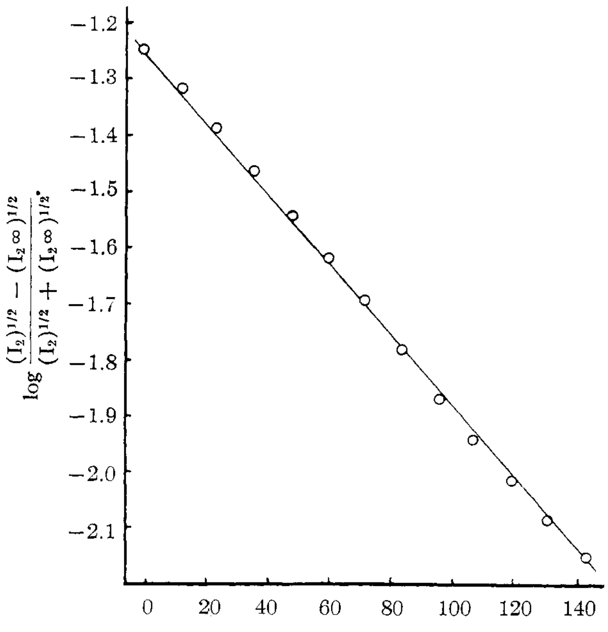

Fig. 3.—Decrease in iodine concentration, plotted according to equation 3.

Evidence for a Simultaneous Non-chain Mechanism.—The compound 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been used successfully to study rates of initiation in polymerizing systems. As long as oxygen is excluded the results are reproducible. The formation of styrene diiodide in carbon tetrachloride was strongly retarded by DPPH. By following the reaction at two different wave lengths it was possible to study the disappearance of iodine and of DPPH separately. The rate of iodine consumption in run 31 was the lowest observed in this work (see Table I) and very similar to that for inhibition by impure quinone and high concentrations of oxygen. Both the iodine and DPPH in run 31 disappeared linearly with time, *iodine reacting 15 times as fast as DPPH.* The rate of initiation as measured by the consumption of DPPH was 1.15 × 10^{-8} M sec.$^{-1}$. Combining this result with the initial rate of reaction in run 52 one obtains a kinetic chain length of about 1750. These data strongly suggest that the substances DPPH, impure quinone and oxygen in saturated solution scavenged most of the radicals produced during initiation while styrene diiodide was being formed by an alternate non-radical path.

The Chain Mechanism.—It can be shown easily that the rate of initiation of run 31 was much too high to be accounted for by either thermal dissociation of iodine or thermal initiation by styrene molecules. Noyes has shown by a kinetic method, in at least one case, that the degree of thermal dissociation[16] of iodine in non-polar solvents is very close to that in the gas phase. The equilibrium constant for $I_2 \rightleftarrows 2I\cdot$ in the gas phase is calculated from statistical mechanics[17] to be 2.98 × 10^{-23} M at 25°. Combining this result with Davidson's value[18] for the recombination rate constant of iodine atoms at 25° in carbon tetrachloride solution ($0.72 \pm 0.11 \times 10^{10}$ M^{-1} sec.$^{-1}$), we calculate the rate of dissociation of 0.01 M iodine in the same solvent to be 2.2 × 10^{-15} M sec.$^{-1}$.

Russell and Tobolsky[12] have determined the rates of thermal initiation in pure syrene, using the DPPH method, at 50, 60 and 75°. On extrapolation of their results, styrene is found to produce radicals at a rate of 2.64 × 10^{-10} M sec.$^{-1}$ at 25°. Assuming that the solvent carbon tetrachloride does not participate in the reaction, for second and third-order initiation in monomer the rates of radical production by 0.174 M styrene would be 1.05 × 10^{-14} and 2.09 × 10^{-15} M sec.$^{-1}$, respectively. The larger of these predictable rates of initiation is still too low by a factor of 10^6 to account for our results. Therefore both iodine and styrene are involved in the initiation of the chain reaction. It is possible to explain our observations on the basis of a radical-chain reaction involving a mode of initiation (a) in which styrene and iodine both take part.

$$\text{(a)}\quad 2C_6H_5CH{=}CH_2 + I_2 \longrightarrow 2C_6H_5\dot{C}HCH_2I$$

Such a scheme is written

$$\begin{array}{lrcll}
\text{a} & 2S + I_2 & \longrightarrow & 2SI\cdot & k_i \\
\text{b} & S + I\cdot & \longrightarrow & SI\cdot & k_2 \\
\text{c} & SI\cdot & \longrightarrow & S + I\cdot & k_5 \\
\text{d} & SI\cdot + I_2 & \longrightarrow & SI_2 + I\cdot & k_3 \\
\text{e} & SI_2 + I\cdot & \longrightarrow & SI\cdot + I_2 & k_4 \\
\text{f} & SI\cdot + I\cdot & \longrightarrow & SI_2 \text{ or } S + I_2 & k_t
\end{array}$$

The symbols S, I_2, I· and SI· stand for styrene, iodine. iodine atom and *α*-phenyl-*β*-iodoethyl radical, respectively. Equilibrium concentrations are marked sub-infinity, initial concentrations sub-zero. Since styrene is in great excess its concentration is regarded as constant. It is assumed that the kinetic chain length is great, that termination and initiation are slow compared to propagation.

The steady state expressions for SI· and I· are:

$$0 = \frac{d(SI\cdot)}{dt} = 2k_i(S)^2(I_2) + k_2(S)(I\cdot) - k_5(SI\cdot) \quad (4)$$
$$- k_3(SI\cdot)(I_2) + k_4(SI_2)(I\cdot) - k_t\,(SI\cdot)(I\cdot)$$

$$0 = \frac{d(I\cdot)}{dt} = -k_4(SI_2)(I\cdot) - k_t\,(SI\cdot)(I\cdot) - k_2(S)(I\cdot) \quad (5)$$
$$+ k_5(SI\cdot) + k_3\,(SI\cdot)(I_2)$$

Equation 5 is solved for (SI·)

$$(SI\cdot) = \frac{k_2(S)(I\cdot) + k_4(SI_2)(I\cdot)}{k_3(I_2) + k_5 - k_t\,(I\cdot)} \quad (5a)$$

and the term $k_t(I\cdot)$ in the denominator of 5a is dropped through the assumption that the chain length is great.

