schemes for the reclamation of tsetse-infested land in Kenya, Uganda and Tanganyika are allotted £70,000 over four years, and £38,000 over four and a half years is granted for the establishment of a Fisheries Research Unit at the University of Hong Kong. Other grants include £34,500, also over four and a half years, for research into the incidence of maize rust in West Africa, £31,500 (over the period January 1, 1952–March 31, 1956) for physiological and biochemical research at Makerere College, Uganda, £34,000 for the establishment of a training centre for ecologists selected for work in Colonial territories, £28,750 for the Anti-Locust Research Centre, and a supplementary £26,620 for the East African Agriculture and Forestry Research Organization for the year ending December 31, 1952.

The only other grants exceeding £20,000 are: £25,000 for hiring and equipping aircraft for disseminating insecticides in East Africa, £23,000 for further research over four and a half years by Dr. C. A. Walton into relapsing fever in East Africa, £24,403 (supplementary) for the Nutrition Field Station, Fajara, Gambia, £22,083 over four years for re-establishment of the Herbarium at Sandakan, North Borneo, and appointment of a botanist, and £21,000 over three years for the Ecological Land Use Survey, British Honduras. Reference should also be made to the grants of £19,300 for investigation, over five years, of seismic activity in the Windward and Leeward Islands, £17,500 to extend clove research at Zanzibar until August 31, 1953, £15,400 for experiments in East Africa on the dissemination of insecticides from fixed-wing aircraft, and £14,000 for the establishment of a Colonial pool of plant pathologists at the Commonwealth Mycological Institute.

Grants of particular scientific interest for development and welfare schemes, apart from those for scholarship training schemes and the like, include £31,000 for the establishment of an Applied Nutrition Unit at the London School of Hygiene and Tropical Medicine, £150,000 for a Technical College at Nairobi, a further £202,500 for Makerere College, £130,000 for tsetse and trypanosomiasis reclamation in East Africa, £55,300 for the Geological Survey of Somaliland Protectorate, £21,911 for a survey of timber resources in Northern Rhodesia, £9,283 for the extension of the Government Veterinary Research Station, Mazabuka, £52,500 for the Geological Surveys Department of Nyasaland, and £150,000 for the comprehensive survey of the Shire Valley project. A further grant of £52,234 is to University College, Ibadan, Nigeria, and £87,700 for the development of medical and health services in Gambia, while of £6,784,700 for the revised Ten-Year Development Plan for Nigeria, £1,049,832 is for agriculture, £853,053 for technical education, £154,674 for forestry, £395,899 for leprosy control, £1,587,861 for medical and health, and £223,261 for veterinary services. £43,163 is granted for animal husbandry in Sierra Leone, £30,000 for agricultural development in Basutoland, £51,474 for anti-malarial works in Mauritius, £200,000 to the University of Hong Kong, £42,706 for meteorological services in South-East Asia, £55,000 for the Eastern Caribbean Farm Institute, £58,337 for meteorological services in the West Indies, £25,867 for cocoa development in British Guiana, and various sums totalling £311,050 to the University College of the West Indies and its teaching hospital. Grants for road development schemes, rural water supplies, the establishment of local broadcasting services and the like figure prominently among the remainder.

REACTIONS OF PHENYL RADICALS IN SOLUTION AND IN THE GASEOUS PHASE

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THE reactions of phenyl radicals in solution have been extensively investigated by many workers. A comprehensive summary of these studies has been presented in a monograph by Waters[1]. It appears that phenyl radicals react differently with aliphatic and with aromatic solvents. With the former they seem to undergo an atom transfer reaction; for example:

$$n - C_6H_{14} + Ph\cdot \rightarrow C_6H_{15}\cdot + Ph.H.$$
$$CCl_4 + Ph\cdot \rightarrow CCl_3. + Ph.Cl,$$

while the reactions with aromatic solvents lead to the formation of substitution products. Waters[2] interpreted the course of this substitution reaction by the equation

$$Ph\cdot + C_6H_5X \rightarrow Ph.C_6H_4.X + H. \qquad (1)$$

It is particularly interesting to note that the reaction of phenyl radicals with toluene leads to the formation of the isomeric methyl-diphenyls $CH_3.C_6H_4.C_6H_5$, and that dibenzyl was never detected among the products of the reaction[3]. This observation seems to exclude the alternative interpretation of the reaction, namely,

$$Ph\cdot + C_6H_5.CH_3 \rightarrow Ph.H + \cdot C_6H_4.CH_3 \qquad (2)$$
$$Ph\cdot + \cdot C_6H_4.CH_3 \rightarrow Ph.C_6H_4.CH_3, \qquad (3)$$

since the inequality:

$$C_6H_5.CH_2{-}H \text{ dissociation energy} < CH_3.C_6H_4{-}H \text{ dissociation energy}$$

requires that phenyl radicals should abstract preferentially the hydrogen atom from the methyl group rather than from the benzene ring. Such a reaction, however, would lead to the formation of benzyl radicals:

$$C_6H_5.CH_3 + Ph\cdot \rightarrow C_6H_5.CH_2\cdot + Ph.H, \qquad (4)$$

and thus dibenzyl or diphenyl-methane would be expected as products of the reactions, contrary to the observations.

