134. *The Photochemical Decomposition of Aromatic Ketones: the Phenyl Radical.*

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Free methyl and phenyl radicals formed during the photolysis of aceto- and benzophenones have been detected and identified by their reactions with tellurium. The possible intermediate formation of the benzoyl radical $C_6H_5{\cdot}CO$ and of the phenacyl radical $C_6H_5{\cdot}CO{\cdot}CH_2$ has also been indicated. The preparation of phenyl methyl telluride and its *mercuric halide* derivatives is described.

It was expected that the aromatic ketones would yield aryl radicals on irradiation with ultra-violet light, but the possibility of identifying them seemed small in view of the conflicting results of previous workers. Zarlman and Adkins (*J. Amer. Chem. Soc.*, 1932, **54**, 3398) decomposed tetraphenyl-lead at 200° under 100 atm. in the presence of nickel as a catalyst and obtained pure diphenyl, and Dull and Simons (*ibid.*, 1933, **55**, 4328) found the same result at atmospheric pressure even at 252° and in the absence of nickel. They also made the experiment at a low pressure in a silica chamber (*ibid.*, p. 3898), and on allowing the volatile products to react with mercury, obtained diphenylmercury, m. p. 120°, and concluded that phenyl radicals must have been present. On the other hand, Paneth and Lautsch (J., 1935, 380) carried tetraphenyl-lead in a hydrogen stream at 2 mm. pressure through a silica tube heated over a short zone; the lead mirror had not the sharp edge remote from the flame usually associated with the presence of free radicals, and neither lead nor tellurium mirrors were attacked by the products which passed along the tube. They concluded that " since carbon was deposited at the place of decomposition of the tetraphenyl-lead, the phenyl apparently underwent extensive decomposition without giving rise to radicals of appreciable life," and " the free phenyl has a much shorter life than methyl or ethyl, or else does not attack tellurium." In the same communication, Paneth and Lautsch examined the reaction between bromobenzene and sodium vapour from which Horn, Polanyi, and Style (*Naturwiss.*, 1932, **20**, 401; *Z. physikal. Chem.*, 1933, *B*, **23**, 291; 1934, *B*, **25**, 151) considered that they had obtained the phenyl radical. Paneth and Lautsch found no evidence of the existence of the phenyl radical, although in similar experiments with benzyl chloride, benzyl radicals were easily detected and their half-value period measured.

In view of the conflicting opinions, it was considered worth trying to obtain the phenyl radical from the products of photolysis of aromatic ketones, as we had previously been successful in isolating certain radicals (J., 1936, 253, 1777; 1937, 567) which were not obtainable by thermal methods.

It is shown below that the photolysis of benzophenone yields active fragments which react with tellurium mirrors. The low volatility of benzophenone (m. p. 49°) introduced complications which prevented the ready identification of the organo-tellurium compounds, and attention was transferred to acetophenone. The products were first examined in the absence of tellurium. The probable presence of diphenyl, benzil, and dibenzoylethane was indicated. In the presence of tellurium, diphenyl, dimethyl, and phenyl methyl tellurides were readily identified. It is evident, therefore, that the ketone molecule had split up to yield methyl and phenyl radicals, which had reacted with the tellurium. The reaction between phenyl and tellurium is contrary to Paneth and Lautsch's conclusion, but is in harmony with Waters' recent discovery (J., 1938, 1078, published after the conclusion of our experiments), that the free phenyl radicals formed during the decomposition of benzenediazonium chloride in acetone solution react with metallic tellurium to yield diphenyl telluride. The occurrence of benzil would suggest the intermediate formation of benzoyl radicals, which, by analogy with the acetyl radical, dissociate to give phenyl and carbon monoxide, so that the decomposition of the ketone proceeds by a mechanism similar to that obtaining in the case of acetone :

$$\text{(i)}\ C_6H_5{\cdot}CO{\cdot}CH_3 \longrightarrow C_6H_5{\cdot}CO + CH_3 \qquad \text{(iii)}\ 2C_6H_5 \longrightarrow C_6H_5{\cdot}C_6H_5$$

$$\text{(ii)}\ C_6H_5{\cdot}CO \longrightarrow C_6H_5 + CO \qquad \text{(iv)}\ 2CH_3 \longrightarrow C_2H_6$$

$$\text{(v)}\ C_6H_5 + CH_3 \longrightarrow C_6H_5{\cdot}CH_3$$

The presence of a small amount of a substance which was probably dibenzoylethane is interesting, and, by analogy, lends weight to Spence and Wild's suggestion (J., 1937, 352) that the radical $CH_3{\cdot}CO{\cdot}CH_2$ participates in the photodecomposition of acetone.

