tration of oxygen arising due to leaks into the system. With the normally encountered leak rates, this flow rate is about 1 l./h.

The high value for the oxygen partial pressure obtained directly from cylinder (99·995 per cent) argon is attributed to the dissociation of water vapour at the measuring temperature 950° C, and may be greatly reduced by drying treatment only. It will also be observed that the ultimate partial pressure of oxygen obtained in this system, 10^{-14}, is about four orders of magnitude lower than that attained in a very good high vacuum system. It may be seen, then, that purified argon provides a very much better protective atmosphere at high temperatures than does a high vacuum system.

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Photodecomposition of 1,4-Dialkyl-1,4-diphenyl-2-Tetrazenes

DURING the course of chromatographic studies on 1,4-dimethyl-1,4-diphenyl-2-tetrazene (I), $C_6H_5(CH_3)N—N{=}N—N(CH_3)C_6H_5$, a new experimental anti-cancer agent[1], there was noticed a blue colour developing on the window side of a column containing solutions of (I). Subsequent investigation revealed that (I) and certain other 2-tetrazenes undergo extensive photochemical decomposition. The crude end-products of the decomposition show no activity in our anti-cancer screening programme[2,3]. The recent report by Schoental[4] that certain carcinogenic *N*-alkyl-*N*-nitroso-urethanes are phototransformed to 2-tetrazenes (presumably photostable) enhances the importance of our observations to workers interested in the biological properties of 2-tetrazenes.

When solutions of (I) in organic solvents are exposed to sunlight or light from a mercury-vapour lamp, one equivalent of nitrogen is released over the course of a few days. Concentration of the remaining solution leaves a thick dark oil from which two substances are separated: *A*, *N*-methylaniline, b.p. 45°–48° C/1·25 mm and 192° C/760 mm, n_D^{24} 1·569, infra-red spectrum and picrate salt (m.p. 145° C), identical to authentic *N*-methylaniline; *B*, 1,2-dimethyl-1,2-diphenylhydrazine, b.p. 122°–124° C/0·20 mm, n_D^{24} 1·601, identical to the product obtained by Wieland and Fressel[5] by thermal decomposition of (I). However, the infra-red and nuclear magnetic resonance spectra of *B* were best explained by a mixture of 10 per cent *N*-methylaniline in 1,2-dimethyl-1,2-diphenylhydrazine. Crystallization of *B* from methanol gave colourless, but thermally and photochemically unstable, crystals, m.p. 32° C[6]. Found: C, 79·17; H, 7·63; N, 13·02 per cent; calculated for $C_{14}H_{16}N_2$: C, 79·21; H, 7·60; N, 13·20 per cent. It was apparent then that on distillation 1,2-dimethyl-1,2-diphenylhydrazine decomposed in part to *N*-methylaniline.

Ultra-violet spectra of (I) undergoing photolysis in solution reveals a progressive and ultimately complete loss of the azo chromophore (345 mμ)—the reaction mixture then possessing a spectrum indicative of a *N*-methylaniline function.

Photolysis of (I) in hydroxylated solvents such as methanol or *t*-butanol proceeds as described with an additional oxidative process (inhibited by ascorbic acid) generating first a brilliant blue colour, followed by progressive darkening. Chromatography of the end product on neutral alumina reveals at least eight uncharacterized components ranging in colour from violet to red.

Other 1,4-dialkyl-1,4-diphenyl-2-tetrazenes, for example, 1,4-diethyl,1,4-di-*n*-propyl, and 1,4-di-*n*-butyl, undergo photolysis in a similar fashion. The oxidative coloration process drops off rapidly with increasing alkyl chain length. On the other hand, a nitro group in the phenyl ring confers photostability to the tetrazene chain; for example, 1,4-dimethyl-1,4-*bis*(4-nitrophenyl)-2-tetrazene and its *bis*-2,4-dinitrophenyl analogue are photostable. In confirmation of Schoental's[4] photosynthesis of a tetrazene from an *N*-nitrosoamine we found that *N*-methyl-*N*-nitroso-4-nitroaniline on exposure to sunlight for 19 days gives a 3 per cent yield of 1,4-dimethyl-1,4-*bis*(4-nitrophenyl)-2-tetrazene, m.p. 237° C.

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BIOCHEMISTRY

Identification of Calcium Hydrogen Phosphate Dihydrate Crystals in Human Fibrocartilage

RECENTLY, we identified microcrystalline calcium pyrophosphate dihydrate in certain pathological human synovial fluids[1]. Roentgenograms of the involved joints showed calcifications in cartilaginous structures; the clinical picture was distinctive enough to suggest a specific syndrome, which we named 'pseudogout'[2]. In two cases multiple cartilages were examined *post mortem* and most contained localized deposits of these crystals[3]. The interplanar spacings found on X-ray diffraction powder pattern are virtually identical with those reported for calcium pyrophosphate dihydrate prepared by Brown *et al.*[4] by hydrolytic degradation of calcium polymetaphosphate gel. Monoclinic and triclinic dimorphs have been identified by these same workers[5]. In human material, the triclinic dimorph predominates although interplanar spacings indicative of the monoclinic form are detected frequently[6].

Crystallographic analysis of localized deposits of calcific material in fibrocartilaginous structures excised from human beings *post mortem* revealed deposits of calcium pyrophosphate dihydrate and, more commonly, another microcrystalline substance. These crystals exhibited strong positive birefringence under crossed Nicols using a first-order red plate compensator and varied from 0·5μ to 3μ in size. The interplanar spacings and relative intensities of powder patterns prepared from 7 different specimens showed virtual identity with calcium hydrogen (ortho) phosphate dihydrate ($CaHPO_4.2H_2O$) listed in the standard *Index of X-ray Diffraction Patterns*[7] (Table 1).

Analysis of the crystals by infra-red spectrophotometry confirmed the identification as calcium hydrogen orthophosphate dihydrate. Emission spectroscopy showed calcium as the only metallic cation present[8].

A clue to the origin of microcrystalline calcium orthophosphate crystals in human cartilage may be obtained from the work of Brown *et al.*[4], who found that 'inter-