

PHOTOCHEMICAL TRANSFORMATIONS — v<sup>a</sup>

ORGANIC IODIDES (Part 4) : SOLUTION PHOTOCHEMISTRY OF  
4-PHENYL-1-IODOBUTANE AND 4-PHENYL-1-BROMOBUTANE<sup>b,c</sup>

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**Abstract** — Evidence is presented to show that product development from photolysis of 4-phenyl-1-iodobutane occurs essentially from an ionic species. This conclusion is in accord with our earlier suggestion that in the photocyclization of citronellyl iodide and related compounds, carbocations are involved.

Up to the close of the sixties, the solution photochemistry of alkyl iodides, like that of their gas phase counterparts, was considered to be essentially a radical reaction, though data pertaining to involvement of ionic species have started accumulating since then.<sup>1</sup> It appears the first example of possible operation of an ionic mechanism in solution photochemistry of an organic halide is due to Cristol and co-workers, who investigated sensitized-photoisomerization of 3,4-dichlorodibenzobicyclo(3.2.2)nona-2,6,8-triene.<sup>2</sup> Subsequently (1973+) Kropp *et al.*, in a series of papers, have adduced compelling evidence regarding the major intervention of an ionic pathway in the solution photochemistry of a number of alkyl and cycloalkyl iodides.<sup>3</sup> Our own work on the photorearrangement of longibornyl iodide and photocyclization of a number of terpene iodides had led us to similar conclusions.<sup>4</sup> As a result of these and other similar investigations<sup>1</sup>, it is now generally believed that, at least in the case of alkyl and cycloalkyl iodides, irradiation leads to homolysis of the carbon-iodine bond, followed by rapid electron transfer within the solvent-caged radical pair to generate an ion pair. Product development takes place from both the radical and ionic species, with the former playing only a minor role.

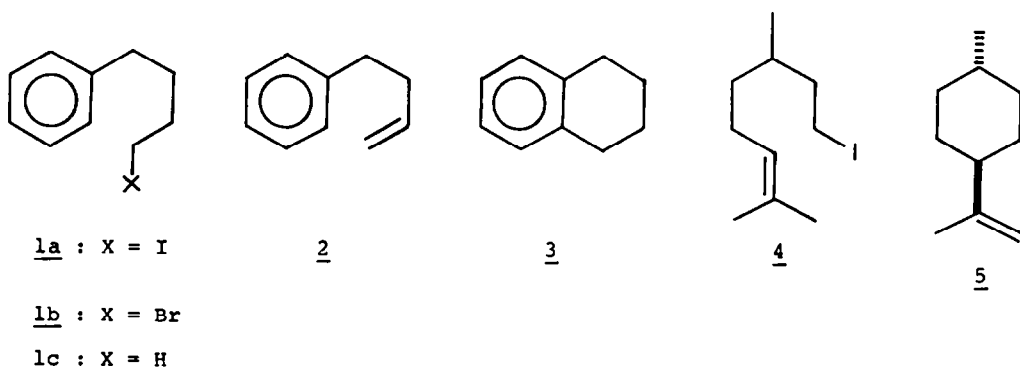
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Sometime back Charlton *et al.*<sup>5</sup> studied the photolysis of 4-phenyl-1-iodobutane (1a) in benzene, and in acetonitrile under a variety of conditions and found that in the absence of oxygen and with scavenging of HI, the major product (88-99%) of the reaction was the simple elimination product 2. These authors specifically looked for the cyclization product, tetralin (3), and concluded that the yield of tetralin in either of the solvents was less than 2%. These results were explained by the authors in terms of radical intermediates, and the authors questioned our conclusions<sup>4a</sup> concerning photocyclization of citronellyl iodide (4) to *trans*-p-menth-8-ene (5), where we had invoked the intermediacy of cationic species. The work to be discussed below was carried out to clarify this situation.




