Tetrahedron Vol 32, pp 1391 to 1393. Pergamon Press 1976 Printed in Great Britain

PHOTOCHEMICAL TRANSFORMATIONS—I
REACTIONS OF SOME TERPENE IODIDES†

P. D. GOKHALE, A. P. JOSHI‡, R. SAHNI‡, V. G. NAIK, N. P. DAMODARAN‡,
U. R. NAYAK and S. DEV*‡
National Chemical Laboratory, Poona, India

(*Received in the UK* 15 *September* 1975; *Accepted for publication* 2 *January* 1976)

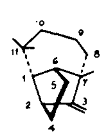
Abstract—Photo-irradiation of longibornyl iodide in *n*-heptane containing some triethylamine as scavenger for hydrogen iodide, furnished rearranged hydrocarbons (longifolene, longicyclene and longiborn-8-ene). Citronellyl iodide, under similar conditions, led to simple elimination (to furnish 2,6-dimethylocta-2,7-diene) and π-participation (to yield *trans*-*p*-menth-8-ene) to almost equal extent. A possible mechanism for these reactions is discussed.

Photochemistry of simple alkyl iodides has been fairly extensively investigated.[1] It is generally believed that absorption of light by an alkyl iodide (at ~250 nm) leads to homolytic dissociation of the carbon–iodine bond generating a "hot" alkyl radical which undergoes typical radical reactions; in the case of higher alkyl iodides, elimination of hydrogen iodide leading to an alkene becomes an important reaction and is considered to be a cage reaction.[1c] In a recent study, Kropp *et al.*[2] concluded that in some cases photoreactions of alkyl iodides are best explained in terms of cationic intermediates. Our own investigations, described below, lead us to a similar conclusion.

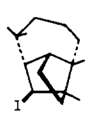
LONGIBORNYL IODIDE§

The longibornyl cation (**1**) is important in the chemistry of longifolene (**2**).[3] Since, photolysis of a carbon–iodine bond is considered to proceed by homolytic cleavage,[1] photolysis of longibornyl iodide (**3**) should generate the radical corresponding to **1**, the subsequent fate of which is of obvious interest. Longibornyl iodide[4] in *n*-heptane containing some triethylamine (to act as HI scavenger) was irradiated till all of longibornyl iodide had disappeared (TLC). The product was worked up to furnish a hydrocarbon mixture (yield 84%), which was found to consist of longifolene (**2**, 40%), longicyclene (**4**, 44%) and a new hydrocarbon (14%), which has been shown to be **5** (longiborn-8-ene, *vide infra*). It must be pointed out that when a mixture of longibornyl iodide and triethylamine in *n*-heptane was kept aside in the dark for as long as 30 days, no change was detected.

1

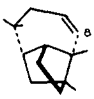


2

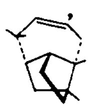


3

4

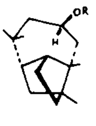


5

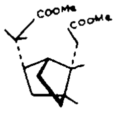


6

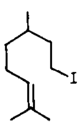
The new hydrocarbon, from its spectral data (PMR: 4 tert. Me, 3H singlets at 0.77, 0.81, 0.87 and 1.02 ppm. *Cis*-CH=CH—CH$_2$, 2H, bm, 4.70–5.35 ppm; IR, 1660, 704 cm^{-1}) was clearly **5** or **6**. That this is so, was confirmed by preparation of authentic samples of **5**, **6** from longibornan-9-ol (**7**).[6] Pyrolysis of the acetate **8** at ~500° furnished a mixture of two hydrocarbons having RRT 1.00(76%) and 1.20(24%). Of these, the hydrocarbon with RRT 1.20, was found to be identical with the photoproduct. It was not possible to distinguish between structures **5** and **6** on the basis of spectral data alone. Hence, the major product from the pyrolysis of the acetate **8** was ozonized followed by chromic acid oxidative work-up,[7] to yield a crystalline dicarboxylic acid (m.p. 177–178°). Its dimethyl ester ($C_{17}H_{28}O_4$; M$^+$, *m/e* 296) shows in its PMR spectrum two tert. methyls relatively down-field (PMR: Me, 3H singlets at 0.88, 0.88, 1.12 and 1.20 ppm; COOMe, 3H singlets at 3.58 and 3.63 ppm). Keeping in view the fact[8] that a Me attached to a carbon carrying a methoxycarbonyl group is deshielded, structure **9** should represent the product of ozonolysis and hence, the photo-olefin must be **5**. Since an authentic sample of olefin **6** was on hand, it was possible to show (GLC) that this is also a product of this photoreaction, but a minor product (< 2%).