$$(SI\cdot) = \frac{k_2(S)(I\cdot) + k_4(SI_2)(I\cdot)}{k_3(I_2) + k_5} \quad (6)$$

By combining equations 4 and 5 we obtain a second relation between (SI·) and (I·), namely

$$(SI\cdot) = k_i(S)^2(I_2)/(k_t(I\cdot) \quad (6a)$$

Solution of (6) and (6a) yields expressions for (SI·) and (I·) which are substituted into the equation 7 for the rate of iodine disappearance

$$- d(I_2)/dt = k_3(SI\cdot)(I_2) - k_4(SI_2)(I\cdot) \quad (7)$$

to yield

$$-\frac{d(I_2)}{dt} = \left[\frac{k_i}{k_t}\right]^{1/2}(S)(I_2)^{1/2} \times$$
$$\left[\frac{k_2k_3(S)(I_2) - k_4k_5(SI_2)}{(k_3(I_2) + k_5)^{1/2}(k_2(S) + k_4(SI_2))^{1/2}}\right] \quad (8)$$

At the beginning of a reaction, when k_4 and k_5 are relatively unimportant, (8) reduces to

$$- d(I_2)/dt = (k_ik_2k_3/k_t)^{1/2}(S)^{3/2}(I_2) \quad (9)$$

which is identical in form to the experimental rate equation 1.

Integration of Equation 8—Equation 8 may be converted into manageable form as follows: The equilibrium constant K_r, for the over-all reaction

$$K_r = \frac{(SI_2)_\infty}{(S)(I_2)_\infty} = \frac{(I_2)_0 - (I_2)_\infty}{(S)(I_2)_\infty} = k_2k_3/k_4k_5 \quad (10)$$

which is known (1.1 at 22°) from our data and those of others, is used to transform the numerator of the fraction in (8) into

$$k_4k_5(K_r(S) + 1)\,[(I_2) - (I_2)_\infty] \quad (11)$$

Hence (8) becomes on integration

$$-\frac{(k_3(I_2) + k_5)^{1/2}[k_2(S) + k_4(SI_2)]^{1/2}d(I_2)}{(I_2)^{1/2}[(I_2) - (I_2)_\infty]} \quad (12)$$
$$= (k_i/k_t)^{1/2}k_4k_5(K_r(S) + 1)(S)t + c_3$$

Since none of the simplifying assumptions have any meaning here it is necessary to integrate (12) as a whole. Thus a suitable choice must be made for the ratio k_2/k_4.

$$k_2/k_4 = a \quad (13)$$

Using (13) and (10), (12) becomes

$$-\int \frac{(a(S) + (I_2)_0 - (I_2))^{1/2}(K_r(I_2)/a + 1)^{1/2}\,d(I_2)}{(I_2)^{1/2}((I_2) - (I_2)_\infty)} \quad (14)$$
$$= (k_ik_4k_5/k_t)^{1/2}(K_r(S) + 1)(S)t + c_3$$

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(16) J. Zimmerman and R. M. Noyes, *J. Chem. Phys.*, **18**, 656 (1950).

(17) J. E. Mayer and M. G. Mayer, "Statistical Mechanics," John Wiley and Sons, Inc., New York, N. Y., 1946.

(18) R. Marshall and N. Davidson, *J. Chem. Phys.*, **21**, 2086 (1953).

The numerator in the integrand of (14) is expanded

$$f(I_2) = [a(S) + (I_2)_0 - (I_2)]^{1/2}[K_r(I_2)/a + 1]^{1/2} \quad (15)$$

as a Taylor's series in terms of $((I_2) - (I_2)_\infty)$. Since the latter numbers are always close together compared to other quantities in the integrand the expansion might be expected to converge rapidly.

$$f(I)_2 = f(I_2)\infty + f'(I_2)\infty[(I_2) - (I_2)\infty] + \frac{f''(I_2)\infty}{2!}[(I_2) - (I_2)\infty]^2 \quad (16)$$

The symbols f′ and f″ refer to the first and second derivatives of $f(I_2)$. The integral is now expanded.

$$\int \frac{f(I_2)_\infty\, d(I_2)}{(I_2)^{1/2}[(I_2) - (I_2)\infty]} + \int \frac{f'(I_2)\infty d(I_2)}{(I_2)^{1/2}} + \int \frac{f''(I_2)[(I_2) - (I_2)\infty]d(I_2)}{2!(I_2)^{1/2}} = -(k_ik_4k_5/k_t)^{1/2}[K_r(S) + 1](S)t + c_3 \quad (17)$$

The series does indeed converge and only the first term, (18), need be used. It is noticed that this first term (18) has exactly the same form as

$$\frac{[a(S) + (I_2)_0 - (I_2)_\infty]^{1/2}[K_r(I_2)_\infty/a + 1]^{1/2}}{(I_2\,\infty)^{1/2}} \times \ln\left[\frac{(I_2)^{1/2} - (I_2)_\infty{}^{1/2}}{(I_2)^{1/2} + (I_2)_\infty{}^{1/2}}\right] = -(k_ik_4k_5/k_t)^{1/2}[K_r(S) + 1](S)t + c_4 \quad (18)$$

equation 3 apart from the constant in front which depends on the arbitrary parameter, a. The agreement here applies when $a = 0.008$; see Table III. In an attempt to improve the value of the arbitrary parameter, its variation between 0.0050 and 0.015 in intervals of 0.001 with $(k_ik_4k_5/k_t{}^{1/2})$ was compiled for all runs using the slopes of the plots of equation 3, with the aid of UNIVAC.

TABLE III

Run	$10^2x(k_ik_4k_5/k_t)^{1/2}$(m./l.)$^{-1}$ sec.$^{-1}$
53	7.6
58	7.5
62	8.0
66	7.8
68	8.2
73	7.2
72	5.2
64	11.9
Av.	7.9

$$d\ln\left[\frac{(I_2)^{1/2} - (I_2\infty)^{1/2}}{(I_2)^{1/2} + (I_2\infty^{1/2})}\right]dt = \frac{-(I_2\infty)^{1/2}[K_r(S) + 1](S)}{[a(S) + (I_{2\,0}) - (I_2\infty)]^{1/2}[K_r(I_2\infty)/a + 1]^{1/2}} \cdot (k_ik_4k_5/k_t)^{1/2} \quad (19)$$

This procedure changed the arbitrary parameter to 0.0078.