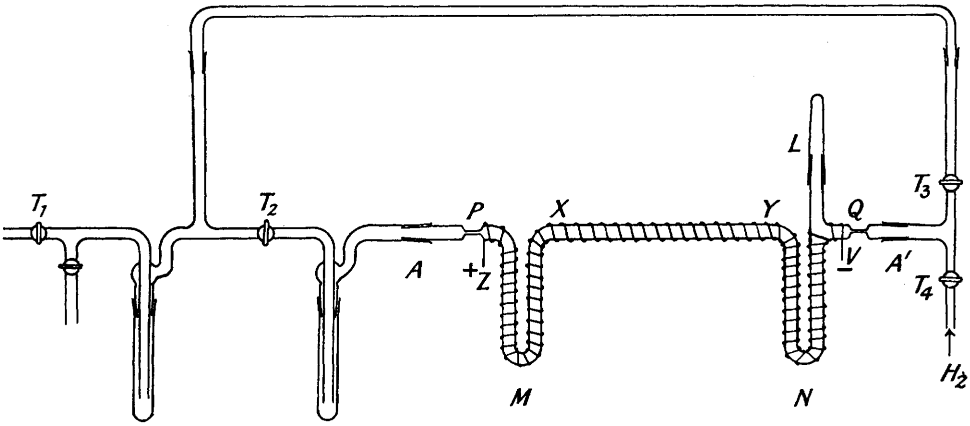
Because benzophenone yields diphenyl on exposure to ultra-violet light and gives evidence of free radicals with tellurium mirrors, it may be argued by analogy that it also undergoes simple fission like the ketone just examined.

EXPERIMENTAL.

Benzophenone is a solid (m. p. 49°, b. p. 306°), for the manipulation of which the apparatus previously used (J., 1934, 1718; 1936, 254) was inadequate. Experiments were first made with a straight quartz tube heated by resistance wire, but modifications were necessary because the ketone condensed in the taps and prevented the maintenance of a vacuum. The apparatus shown in the figure was therefore built.

A quartz tube *AA'*, 12 mm. in diameter, and fitted with ground joints, was bent into the two U-tubes *M* and *N*, separated by the straight length *XY*, 60 cm. long. The U-tubes could be immersed in a liquid-air vessel, and *N* was fitted with an extended side arm *L*, provided with a ground joint to allow of the introduction of the benzophenone. On each end of the quartz tube *PQ*, a capillary was formed which could be sealed with the benzophenone and thus prevent it distilling about the system. The whole of the tube was wound with nichrome wire, and temperatures up to 150° could be maintained. A metallic mirror could be formed in the quartz tube from the reservoir at *X*. To facilitate this process, a supply of pure hydrogen was available through T_4. A hot and a cold mercury arc, burning on opposite sides of the tube, were employed as sources of ultra-violet light, and the ketone was caused to stream from the vessel *N* into *M* (cooled in liquid air) by heating the wiring between *X* and *V* to about 80°, under which conditions the capillary *Q* became blocked. It was found that brown opaque tellurium mirrors 2 mm. wide and 5 cm. from the irradiated zone could be moved in times between 2 and 5 minutes. To carry out a further series of runs, more benzophenone was introduced through *L*, or that in *M* was distilled back into *N* by cooling the latter in liquid air, heating the system between *Z* and *Y*, and pumping through T_3 with T_2 closed. The capillary *Q* was opened by melting the benzophenone contained in it, whilst *P* was blocked by cooling with water. Blank experiments were made to ascertain (*a*) if the heat of the wiring was sufficient to remove a tellurium mirror by distillation, and (*b*) whether a tellurium mirror was affected by benzophenone in the absence of ultra-violet light. Both these experiments were negative, and the presence of free radicals in the photodecomposition of benzophenone is thus established.