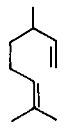
7 R=H
8 R=OAc



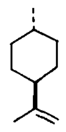
9



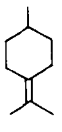
10



11



12a trans
b cis



13

---

†Communication No. 1963, National Chemical Laboratory, Poona, India.

‡Present address: Malti-Chem Research Centre, Nandesari, Vadodara, India.

§Abstracted from the Ph.D. Thesis of A. P. Joshi, Poona University (1972) and presented at the *Second Indo-Soviet Symposium on the Chemistry of Natural Products*, New Delhi (1970) Abstract Book, p. 97.

CITRONELLYL IODIDE[†]

Photolysis of citronellyl iodide (**10**) was investigated to see if any product of π-participation leading to say **12a** was formed.[9] Though photocyclization of certain aromatic iodo compounds has been achieved,[10] no example of the type outlined earlier, is on record.

Citronellyl iodide (**10**), obtained from citronellyl tosylate[11] and NaI, was irradiated (N_2) as a 1% soln in *n*-heptane containing some triethylamine, till a photostationary state was reached (15 h). The product consisted essentially of two major and two minor hydrocarbons with RRT of 1.00 (52%), 1.45 (35%), 1.80 (6.5%) and 2.00 (6.5%). The hydrocarbon with RRT 1.0 proved to be the simple elimination product **11** and this was confirmed by comparison with an authentic sample prepared by the Wolff–Kishner reduction of citral.[12] The second major component, from its spectral data (IR, PMR), was clearly the expected cyclization product and by comparison of its IR and PMR spectra with those reported in the literature[13,14] for *cis*- and *trans*-*p*-menth-8-ene it was identified as the *trans*-isomer (**12a**). The two minor constituents were identified as the *cis*-isomer **12b** (RRT, 1.80) and **13** (RRT, 2.00), only by mixed GLC with authentic samples.[15] No change was detected when citronellyl iodide and triethylamine were kept aside in heptane soln in the dark (15 days).

In an attempt to raise the yield of the cyclized products, irradiation was carried out in two other solvents, benzene and methanol. Benzene soln gave essentially the same results, whereas irradiation of methanol soln resulted in a very complex product (at least 12 components by GLC) which was not investigated further. However, a definite temperature effect was noticed. When the irradiation of heptane soln was carried out at 55–60°, instead of the usual room temp. (24–28°) the total yield of the cyclized products (in essentially the same ratios) increased to 55% at the expense of **11**. This photocyclization reaction has interesting possibilities and is being investigated further.

DISCUSSION

Though it may be possible to rationalise the formation of the various products from the two photoreactions described above, by a radical pathway involving photodissociation, radical cyclization[9] (leading to a precursor for **12a,b** and **13**), elimination-readdition sequence[16] (finally leading to **2**), transannular shift[17] (for generating **5**), the almost complete absence of any reduced product (such as 2,6-dimethyl-oct-2-ene from **10**), in each case, in the reaction mixture, mitigates against such a mechanism. A cationic intermediate is not only fully consistent with the products in each case, but explains best the formation of longicyclene (**4**; 1,3-elimination) from longibornyl iodide. It is conceivable that initially homolytic photodissociation occurs, rapidly followed by a fast electron-transfer process in the solvent cage.

It may be pertinent to point out here that solvolysis of longibornyl chloride[18] or bromide[19] in buffered refluxing aq. ethanol is known to give longifolene only, whereas in presence of alkali both longicyclene (26%) and longifolene are produced. We now find that longibornyl iodide, also, behaves similarly and no transannular product (cf. product composition from photo reaction) was formed. It is suggested that the photoreaction generates "hot" carbonium ions,[20] which are expected to be less discriminating, resulting in a greater product complexity.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Light petroleum refers to the fraction b.p. 60–80°. Optical rotations were measured in $CHCl_3$. The following instruments were used for spectral data: Perkin-Elmer Infracord Model 137E (IR); Varian Associates A-60 Spectrometer (PMR); CEC Mass Spectrometer, model 21-110B (Mass; 70 eV, direct inlet system); "Aerograph" model A-350-B (GLC; 300 cm × 0.5 cm Al columns packed with 20% diethylene glycol succinate on Chromosorb W of 60–80 mesh. H_2 as carrier gas). All PMR spectra were taken in 15–20% solnin CCl_4 with TMS as internal standard; signals are reported in ppm (δ). While citing PMR data the following abbreviations have been used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and b (broad). To summarise the mass spectral data only the molecular ion and the ten most abundant ions (above *m/e* 50) are given with their relative intensities. Photoirradiation was carried out with Hanovia high pressure mercury vapour lamps using an immersion-type water-cooled set-up.

