374. *The Photoreactions of Liquid and Dissolved Ketones. Part III.*

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In Parts I and II (Bowen and de la Praudière, J., 1934, 1503; Bowen and Horton, *ibid.*, p. 1505) it was shown that acetone and diacetyl give no gaseous products on exposure in the pure liquid state to ultra-violet light from the mercury arc, and that in hexane solution a photo-reaction occurs, giving dissolved products. The quantum efficiency of this reaction with diacetyl diminished with increasing concentration of the ketone, and the results for acetone seemed to point in the same direction.

We have now confirmed this result for acetone (see Table I, where γ is the quantum efficiency), and have found that the two chief products resulting from exposure of its solutions in *n*-hexane or *cyclo*hexane are (1) an alcohol, and (2) a substance capable of absorbing bromine rapidly from a moist solution in carbon tetrachloride, liberating an equivalent of hydrogen bromide. Table I shows that the relative amounts of these two products are independent of the acetone concentration.

The arrangement of light sources and filters, and the methods of measuring light absorptions and intensities have already been described (see Part I; and Bowen, J., 1935, 76). The radiation used was 3135—2480 A.

In order to obtain reproducible results it was necessary to purify the acetone very carefully, the following method being convenient. The acetone was treated with successive small quantities of potassium permanganate for several days, the manganese dioxide filtered off, and the filtrate distilled through a " Dufton " column about 80 cm. long. The distillate was shaken with potassium carbonate and again distilled through the same column, and then the drying and final distillation were repeated. The methyl alcohol content of this acetone, determined by Fischer and Schmidt's method (*Ber.*, 1924, **57**, 693; 1926, **59**, 679), was less than 0·15 mol. %.

The last column of the table was calculated from the difference between the hydroxyl content of each solution before and after exposure. This content was determined by a modification of a method used by Bell (J., 1932, 2903) for estimating water, *viz.*, adding the substance to a solution of α-naphthoxydichlorophosphine dissolved in chlorobenzene, drawing off the hydrogen chloride so produced in a current of air, collecting it in water, and estimating its amount by titration. The reaction is quantitative for water, but does not seem to be so for other hydroxylic compounds. It is, however, fairly consistent; *e.g.*, *iso*propyl alcohol in amounts of the order of 0·1 g. gave 58, 60, 64, 58% of the expected yield of hydrogen chloride. No correction for this incomplete reaction has been applied to any of the results of hydroxyl determinations given in this paper, and so they are all minimum values.

Dissolved air was removed from the solutions by bubbling nitrogen through them for an hour before exposure. If oxygen was bubbled through, it was found that the observed quantum efficiency was reduced by a factor of about 2, the effect being greatest in solutions containing the smallest proportion of acetone. This was presumably due to the inner-filter action of oxidation products.

TABLE I.

Solutions of Acetone in n-*Hexane.*

Acetone, % by wt.	10	35	65	87	96	100	34
Apparent γ, as measured by Br titration	0·15	0·12	0·08	0·04	0·01	0·004	0·12
Apparent γ, as measured by OH detmtn.	0·27	0·21	0·12	0·08	0·02	0·02	0·20

The last result of Table I was obtained by using monochromatic light of wave-length 3135 A., whereas the other results were obtained by using the full radiation from 3135 to 2480 A.

On distillation of an exposed solution of acetone in *n*-hexane, a small quantity of a colourless and somewhat viscous liquid, b. p. 180—190°, was obtained. From an exposed solution of acetone in *cyclo*hexane a liquid of similar odour and appearance was obtained, having a b. p. about 5° higher. The properties of these liquids suggested that they were dimethyl-*n*-hexylcarbinol and *cyclo*hexyldimethylcarbinol respectively. For comparison, these substances were synthesised by Grignard reactions, and the properties of the synthetic compounds and the photo-products are given in Table II. The analyses and molecular weights for the synthetic compounds are the theoretical values and were not determined experimentally.

TABLE II.

	From *n*-hexane.		From *cyclo*hexane.	
	Photo-product.	Synthetic compound.	Photo-product.	Synthetic compound.
B. p.	180—190°	180—183°	185—195°	188—195°
n_{D}	1·437 (17·5°)	1·429 (17·5°)	1·469 (14°)	1·470 (14°)
Analysis, % C	76·3, 75·8	(74·9)	74·7, 75·3	(76·0)
Analysis, % H	13·6, 13·0	(14·0)	12·2, 12·4	(12·8)
M	148, 142	(144)	134, 143	(142)
Br absorbed (mols. %)	11, 15, 13	<1	12	<1
OH content (mols. %)	75, 70	67	75	—

The " hydroxyl content " gives the amount of hydrochloric acid collected, expressed as a percentage of the theoretical yield to be expected if Bell's method gave complete reaction and all the substances concerned contained one hydroxyl group per molecule.