Numerical integrations of equation 14 by Simpson's rule[19] yielded identical results; see Fig. 4.

The linearity of the integrated plots provides confirming evidence for the suggested mechanism and also the relationships between k_2 and k_4, k_3 and k_5.

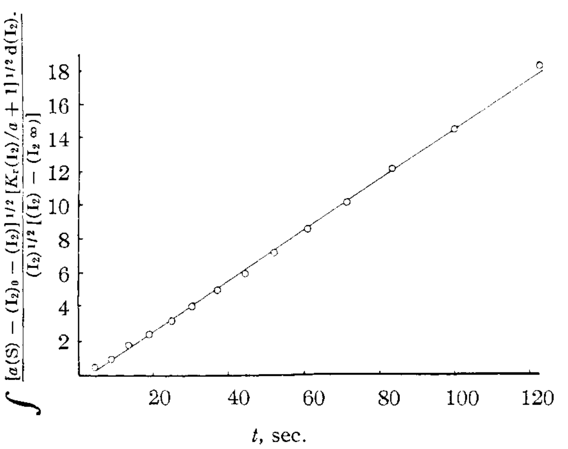

Fig. 4.—Data for a kinetic run plotted according to the integrated form (18) of equation 14.

The experimental equation 1 is also consistent, in the early stage of reaction, with an initiating reaction

$$S + 2I_2 \longrightarrow SI_2 + 2I\cdot \text{ or } SI\cdot + I_2 + I\cdot$$

together with a terminating reaction

$$2I\cdot \longrightarrow I_2$$

However, the integrated kinetic equation for this case yields a very inferior fit to the data, with curved plots and inconstant rate constants from run to run. This mechanism would also be inconsistent with the photodisplacement observed in Part I, and it will not be considered further here.

Oxygen Retardation.—Earlier during these studies, a number of supposedly uninhibited reactions between iodine and styrene in carbon tetrachloride were followed with the Beckman DU spectrophotometer. These runs had half-times of about thirty minutes, yielded equilibrium concentrations of iodine consistent with styrene diiodide formation, but later were found to have been retarded by oxygen due to incomplete degassing. Although the oxygen concentrations were not known, it was possible to fit the results from any particular run to our theory by replacing step (f), $SI\cdot + I\cdot \rightarrow SI_2$ or $S + I_2$, with (g).

$$\text{(g)} \qquad SI\cdot + O_2 \xrightarrow{k_8} SIO_2{}^{20}$$

The resulting rate equation

$$-\frac{d(I)_2}{dt} = \left[\frac{2k_ik_4k_5}{k_8}\right]\frac{(S)^2(I_2)[K_r(S) + 1][(I_2) - (I_2\,\infty)]}{(O_2)[k_2(S) + k_4(SI_2)]} \quad (20)$$

is integrated to

$$\frac{a(S) + (I_{2\,0})}{(I_2\infty)}\ln\frac{(I_2) - (I_2\infty)}{(I_2)} - \ln[(I_2) - (I_2\infty)] = \left[\frac{2k_1k_5}{k_8(O_2)}\right][K_r(S) + 1](S)^2t + c_5 \quad (21)$$

which is the only relationship found to yield linear plots for runs retarded by oxygen (see Fig. 5). Though in harmony with the suggested mechanism, this result provides no independent measurement of the over-all rate constant, k_ik_5/k_8.

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[19] R. S. Burington, "Handbook of Mathematical Tables and Formulas," 3rd ed., Handbook Publishers, Inc., Sandusky, Ohio, 1956, p. 13.

[20] Followed immediately by either $2SIO_2\cdot \rightarrow ISOOSI + O_2$ or $SIO_2\cdot + SI\cdot \rightarrow ISOOSI$. The former is a common chain termination in autoxidation systems with abundant oxygen; the latter is more likely in oxygen deficiency [F. R. Mayo, THIS JOURNAL, **80**, 2470 (1958)]. Under equilibrium conditions, the concentration of oxygen molecules can be much higher than that of any radical, and hence *irreversible* disappearance of SI· by (g) becomes faster than by the coupling of SI· in the absence of oxygen. See the discussion of the styrene–iodine–oxygen reaction in Part I.

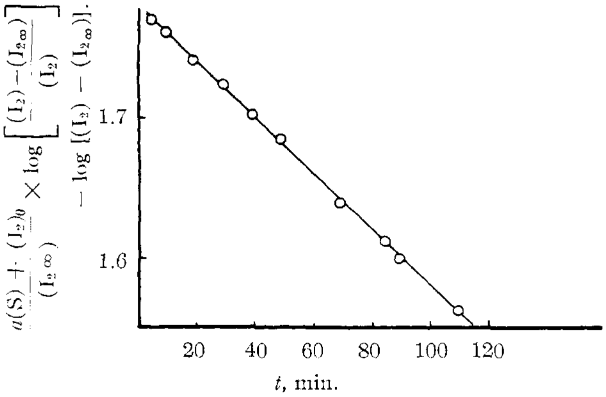


Fig. 5.—Iodination of styrene retarded by oxygen, plotted according to equation 21.

Although not implicit in the results it might be guessed that the attack of iodine atoms on styrene molecules would be the slow step in the mechanism. The resonance energy of styrene would have to be overcome but the α-phenyl-β-iodoethyl radical would also be stabilized, possibly to the extent of 24 kcal. The speed of the reaction must be ascribed to the stability of SI· together with the unique mode of termolecular initiation.

Inhibition by Quinone.—The normal behavior of inhibitors in free radical reactions is to provide a mode of chain termination

$$2R\cdot + Q \longrightarrow X$$

much faster than that originally present

$$2R\cdot \longrightarrow X$$

which alters the kinetics of the reaction in a simple predictable way. In reactions with long kinetic chains the action of an inhibitor may appear as a total inhibition, with the attendant induction period, or as varying degrees of retardation.