This peculiar behaviour of phenyl radicals induced us to investigate their reactions in the gaseous phase. Several sources of phenyl radicals were explored by using pyrolytic methods. We found that iodo-benzene, bromo-benzene, mercury-diphenyl, benzyl-benzoate, benzoyl-bromide and benzil generate phenyl radicals in our experimental arrangement, whereas benzo-phenone and azo-benzene required for their decomposition temperatures higher than our experimental conditions permitted. All experiments were carried out in a flow system, described in previous communications[4], the total pressure being of the order 10–20 mm. mercury, and the time of contact of the order of half a second.

Iodo-benzene decomposes rapidly at temperatures of about 600° C. The decomposition is complicated by the presence of iodine atoms and molecules, and therefore is not suitable for studying the reactions of phenyl radicals. Neither is it convenient to use bromo-benzene as a source of phenyl radicals, since the decomposition requires rather high temperatures (800–900° C.) and consequently is complicated by the considerable amount of products formed by the decomposition of toluene used as a carrier gas.

The decomposition of benzyl-benzoate (studied in our laboratories by Mr. J. W. Taylor) seems to take place according to the expression :

$$\mathrm{Ph.CO.O.CH_2.Ph} \rightarrow \mathrm{Ph.CO_2} + \mathrm{Ph.CH_2}\cdot, \qquad (5)$$

followed by the rapid reaction

$$\mathrm{Ph.CO_2} \rightarrow \mathrm{Ph}\cdot + \mathrm{CO_2}.$$

In the presence of toluene, phenyl radicals react according to (4), producing benzyl radicals :

$$\mathrm{C_6H_5.CH_3} + \mathrm{Ph}\cdot \rightarrow \mathrm{C_6H_5.CH_2}\cdot + \mathrm{Ph.H}, \qquad (4)$$

and the dimerization of the latter yields dibenzyl. The experimental results are given in Table 1, which shows that two benzyl radicals, that is, one molecule of dibenzyl, are produced for each molecule of benzyl-benzoate decomposed (or for each molecule of carbon dioxide formed in the pyrolysis). The initial decomposition (5) accounts for half the amount of dibenzyl collected, whereas the second portion is undoubtedly produced by reaction (4).

TABLE 1. DIBENZYL SEPARATED FROM BENZYLBENZOATE BY CHROMATOGRAPHIC TECHNIQUE

T °C.	Carbon dioxide (m.mol.)	Dibenzyl (m.mol.)	Ratio of dibenzyl to carbon dioxide
674	0·448	0·407	0·91
666	0·322	0·312	0·97
704	0·481	0·482	1·00
698	0·404	0·389	0·96
691	0·323	0·321	0·99
687	0·293	0·339	1·16 (?)
699	0·430	0·428	1·00
700	0·399	0·425	1·06
697	0·423	0·404	0·95

m.p. 51° C. after a gentle pressing on a porous tile

The decomposition of benzoyl bromide, investigated by Ladacki, Leigh and Szwarc[5], appears to be a clean-cut reaction proceeding according to the following mechanism :

$$\mathrm{Ph.CO.Br} \rightarrow \mathrm{Ph.CO} + \mathrm{Br},$$

followed by the rapid reaction

$$\mathrm{Ph.CO} \rightarrow \mathrm{Ph}\cdot + \mathrm{CO}.$$

Under conditions prevailing in our experiments, bromine atoms react with toluene yielding hydrogen bromide and benzyl radicals[8] :

$$\mathrm{C_6H_5.CH_3} + \mathrm{Br} \rightarrow \mathrm{C_6H_5.CH_2}\cdot + \mathrm{HBr}. \qquad (6)$$

However, the amount of dibenzyl collected in the pyrolysis of benzoyl bromide exceeds that anticipated on the basis of reaction (6) only (see Table 2), and this observation indicates that phenyl radicals reacting with toluene produce benzyl radicals. Moreover, benzene was detected among the products of the decomposition, and this proves definitely that reaction (4) takes place (we are indebted to Anglo-Iranian Oil Co. for their help in analysing toluene for its benzene content).

