which are close to the molar volume of pure liquid chlorine at the respective temperatures.

2. The new solubility measurements have been tabulated together with existing data in four other solvents and it has been shown that the equation $\ln a_2 = \ln \phi_2 + (1 - (v/v_1)\phi_1 + (v_2 \phi^2/RT)(\delta_1 - \delta_2)^2$ accounts fairly well for the observed values of the solubility without empirical adjustment of the parameters.

3. The temperature coefficient of solubility is in reasonable accord with the above equation.

BERKELEY, CALIFORNIA RECEIVED AUGUST 6, 1949

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

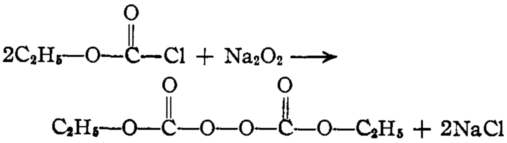
Some Reactions of Diisopropyl Peroxydicarbonate

BY SAUL G. COHEN* AND DONALD B. SPARROW†

Introduction

Dialkyl peroxydicarbonates of the structure $R{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}R$, I, are formally similar to the diacyl peroxides, $R{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}\overset{\overset{O}{\|}}{C}{-}R$, (II), the hydrocarbon groups in (II) being replaced by alkoxy groups in (I). The peroxydicarbonates and the free radicals, $R{-}O{-}\overset{\overset{O}{\|}}{C}{-}O\cdot$ which appear to be formed in their decomposition are derivatives of the thermally, unstable monoalkyl carbonic acids, $R{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}H$, just as the diacyl peroxides and the carboxylate free radicals[1] are related to the more stable carboxylic acids.

Diethyl peroxydicarbonate was apparently prepared both by the decomposition of ethyl triphenylmethyl-azo-carboxylate, $(C_6H_5)_3C{-}N{=}N{-}COOC_2H_5$, in the presence of oxygen, and by the interaction of sodium peroxide and ethyl chlorocarbonate.[2]



$$2C_2H_5{-}O{-}\overset{\overset{O}{\|}}{C}{-}Cl + Na_2O_2 \longrightarrow C_2H_5{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}O{-}\overset{\overset{O}{\|}}{C}{-}O{-}C_2H_5 + 2NaCl \quad (1)$$

The latter reaction was utilized in the Columbia Chemical Division, Pittsburgh Plate Glass Company, in the preparation of many such esters, which were found to be efficient polymerization initiators.[3,4]

We are reporting the results of a study of the reactions of diisopropyl peroxydicarbonate in ethylbenzene and in the polymerization of styrene in ethylbenzene and in both systems in the presence of quinone and hydroquinones.

Rates of Decomposition and Polymerization.—The rates of decomposition of diisopropyl peroxydicarbonate were determined (a) in ethylbenzene, and (b) in 3.46 m./l. of styrene in ethylbenzene at 54.3°, and (c) in 3.46 m./l. of styrene in benzene at 54.0°. The data are plotted in Fig. 1 according to a first order rate expression. The decompositions showed apparent first order kinetics to about 75% of completion, and slowed up at higher conversion. The over-all kinetic order was less than three halves and it may well be that, as in the case of benzoyl peroxide,[5,6] a first order "thermal" decomposition and a radical induced decomposition of higher order occur concomitantly. The first order rate constants, calculated from the curves, are (a) 4.5×10^{-5}, (b) 5.2×10^{-5}, and (c) 5.0×10^{-5} sec.$^{-1}$ (respectively). The rate of decomposition in 3.46 m./l. of styrene in benzene at 54.0° is equal to that of benzoyl peroxide in a similar medium at 82.0° as calcu-

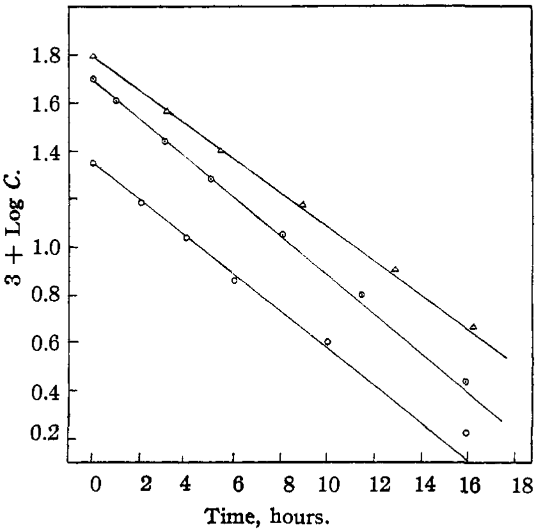


Fig. 1.—Decomposition of diisopropyl peroxydicarbonate: Δ, in ethylbenzene, 54.3°; ⊙, in 3.46 mil. styrene in ethylbenzene, 54.3°; O, in 3.46 mil. styrene in benzene, 54.0°.

