

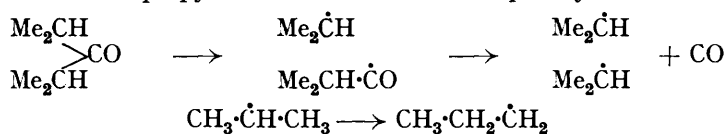
394. Free Radicals and Atoms in Primary Photochemical Processes.
The Free Propyl Radical from Diisopropyl Ketone.

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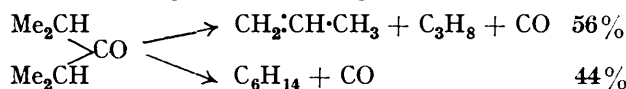
THE primary products of the photochemical dissociation of acetone, diethyl ketone, and di-*n*-propyl ketone are carbon monoxide and the free radicals methyl, ethyl, and *n*-propyl respectively (Norrish, *Trans. Faraday Soc.*, 1934, **30**, 108; Norrish and Appleyard, *J.*, 1934, 874; Pearson, *ibid.*, p. 1718; Pearson and Purcell, *J.*, 1935, 1151; this vol., p. 253; Prileshajeva and Terenin, *Trans. Faraday Soc.*, 1935, **31**, 1483).

In an endeavour to prepare the *isopropyl* radical, diisopropyl ketone was allowed to stream through a silica tube at low pressures, wherein it was irradiated by mercury-vapour arcs, and the products of photolysis were allowed to impinge on mirrors of tellurium or lead. These were completely removed in times comparable with those taken by the radicals from the other aliphatic ketones. Although the reaction with tellurium might be ascribed to atomic hydrogen, that with lead can be due only to organic radicals, and these were identified by allowing them to react with metallic mercury. A liquid considerably less volatile than the ketone could be isolated which at room temperature had the faint unpleasant odour of the higher mercury alkyls. This liquid, which was dissolved in much unchanged ketone, was treated with an excess of mercuric bromide and kept overnight, the ketone removed, the solid white residue fractionally sublimed, and the behaviour of the sublimates during heating observed with a microscope. They were similar in all respects to synthetic mixtures of *n*-propylmercury bromide, mercuric bromide, and diisopropyl ketone, but the complexity of the phenomena did not allow of an unequivocal identification. Therefore the experiments were repeated, with mercuric iodide in place of the bromide. The product was identical with *n*-propylmercury iodide; it melted at 127°, alone or mixed with authentic *n*-propylmercury iodide (m. p. 127°).

The result may be interpreted in two ways: either *n*-propyl results during the primary act of dissociation, or *isopropyl* is first formed and subsequently isomerises:



The former hypothesis is untenable as shown by the experiments of Dr. Bamford and Dr. Norrish, who have kindly allowed us to use their unpublished results. They conclude that the process proceeds according to the following scheme:



The hydrocarbon C₆H₁₄ consists mainly of diisopropyl (v. p. and b. p.), and they were unable to detect an appreciable quantity of *n*-hexane in the products of the reaction. *iso*Propyl

radicals are therefore liberated in the primary act, and thereafter combine with one another to yield diisopropyl without tautomerising. It thus appears that the tautomerism which occurred in our experiments was a consequence of the mercury which was used.

A closely related series of transformations involving alkyl bromides has been investigated by Eltekoff (*Ber.*, 1873, **6**, 1258; 1875, **8**, 1244) and others (Michael and Leupold, *Annalen*, 1911, **379**, 263). The vapour of *n*-propyl bromide when heated for 1 hour at 262° is converted to the extent of 23% into isopropyl bromide. The reverse reaction occurs, but is much slower. Liquid isobutyl bromide after 48 hours' irradiation with ultra-violet light (Lucas and Salmon-Legagneur, *Compt. rend.*, 1928, **186**, 39) gave 14% of *tert.*-butyl bromide, and similar reactions occurred (no values are given) with *n*-propyl bromide. All these reactions proceed most rapidly in the direction, normal \rightarrow *iso* \rightarrow tertiary, *i.e.*, opposite to that observed in our experiments. It has been shown in this laboratory (unpublished experiments with Mr. F. Carr) that radicals occur as intermediates in the photolysis of the alkyl halides, and if it be allowed that tautomerism is always preceded by fission of the halide molecule, then combination of the radical with a halogen evidently favours the formation of the branched-chain radical, *i.e.*, *n*-propyl \rightarrow isopropyl. It thus seems that the form in which the radical ultimately appears in a compound is governed by the nature of the element with which it has combined.