Longibornyl iodide

A soln of longifolene (8.0 g) in gl. AcOH (55 ml) cooled to ~ 10° was saturated with gaseous hydrogen iodide[21] (swept over with oxygen-free N_2). The soln, from which some solid had started separating, was kept overnight (~ 14 h) at 10°. The solid (7.5 g) was collected by filtration and recrystallised from EtOH to furnish white needles, m.p. 70–71°. (Lit.[4], m.p. 70°). λ_{max}^{EtOH} 261 nm (ϵ 665). IR (Nujol): 708, 762, 800, 850, 900, 915, 945, 980 and 1026 cm^{-1}. PMR: 4 tert. Me's (3H, s, 0.83, 0.95, 1.02 and 1.12 ppm), –CH·CHI (1H, q, 4.23 ppm, $J_1 = 6$ Hz, $J_2 = 2$ Hz).

Photoirradiation of longibornyl iodide

Longibornyl iodide (1.35 g) in pure *n*-heptane (130 ml) containing Et_3N (1.5 ml) was irradiated with a 100-W lamp, suspended in a double-walled, water-cooled, clear-fused quartz well, using a Vycor filter sleeve. A minute steady flow of oxygen-free dry N_2 was passed through the reaction mixture. The progress of the reaction was followed by GLC. After all longibornyl iodide had disappeared (6 h), the soln was filtered, the filtrate washed with 10% aq $Na_2S_2O_3$ (100 ml × 2), water (100 ml × 3), dried (Na_2SO_4) and freed of solvent (at 40–50 mm) to furnish a yellowish liquid (0.84 g). This material was passed through a column of silica gel (**2a**[22], 51 × 2 cm) which was washed with light petroleum (100 ml × 3). Removal of solvent yielded a hydrocarbon mixture (0.69 g), which was chromatographed on a column of 15% $AgNO_3$-on-alumina (70 × 2 cm):

Fr. 1	Light petroleum	10 ml × 12	238 mg, longicyclene (**4**; GLC, PMR)
Fr. 2	Light petroleum	10 ml × 4	11 mg, mixture (**4** + **2**)
Fr. 3	Light petroleum	10 ml × 23	254 mg, longifolene (**2**, GLC, PMR)
Fr. 4	Light petroleum	10 ml × 8	108 mg, **5**(+ traces of **4**, GLC).

Fraction 4 was further purified by rechromatography over $AgNO_3$–Al_2O_3 (90 × 2 cm) to furnish 61 mg of pure **5**, b.p. 122° (bath)/10 mm. MS: *m/e* 204 (M^+, 100%), 189 (61%), 161 (59%), 148 (57%), 147 (53%), 133 (50%), 94 (50%), 119 (49%), 105 (49%), 107 (46%) and 149 (44%). (Found: C, 88.06; H, 11.69. $C_{15}H_{24}$ requires: C, 88.16; H, 11.84%).

Pyrolysis of longibornan-9-ol acetate (**8**): *longiborn-8-ene* (**5**) *and longiborn-9-ene* (**6**)

A mixture of longibornan-9-ol (12 g),[6] dry pyridine (18 ml) and acetic anhydride (36 ml) was set aside at room temp (~27°) for 24 h and worked up in the usual way to furnish the required acetate (13.7 g), b.p. 132–134°/3 mm.

The above product (13.5 g) was passed during 90 min through a bed (48 × 2 cm) of broken Pyrex glass pieces maintained at 500 ± 5°; the addition was carried out under a mild suction (pressure:

[†] In part abstracted from the Ph.D. Thesis of P. D. Gokhale, Poona University (1971) and presented at the *Eighth I.U.P.A.C. Symposium on the Chemistry of Natural Products*, New Delhi (1972). Abstract Book, p. C-88.