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* Harvard University Ph.D. 1940.

† Harvard College, A.B. 1943.

(1) Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

(2) Wieland, vom Hove and Borner, *Ann.*, **446**, 31 (1926).

(3) Strain, U. S. Patent 2,370,588, February 27, 1945; Strain, U. S. Patent 2,464,062; Pechukas, U. S. Patent 2,464,056, March 8, 1949.

(4) Strain, Bissinger, Dial, Rudoff, DeWitt, Stevens and Langston, THIS JOURNAL, **72**, Feb. (1950).

(5) Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(6) Cass, *ibid.*, **68**, 1976 (1946).

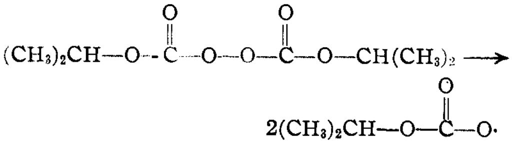
lated by extrapolation of data obtained at 54°, 64°, and 74°.[7]

In 3.46 m./l. of styrene in benzene an average rate of peroxydicarbonate decomposition of 1.02×10^{-6} m./l./sec. (5.0×10^{-5} sec.$^{-1}$ $\times$ 0.0204 m./l.) led, after one hour at 54° to 6.31% of methanol insoluble polystyrene, $\eta_{sp}/c_g = 0.110$. We have previously reported[7] that in the same system an average rate of benzoyl peroxide decomposition of 4.25×10^{-7} m./l./sec. (1.83×10^{-6} sec.$^{-1}$ $\times$ 0.233 m./l.) led, after one hour at 54° to 3.9% of polystyrene, $\eta_{sp}/c_g = 0.148$. With the approximation that the rates of polymerization of styrene are proportional and the molecular weights are inversely proportional to the square roots of the rates of peroxide decomposition,[8] the corresponding values may be calculated for polymerization in the presence of benzoyl peroxide decomposing at the same rate as is now being reported for the peroxydicarbonate. These values are 6.17% polymerization, $\eta_{sp}/c_g = 0.096$. Despite the eleven-fold difference in concentrations and the twenty-seven-fold difference in rate constants, the two initiators lead to quite similar rates of polymerization and molecular weights and thus appear to have approximately equal efficiencies as initiators of the polymerization of styrene at 54°.

Products of decomposition of diisopropyl peroxydicarbonate in dilute solution were determined at 54.3°. In ethylbenzene the following products were obtained: carbon dioxide, 88%, 1.76 moles per mole of peroxydicarbonate; isopropyl alcohol, as its N-phenyl carbamate, 59% yield, 67% based on evolved carbon dioxide; meso-2,3-diphenylbutane, 21%. No acetone was found.

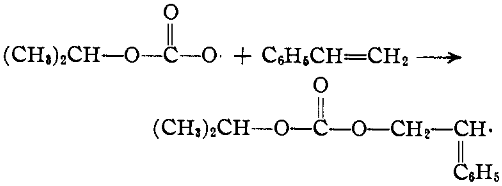
In the decomposition of 0.052 m./l. of diisopropylperoxydicarbonate in 3.46 m./l. of styrene in ethylbenzene the yield of carbon dioxide was diminished markedly to 10.8%, and 78% polymerization occurred. Isopropyl alcohol was obtained, 5% yield, 50% based on evolved carbon dioxide. The polymer solution was then subjected to an ester interchange reaction with sodium myristylate and myristyl alcohol, and isopropyl alcohol was isolated as its N-phenyl carbamate, 68% yield, 77% yield corrected for liberated carbon dioxide. Isopropyl β-phenylethyl carbonate was prepared as a model compound with which the procedure was worked out for removal of initiator fragments from the polystyrene.