It is the experience of organic chemists that the carbon atom \dot{C} in a *normal* group (I) is less negative than that in the corresponding *iso*-group (II) (*Ann. Reports*, 1932, **29**, 96; 1933, **30**, 181; Baker and Nathan, *J.*, 1935, 1845). Hence, it is reasonable that the tautomerism which occurs on combination with an electropositive element (metal) involves the migration of hydrogen to yield the *n*-propyl derivative, whilst with an electronegative element (halogen) the *iso*-derivative is obtained.



From these considerations the life-period measurements recorded in the experimental section refer to isopropyl. The value obtained for its half-life period, 4.4×10^{-3} sec., does not differ appreciably from that of *n*-propyl, 4.0×10^{-3} sec., measured under similar experimental conditions in the same apparatus.

Whether rearrangement occurs during the formation of the metal alkyl or afterwards, is a fine point on which the present experiments do not give information. These and related tautomeric changes are being further investigated.

EXPERIMENTAL.

Diisopropyl ketone was dried over calcium chloride and distilled at atmospheric pressure through a bead column, the middle fraction, b. p. 123–124°, being collected. Mercury was purified with nitric acid, dried, and redistilled in a vacuum. Commercially pure mercuric bromide was recrystallised from water.

The apparatus employed for the experiments with tellurium and lead was that previously described (*J.*, 1935, 1153). Manometers containing butyl phthalate were used, to avoid the presence of mercury in the apparatus. In the absence of ultra-violet light, the ketone was without action on tellurium or lead, but in its presence brown mirrors of tellurium, about 2 mm. wide and situated 3–4 cm. from the irradiated zone, were removed in 1–2 minutes. Lead mirrors were removed in longer but comparable times.

The radicals were identified in the transparent quartz apparatus previously described (this vol., p. 253, Fig. 2). It was soon appreciated that the alkylmercury obtained was much less volatile than the diisopropyl ketone and could be retained as a tail fraction during the distillation of the ketone through the apparatus (diisopropyl ketone, b. p. 123.5°; dimethylmercury, b. p. 96°; diethylmercury, b. p. 159°; di-*n*-propylmercury, b. p. 190°; diisopropylmercury, b. p. 119–121°/125 mm.). About ten passages of ketone over the mercury were therefore made before distilling the alkylmercury on the mercuric bromide. This was contained in a glass vessel having a neck of uniform quill tubing. The mixture of ketone, mercuric bromide, and the alkylmercury was kept overnight. After removal of the ketone, the vessel was surrounded with a water-bath at 80°; a white product then sublimed into the quill, leaving a residue of mercuric bromide in the bottom of the vessel. The vessel was removed from the apparatus, and the quill tubing cut just below the level of the sublimate. By pushing a piece of glass rod through the quill, the white solid was transferred without appreciable loss to the micro-sublimation apparatus,

wherein it was separated into a large number of small fractions, each of which was collected on a separate cover slip (Hans Meyer, "Nachweis und Bestimmung organischer Verbindungen," Leipzig, 1935). The first ten fractions were identical and consisted of minute colourless isotropic nodules, like sections through regular garnets. The cover-slips were placed in turn in a copper block on the microscope stage and gradually heated. The majority of the specimens melted over a range (124—128°), and left an infusible residue, a behaviour which does not correspond with that of any pure alkylmercury bromide (methyl derivative, m. p. 160—164°; ethyl, m. p. 193·5°; *n*-propyl, m. p. 138°; isopropyl, m. p. 98°), but is nearly reproduced in a mixture of *n*-propylmercury bromide and mercuric bromide recrystallised from diisopropyl ketone and subsequently sublimed (cf. this vol., p. 255). It thus appeared that the main constituent of our product was *n*-propylmercury bromide, but the presence of less than 5% of the *iso*-compound would have escaped detection.