The formation of styrene diiodide in carbon tetrachloride was retarded by quinone to one-tenth the rate of the uninhibited process. The initial rate shows a half-order dependence on both reactants and in the concentration range from 10^{-4} to 10^{-1} *M* is zero order in quinone (see equation 22, Table IV, and Fig. 6).

$$-d(I_2)/dt = k_a(S)^{1/2}(I_2)^{1/2} \qquad (22)$$

A more satisfactory relationship is provided by equation 23 (see Fig. 7).

$$\frac{-d(I_2)}{dt} = \frac{a(S)^{1/2}(I_2)^{3/2}}{b + (I_2)} \qquad (23)$$

TABLE IV

THE REACTION OF STYRENE WITH IODINE IN THE PRESENCE OF QUINONE AT 25°

Run	$(S)_0$	$(I_2)_0$ $\times 10^{-3}$	$(Q)_0$	v_i, m./l. sec. $\times 10^{-7}$
38	0.1736	10.0	9.14×10^{-2}	20
40	.1736	10.0	6.48×10^{-3}	21
42	.1736	10.0	7.11×10^{-5}	22
43	.1736	10.0	6.88×10^{-4}	19
44	.1736	10.0	6.88×10^{-6}	25
46	.1736	4.37	9.51×10^{-4}	15
45	.1736	19.8	9.51×10^{-4}	33
47	.0868	11.1	9.33×10^{-4}	17
48	.3472	4.10	9.37×10^{-4}	19
51	.0868	9.93	12.2×10^{-3}	16

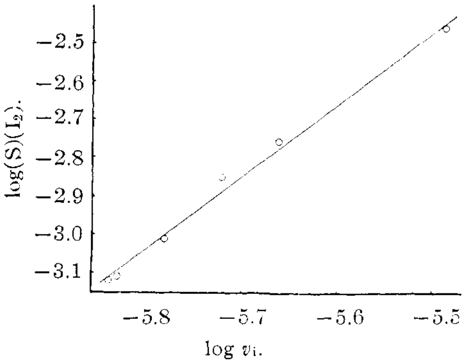


Fig. 6.—Quinone-retarded iodination of styrene, plotted according to equation 22 (logarithmic scale).

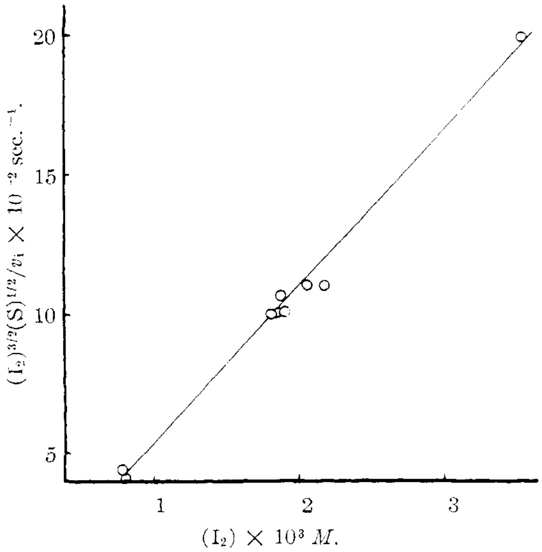


Fig. 7.—Quinone-retarded iodination of styrene plotted according to Equation 23.

It seemed likely that the process was still a free radical reaction but from the zero-order dependence on quinone this retarder must have been acting in an unusual manner. Either quinone was involved in two or more propagation steps, *i.e.*, consumed by one and returned by another, or the quinone entered both the initiation and termination steps. Quinone might also complex with both the intermediate radicals to lower their effective concentrations. The results are most closely in accord with the first suggestion.

The Photochemical Reaction of Iodine and Styrene.—In strong light iodine was irreversibly consumed from equilibrium mixtures of styrene, iodine and styrene diiodide (see Part I). The color of our irradiated solutions never completely disappeared but remained a light amber. In most of these experiments the solutions were prepared in a stream of nitrogen, transferred into the reaction vessel, degassed, sealed off under vacuum and irradiated for as long as it took the iodine color to disappear.

The product from 100 cc. of an irradiated styrene solution, 0.1 *M* in iodine, consisted of several grams of a dark brown oil together with a small quantity of crystalline material. No hydrogen iodide was found and the bulk of unreacted styrene could be recovered.

The dark brown oil, I, readily lost iodine on exposure to air. It was converted into a light orange oil II on treatment with alcoholic potassium hydroxide. This product had a molecular weight of 330 ± 2 determined by cryoscopic measurements in benzene and showed an ultraviolet maximum at 253 mμ ($\epsilon = 1.6 \times 10^4$) quite close to that of styrene ($\lambda_{\max} = 242$ mμ, $\epsilon = 1.3 \times 10^4$).[21a,b]

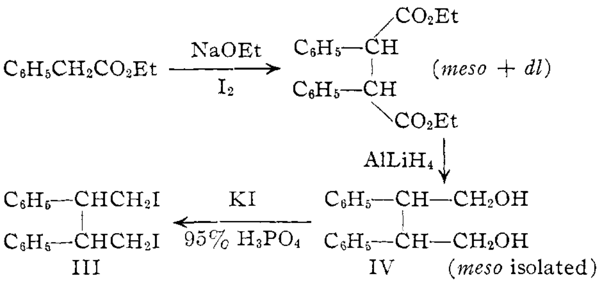
The evidence strongly indicates that the bulk of the photochemical product is a diiodo-styrene trimer. The stoichiometry of the reaction of I with base supports this suggestion—one mole of $(C_8H_8)_3I_2$ with two of KOH.

The crystalline product III melted at 199° and appeared to be the same material isolated in Part I[13] under comparable conditions. Its analysis corresponded to diphenyl-diiodobutane and it absorbed in the ultraviolet at $\lambda_{\max}$ 256 mμ (ϵ = 1200). The yield of this material was greater at lower temperature (Table V). The structure III, assigned in Part I, was confirmed by the synthetic route

TABLE V

AMOUNT OF PRODUCT III ISOLATED FROM 100 CC. OF 0.1 M IODINE SOLUTION IN STYRENE, IRRADIATED

T, °C.	Yield, g.
0	0.30
10	.15
23	.030



The coupling of ethyl phenylacetate by sodium ethoxide and iodine has been described already by Wren and Still[22] who identified the isomers by hydrolysis to α,α'-diphenylsuccinic acids followed by resolution of the d,l-mixture. Reduction of the diester went smoothly in 75% yield.