It seems likely that the first step in the decomposition involves in part an induced decomposition but is in large part a unimolecular formation of monoalkyl carbonate radicals.



$$\mathrm{(CH_3)_2CH{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH(CH_3)_2 \longrightarrow 2(CH_3)_2CH{-}O{-}\overset{O}{\overset{\|}{C}}{-}O\cdot} \quad (2)$$

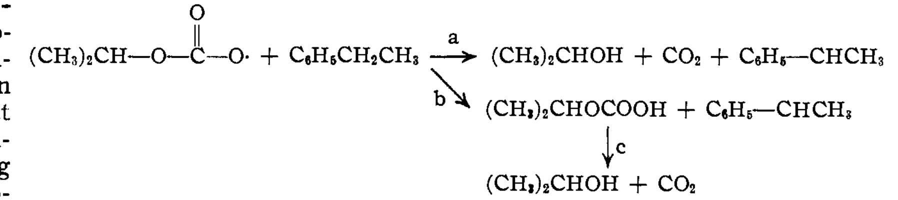
The low yield of carbon dioxide and the recovery of isopropyl alcohol by ester interchange indicates that in the presence of styrene these radicals largely survive without loss of carbon dioxide the short time which elapses and the collisions which they undergo prior to their addition to styrene in the polymerization initiation process.



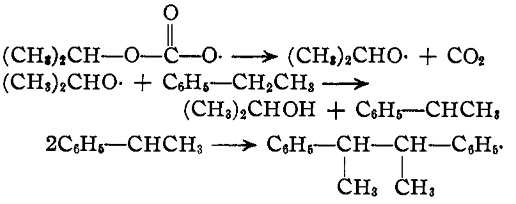
$$\mathrm{(CH_3)_2CH{-}O{-}\overset{O}{\overset{\|}{C}}{-}O\cdot + C_6H_5CH{=}CH_2 \longrightarrow (CH_3)_2CH{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\underset{C_6H_5}{\underset{\|}{CH}}\cdot}$$

The alkyl carbonate radicals may have stability intermediate between that of the unstable carbonic acid and the relatively stable carbonate ion.[9] Benzoyl peroxide similarly initiates the polymerization of styrene at 74° with evolution of not more than 19% of its carbon dioxide.[10]

In ethylbenzene in the absence of styrene several reactions may occur



$$\begin{array}{lll} \mathrm{(CH_3)_2CH{-}O{-}\overset{O}{\overset{\|}{C}}{-}O\cdot + C_6H_5CH_2CH_3} & \xrightarrow{a} & \mathrm{(CH_3)_2CHOH + CO_2 + C_6H_5{-}\dot{C}HCH_3} \quad (4) \\ & \searrow^{b} & \mathrm{(CH_3)_2CHOCOOH + C_6H_5{-}CHCH_3} \\ & & \quad \downarrow c \\ & & \mathrm{(CH_3)_2CHOH + CO_2} \end{array}$$



$$\mathrm{(CH_3)_2CH{-}O{-}\overset{O}{\overset{\|}{C}}{-}O\cdot \longrightarrow (CH_3)_2CHO\cdot + CO_2} \quad (5)$$

$$\mathrm{(CH_3)_2CHO\cdot + C_6H_5{-}CH_2CH_3 \longrightarrow (CH_3)_2CHOH + C_6H_5{-}CHCH_3} \quad (6)$$

$$\mathrm{2C_6H_5{-}CHCH_3 \longrightarrow C_6H_5{-}\underset{CH_3}{\underset{|}{CH}}{-}\underset{CH_3}{\underset{|}{CH}}{-}C_6H_5} \quad (7)$$

It is difficult to assess the relative importance of the several reactions which may lead to the observed carbon dioxide and isopropyl alcohol Some alkyl carbonic acid may well be formed in reaction (4b) by analogy with the formation of benzoic acid from benzoyl peroxide under similar conditions.[6,10] However, the yields of benzoic acid have been such as to indicate that a large part of the carbon dioxide and isopropyl alcohol are probably formed in this case in reactions (4a), (5) and (6) without prior formation of the alkyl carbonic acid. The formation of 2,3-diphenylbutane indicates that the radicals derived from the peroxydicarbonate extract alpha hydrogen atoms from ethylbenzene, leading to alpha phenylethyl radicals.

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(7) Cohen, This Journal, **67**, 17 (1947).

(8) Schulz and Husemann, *Z. physik. Chem.*, **B39**, 246 (1938).

(9) Faurholt, *J. chim. phys.*, **21**, 400 (1924); *Z. physik. Chim.*, **126**, 72, 85, 211 (1927).

(10) Cohen, *J. Pol. Sci.*, **2**, 511 (1947).