TABLE 2

T °C.	Carbon monoxide (m.mol.)	Dibenzyl (m.mol.)	Melting point	Ratio of dibenzyl to carbon monoxide
662	1·44	1·15	50–51° C.	0·80
662	1·05	0·84	50–51° C.	0·80
617	0·65	0·49	51–52° C.	0·75
638	1·58	1·20	48–50° C.	0·76
657	1·20	0·97	49–50° C.	0·81

Pyrolysis of benzil appears to be the most convenient source of phenyl radicals. The reaction takes place according to the expression :

$$\mathrm{Ph.CO.CO.Ph} \rightarrow 2\mathrm{Ph.CO},$$

followed by the rapid reaction

$$\mathrm{Ph.CO} \rightarrow \mathrm{Ph}\cdot + \mathrm{CO}.$$

Thus, the rate of formation of phenyl radicals can be measured conveniently by the rate of formation of carbon monoxide. The investigation is simplified by the fact that phenyl radicals are the only reactive species produced initially in the system. Dibenzyl was the only non-volatile product produced in the pyrolysis taking place in the presence of toluene, which proves beyond any doubt that phenyl radicals react with toluene according to (4).

$$\mathrm{C_6H_5.CH_3} + \mathrm{Ph}\cdot \rightarrow \mathrm{C_6H_5.CH_2}\cdot + \mathrm{Ph.H}. \qquad (4)$$

The experimental results are given in Table 3. The melting points of the non-volatile products collected indicate that they contain more than 95 per cent of dibenzyl (in this connexion see also Tables 1 and 2). It has been shown that a mixture containing 95 per cent of dibenzyl and 5 per cent of diphenyl melts at 46–47° C.

TABLE 3

T °C.	Carbon monoxide (m.mol.)	Dibenzyl (m.mol.)	Melting point	Ratio of dibenzyl to ½ carbon monoxide
603	2 × 0·336	0·324	48–50° C.	0·965
593	,, 0·434	0·417	49–51° C.	0·96
600	,, 0·654	0·626	49–51° C.	0·96
723	,, 0·598	0·560	48–50° C.*	0·94

* After gentle pressing on porous tile

We conclude, therefore, that phenyl radicals reacting with toluene in gaseous phase and at high temperatures abstract hydrogen atoms from methyl groups. On the other hand, the reaction in solution and at room temperature leads to their addition to benzene ring. We suggest tentatively the following explanation for the divergence of the behaviour of phenyl radicals. Phenyl radicals, having one hydrogen atom removed from the ring, might approach sufficiently close to the nucleus of an aromatic compound for a relatively strong π—π bond to be formed. To appreciate the strength of such a bond, let us compare $D(\mathrm{CH_3}$—$\mathrm{CH_3})$ with $D(\mathrm{C_6H_5}$—$\mathrm{C_6H_5})$. The C—C dissociation energy of the former is 83 kcal./mole, while we estimate the magnitude of the latter at about 97 kcal./mole. (Investigation of the pyrolysis of bromo-benzene carried out in our laboratories by Mr. D. Williams leads to $D(\mathrm{C_6H_5}$—$\mathrm{Br}) \sim 71$ kcal./mole. This value, in conjunction with the relevant thermochemical data, leads to $D(\mathrm{C_6H_5}$—$\mathrm{H}) \sim 102$ kcal./mole and $D(\mathrm{C_6H_5}$—$\mathrm{C_6H_5}) \sim 99$ kcal./mole.) This remarkable increase in the C—C dissociation energy probably measures the strength of the π—π bond in diphenyl[6]. The formation of a π—π bond between a phenyl radical and an aromatic compound leads to a 'hot' complex which contains all the energy of the interaction. Such a 'hot' complex is certainly unstable at the high temperatures and low pressures prevailing in our experiments, and thus it decomposes rapidly. On the other hand, in solution and at room temperatures the excess of energy might be removed by collisions with molecules of solvent, and thus the stabilized complex might survive until a collision with another phenyl radical would lead to the abstraction of hydrogen atom and completion of the reaction.

The fact that the addition reaction prevails at room temperature indicates that its activation energy is probably lower than that of the hydrogen abstraction reaction. Indeed, the analogy with the corresponding reaction of methyl radicals[7] might suggest an activation energy of the order of 8 kcal./mole for reaction (4). [March 20.

[1] Waters, W. A., "The Chemistry of Free Radicals" (Oxf. Univ. Press, 1948).

[2] Waters, W. A., see ref. 1, p. 147 and p. 149.

[3] Hey, D. H., *et al.*, *Research*, 4, 386 (1951).

[4] Szwarc, M., *J. Chem. Phys.*, **17**, 431 (1949); *Proc. Roy. Soc.*, A, **198**, 267 (1949).

[5] Ladacki, M., Leigh, C. H., and Szwarc, M., *Proc. Roy. Soc.* (in the press).