The proportion of bromine-absorbing substance to hydroxy-compound is smaller with the distilled products than with the exposed solutions. This difference may be due, in part, to separation (though no further separation took place on redistillation), and, in part, to removal of excess acetone which might have taken up bromine by an " induced " reaction. It was not possible to separate the bromine-absorbing substance from the hydroxy-compound by bromination followed by distillation, or even by evaporation at a low temperature, as this led to tar formation. Neither could the 3 : 5-dinitrobenzoyl esters of the photo- or synthetic products be prepared, although the reaction with the chloride was tried at high temperatures with and without a solvent (quinoline, nitrobenzene). It seems that the tertiary structures of the alcohols are responsible for their failure to form identifiable crystalline esters. No reaction could be observed with α-naphthyl *iso*cyanate. The bromine-absorbing substance may be a ketone capable of bromination. By reaction of the distilled product with 2 : 4-dinitrophenylhydrazine, a very small quantity of crystals was separated, and these charred when heated to 200°; no reaction for aldehyde or enolic substance was obtained. In view of the presence of this substance in the distilled products to the extent of some 15%, the agreement in properties between each photo-product and the corresponding synthetic carbinol seems to be as good as could be expected.

Unequivocal evidence that the solvents had taken part in the reaction was obtained by oxidising the photo-products with chromic acid. From the product from *cyclo*hexane was obtained a 20% yield of adipic acid, identified by m. p. (151°), analysis (Found : C, 48·98; H, 7·06. Calc. : C, 49·23; H, 6·90%), and the m. p. of its *p*-bromophenacyl ester (153°; Kelley and Kleff, *J. Amer. Chem. Soc.*, 1932, **54**, 4444, give 154°). A similar oxidation of the product from *n*-hexane would be expected to give a mixture of straight-chain monobasic acids; and this was in fact found. The oxidation product was a liquid which was fractionated into portions, b. p. 140—170° and 170—210°, having odours indistinguishable from those of the aliphatic acids. The first fraction gave a *p*-bromophenacyl ester, m. p. 51°, and the second, one of m. p. 63°. These values may be compared with the following, from the literature :

Acid	Propionic	*n*-Butyric	*n*-Valeric	*n*-Caproic
B. p.	140°	163°	186°	205°
M. p. of *p*-bromophenacyl ester	63°	63°	75°	72°

The results described above seem to show that the chief photo-product formed in solutions of acetone in *n*-hexane or *cyclo*hexane is a carbinol formed from one molecule of acetone and one of the hydrocarbon. From the absorption spectrum and the photo-products of acetone in the gaseous state, *viz.*, ethane, carbon monoxide, and diacetyl (Norrish, Crone, and Saltmarsh, J., 1934, 1456; Barak and Style, *Nature*, 1935, **135**, 307), it is generally concluded that the primary photo-process is $CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_3 + CH_3{\cdot}CO$. The dissociation may be of the delayed type, and the very small quantum efficiency in the pure liquid state may be due either to deactivation by collision in the delay interval or to " primary recombination " of the radicals (Franck and Rabinowitsch, *Trans. Faraday Soc.*, 1934, **30**, 120). For the reaction in solution there are the possibilities of combination of the dissociation products with the hydrocarbon molecule or the interaction with the hydrocarbon of an excited acetone molecule. Until the spectrum of acetone is more fully interpreted, it does not seem possible to distinguish between these mechanisms.

The very specific nature of these reactions is further shown by the following experiments on other ketones and other solvents.

Experiment 1. A solution containing 33% acetone in benzene was exposed to the 3135 A. region. No appreciable change occurred, as judged by hydroxyl determination, bromine titration, or distillation, and no gas was evolved.

Experiment 2. A solution containing 29% acetone in carbon tetrachloride was similarly exposed. No gas was evolved, but the exposed solution had an odour similar to that of chlorine, and slowly liberated iodine from potassium iodide.

Experiment 3. A solution containing 19% diethyl ketone in *n*-hexane was exposed to unfiltered ultra-violet light. Gas was evolved at a rate corresponding to a quantum efficiency of about 0·1. On distillation, the product, b. p. 160°/20 mm., was different in odour and appearance from the acetone products, and gave only 11% reaction by Bell's method.

Experiment 4. A solution containing 19% methyl ethyl ketone in *n*-hexane was similarly exposed. Gas was evolved at a rate corresponding to a quantum efficiency of about 0·01. On distillation, up to 70° the distillate was colourless, but after that, fractions up to 200° were obtained having a yellow colour and the characteristic odour of diacetyl. It is clear that α-diketones are formed in this case, and this may be compared with Barak and Style's results (*loc. cit.*) on the non-gaseous products formed on exposure of simple ketones in the gas phase, though we found no trace of α-diketones in the case of acetone solutions.

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