83. *Free Organic Radicals in the Gaseous State. Part VI. Attempts to prepare Various Free Radicals : the Existence of Free Benzyl.*

By F. A. PANETH and W. LAUTSCH.

OUR attempts to prepare free radicals other than methyl and ethyl (described in previous communications) having had to be temporarily abandoned, we report some results because in one instance a new free radical (benzyl) of comparatively long life has been found, and in other cases there are definite indications that the desired radicals are much less stable than free methyl or ethyl, if capable of existence at all.

I. *Attempts to prepare Free Propyl.*—As already mentioned (Part II, *Ber.*, 1931, **64**, 2707), we decomposed tetra-*n*-propyl-lead at about 400°, using exactly the same method as that yielding free methyl and ethyl, and investigated the action of the products upon mirrors of lead, antimony, and zinc.

With lead, a yellow liquid was produced (presumably chiefly a trialkyl-lead, since the tetra-alkyls are volatile) which decomposed above 100° with separation of metallic lead and formation of minute amounts of a liquid non-volatile in vacuum at room temperature. Antimony yielded a compound which, as judged by the colour, was bisdimethylantimony (Part IV). With zinc, in addition to hydrocarbons, there was formed chiefly dimethylzinc, identified by its m. p. and inflammability in air. It is possible that a higher zinc alkyl was also produced in traces.

From these experiments it follows that free propyl, which must be assumed to be formed transiently in the decomposition of tetrapropyl-lead, very rapidly decomposes, at least for the most part, producing considerable quantities of free methyl. It seems probable that the decomposition follows the equation $CH_3{\cdot}CH_2{\cdot}CH_2{-} \longrightarrow CH_3{-} + C_2H_4$ (cf. Rice, *Trans. Faraday Soc.*, 1934, **30**, 152).

Since we had observed (see Part IV, p. 369) that elevation of the temperature above 600° sufficed to decompose free ethyl completely into free methyl, it seemed likely that the decomposition of the free propyl might be due to the high temperature of the decomposition zone. We therefore attempted to lower the decomposition temperature of the tetra-*n*-propyl-lead by the use of catalysts (lead and copper). These attempts were fruitless, as also were attempts to produce free propyl by the electrical decomposition of tetra-*n*-propyl-lead vapour by means of high-frequency discharges.*

II. *Attempts to prepare Free Butyl.*—By the decomposition of tetra*iso*butyl-lead at about 300°, there resulted a reactive agent which attacked antimony mirrors. As with propyl, however, the resulting product consisted chiefly of bisdimethylantimony. It follows that, like free *n*-propyl, the *iso*butyl freed momentarily decomposes with formation of free methyl.

III. *Attempts to prepare Free Phenyl.*—Tetraphenyl-lead was decomposed in a hydrogen stream, at 2 mm. pressure, at a red heat. The lead mirror formed showed no sharp edge on the side remote from the flame, thus precluding the formation of an " aggressive " agent (cf. Part I, p. 1339). Lead and tellurium mirrors deposited a short distance away were not attacked, either when cold or when hot. Since carbon was deposited at the place of decomposition of the tetraphenyl-lead, the phenyl apparently underwent extensive decomposition without giving rise to free radicals of appreciable life.

We attempted also to obtain free phenyl by the action of sodium vapour on bromobenzene, using for the purpose a simplification of the technique developed by Horn, Polanyi, and Style (*Naturwiss.*, 1932, **20**, 401; *Z. physikal. Chem.*, 1933, *B*, **23**, 291). A tellurium mirror a short distance from the reaction zone served as a test for resulting free phenyl. Since this was not attacked either in the cold, or when hot, we must conclude that free phenyl either has a much shorter life than methyl or ethyl, or else does not attack tellurium.

The existence of free phenyl seems to be indicated by recent experiments of Horn and Polanyi (*ibid.*, 1934, *B*, **25**, 151; cf. also *Trans. Faraday Soc.*, 1934, **30**, 199). These authors also allowed bromobenzene to react with sodium vapour, the reaction products being caused

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* We had previously observed (cf. Part I) that electrical discharges in a mixture of methane and hydrogen produced free radicals. These experiments were continued by Hofeditz, but are not yet published. The essential result is that glow discharges (50 cycles) in pure methane, as well as in mixtures of methane with various hydrocarbons, alcohols, and ethers, produce free radicals. These may be readily detected beyond the discharge by their action on metallic mirrors, if a stream of gas at about 1 mm. pressure is passed through the discharge tube at a velocity of 10—20 m. per sec.

to impinge upon iodine. They assumed the presence of iodobenzene in the organic reaction products, since they could not detect aliphatic iodo-compounds in the organically bound iodine. It is surprising that, with this experimental arrangement, the life of the phenyl appears to be not notably shorter than that of methyl or ethyl in similar experiments. In view of the interest attaching to the preparation of free phenyl, a more direct analytical identification of the iodobenzene is clearly desirable.

