The acetyl derivative, 4-nitro-2,5-dimethylacetanilide, was prepared by nitration of 2,5-dimethylacetanilide (numerous crystallizations were required to remove the 2-nitro isomer), and by acetylation of 4-nitro-2,5-dimethylaniline; the m. p. was 168–169°.

4-Nitro-2,5-xylonitrile.—The method of Bogert and Hand[12] was used to convert the amine into the nitrile. After crystallization from alcohol the m. p. was 160–161°. The nitrile may be purified also by sublimation.

Anal. Calcd. for $C_9H_8O_2N_2$: C, 61.36; H, 4.58. Found: C, 61.18; H, 4.63.

4-Nitro-2,5-xylic Acid.—The cyanide was hydrolyzed with sulfuric acid, and the product was crystallized from alcohol and from ligroin; the m. p. was 165.5–166.5°.

Anal. Calcd. for $C_9H_9O_4N$: C, 55.38; H, 4.65. Found: C, 55.48; H, 4.71.

5-Nitro-2,4-xylic Acid.—Ten grams of 2,4-dimethylacetophenone was nitrated by a method purported to yield mainly 5-nitro-2,4-dimethylacetophenone.[13] The crude

(12) Bogert and Hand, THIS JOURNAL, **24**, 1035 (1902).
(13) Claus, *J. prakt. Chem.*, [2] **41**, 495 (1890).

product thus obtained was agitated with sodium hypobromite (11 cc. of bromine in 300 cc. of 10% sodium hydroxide) during four hours. The product was crystallized from alcohol and from benzene and ligroin; the m. p. was 197.5–198.5°. The melting point previously reported[5] for this acid, prepared from 5-nitro-2,4-xylonitrile, is 196–197°.

Summary

The oxidation product of 5-bromopseudocumene, previously claimed to be 5-bromo-2,4-xylic acid, is a sharply-melting mixture of this acid and an isomeric compound, 4-bromo-2,-5-xylic acid.

In the oxidation of 5-nitropseudocumene the methyl group meta to the nitro group is attacked chiefly, yielding 5-nitro-2,4-xylic acid.

Some new substituted xylic acids and related compounds are described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photochlorination of Pentane

BY T. D. STEWART AND BERNARDT WEIDENBAUM

In connection with other work we had occasion to measure the quantum efficiency of the photochlorination of *n*-pentane in the liquid phase, and with the rigid exclusion of oxygen. Great care was taken in purification and handling of the reagents. The consistency of the results together with the apparent absence of an induction period point to the absence of disturbing factors in this measurement.

Purification of Chemicals.—The pentane was obtained from a commercial source. It was first treated with alkaline potassium permanganate with constant agitation until no more reaction was obtained, then treated with chlorosulfonic acid to remove isomers other than normal pentane[1] and finally fractionated very carefully in a 6.1-meter packed fractionating column which Dr. R. E. Cornish kindly placed at our disposal. The temperature of distillation (uncorrected) was 36.0°, and no drop in temperature was observed if the distillation continued for so long as ten hours with total reflux. The pentane was dried and deoxygenated by allowing it to stand over sodium–potassium alloy for at least three months,

(1) Shepard and Henne, *Ind. Eng. Chem.*, **22**, 356 (1930).

and then distilled, as needed, from an all-glass distilling apparatus into a large bulb in the line.

The chlorine was from a commercial cylinder of liquid chlorine and was known to be free of hydrochloric acid. It was dried by passing over calcium chloride and magnesium perchlorate, and then was frozen in a liquid air trap. A first portion was distilled away; the bulk of the chlorine was then distilled into a liter bulb which was thereafter used as the source of supply for these experiments.

The nitrogen was from a commercial cylinder. To remove oxygen it was bubbled through an alkaline solution of pyrogallol and then through a solution of ammonium carbonate in which copper wire was suspended; it was then scrubbed with concentrated sulfuric acid, dried with phosphorus pentoxide, and stored in two one-liter bulbs at about 100 cm. pressure. The nitrogen was used to force the pentane into the reaction flask when the chlorine solution was being made. It was also used to force the solution from the reaction flask into the quenching solution of potassium iodide at the conclusion of the experiment, as well as being used to flush the line prior to its evacuation.

Experimental Procedure.—Figure 1 is a diagrammatic representation of the reaction system. The reaction vessel, A, was a cylindrical Pyrex cell, 3.6 cm. in diameter and 2.1 cm. long, which had carefully ground plane windows sealed at both ends. The volume of the reaction vessel and the capillary leads between stopcocks 2 and 3 was experimentally determined to be 21.5 cc. B was a phototronic cell (Weston), whose area was 1260 sq. mm., and fitted very snugly on the reaction flask; it was connected directly to a high sensitivity Leeds and Northrop galvanometer. The reaction flask was enclosed by a wooden box, S, with a detachable top and end, in order to eliminate stray radiations and sudden temperature changes; a Corning Ultra Violet No. 586 filter, F, and an infra-red filter, C, also fitted in the box. A 220-volt mercury arc, L, was used in conjunction with this filter to give a source of monochromatic light of wave length 3650 Å. The light was shown to be monochromatic by photographing the incident light in a Hilger E3 quartz spectrograph; with a thirty minute exposure the photographs failed to show the transmission of light other than the group of lines at 3560 Å.

The phototronic cell was calibrated against a Moll large surface thermopile, which in turn was calibrated against a Bureau of Standards lamp.

The phototronic cell and the thermopile were mounted on a slide which operated in an air thermostat. In this way first the photocell and then the thermopile could be placed in the optical path at the same distance from the light source, and in addition the thermopile readings would not be subject to error due to extraneous sources of heat. Variation of light intensity was obtained with a set of calibrated wire screens whose calibration was checked by the thermopile readings.