~650 mm) under N_2 atmosphere. The pyrolysate was taken up in light pretroleum (150 ml), washed with water (100 ml × 3), dried, freed of solvent and distilled to give a liquid (6.64 g), b.p. 136–138°/15 mm. The product consisted of two components (GLC: temp. 160°; H_2 flow 30 ml/min) having RRT of 1.00 (76%) and 1.20 (24%). These were separated by preparative GLC (30% diethylene glycol succinate on 30–60 mesh Chromosorb W; column 300 × 1 cm; temp 150°; H_2 flow, 150 ml/min).

Longiborn-9-ene (**4**; *RRT*, 1.00). B.p. 120° (bath/10 mm, $[\alpha]_D$ −5.75 (c, 5.2%). IR (Film): -CH=CH- (*cis*) 1650, 708 cm^{-1}. PMR (CCl_4): four tertiary Me's (3H singlets at 0.82, 0.88, 0.88 and 0.93 ppm), $-CH_2-CH=CH-$ (2H, bm, 5.03–5.70 ppm). MS: *m/e* 204 (M^+, 100%), 93 (62%), 105 (58%), 91 (58%), 95 (57%), 133 (55%), 119 (53%), 161 (51%), 94 (48%), 189 (45%) and 107 (43%). (Found: C, 88.35; H, 11.74. $C_{15}H_{24}$ requires: C, 88.16; H, 11.84%).

Longiborn-8-ene (**5**; *RRT*, 1.20). B.p. 125° (bath/10 mm, $[\alpha]_D$ +9.6° (c, 4.85). IR (Film): -CH=CH- (*cis*), 1660, 704 cm^{-1}.

Degradation of longiborn-9-ene to **9**

The hydrocarbon **6** (1.1 g) in EtOAc (130 ml) was ozonised (O_3 conc. in the oxygen stream 0.8 g/h) at 0° till no more O_3 was absorbed (20 min). The solvent was removed (~40°/50 mm), the residue taken up in acetone (15 ml), chilled in an ice-salt bath and treated[7] with Jones reagent till a slight excess was present (~8 ml). The reaction mixture was diluted with water (100 ml), product taken up in ether (100 ml × 3) and separated into acidic and neutral products with aq Na_2CO_3. The acid part (0.53 g) was recrystallised from CH_3CN to furnish white prisms, m.p. 177–178°, of the required acid (Found: C, 67.39; H, 9.04. $C_{15}H_{24}O_4$ requires: C, 67.13; H, 9.02%). Esterification with diazomethane gave the dimethyl ester **9**: b.p. 152°/1 mm, $[\alpha]_D$ +7.2° (c, 5.0%). MS: *m/e* 296 (M^+, 14%), 223 (100%), 181 (68%), 222 (43%), 265 (18%), 182 (18%), 179 (17%), 237 (16%), 224 (16%) and 183 (16%).

Citronellyl iodide (**10**)

A mixture of citronellyl tosylate[11] (10 g), acetonitrile (60 ml) and dry NaI (12 g; dried by azeotropic removal of water with xylene) was refluxed (3 h), the bulk of solvent distilled off and the residue treated with water (50 ml). The product was taken up in ether (50 ml × 4), the extract washed with 10% aq sodium thiosulphate (25 ml × 2), brine and dried (Na_2SO_4). The solvent was flashed off and the residue distilled to furnish **10** as a pale yellow oil (8.1 g): b.p. 116–118°/10 mm, n_D^{20} 1.5040, $\lambda_{max}^{heptane}$ 256 nm (ϵ, 444). PMR: $CH_3 \cdot CH$ (3H, d, 0.90 ppm, J = 6 Hz), $(CH_3)_2$ C=C (3H singlets at 1.60 and 1.67 ppm), $(CH_3)_2$ C=CH (1H, t, 5.53 ppm, J = 7 Hz), $-CH_2I$ (2H, t, 3.17 ppm, J = 7 Hz). (Found: C, 45.62; H, 7.60. $C_{10}H_{19}I$ requires: C, 45.11; H, 7.14%).