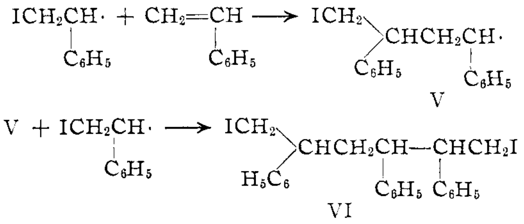
The *meso*-diol IV was converted with potassium iodide in 95% phosphoric acid at 140°, the method of Stone and Shechter,[23,24] into a material, *meso*-1,4-diiodo-2,3-diphenylbutane (IV) which had an identical infrared absorption and melting point with that of the photochemical dimer.

Although the photochemical product seemed to consist chiefly of tristyrene-diiodide and *meso*-1,4-diiodo-2,3-diphenylbutane, it was not to be excluded that small quantities of other possible products, *e.g.*, 1,4-diiodo-1,3-diphenylbutane, were also present.

The dehydroiodination product II gave no isolable addition product with maleic anhydride.

The primary photochemical product I was treated with sodium acetate in glacial acetic acid in the hope of preparing solid diacetates. Infrared examination of the product failed to show the presence of anything but hydrocarbons. Thus there was no evidence for any dimers in the photochemical product other than 1,4-diiodo-2,3-diphenylbutane.

1,4-Diiodo-2,3-diphenylbutane is surely the product of recombination of α-phenyl-β-iodoethyl radicals. The fact that more dimer was isolated at lower temperatures is entirely consistent with the very low activation energies found for radical recombinations compared to those of radical propagation. The product of the photochemical reaction must consist mostly of diiodo-styrene trimer. Although the homogeneity and structure of the tri-styrene diiodide have not been established, certain conclusions can be drawn from the fact that it seems to represent the dominant chain termination product and the only one other than 1,4-diiodo-2,3-diphenylbutane. Each of these products must arise by the union of two monoiodo-radicals. The most obvious way to obtain a diiodo-trimer is by addition of an SI· radical to a styrene molecule and the coupling of the resulting chain-carrier with a second SI· radical.



We may wonder why, if the radical V is a precursor of this trimeric product, termination of V by iodine is not the most important reaction of all, producing substantial quantities of the missing 1,4-diiodo-1,3-diphenylbutane. This would be intelligible if this product, as a secondary benzylic iodide, were either thermally or photochemically so dissociable that when formed under the conditions of this reaction it undergoes cleavage again at the C–I bond just as styrene diiodide does. If only primary iodides can survive the conditions, then III and VI are the two simplest termination products which this reaction can yield.

It is known that benzyl iodide undergoes photolysis more readily than other iodides,[25,26] whereas 1,4-diiodo-2,3-diphenylbutane is quite stable in solution. The ease with which iodine is produced by the trimeric product suggests that benzylic products, formed by the attack of iodine on V or on an analogous iodotrimer radical, were not entirely absent.

In Part I it was mentioned that the small but definite alteration of the concentration of iodine produced by illuminating an equilibrated solution of styrene and iodine was inconsistent with any chain mechanism in which diiodide is produced *only* in the chain-propagating steps. The reasoning is:

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(21) (a) H. P. Koch, *J. Chem. Soc.*, 387 (1949); (b) W. W. Robertson, J. F. Music and F. A. Matsen, THIS JOURNAL, **72**, 5260 (1950).

(22) H. Wren and C. J. Still, *J. Chem. Soc.*, 446 (1915).

(23) R. B. Wagner and H. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 90.

(24) H. Stone and H. Shechter, *Org. Syntheses*, **31**, 31 (1951).

(25) R. M. Noyes and D. J. Sibbett, THIS JOURNAL, **75**, 769 (1953).

(26) O. H. Gellner and H. A. Skinner, *J. Chem. Soc.*, 1145 (1949).

In the equilibrated system each step in the chain reaction is going forward and backward at identical rates, and the same is true of the steady state developed under constant illumination. The equilibrium $I_2 \rightleftarrows 2I\cdot$ will of course be shifted under light which excites I_2 but not $I\cdot$. However, a shift of 1% of I_2 to $I\cdot$ at the steady state in a solution 7×10^{-4} *M* in iodine would require that $(I\cdot)^2/(I_2) = 49 \times 10^{-12}/7 \times 10^{-4} = 7 \times 10^{-8}$ under illumination. This would mean that $k_{\text{diss}}/k_{\text{assoc}} = 7 \times 10^{-8}$ and $k_{\text{diss}} = k_{\text{assoc}} \times 7 \times 10^{-8} = 7 \times 10^9 \times 7 \times 10^{-8} = 490$ sec.$^{-1}$, corresponding to a light intensity which would dissociate half the iodine in 1.3×10^{-3} second. Any such light intensity would multiply the steady state concentrations of $I\cdot$ and $SI\cdot$ by a factor of $7 \times 10^{-6}/6.3 \times 10^{-10} \cong 10^4$, and the rate of formation of diiododimer would be increased by a factor of 10^8. None of these effects being observed, it is clear that the iodine which is disappearing reversibly under illumination is going to styrene diiodide and not to iodine atoms.

Now, if styrene diiodide and $SI\cdot$ are formed and consumed only in the reversible step

$$SI\cdot + I_2 \rightleftarrows I\cdot + SI_2$$

then there is no way in which a photodisplacement of the iodine dissociation equilibrium can increase the steady state concentration of SI_2. On the other hand, if the reaction

$$SI\cdot + I\cdot \rightleftarrows SI_2$$

is an important mode of termination, then an increase in $[I\cdot]$ and its attendant increase in $[SI\cdot]$ will produce an increase in $[SI_2]$ which may readily become detectable.