An attempt to identify the radical was made in the same apparatus by allowing the radicals to impinge on lead and tellurium. Diphenyl-lead is a blue solid (m. p. 200°), whereas diphenyl telluride is a high-boiling liquid forming stable salts with mercuric halides (Lederer, *Ber.*, 1915, **48**, 1422). The mercury arcs were operated in the centre of *XY*, and a heavy tellurium mirror formed on each side of them from deposits of the metal placed along the tube; the benzophenone was then allowed to stream backwards and forwards between *X* and *Y* in the manner described above. After six runs with 5 g. of benzophenone, the apparatus was dismantled, the quartz tube thoroughly extracted with ether, and to this extract was added a concentrated solution of mercuric iodide, but the quantities of aryl telluride, if present, were too small to allow of identification, which was rendered especially difficult by the fact that benzophenone is a solid.



A final experiment was undertaken, an opaque mirror of pure lead 2 mm. wide, formed in the same way as the tellurium mirrors, being used. Although irradiated benzophenone was streamed over it, it was apparently unaffected and there was no appearance of the blue diphenyl-lead.

In order to obtain greater light absorption, the identification experiments were continued in the apparatus shown in Fig. 2 (J., 1936, 254), or in a silica circulating system which allowed the experiments to be made continuously over a considerable period. In view of the difficulty experienced with benzophenone, it was decided to investigate the products of the decomposition of acetophenone, which is a liquid at room temperature in summer (m. p. 19·5°) and may be distilled through the apparatus in the ordinary way. The acetophenone (B.D.H.) was fractionally distilled, and a small centre portion (b. p. 200°) retained.

The first experiment was carried out in the absence of tellurium. Acetophenone was streamed back and forth through the quartz irradiation tube four times, in each case distilling from lukewarm water to liquid air. At the conclusion of the experiment, a yellowish solid was noticed in the side-arms of the irradiation vessel. It was dissolved in a little warm alcohol and allowed to recrystallise. The first deposition consisted of faintly yellow needles which appeared colourless under the microscope. On being heated on the copper block under the microscope, they melted sharply at 70° (probably diphenyl, m. p. 69—71°). Later deposits of crystals were obtained which appeared under the microscope as yellow, fern-like clusters, identical with benzil, and melting sharply at 95—97°. A third specimen was obtained in the form of a white material, insoluble in the amount of alcohol used in the recrystallisation. After being washed thoroughly with cold alcohol, it melted sharply at 144—145°, and may have been dibenzoylethane (m. p. 144—145°). These compounds afford some evidence of the intermediate formation of phenyl, benzoyl, and phenacyl radicals during the photodissociation of acetophenone.

It was next decided to identify the radicals directly by allowing the decomposition products to react with tellurium. The apparatus used consisted of the silica irradiation vessel previously described (J., 1936, 254, Fig. 2), which was incorporated by means of ground joints in an apparatus similar to that shown in Fig. 1, J., 1935, 1153, in place of the quartz tube *XZ*. The capillary tube *D* was, however, found to be superfluous, and was replaced by a length of 10-mm.-bore tubing. The manometers were filled with dibutyl phthalate to avoid the presence of mercury in the irradiation apparatus. As in the acetyl investigation (J., 1937, 567), the whole of the inner surface of the outer wall of the irradiation vessel was covered with sublimed tellurium. The acetophenone was distilled from the vessel *E* immersed in tepid water to the trap *B* cooled in liquid air, so that a pressure of a few mm. of butyl phthalate was indicated by the manometer *C*. In order to prevent the condensation of acetophenone in the irradiation vessel, this was held at 40° by controlling the rate of flow of the cooling water in the jacket. In the laboratory at about 20°, the rate of distillation was very slow, 12 hours being required to distil 20 g. of acetophenone through the system. Even at this low rate it was soon apparent that the tellurium mirror was being eroded, and the condensate in *B* was bright yellow. At the completion of the run, the reaction products were fractionally distilled in the system, but no sharp colour separation could be achieved. The whole product was therefore removed from the apparatus, whereupon the unmistakable odour of dimethyl telluride was noticed. A saturated solution of mercuric iodide in acetone was added, and a bright yellow precipitate separated, similar in every respect to dimethyl telluride mercury iodide obtained under identical conditions from the products of the photodecomposition of acetone in the presence of tellurium (J., 1937, 567). Considerable melting was observed under the microscope at 105—110°, which was not affected by admixture with the authentic material (m. p. 107°, J., 1938, 282), but the product was obviously contaminated with small amounts of other materials which could not be removed. Repetition of the experiment confirmed this behaviour.