Effects of Inhibitors.—The presence of 0.06 m./l. of toluhydroquinone or 0.10 m./l. of quinone in ethylbenzene increased the yield of carbon dioxide from 88 to 95% and 94%, respectively, presumably by donation of hydrogen to the peroxydicarbonate molecule or the alkyl carbonate radicals, thus decreasing the probability of their being converted to stable carbon dioxide containing molecules.

In the styrene–ethylbenzene system, the presence of 0.06 m./l. of quinone led to inhibition, less than 0.5% of methanol insoluble polystyrene being formed, while the carbon dioxide yield rose from 10.8% to 36.4%. Toluhydroquinone (0.06 m./l.) led to similar strong inhibition, but the yield of carbon dioxide rose to 73.3%. In the presence of 0.06 m./l. of di-*t*-butylhydroquinone the yield of carbon dioxide rose to 88%, while 7% of methanol insoluble polymer was formed. To the extent that the additives increased the yields of carbon dioxide they apparently reacted with the peroxydicarbonate or the alkyl carbonate radicals. Thus quinone showed moderate interaction with the initiator, about 60% of the normal chain initiation reactions took place, and inhibition of these chains resulted from their interaction with quinone. Toluhydroquinone showed considerably more interaction with the initiator, presumably by donation of hydrogen atoms, and effectively inhibited those chains which were started. Di-*t*-butylhydroquinone, with probably a lower oxidation potential, appeared to be oxidized readily and the initiator was converted largely to the easily decarboxylated mono-isopropylcarbonic acid. However, some chain initiation occurred and this hydroquinone and its quinone were not particularly effective in stopping chain growth.

Experimental

Diisopropyl Peroxydicarbonate.—Directions for the preparation and handling of this sensitive material were supplied by Dr. F. Strain, Pittsburgh Plate Glass Company, and will appear shortly in a publication from that laboratory.[4]

Isopropyl β-phenylethyl carbonate was prepared by the addition at 5–10° of 22 g. of isopropyl chlorocarbonate to a stirred solution of 20 g. of Eastman Kodak Co. β-phenylethanol in 15 g. of pyridine. The mixture was left at room temperature for one hour, washed with water, 10% hydrochloric acid and 10% sodium bicarbonate, dried and distilled, b. p. 122–123° (3.5 mm.), 20 g., 59% yield. *Anal.* Calcd. for $C_{12}H_{16}O_3$: C, 69.3; H, 7.7. Found: C, 69.4; H, 7.9.

α-Phenylethyl chloride was prepared by the method of Kharasch and Brown,[11] b. p. 90–94° (28–30 mm.).

2,3-Diphenylbutane was prepared by the interaction of α-phenylethyl chloride and magnesium in moist ether.[12] The *meso* product was obtained in 17% yield, sintering at 121°, melting at 124–125°.

Styrene, Dow-*N*-100, and **ethylbenzene**, Eastman Kodak Co. were distilled and used immediately or were stored in a refrigerator for not more than twenty-four hours in nearly full glass-stoppered flasks.

Analyses for diisopropyl peroxydicarbonate were carried out essentially as described previously for benzoyl peroxide.[7]

Rates of Decomposition.—Solutions of peroxydicarbonate were prepared in the desired solvents at 0°. Aliquots were sealed in vacuum and stored at −45°. Prior to being heated at 54.3° they were warmed in cold water and shaken well. Samples were titrated at this point and after stated periods of heating.

Specific viscosities were measured in benzene at 30°.

Carbon Dioxide Evolution.—Nitrogen, freed from oxygen, moisture and carbon dioxide, was passed through a gas inlet tube nearly to the bottom of the reaction vessel, which was a tube of 20 cc. useful capacity, fitted with a ground glass stopper, the nitrogen inlet tube and a gas exit tube. The reaction vessel was immersed in water in a larger tube, which was maintained at constant temperature by the vapors of boiling ethyl formate. From the reaction vessel, the nitrogen passed through a reflux condenser, dry ice traps, a dehydrite tube, and two ascarite tubes. The gain in weight of the first ascarite tube was determined. The additives, when used, were placed in the reaction vessel, the peroxydicarbonate solution in ethylbenzene or 3.46 m./l. of styrene in ethylbenzene was run in, the parts of the system were connected and nitrogen flow and heating started. Nitrogen flow and heating were continued until there was no further gain in weight of the carbon dioxide absorption tube.