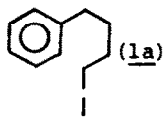
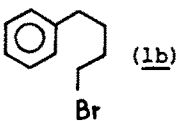


#### RESULTS AND DISCUSSION

Charlton *et al.*<sup>5</sup> had investigated the photolysis of 4-phenyl-1-iodobutane (1a) under conditions which were somewhat different from those under which we had studied cyclization of citronellyl iodide. Hence, we first investigated photolysis of 1a under our conditions. We had studied photocyclization of citronellyl iodide (4) under various conditions and had concluded that photolysis in tetrahydrofuran (THF) at 50° and in presence of triethylamine as HI scavenger, was a good preparative procedure.<sup>4b</sup> Under these conditions, photolysis of 4-phenyl-1-iodobutane furnished (Table 1) besides the elimination and reduction products, ~20% tetralin (3), the cyclization product. Thus the failure of Charlton *et al.* to get any significant amounts of the cyclization product must be attributed to the different reaction conditions employed by them. In agreement with their results, photolysis of 1a in benzene gave mainly elimination and reduction products (Table 1). Charlton and co-workers had preferred to trace the genesis of the olefin (2) to the 4-phenylbutyl radical rather than to the corresponding cation arising from electron transfer. An unambiguous indication that at least the bulk of the elimination product must be arising from the carbocation became apparent from the following.

Comparative photochemistry of alkyl bromides and the corresponding alkyl iodides has revealed that whereas the photochemistry of iodides proceeds essentially via cationic species, the photoproducts from bromides, excepting benzylic and bridgehead bromides, were typical of radical reactions.<sup>3a,3b,6</sup> Photoirradiation of 4-phenyl-1-bromobutane (**1b**), under exactly the same conditions as used for the iodide **1a** led to the reduction product **1c** as the major photoproduct (72%), with elimination, and cyclization accounting for 9%, and 18% respectively (Table 1). These results are consistent with the operation of radical pathway. Reduction to **1c** is a typical radical reaction, while the vast difference between the elimination/cyclization ratios (iodide: 2.8; bromide: 0.5) clearly points to different species as progenitors of these products in the two cases. Propensity of the 4-phenylbutyl radical to cyclization against olefin generation has been earlier demonstrated by DeTar and Weis<sup>7</sup> who investigated the fate of this radical, which was generated from di- $\delta$ -phenylvaleryl peroxide in refluxing benzene; olefin (**2**)/tetralin (**3**) ratio of 0.13 was obtained.

Table 1. Photo-irradiation of 4-phenyl-1-iodobutane and 4-phenyl-1-bromobutane<sup>a</sup>

No.	Compound	Solvent	HI scavenger	Product Composition (%)			
				 ( <b>2</b> )	 ( <b>3</b> )	 ( <b>1c</b> )	Unidentified
1	 ( <b>1a</b> )	THF	Et <sub>3</sub> N	56	20	21	3
2	<b>1a</b>	C <sub>6</sub> H <sub>6</sub>	None	80	3	13	4
3 <sup>b</sup>	<b>1a</b>	C <sub>6</sub> H <sub>6</sub>	None	61	<2	27	?
4 <sup>b</sup>	<b>1a</b>	CH <sub>3</sub> CN	K <sub>2</sub> CO <sub>3</sub>	99	-	-	-
5	 ( <b>1b</b> )	THF	Et <sub>3</sub> N	9	18	72	1

<sup>a</sup> 1% soln in the appropriate solvent; 400 watts medium pressure lamp; temp. of irradiation, 50<sup>o</sup>; N<sub>2</sub> blanket. The combined yield of photo-products was around 60% in each case.

<sup>b</sup> Data from reference 5

The above results are consistent with our earlier conclusion that product development resulting from photolysis of alkyl and cycloalkyl iodides proceeds essentially by the ionic pathway. Failure to observe cyclization reaction to any significant extent by Charlton *et al.* must now be attributed to generation of a high energy cation of exceedingly short half-life, under the reaction conditions employed, which rapidly deprotonates to the olefin 2. In benzene the cationic species is expected to be unencumbered and hence highly unstable.<sup>3b,8</sup> On the other hand, in tetrahydrofuran, a solvent of good nucleophilic solvating power (Lewis basicity = 142)<sup>9</sup>, the cationic species is expected to be solvated and hence relaxed, thus permitting it to adopt a conformation suitable for cyclization. However, it is difficult to reconcile the results obtained by Charlton *et al.* in acetonitrile, which also has good nucleophilic solvating power (Lewis basicity = 101) as compared to that of benzene (Lewis basicity = 52)<sup>9</sup>. It may be that triethylamine, used by us as HI scavenger, has a role to play.