Discussion

Reasonable consistency can be established between the proposed mechanism for the formation of styrene diiodide and the absolute rate constants which have been determined for the recombination of iodine atoms[18] and for the steps in the polymerization of styrene.[27] Considering only the early stage of iodine addition, we may neglect all reverse rates and apply a steady-state treatment to equations a, b, d and f. This yields the equations

$$V_i = \text{initiation rate} = 2k_i(S)^2(I_2) \qquad (24)$$

$$(I\cdot) = V_i/k_t(SI\cdot) \qquad (25)$$

$$(SI\cdot) = \sqrt{\frac{k_2(S)V_i}{k_3k_t(I_2)}} \qquad (26)$$

$$-\,d(I_2)/dt = k_3(SI\cdot)(I_2) \qquad (27)$$

In the combination of unlike radicals, the ratio ϕ, defined as the ratio of the cross-termination rate constant to twice the geometric mean of the rate constants for homo-termination

$$\phi = \frac{k_{t12}}{2(k_{t11}k_{t22})^{1/2}}$$

is commonly greater than one. Walling[28] lists a number of values of ϕ involving styrene-type radicals with others, the values ranging from 1 to 150. If we assume that $\phi = 50$ for iodine atoms and β-iodo-α-phenyl-ethyl radicals, and that the rate constant for union of two $SI\cdot$ radicals is the same as that for the union of growing polystyrene radicals, then

$$k_t = 100\sqrt{7.2 \times 10^9 \times 9.4 \times 10^7} = 8.2 \times 10^{10} \text{ l./mole sec.}$$

In run 61, $-d(I_2)/dt = 6.4 \times 10^{-5}$ mole/l. sec.

If the kinetic chain length was 1750, then

$$V_i = \frac{6.4 \times 10^{-5}}{1750} = 3.65 \times 10^{-8}$$

An arbitrary choice of rate constants to maximize the dominance of cross termination then yields the values

$$k_2 = 3 \times 10^6 \text{ and } k_3 = 1 \times 10^7$$

Inhibitory constant[29] of iodine $= k_3/k_p = 2.5 \times 10^5$. Dark rate of formation of diiododimer, uncatalyzed

$$= k_{t11}(SI\cdot)^2 = 9.4 \times 10^7 \times 4 \times 10^{-19} = 4 \times 10^{-11} \text{ m./l.sec.}$$

(Here k_{t11} is taken as the termination rate constant in styrene polymerization.)[27] All these values seem permissible within the known facts, but the individual rate constants may vary widely from those assumed. The value of ϕ may be different from 50; the presence of iodine may stabilize the β-iodo-α-phenylethyl radical; and k_2/k_3 may vary over at least three powers of ten without destroying the dominance of cross-termination. Thus these possible rate constants have only illustrative value.

The oxygen retardation of the formation of styrene diiodide does not necessarily mean that oxygen reacts with $SI\cdot$ faster than iodine does. If $[O_2] = 7.1 \times 10^{-3}$ *M*[30] at saturation at 25°, it is comparable in concentration to iodine (0.0107 *M*) in run 17. If $(SI\cdot)$ reacts at the same rate with iodine and with oxygen, the effect is to cut the average kinetic chain length down to 2. If the rate of disappearance of iodine in run 17 is, as suggested, due mostly to a non-chain reaction, the results could be explained by a rate constant k_8 similar in magnitude to k_3. On the other hand, if the iodination in runs 17, 30 and 31 (Table I) is by an incompletely inhibited chain, by chance retarded to the same extent by three different agents, then k_8 need be only about about one-fourteenth as great as k_3. Within these limits, we can conclude that the reaction rate constants for reaction of the $SI\cdot$ radical with the various species present stand in the approximate order: $I\cdot$, 10^{11}; $SI\cdot$, 10^8; I_2, 10^7; O_2, 10^7; styrene. 10^3.

Experimental

Materials.—Styrene monomer, Eastman Kodak Co., contained added *t*-butylcatechol which was washed out with several portions of aqueous sodium hydroxide until the washings failed to show color. The monomer then was washed with water, dried for several hours with magnesium sulfate, and then distilled through a four-foot vacuum jacketed column packed with glass helices (b.p. 49° (23 mm.)). The middle fraction of the distillation was collected and stored under nitrogen in darkness at −25°. Before actual use the monomer was always redistilled over the vacuum line at 0°. Samples used for kinetic runs were treated in the same way but distilled into 8 mm. o.d. Pyrex vials which were sealed off under vacuum and stored at −78° until use. Under these circumstances styrene monomer could be preserved indefinitely.

Iodine, Mallinckrodt Chemical Works analytical reagent, was sublimed before use.

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(27) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1700 (1951).

(28) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 145, 146.

(29) P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950).

(30) F. R. Mayo and A. A. Miller, *ibid.*, **80**, 2483 (1958).

Bromanil was prepared by the method of Torrey and Hunter[31] in 65% yield and recrystallized from toluene (m.p. 299–302° dec.).

Carbon tetrachloride, Merck "reagent grade," contained small quantities of olefins and sulfur compounds. The material was exhaustively photochlorinated, washed with aqueous sodium hydroxide, with water, dried with magnesium sulfate, and distilled through a three-foot column packed with glass helices (b.p. 77–77.5° (762 mm.)).

Benzoquinone was sublimed twice and recrystallized from normal pentane.

2,2-Diphenyl-1-picrylhydrazyl (DPPH) was furnished by Dr. R. R. Hiatt.

The Photochemical Reaction of Iodine and Styrene. General Procedure and Isolation of *meso*-1,4-Diiodo-2,3-diphenylbutane (IV).—Iodine (2.5 g., 0.01 mole) was dissolved with vigorous swirling in a stream of nitrogen in 100 cc. of freshly distilled styrene which had been further purified by a bulb-to-bulb distillation on the vacuum line. The solution was transferred to a U-shaped vessel, degassed, and sealed off under vacuum. Degassing was accomplished by alternately thawing and freezing (Dry Ice–ethanol) the solution, with pumping only during the frozen periods.

After irradiation for 60 hours at 10° with a General Electric Sunlamp, the solution changed from an initial dark red to a final light amber color. The arm of the vessel away from the delivery tube was cooled in Dry Ice–ethanol and when 90% of the excess styrene had distilled into it (*ca.* 85 cc.), with the distillate frozen, the delivery tube was opened, and the product in 10 cc. of styrene poured into a small flask. The latter was attached to the vacuum line, degassed and, with the system isolated from the pump, the remaining volatile materials were allowed to distil into a trap cooled by liquid nitrogen. There now remained a quantity (5.8 g.) of brown oil containing some crystalline material. This was treated with 20 cc. of ether. The solution was boiled slowly for about 15 seconds to remove excess air, stoppered, and stored in darkness at −25° for an hour. The solid material, *ca.* 0.1 g., was recrystallized twice from ether (m.p. 199–200°). The material had an ultraviolet absorption maximum at 256 mμ in ethanol and on the basis of structure IV, ϵ 1200.