IV. *Attempts to prepare Free Methylene.*—We first attempted to obtain methylene by the decomposition of keten. This seemed hopeful, since Schmidlin and Bergmann (*Ber.*, 1910, **43**, **2821**) have shown that above 600° acetone yields, not keten (reaction *a*), but ethylene, the formation of which can be most simply explained by the disruption of keten and transient formation of the free methylene radical (reaction *b*) :

$$(a)\ CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_2{:}CO + CH_4;\quad (b)\ 2CH_2{:}CO \longrightarrow C_2H_4 + 2CO.$$

By passing keten in a rapid gas stream through a strongly heated quartz tube, we were unable to raise the temperature sufficiently to effect any appreciable decomposition, with formation of free methylene. As the following shows, however, free methylene decomposes at relatively low temperatures, with separation of carbon (compare also Williamson, *J. Amer. Chem. Soc.*, 1934, **56**, 2216). In the experiments with keten, this was never observed.

Another reaction in which the intermediate formation of free radicals is probable is the decomposition of diazomethane, which often reacts as would be expected of free methylene, *e.g.*, $CH_2N_2 + I_2 = CH_2I_2 + N_2$, $CH_2N_2 + R{\cdot}CO_2H = R{\cdot}CO_2CH_3 + N_2$. Staudinger and Kupfer (*Ber.*, 1912, **45**, 501, 504, 508) have already attempted to capture by means of carbon monoxide the nascent methylene formed by passing diazomethane through a heated silica tube, and indeed obtained keten in very small amounts, apparently according to the equation $CH_2 + CO = CH_2{:}CO$. The transient formation of methylene is thereby virtually proved, but no information is gained as to its stability.

We passed diazomethane through a quartz tube, heated to 600° over a length of 15 cm., using first hydrogen and then helium as transport gas. Any methylene so formed we sought to identify by passing the products of pyrolysis over benzoic acid, but could detect no smell of methyl benzoate. Carbon mirrors were also unattacked, although one might expect the formation of allene, $CH_2{:}C{:}CH_2$, by free methylene; as the diazomethane was quantitatively decomposed, presumably with initial formation of free methylene, we must conclude that the methylene radical is very unstable.

Since the hot quartz wall was possibly responsible for the disappearance of the methylene primarily formed, we also decomposed diazomethane by electric discharges, to exclude the influence of temperature. A solid product, rich in carbon, was formed, but methylene could not be detected.

A further possibility for the production of methylene lay in the gas reaction $CH_2Cl_2 + 2Na = CH_2 + 2NaCl$, studied by von Hartel and Polanyi (*Z. physikal. Chem.*, 1930, *B*, **11**, 97). An advantage of this reaction is its applicability at relatively low temperatures. We carried out the experiment in a helium atmosphere, taking care to cool the tube rapidly behind the place where the sodium vapour and methylene chloride diffused into one another, in order to preserve any methylene formed. Here also, considerable deposition of carbon occurred even at 300°, from which one must conclude that the methylene formed initially decomposes further on collision with the wall, if not before. Various alterations in the reaction conditions (altered concentration of the reacting gases, water-cooling of the quartz immediately behind the reaction place) gave no better results.

To summarise, it may be said that, according to our results, the methylene radical is far inferior to methyl and ethyl in stability, since where its formation is to be expected with some probability, carbon deposition occurs instead. Nevertheless, since our experimental method permits of free radicals being first detected some distance from the reaction place, *i.e.*, after many collisions with gas molecules and the tube walls, it is possible that free methylene might be detected with more refined methods. Indications of this are available in the work of Belchetz (*Trans. Faraday Soc.*, 1934, **30**, 170) and especially of Rice and Glasebrook (*J. Amer. Chem. Soc.*, 1933, **55**, 4329; 1934, **56**, 2381).

V. *Preparation of Free Benzyl.*—(i) *By thermal decomposition of tetrabenzyltin.* Free benzyl may be obtained by exactly the same procedure as free methyl and ethyl.* We decomposed

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* That the benzyl radical possesses a relatively high stability has already been concluded by Emde (*Helv. Chim. Acta*, 1932, **15**, 1330) from experiments on fission during hydrogenation.

tetrabenzyltin and allowed the products to react with mirrors of selenium, tellurium, and mercury. By reaction with selenium there resulted a yellowish substance of m. p. 75—76°. Since benzyl selenide melts at 45·5°, and dibenzyl diselenide at 90°, a mixture of both substances was apparently present. Indeed, by fractionation in a high vacuum, we could isolate an almost colourless substance containing selenium and melting sharply at 44—45°. This substance was therefore dibenzyl selenide, and the formation of the benzyl radical by the decomposition of tetrabenzyltin may be regarded as confirmed.

Gently-heated tellurium mirrors were also attacked by the decomposition products of tetrabenzyltin. A yellowish oil, in which tellurium was detected, and which after solidifying melted at 40°, was thereby produced. It was probably impure dibenzyl telluride (m. p. 53°), but could not be further purified on account of its minute quantity.