A typical experiment was performed in the following manner. The system was evacuated and flushed out with nitrogen, both sides of the sulfuric acid manometer being pumped out. The initial light intensity was obtained from the galvanometer reading. After stopcocks 1 and 2 were closed, chlorine was introduced until the pressure in the reaction flask was approximately one-tenth of an atmosphere. The galvanometer reading was now determined by the amount of chlorine present and could be used to evaluate the absorption coefficient at the wave length employed, as the concentration of the chlorine could be ascertained. Pentane was then introduced

from the pentane supply through stopcocks 1 and 2. Next the reaction vessel was illuminated for a definite time interval; galvanometer readings were taken at the start and conclusion of this interval. The reaction mixture was forced from the reaction flask with a stream of nitrogen into a vessel containing a solution of potassium iodide. The iodine formed was titrated with 0.01 N sodium thiosulfate.
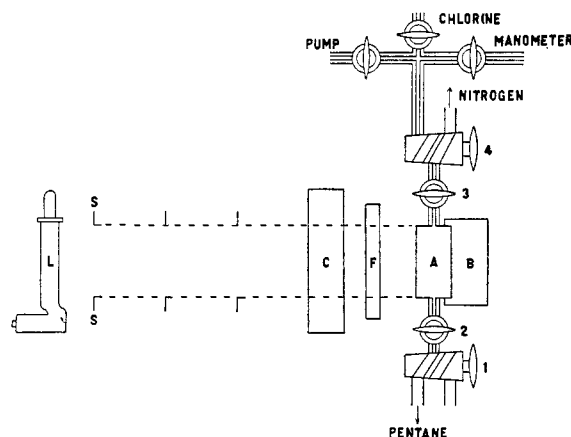

Fig. 1.—Apparatus.

This method of making the chlorine solution was entirely satisfactory, as was shown by the fact that fifteen preparatory trials gave a sodium thiosulfate titer of 18.19 cc. with a probable error of 0.07 cc. The phototronic cell also appeared to be satisfactory, since no drifts or constant changes could be observed from it after it had been illuminated.

Experimental Results.—The results obtained are listed in Table I.

The average of these values for the quantum yield is 192, with a probable error of 14.

The absorption coefficients were calculated from the data collected in seventeen of these experiments.

An average value for ϵ of 28.2 was obtained for the wave length of 3650 Å., with a probable error of 0.6. This is in good agreement with the value of 27.9 given by Gibson and Bayliss[2] for the absorption coefficient of gaseous chlorine at a wave length of 3650 Å. and a temperature of 18°. The temperature coefficient is very small, 3% for a change of 150° from room temperature at this wave length, and can be disregarded for this comparison.

The number of moles of chlorine at any time that remained in the reaction flask was plotted on

(2) Gibson and Bayliss, *Phys. Rev.*, **44**, 188 (1933).

TABLE I

MOLES OF CHLORINE REACTING, γ, PER QUANTUM AB-
SORBED

| Experiment	Time of exposure, min.	Moles of chlorine remaining $\times 10^{-5}$	γ
19-2	30	5.94	198
19-3	20	6.53	215
19-5	5	8.29	186
24-1	5	8.17	214
24-2	10	7.96	154
24-3	20	6.68	175
24-4	30	6.50	175
27-1	5	8.16	215
27-2	10	7.96	184
27-3	20	6.81	200
27-4	30	6.09	182
31-1	5	8.14	200
31-3	5	8.14	248
31-4	10	7.64	184
31-5	10	7.65	182
31-6	10	7.64	184
31-7	20	6.88	168
31-8	20	7.07	154

semi-logarithmic paper against the time as the abscissa for those experiments having the same initial concentration of chlorine. A straight line was obtained, indicating that the reaction is first order with respect to chlorine. The rate of decrease of chlorine can then be expressed by the equation

$$-d(Cl_2)/dt = kI_0(Cl_2)$$
$$= k'I_{abs.}$$

and the reaction mechanism may be represented in the usual way

$$Cl_2 + h\nu = Cl + Cl$$
$$Cl + C_5H_{12} = HCl + C_5H_{11}$$
$$C_5H_{11} + Cl_2 = C_5H_{11}Cl + Cl$$
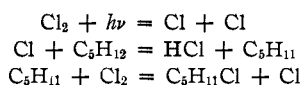
This mechanism fulfils the necessary condition that the over-all reaction be exothermic, as well as the requirement that every step in the chain cycle be exothermic, or in any event have a very small energy requirement. The correct rate law is derivable from this mechanism if the chain terminating step is taken to be

$$Cl + W = \frac{1}{2}Cl_2$$
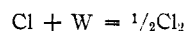
where W denotes either the wall or some unreactive molecule.

The experiments described were performed with the rigorous exclusion of oxygen. An effect, which may be ascribed to the presence of oxygen, is the fact that the chlorination of pentane does not occur ordinarily in diffuse daylight, but occurs very rapidly in bright sunlight. A possible explanation for this phenomenon is that exposure to diffuse light is probably insufficient to remove oxygen; but once chlorination starts, its rate is appreciable even in comparatively weak light. Evidence for this is given by the sensitivity of a vessel which has been previously used in photochemical chlorination; when fresh chlorine solution, made with pentane that is oxygen free, is introduced into such a vessel, the chlorination proceeds even in diffuse light.

Summary

The photochlorination of pentane in the liquid phase, with light of 3650 Å., has a quantum efficiency of 192 ± 14, at 25°. The reaction rate is proportional to the first power of the chlorine concentration at constant light intensity.