Anal. Calcd. for $C_{16}H_{16}I_2$: C, 41.58; H, 3.49. Found: C, 41.70; H, 3.72.

There remained approximately 5.8 g. of a dark brown oil, I. When a small quantity of either distillate was equilibrated with water the *p*H of the water remained unchanged.

The distillate turned out to consist almost entirely of styrene as determined by redistillation and refractive index comparison.

The extreme precaution employed here derives from exploratory experiments on the photochemical product. It was found that dimeric material could not be isolated when the reaction was run in benzene. The second product lost iodine very rapidly when exposed to air, especially so when dissolved in oxygenated solvents. The infrared spectrum of I was very similar to that of polystyrene. The material absorbed very strongly in the ultraviolet, showing only end absorption from 3000 Å. down.

Reaction of the Photochemical Product I with Potassium Hydroxide.—The photochemical product (5.1 g.) was dissolved in 50 cc. of 95% ethanol containing 3% by weight of potassium hydroxide and refluxed for two hours. The color changed from dark brown to a light orange. Water was added and excess base neutralized with dilute sulfuric acid. The solvent was removed under reduced pressure. There remained a quantity of oil and solid material which was taken up in water and ether. The ether phase was washed with aqueous sodium thiosulfate, with water and dried with magnesium sulfate. The product II consisted of a light brown oil. This material absorbed light in the ultraviolet at λ_{max} 253 mμ in cyclohexane. Freezing point depression studies in benzene indicated a molecular weight of 336 ± 2. The infrared spectrum was very similar to that of polystyrene.

Reaction of II with Maleic Anhydride.—The oil II (2 g.) was dissolved with maleic anhydride (2 g., 0.02 mole) in 40 cc. of benzene and refluxed for 15 hours. The solution was treated with hot aqueous potassium hydroxide. The combined aqueous extracts were acidified to *p*H 2 and evaporated to dryness under reduced pressure. A quantity of solid material remained. It was taken up in ether, the solution was dried with magnesium sulfate, and the ether removed leaving crystals (1 g., m.p. 130–131°). The material was identified with an authentic sample of maleic acid by the method of mixed melting points. Furthermore, the ultraviolet spectrum showed no sign of any absorption above 2500 Å.

Reaction of the Photochemical Product I with Sodium Acetate.—The photochemical product I (5.8 g.), was dissolved in a deoxygenated solution of 3 g. of sodium acetate in 40 cc. of cold glacial acetic acid. The solution was stoppered and allowed to stand in darkness for three hours at 0°. It then was heated to 50° for two minutes, neutralized with sodium carbonate, and extracted with ether. The combined ether extracts were dried with magnesium sulfate and the solvent removed. There remained 3.9 g. of a brown oil. The infrared spectrum showed no carbonyl absorption.

***meso*-Diethyl-α-α'-diphenylsuccinate** was prepared by the method of Wren and Still.[22]

***meso*-2,3-Diphenyl-1,4-butanediol (VI).**—Lithium aluminum hydride (1.02 g., 0.027 mole) was added to 250 cc. of ether in a three-necked flask equipped with Soxhlet extractor and sealed stirrer. The ether was allowed to reflux with stirring for 10 minutes to achieve suspension. Since it was not very soluble in ether, *meso*-α-α'-diphenyldiethylsuccinate (6 g., 0.018 mole) was eluted from the Soxhlet cup into the reaction mixture over a period of several hours. The system was allowed to reflux with stirring overnight, 12 hours, and yielded a thick white suspension. This was decomposed with 75 cc. of 10% sulfuric acid at 0°. The ether layer was combined with several ether extracts of the water layer, dried with magnesium sulfate, and the ether removed. The product, *meso*-2,3-diphenyl-1,4-butanediol, was recrystallized from chloroform, 3.4 g., 77% yield, m.p. 153–154°. Infrared absorption at 2.83 and 2.95 mμ together with the absence of absorption in the carbonyl region indicated that total reduction had taken place.

***meso*-2,3-Diphenyl-1,4-diiodobutane.**—Phosphorus pentoxide (0.8 g., 0.006 mole) was dissolved in phosphoric acid (1 cc., 0.009 mole) to form a 95% solution of H_3PO_4. After cooling the phosphoric acid, potassium iodide (2.6 g., 0.016 mole) and *meso*-2,3-diphenyl-1,4-butanediol (1 g., 0.0041 mole) were intimately mixed in the phosphoric acid. The reaction was heated at 140° for two hours with rapid stirring. The product was extracted into ether and water. The combined ether extracts were washed with aqueous sodium thiosulfate, with water, and dried with magnesium sulfate, yielding 0.5 g. of crystals, m.p. 196–197°; mixed melting point with dimer from photochemical reaction 196–197°. The infrared spectrum was identical to that of the photochemical dimer.

Kinetic Procedure. Thermostat.—The thermostat consisted of a Plexiglas tank, 6" × 17" × 12", fitted with two plane polished Pyrex windows. These were cemented to rubber gaskets and clamped into position. An open rectangular copper tube or beam guide spanned the distance between the windows and each end held a closely fitting copper sleeve which could be pushed flush against the window. The cell holder was built from a section of the same copper tubing. It fitted smoothly into a vertical slot built into the center of the beam guide. The tank was equipped with a large paddle mounted from without, a 40-ohm intermittent heater, a mercury–toluene regulator, and a thyratron control circuit. The apparatus was mounted on an adjustable tray between the light source and the phototube housing of a Beckman DU spectrophotometer. The whole array was held fast by means of brass pins. Under normal operation deaerated distilled water was used as medium. This precaution and that of the beam guide were found necessary to minimize errors due to light scattering from bubbles and circulating debris in the water. During runs the temperature was held to within ±0.01°.

Reaction Cells.—Two kinds of cells were used (Fig. 8). The first, cell 1 (Fig. 8), was essentially a forked tube sealed to a 1-cm. Beckman cell. A short side-arm held a ball joint at b. During runs and degassing procedures a side tube t, with joints at each end and 0.5 mm. oblique bore stopcock near the middle, was attached at b. Cell 2 (Fig. 8) is of smaller construction but is built to be sealed off at a and c. The breakseal and weight (b, d) permit mixing of reactants while the system remains evacuated. All runs except those inhibited by oxygen were conducted in the second cell.