By reaction with mercury, the surface of which was continually renewed by distillation, a well-defined substance was formed in quantity sufficient to permit of fractionation in a high vacuum and its separation from dibenzyl. The m. p. was 115—117°, the recorded m. p. of dibenzylmercury being 117°. Mercury and dibenzyl were formed from the substance on heating, confirming the identification as dibenzylmercury. This reaction therefore also demonstrates the stability of free benzyl over a certain period. The possibility that dibenzylmercury might be formed by back diffusion of mercury into the zone of already decomposed tetrabenzyltin, against the gas stream, was disposed of by the fact that the compound is unstable at high temperatures, and that at low temperatures—up to 100°—mercury does not react with the tin aryl.

The yield of free benzyl by this reaction appears to be considerably less than that of free methyl and ethyl, since tellurium was only slowly attacked even when considerable amounts of the compound were decomposed. The greater proportion of free benzyl apparently passes directly into dibenzyl. In a 22-hour experiment, at dull red heat and 2 mm. pressure, 0·241 g. of dibenzyl was formed from 0·336 g. of tetrabenzyltin (87% yield).

(ii) *By thermal decomposition of dibenzyl ketone.* Since Rice (*J. Amer. Chem. Soc.*, **1932**, **54**, 3529) obtained free methyl by the decomposition of acetone, we attempted to apply the same method to the preparation of free benzyl. We decomposed dibenzyl ketone in a red-hot silica tube, using hydrogen as carrier gas. Much dibenzyl was formed (identified by m. p., volatility, and smell). When a tellurium mirror heated at 80—100° was placed behind the decomposition place, it was attacked and a yellowish oil resulted. This was soluble in benzene, but the solution became turbid on standing, metallic tellurium separating. Owing to the very minute amounts of the oil available, no purification was attempted; since, however, it was a tellurium compound and not volatile at room temperature, it may be assumed from its mode of formation to be benzyl telluride.

(iii) *By reaction of benzyl chloride with sodium vapour.* When these two reactants diffused into one another, in a stream of helium, tellurium mirrors were attacked at a distance of 15 cm. from the reaction point. Blank experiments (passage of sodium vapour or benzyl chloride alone) left the mirrors unaltered. In the attack on the tellurium, a solid substance was formed which decomposed on warming in air, with separation of a grey deposit and an odour of benzaldehyde. It was thereby shown that free benzyl may be obtained in this manner also, but the method offered no advantages over the simpler methods described above.

The Life Period of Free Benzyl.—The reproducibility of results necessary for the determination of life periods was best achieved when the radical was obtained by method (ii), and allowed to react with tellurium mirrors at various distances. The formation of yellow, oily benzyl telluride of peculiar properties (see above) was taken as evidence of the production of free benzyl, since mere disappearance of the tellurium mirror could be produced likewise by hydrogen, methyl, or ethyl.

The experiments were made in a quartz tube of 0·5 cm. diameter, with a gas velocity of 20 m. per sec., at a pressure of 2 mm., using hydrogen as carrier gas. An action on gently heated tellurium mirrors was evident close (5 cm.) behind the decomposition point of the ketone. With a length of 25 cm. of unheated tube between the decomposition zone and the mirror, however, no free benzyl could be detected; but if the tube between decomposition place and mirror were heated to 200°, benzyl could still be detected at a distance of 25 cm.

After the life of free benzyl had thus qualitatively been shown to be considerable in a heated tube, we attempted to make the method quantitative. Tellurium, converted into dibenzyl telluride, was weighed as its dioxide after destruction of the organic matter. The results were as follows :

Expt. No.	Distance of mirror from decomposition point, cm.	Time of expt., t (hrs.).	Weight of TeO_2, g.	Activity, $A = g . 10^4/t$.
1	5	6·5	0·038	58
2	5	7·75	0·0185	24
3	25	14	0·0086	6
4	25	15·75	0·0111	7

The last column shows the weight of tellurium dioxide (g. × 10^4) formed per hour, and so gives a measure of the activity A. Under constant conditions, the values of A in the pairs of experiments 1 and 2, 3 and 4, should be the same. The discrepancy between Expts. 1 and 2 is probably to be explained by variations in the temperature of the heating bath used to vaporise the ketone. Taking into account a streaming velocity of 15 m. per sec., and assuming a first-order reaction, the reaction constant K and half value period T may be calculated (from the mean of our experiments) as $K = 130$ and $T =$ approx. 6×10^{-3} sec.

It would be interesting to know how the half-value period of free benzyl compares with that of free methyl. Considering the inaccuracy of our experiments with free benzyl, and the numerous conditions upon which the life of the radicals depends (cf. Part V), we can only say that the life of benzyl in a cold tube is considerably shorter than, and in a heated tube is of the same order as, that of methyl. Corresponding to the view developed in Part V, it is probable that the more rapid decomposition in a cold tube is due to the higher accommodation coefficient. Only a direct comparison, however, of methyl and benzyl under identical conditions can decide the relative stabilities in a heated tube. Such an investigation would be, moreover, of particular interest in that we can regard benzyl, " monophenylmethyl," as a transition stage between the free methyl radical, comparatively stable in the gaseous state, and triphenylmethyl, stable in solution. To this question we hope to return later.

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Chemisches Institut der Universität, Königsberg i. Pr.
Imperial College of Science and Technology, London.

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