## EXPERIMENTAL

### General

For general remarks see reference 4b.

Solvents used in photoirradiation were purified as under : tetrahydrofuran was refluxed over LAH and then distilled from it;<sup>10</sup> benzene was made thiophene-free.<sup>11</sup> Triethylamine was refluxed over KOH pellets and then distilled over Na.<sup>12</sup>

Equipment used for photoirradiation was an Applied Photophysics medium-pressure mercury lamp 400 LQ (400 W), suspended in a double-walled, water-cooled, clear-fused quartz well, without filter.

For gas-liquid-chromatography a Hewlett-Packard 5712A machine was used (Al columns 360 cm x 0.6 cm; support, 60-80 mesh Chromosorb W; stationary phases, 10% Carbowax-400, 10% diethyleneglycol succinate, or 10% SE-30; carrier gas, H<sub>2</sub>).

### 4-Phenyl-1-iodobutane (1a)

4-Phenyl-1-butanol<sup>5b</sup> (2.0g, 0.0133 mole) in dry pyridine (10 ml) was reacted with *p*-toluenesulphonyl chloride (3.6 g, 0.0169 mole) at 4° (20 hr) in the usual manner. Work up furnished the crude tosylate (4.0 g, 100%), which was converted to the required iodide by reaction with dry NaI (4.0 g) in acetone (40 ml) at room temp (~35°) for 12 hr. Usual work up<sup>4b</sup> gave a product (2.3 g) which was passed through a column of SiO<sub>2</sub>gel-IIB<sup>13</sup> (25 cm x 1.5 cm). Elution with hexane yielded, after solvent removal, pure iodide 1a (2.1 g, 82%). PMR (CCl<sub>4</sub>): Ar-CH<sub>2</sub> (2H, m, 2.57 ppm), CH<sub>2</sub>I (2H, m, 3.09 ppm), Ar-H (5H, essentially s, 7.15 ppm). (Lit. <sup>5b</sup>:PMR)

4-Phenyl-1-bromobutane (1b)<sup>14</sup>

4-Phenyl-1-butanol (3.0 g, 0.02 mole) was added to 60% HBr aq (10 ml) and the mixture stirred and heated gradually over a period of 1/2 hr to 120°. The bromide separated as a dark upper layer. After work up with ether in the usual manner, pure 1b (3.4 g, 80%) was obtained after distillation: b.p. 130-132°/12 mm. PMR (CCl<sub>4</sub>): ArCH<sub>2</sub> (2H, t, 2.6 ppm, J = 7 Hz), CH<sub>2</sub>Br (2H, m, 3.32 ppm), Ar-H (5H, essentially s, 7.13 ppm).

General procedure for photoirradiation

The substrate (0.008 mole) was used at 1% conc in appropriate solvent, containing molar equivalent of Et<sub>3</sub>N (except for expt. No. 2, Table 1). A minute, steady flow of oxygen-free N<sub>2</sub> was passed through the soln, while cool water was circulated through the photoreactor jacket at such a rate that irradiation could be carried out at ~50°. Reaction was monitored by tlc (10% C<sub>6</sub>H<sub>6</sub> in light petrol). When the photostationary stage was reached (~2 hr), the reaction mixture was worked up by careful removal of solvent through a short Vigreux column, taking up the residue in light petrol, and washing it first with water, followed by 5% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aq. The solvent was carefully stripped off through an efficient Vigreux column. The product, so obtained, was passed through a short column of SiO<sub>2</sub>-gel/IIB and eluted with light petrol. The eluate was freed of solvent as before and the residue distilled: b.p. 128-130°(bath)/20 mm, yield 55-60%. Individual members of the hydrocarbon mixture, thus obtained, were identified by mixed GLC with authentic samples<sup>15</sup> on the three columns (see under General)

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