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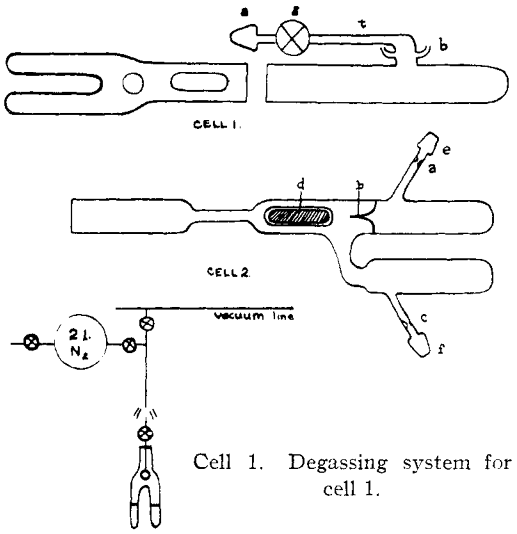
(31) H. A. Torrey and W. H. Hunter, THIS JOURNAL, 34, 706 (1912).



Cell 1. Degassing system for cell 1.

Fig. 8.—Cells used for preparing and following iodination experiments.

Before use, cells were washed with cleaning solution and then boiling distilled water.

Kinetic Runs. Cell 1.—Exactly 1.5 cc. of the iodine solution in carbon tetrachloride was syringed into one fork of the cell. The styrene solution then was prepared rapidly in a 5-cc. volumetric flask and 1.5 cc. of this was syringed into the other fork. The cell was attached to the vacuum line (Fig. 8) by its side-arm. The contents of the cell were degassed in the usual way three times and then prepurified nitrogen was bled in. The stopcock on the side-arm was closed and the cell removed from the vacuum line. In the degassing cycles ethanol–Dry Ice mixtures at −78° were used for freezing, room temperature for thawing. The reactants were equilibrated for five minutes in the thermostat, the side-arm was reversed (see Fig. 8), and the cell rapidly mounted in the beam guide. Prior to each reading the cell holder was lifted out of the light beam and the instrument zeroed against tank water. Suitable optical density corrections for the solvent, cells and tank water had already been made. Usually readings were taken initially as rapidly as possible, about every two minutes, and thereafter less often.

Cell 2.—Operation with the second cell was quite similar. Reactants were in turn separately syringed into each fork, degassed several times through the particular joints e and f, and sealed off under vacuum at constrictions a and c, respectively. After the usual temperature equilibrium seal b was broken and the procedure followed as before. In spite of its tedium this method offered several advantages over the first one. It ensured more complete degassing, one could store the filled cell in Dry Ice for several hours before use, and finally it obstructed premature mixing of reactants by distillation as is possible in cell 1. When *inhibitors* were used these were weighed and dissolved in the styrene solution first. In the DPPH run the optical density of the reactants was followed at 6800 and 6600 Å. Because both these compounds absorbed light in this region and since they both obeyed Beer's law separately and when mixed, it was possible to obtain their concentrations by solving simultaneous expressions at each point.

The raw data from all runs were tabulated and plotted on graph paper. Those for the uninhibited runs had to be corrected for the maximum–minimum scale adjustments and then converted from percentage absorption to optical density units. Infinity values were always taken after at least five half-times except in very slow runs, when for mathematical purposes the number could be calculated from the equilibrium constant.

All the inhibited kinetic runs were followed with the Beckman DU spectrophotometer at 6800 Å., except for run 31, with DPPH. Runs 52-72 were recorded on an automatic spectrophotometer built in these laboratories equipped with thermostat and RCA 6217 photomultiplier.[32] For concentrations of iodine above 0.001 *M* either of the two Baird interference combination filters 6880 or 6810 Å. were used. Below 0.001 *M* iodine it was necessary to substitute a 5145 Å. Baird interference filter in conjunction with a Kodak Wratten No. 72. This combination gave a very sharp cutoff and transmitted only 1/3% of the incident light intensity at the absorption minimum, 5145, Å., compared to 40% for either of the red filters. For this reason and because the data seemed to be internally consistent, photocatalysis by the light source at 5145 Å was discounted.

Acknowledgments.—It is a pleasure to acknowledge support of this work by the National Science Foundation.

[32] H. Kwart and C. Yang, Technical Report No. 3 to the Office of Naval Research, Project No. NR-056-095, Contract No. N5ori-76, Task XX, Harvard University, Cambridge, Mass., 1949.

Cambridge 38, Mass.

[Contribution from the Department of Chemistry of the University of Wisconsin]

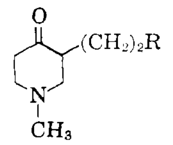
The Reaction of 2-Substituted Cyclohexanones with Organometallic Compounds

By S. M. McElvain and Rodney B. Clampitt[1]

Received April 30, 1959

The reaction products of a series of 2-substituted cyclohexanones (III) with phenylmagnesium bromide and phenyllithium have been determined. When the 2-substituent is a carbethoxymethyl or a 2-carbethoxyethyl group, a major reaction product is the metal enolate of the original ketone. When this substituent is the dimethylaminomethyl group, normal addition of the organometallic compound to the ketone function occurs. If the amino function is separated from the ring by two or three methylene groups, the enolization reaction is the main or only reaction with phenylmagnesium bromide; with phenyllithium these substituents do not interfere with normal addition to the ketone. With non-polar alkyl groups as 2-substituents, both organometallic compounds give the normal addition reactions. A rationalization of these results is proposed. The propionates of two of the aminocarbinols (XIIIc and d) were prepared and screened for analgesic activity.

In earlier work[2] in this Laboratory it was found that neither phenylmagnesium bromide nor phenyllithium would add preferentially to the ketonic group of the 3-substituted-4-piperidone Ia. With the Grignard reagent the main reaction was enolization of the ketone (50%); the only addition



Ia, R is COOEt
Ib, R is $CH_2OCOC_6H_5$
Ic, R is $CONC_5H_{10}$
Id, R is $CH_2NC_5H_{10}$

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[1] Wisconsin Alumni Research Foundation Research Assistant, 1956–1957; United States Rubber Co. Fellow 1957–1958; E. I. du Pont de Nemours and Co. Summer Research Fellow, 1955.

[2] S. M. McElvain, W. B. Dickinson and R. J. Athey, This Journal, **76**, 5625 (1954).