This conclusion was established by allowing the alkylmercury from 12 runs to react with mercuric iodide instead of the bromide. After removal of the ketone in the final stage, the solid residue was bright yellow. On sublimation into the quill tubing from a bath at 80°, a pale yellow solid was deposited, leaving unchanged red mercuric iodide in the vessel. The yellow solid was separated into 15 fractions, the first 13 of which were very pale yellow, irregular, crystalline grains identical in appearance with *n*-propylmercury iodide; they had m. p. 127°, unaffected by admixture with the authentic material (m. p. 127°). The last two fractions contained mercuric iodide. No higher or lower alkylmercury iodides were observed (*isopropylmercury iodide*, m. p. 112°).

The life of the radicals was compared with that of the *n*-propyl radical obtained from di-*n*-propyl ketone under identical experimental conditions, by observing the times of removal of standard tellurium mirrors at various distances along a quartz tube from the irradiated zone (J., 1934, 1721), first the di-*n*-propyl ketone and then the diisopropyl ketone being used. The results obtained are shown in the tables, in which the symbols have the meanings previously attached to them (J., 1934, 1721), the time *t* being calculated from the Herzfeldt relationship (Paneth and Lautsch, *Ber.*, 1931, 64, 2702)

$$t = (X_2 - X_1)/V - a(X_2^2 - X_1^2)/2VP$$

Life period of radical from diisopropyl ketone.

Velocity of gas stream on entering tube (*V*) = 19·12 m./sec. Pressure (*P*) at this point = 0·093 cm. Hg. Average pressure gradient (*a*) = 0·00049 cm. Hg/cm. Diameter of tube = 11·2 mm.

<i>L</i> , cm.	<i>t</i> × 10 ³ .	<i>x</i> (secs.).	log 1000 <i>A</i> .	<i>L</i> , cm.	<i>t</i> × 10 ³ .	<i>x</i> (secs.).	log 1000 <i>A</i> .
1	0·37	45	1·347	10	3·53	86	1·066
1·5	0·55	45	1·347	15	5·24	112	0·951
2	0·73	55	1·260	20	6·85	140	0·854
4	1·46	60	1·222	20	6·85	125	0·903
7	2·52	70	1·155	24·5	8·24	150	0·824

*Life period of radical from di-*n*-propyl ketone.*

V = 16·64 m./sec. *P* = 0·062 cm. Hg. *a* = 0·00031 cm. Hg/cm. Diameter of tube = 11·2 mm.

3	1·34	85	1·071	18·2	7·75	275	0·561
5	2·23	115	0·939	20·5	8·66	288	0·541
10	4·38	156	0·807	21	8·85	330	0·482
16	6·86	250	0·602				

From these results the mean half-life periods of the radicals from diisopropyl ketone and di-*n*-propyl ketone are 4·4 and 4·0 × 10⁻³ respectively. The latter value is in agreement with that previously obtained (this vol., p. 255), *viz.*, 2·3 × 10⁻³ sec., in a tube 8 mm. in diameter.

SUMMARY.

On exposure to ultra-violet light, diisopropyl ketone yields free radicals which combine with mercury to give *n*-propylmercury. It appears that the radical first liberated is *iso*-propyl, which subsequently tautomerises.

The half-life periods of *n*-propyl from di-*n*-propyl ketone and of *iso*propyl from diisopropyl ketone have been compared under identical experimental conditions and found to be 4·0 and 4·4 × 10⁻³ sec., respectively.

The authors are indebted to the Royal Society for a grant.