Products of Decomposition in Ethylbenzene.—A solution of 4.0 g. of diisopropyl peroxydicarbonate in 200 cc. of ethylbenzene was prepared. Two 5-cc. aliquots were titrated, consuming 9.20 and 9.15 cc. of 0.1050 *N* sodium thiosulfate, indicating that the solution contained 0.096 m./l. of peroxide.

A 100-cc. portion was sealed in vacuum and heated at 54.0 ± 0.5° for forty hours. The reaction bulb was opened, a 10-cc. portion was removed, and the remainder was distilled in a Claisen flask, about 7 cc. being collected over the range of 60–134°. This was diluted to 10 cc. and divided into two 5-cc. portions. Of these, one was treated with 1.2 g. of phenyl isocyanate, leading to isopropyl N-phenyl carbamate, melting point and mixed melting point 85–88°, 0.91 g., 59% yield. The second 5-cc. portion was treated with 2 g. of 2,4-dinitrophenylhydrazine. Acetone 2,4-dinitrophenylhydrazone was not obtained.

The undistilled residue of the reaction solution was further concentrated to about 15 cc. This residue was diluted with ethylbenzene to 25 cc. and 20 cc. of this was concentrated in vacuum, leaving a partially crystalline residue. This was dissolved in ethanol and cooled, leading to a white solid, 0.3 g., 21% yield of *meso*-2,3-diphenylbutane, melting at 121–123°, a mixture with an authentic sample sintering at 121°, melting at 123–124°. Concentration of the alcohol washings led to 0.7 g. of an oil which may have contained *dl*-2,3-diphenylbutane.

Alcoholysis of Isopropyl β-Phenylethyl Carbonate.—Myristyl alcohol, 20 g., 0.09 mole, was dissolved in 100 cc. of ethylbenzene and boiled to remove water; sodium, 0.35 g., 0.015 mole, was added, and the mixture was boiled for several hours under oxygen free nitrogen. Isopropyl β-phenylethylcarbonate was added, 1.04 g., 0.005 mole, and the mixture was slowly distilled, 20 cc. being collected fairly rapidly, and a second 20 cc. over a period of one hour. Each distillate was treated with phenyl isocyanate, warmed on the water-bath and concentrated in vacuum. The residues were crystallized from hexane, the first yielding 0.60 g., 67% yield of isopropyl N-phenylcarbamate, m. p. and mixed m. p. 84–86°. The second portion of the distillate led to only traces of product. Repetition of this experiment led to 55% recovery of a less pure product, melting 77–80°.

Products of Diisopropyl Peroxydicarbonate Induced Polymerization of Styrene in Ethylbenzene.—A 200-cc. portion of a solution of 6.79 g. of the peroxydicarbonate in 240 cc. of styrene was diluted with 300 cc. of ethylbenzene. Titration indicated that the solution contained 0.052 m./l. of peroxide.

Two 100-cc. portions were sealed in vacuum and heated at 54.0° for sixty-four hours. A 10-cc. sample of one was

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[11] Kharasch and Brown, This Journal, 61, 2142 (1939).

[12] Ott, *Ber.*, 61, 2141 (1928).

titrated for percarbonate; none was found. Another portion, 2.59 g., was diluted with 50 cc. of methanol, and the precipitated polystyrene was washed with methanol and dried to constant weight in vacuum at 60°, 0.841 g. 78% polymerization, $\eta_{sp}/c_g = 0.103$. A small quantity of hydroquinone was added to the remainder of the solution which was then distilled, about 5 cc. being collected, boiling 130–135°. The distillate was treated with 0.2 g. of phenyl isocyanate, leading to isopropyl N-phenylcarbamate, 0.086 g., 5.4% yield, melting point and mixed melting point, 83–86°. The second 100-cc. portion was distilled similarly. This distillate was treated with 0.4 g. of 2,4-dinitrophenylhydrazine and 10 cc. of 95% ethanol and worked up for acetone dinitrophenylhydrazone. No more than a trace of impure material, melting 110–120° was obtained.

A portion (42.8 g.) of reaction product, from which the low boiling material had been distilled, was added to a sodium myristylate–myristyl alcohol–ethylbenzene solution as described in the preceding section. The solution was boiled, becoming quite dark; about 20 cc. of distillate was collected, the residue was boiled for one-half hour, and 20 cc. more of distillate was taken. The combined distillates were treated with 1.2 g. of phenyl isocyanate, leading to isopropyl N-phenylcarbamate, m. p. 83–85°, mixed melting point 84–87°, 0.66 g., 68% recovery.