[6] Szwarc, M., *Nature*, **161**, 890 (1948).

[7] Trotman-Dickenson, A. D., and Steacie, E. W. R., *J. Chem. Phys.*, **19**, 1097 (1951); see also *J. Amer. Chem. Soc.*, **72**, 2310 (1950).

[8] Szwarc, M., Ghosh, N. B., and Sehon, A. H., *J. Chem. Phys.*, **18**, 1142 (1950).

ARCTIC AEROBIOLOGY

FUNGI AND BACTERIA, ETC., CAUGHT IN THE AIR DURING FLIGHTS OVER THE GEOGRAPHICAL NORTH POLE

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WHEREAS previous contributions[1] have been concerned with material gathered by Polunin while flying over northern Canada in 1947, the present communication reports upon the result of subsequent flights from central Alaska to the North Pole and back which he made in the following years—in the last instance accompanied by Kelly and S. M. Pady. In the meantime, the work had been adopted as an extra-mural research project by the Defence Research Board of Canada, and it is a pleasure to express gratitude for the all-important governmental assistance in Canada and the United States which has thus been obtained and co-ordinated. These flights were special ones in United States Air Force B-29 (Superfortress) aircraft of the 72nd (Very Long Range) Reconnaissance Squadron operating out of Ladd A.F. Base, Fairbanks, Alaska, and in this connexion our warm thanks are due to the late General Dale V. Gaffney, Colonel Neil D. van Sickle, and Lieut.-Col. Charles F. Overstreet, for the unique facilities afforded and the splendid co-operation of all their officers and men concerned. Thanks and appreciation are also due to the Royal Canadian Air Force for much incidental transportation and hospitality, and to the Defence Research Board in general and Lieut.-Col. G. W. Rowley and Mr. C. P. McNamara of the Arctic Research Section in particular, for their efficient handling of many problems involved. Without such support and the co-operation of many other bodies and individuals, in Washington and Ottawa, Montreal and Alaska, the chance to do this work could scarcely have materialized. There were also the pilots on those long (and in the first case arduous) flights, and the five or six busy navigators and radar observers who made up such a large proportion of the picked and trained crews of fifteen or sixteen—not to mention the almost equally essential ground-staffs of many and various categories, among whom were Major Joseph J. Slack (O.C. Base Weather Detachment), Captain Vaughan (operations officer), the Engineering and Intelligence personnel, and Colonel R. R. Stewart (base supply officer).

The first of his polar flights was made by Polunin on September 13–14, 1948. Planning had extended over much of the previous year, with the design and construction of special apparatus for the purpose, and been backed by active work at laboratory techniques by Pady and Kelly[2]. The apparatus, which it is hoped to describe and figure in more detail elsewhere[3], was required for exposure of Petri plates vertically against the unobstructed airstream in front of an aircraft travelling at high speed, with low temperatures outside and possible pressurization inside. Essentially it consisted of a steel plate replacing the front large 'Plexiglas' window in the nose, into which a short piece of steel tube was welded in a horizontal position so as to act as a sleeve and lead to an opening in the plate that could be closed by a metal sliding door. A second steel tube, 68 cm. long and blocked off with a handle at the back, was made to slide within the sleeve; its inside diameter was such that it would just take a standard (10 cm. diameter) Petri dish which rested against a blocking-off metal plate just behind the front end of this inner tube or cylinder and was held in place by lateral steel clips. In the sleeve was cut a loading-breech with an airtight cover to allow changing of the Petri dishes when the inner tube was withdrawn and the sliding door closed. Loading was accomplished by pressing a sterile, unwrapped, but still covered, Petri 'plate' into position and then removing the cover, after which the breech was quickly closed, the sliding door opened, and the inner tube slid forward and locked in the exposing position in which the Petri plate was held flat against the airstream well ahead of anything else on the plane. In connexion with the construction of this apparatus special thanks are due to Prof. J. S. Foster, of McGill University.

The sticky surface for 'catching' was a thin smear of silicone grease (DC-4-ANC-128-A) on the inside of the base of the Petri dish; this particular grease retains its stickiness through the remarkable temperature-range of − 75° C. to more than 200° C. and appears to be neutral to most biological activity. Expert mathematical advice had indicated that we might expect at least 40 per cent of the particles in the atmosphere to penetrate any air-cushion—for example, that might be built up in front of the Petri plate which was already far enough ahead of the nose to avoid its air-cushion—and consequently become stuck on the silicone surface during flight.

Practically throughout the first polar flight and a training and testing preliminary, plates were loaded and exposed for periods of up to ten minutes. Then, on return to the laboratory, the silicone surface was 'poured' with melted agar for observation of the fungi and bacteria the growth and development of which were able to proceed when the nutrient covered the surface to which they had become attached. It

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