Photoirradiation of citronellyl iodide

Citronellyl iodide (3.5 g) in *n*-heptane (350 ml) containing triethylamine (5 ml) was irradiated with a 250-W lamp exactly as described earlier, and worked up (after 15 h) in the same fashion to furnish a product which was distilled: b.p. 180–190° (bath)/710 mm, yield 1.4 g. The major products (**11**, **12a**) were separated by preparative GLC (3 m × 1 cm column packed with 30% diethyleneglycol polysuccinate on 60–80 mesh Chromosorb W; temp. 130°; 30 ml H_2/min; each injection 200 μl). Compd. **11**: n_D^{20} 1.4410. Compd. **12a**: n_D^{20} 1.4540.

REFERENCES

[1] See e.g.: [a] J. R. Majer and J. P. Simons, *Advan. Photochem.* **2**, 137 (1964); [b] J. G. Calvert and J. N. Pitts Jr., *Photochemistry* p. 522. Wiley, New York (1966); [c] P. G. Sammes, In *The Chemistry of the Carbon–Halogen Bond* (Edited by S. Patai), Part 2, p. 747. Wiley-Interscience, New York (1973).

[2] P. J. Kropp, T. H. Jones and G. S. Poindexter, *J. Am. Chem. Soc.* **95**, 5420 (1973); G. S. Poindexter and P. J. Kropp, *Ibid.* **96**, 7142 (1974).

[3] For a Review see: J. Lhomme and G. Ourisson, *Recherches* **15**, 16 (1966).

[4] J. L. Simonsen, *J. Chem. Soc.* **117**, 578 (1920); P. Naffa and G. Durisson, *Bull. Soc. Chim. Fr.* 1410 (1954).

[5] U. R. Nayak and S. Dev, *Tetrahedron* **24**, 4099 (1968).

[6] J. R. Prahlad, U. R. Nayak and S. Dev, *Ibid.* **26**, 663 (1970).

[7] A. S. Narula and S. Dev, *Tetrahedron Letters* 1733 (1969).

[8] C. W. Chien, *J. Am. Chem. Soc.* **82**, 4762 (1960); J. W. ApSimon, O. E. Edwards and R. Howe, *Can. J. Chem.* **40**, 630 (1962); T. S. Santhanakrishnan, U. R. Nayak and S. Dev, *Tetrahedron* **26**, 641 (1970).

[9] For a survey of free-radical cyclizations see: J. W. Wilt, In *Free Radicals* (Edited by J. K. Kochi), pp. 418–446. Wiley-Interscience, New York (1973).

[10] S. M. Kupchan and H. C. Wormser, *J. Org. Chem.* **30**, 3792 (1965); P. W. Jeffs and J. F. Hansen, *J. Am. Chem. Soc.* **89**, 2798 (1967); J. L. Neumeyer, K. H. Oh, K. K. Weinhardt and B. R. Neustadt, *J. Org. Chem.* **34**, 3786 (1969). Also see: P. G. Sammes, In *The Chemistry of Carbon-Halogen Bond* (Edited by S. Patai), Vol. 2, pp. 777–782. Wiley-Interscience, New York (1973).

[11] D. H. R. Barton and L. R. Morgan, *J. Chem. Soc.* 630 (1962).

[12] R. Fischer, G. Lardelli and O. Jeger, *Helv. Chim. Acta* **34**, 1577 (1951).

[13] B. M. Mitzner, E. T. Theimer and S. K. Freeman, *Appl. Spectros.* **19**, 169 (1965).

[14] A. F. Thomas and M. Stoll, *Helv. Chim. Acta* **47**, 413 (1964).

[15] Samples prepared (Dr. A. N. Misra) in this Laboratory from *p*-menthan-8-ol.

[16] See e.g.: J. A. Berson, C. J. Olsen and J. S. Walia, *J. Am. Chem. Soc.* **82**, 5000 (1960); **84**, 3337 (1962).

[17] See e.g.: D. Helminger and G. Ourisson, *Liebigs Ann.* **686**, 19 (1965).

[18] P. Ourisson and G. Ourisson, *Bull. Soc. Chim. Fr.* 1415 (1954).

[19] U. R. Nayak and S. Dev, *Tetrahedron* **24**, 4099 (1968).

[20] See e.g.: J. T. Keating and P. S. Shell, In *Carbonium Ions* (Edited by G. A. Olah and P. Von R. Schleyer), Vol. II, pp. 573–653. Wiley-Interscience, New York (1970).

[21] C. J. Hoffman, *Inorganic Syntheses* **7**, 180 (1963).

[22] R. Hernandez, R. Hernandez, Jr. and L. R. Axelrod, *Analyt. Chem.* **33**, 370 (1961).