Another portion of the polymerization product, 19.3 g., was treated with excess methanol; the liquid was decanted and the precipitated polystyrene was dissolved in benzene and reprecipitated with methanol. The combined supernatant liquids were evaporated in vacuum at room temperature, leaving a small oily residue. This residue was treated with sodium myristylate as described above and worked up for isopropyl N-phenylcarbamate. None was found. The reprecipitated polystyrene was dried to constant weight in vacuum at room temperature, dissolved in 50 cc. of ethylbenzene, added to sodium myristylate–myristyl alcohol in ethylbenzene and worked up for isopropyl N-phenylcarbamate; this product was obtained, m. p. and mixed 81–84°, 0.14 g., 32% yield. Some high melting material contaminated the product, presumably diphenylurea.

Summary

The decomposition of diisopropyl peroxydicarbonate at 54° in styrene–benzene, in ethylbenzene, and in styrene–ethylbenzene appears to be largely a first order reaction accompanied by a reaction of higher order; the rate in styrene–benzene at 54° is equivalent to that of benzoyl peroxide at 82°. Its efficiency in initiating the polymerization of styrene at 54° is similar to that of benzoyl peroxide.

The decomposition in ethylbenzene leads to high yields of carbon dioxide and isopropyl alcohol. In the presence of styrene these products are formed in quite low yields, the alkyl carbonate radicals adding to styrene monomer more rapidly than they may lose carbon dioxide, despite their formal derivation from the unstable alkyl carbonic acid. Isopropyl alcohol may be removed from the polystyrene by saponification.

The effects of quinone and two hydroquinones on these reactions are discussed.

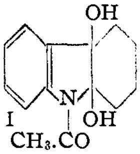
CAMBRIDGE, MASS. RECEIVED MARCH 15, 1949

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

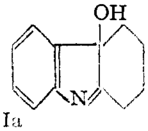
The Structure of the So-called 11-Hydroxytetrahydrocarbazolenine[1]

BY BERNHARD WITKOP*

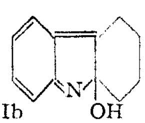
In 1923, Perkin and Plant[2] noticed a "curious and unexpected result" when they treated 9-acetyl-10,11-dihydroxyhexahydrocarbazole (I) with hot aqueous alcoholic potassium hydroxide. They obtained an orange substance, $C_{12}H_{13}NO$ (II), m. p. 79°, to which they ascribed the structure of an 11-hydroxytetrahydrocarbazolenine (IIa), or, less likely, that of the isomeric hydroxy derivative (IIb). In this paper we show that the correct structure of this colored transformation product is that of a spiro-[cyclopentane-1,2'-ψ-indoxyl] (II). Table I summarizes the reactions and further transformations carried out with compound (II).



I



IIa



IIb

Compound (I) was obtained either according to Perkin and Plant[2] by the action of nitric acid on N-acetyltetrahydrocarbazole or by a second unambiguous method to be published later. The transformation product (II), m. p. 79°, see Table I, after distillation in high vacuum, had a pure yellow color with no shade of orange or red. Its absorption spectrum[3] (Fig. 1) shows a characteristic maximum at 400 mμ, whereas the colorless acetyl compound (IV) has its peak of absorption at 340 mμ. Perkin and Plant[2] considered this acetyl compound to be an O-acetyl derivative. The infrared spectra (Fig. 2 and Table II) show clearly that what they assumed to be (II), has a free NH-band (2.9 μ) which is lacking in the case of the acetyl compound (IV). Another important band in the infrared absorption spectrum shows up at 5.85 μ, and is typical of a carbonyl function in a five membered ring (*cf.* oxindole, Table II). The formation of a dinitrophenylhydrazone from the yellow transformation product confirmed this suggestion. The reduction of the "hydroxytetrahydrocarbazolenine" with lithium aluminum hydride furnished two products: a solid colorless compound (V) $C_{12}H_{15}NO$, m. p. 146°, and a liquid colorless base (VI), $C_{12}H_{15}N$. V on dehydrogena-

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* Harvard University Faculty 1948–.

[1] This investigation was supported by a grant-in-aid from Research Corporation, New York.

[2] Perkin and Plant, *J. Chem. Soc.*, 123, 676 (1923).

[3] I am indebted to Dr. E. R. Blout, Polaroid Corporation, Cambridge, for kindly making arrangements for measuring the ultraviolet spectra.