The tellurium was then kept at 150° during the irradiation to favour the formation of ditellurides instead of monotellurides. The liquid products were fractionally distilled before being treated with mercuric iodide. The tail fraction gave an insoluble precipitate which melted in the range 97—110°. It was extracted with several small amounts of acetone. The residue, which was canary-yellow, was heated between cover-slips and observed under the microscope. It became orange at 86°, began to sinter and darken at 92°, was almost black at 96°, and melted to a russet-coloured liquid at 101—102°. This behaviour was identical with that shown by a synthetic specimen of diphenyl ditelluride mercuric iodide, and was not affected by admixture with the synthetic material.

The head fraction gave an orange-yellow precipitate with mercuric iodide (m. p. 86—96°), which, after extraction with hot acetone, melted at 97°, but could not be identified with any known organic tellurium compound. The filtrates from the precipitation and the extraction were combined, and evaporated until crystals began to deposit. These crystals were identical in appearance and properties with diphenyl telluride mercuric iodide, recrystallising to fine needles between 120—130°, sintering at 140°, and melting at 146°.

Attempts to isolate a very soluble mercuric iodide derivative which was evidently present in the residues from the above experiment were unsuccessful. It was always contaminated with large quantities of mercuric iodide, from which we were unable to free it. The presence of phenyl methyl telluride, which forms a very soluble mercuric iodide derivative, was, however, readily demonstrated by using mercuric bromide as a precipitant in place of the iodide. The whole of the liquid products from the photolysis of acetophenone in the presence of tellurium were treated with a solution of mercuric bromide in acetone. A pale cream-coloured precipitate (A) was thrown out, to leave a pale yellow liquid (B). When (A) was heated, the colour intensified up to 90°; there were signs of sintering at 100°, and the substance melted at 116—117° to yield a yellow oil. After extraction with acetone, the compound sintered at 106° and melted at 110°. The liquid (B), on evaporation in a vacuum at room temperature, gave white granular crystals having a pale cream tinge, which melted to a yellow liquid at 125°, and were identical with phenyl methyl telluride mercuric bromide (mixed m. p. 124°).

Phenyl methyl telluride, which has not previously been described, was prepared as follows: A mixed Grignard reagent was formed by adding a mixture of iodobenzene (0·2 mol.) and methyl iodide (0·2 mol.) to magnesium (0·4 atom) in dry ether (350 c.c.). To the clear ethereal solution, free from unchanged magnesium, was added little by little, with constant stirring, a finely powdered solid solution of iodine and tellurium which had been prepared by gently fusing together an intimate mixture of powdered iodine (0·4 atom) and powdered crystalline tellurium (0·2 atom). The mixture was then refluxed for 3 hours, allowed to cool, and decomposed with ice-water. The resulting oily sludge was extracted several times with ether as rapidly as possible to eliminate aerial oxidation, the ethereal extract was rapidly dried over calcium chloride or sodium sulphate, the ether removed by distillation in an inert atmosphere, and the residual oils fractionally distilled in a vacuum. There were present dimethyl telluride, diphenyl telluride, and diphenyl ditelluride, but by far the largest fraction (17 g. = 40% yield) was phenyl methyl telluride, a yellow oil, b. p. 118—122°/22 mm., which combined quantitatively with mercuric halides to yield (i) the iodide $TeMePh,HgI_2$, as sulphur-yellow, acicular crystals, m. p. 89—90°; (ii) the *bromide* as pale cream nodules, m. p. 124—125° (Found : Br, 27·57. $C_7H_8Br_2HgTe$ requires Br, 27·55%); and (iii) the *chloride*, colourless granules, m. p. 132° (Found: Cl, 14·38. $C_7H_8Cl_2HgTe$ requires Cl, 14·45%). All three compounds are readily soluble in alcohol and acetone, from which they may be precipitated by the addition of water. The preparation of phenyl methyl telluride should be undertaken in a good fume-chamber. The vapours evolved have a most objectionable odour, which clings to the clothes for months after the conclusion of the experiment, and continued inhalation of the vapours induces an unpleasant halitosis, and in the authors' experience, debility and headaches.

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[*Received, August 23rd,* 1938.]