geneous case (6) M represents any suitable third body present in the gas phase. In all cases, *viz.*, (4) and (5), (4) and (6), or (4) and (7), the rate is independent of the total pressure. This is consistent with our findings since the total pressure did vary by a factor of about 2 between several of the runs with no significant effect on the calculated rate constant. This independence of pressure supports the postulated first order in benzal chloride for if this order were not unity then the homogeneous mechanisms would involve a pressure dependence. Because of the two-fold variation in pressure and also because good rate constants were not found where the order of benzal chloride was assumed to be other than unity we may take that order as unity without a more direct determination.

The homogeneous chain starter (8)

$$Cl_2 = 2Cl \qquad (8)$$

has not been considered since the half-life of the excited chlorine molecule is smaller than the time between collisions at the pressures used in this investigation.

It is of some interest that if one uses the equilibrium concentration of chlorine atoms[10] and the observed rate constant and, by the method of Pease,[2a] calculates a chain length the value found is 10^8. The assumptions used make this value uncertain even as to order of magnitude. However, and more important, since any such chain length is highly improbable in the present reaction, the calculation argues in favor of the heterogeneously catalyzed reaction (5), *i.e.*, a higher rate for the chain starter than estimated in the calculation.

(10) W. F. Giauque and R. Overstreet, THIS JOURNAL, **54**, 1731 (1932).

In the light of the above considerations one must conclude that either (or both) the heterogeneous, (5), or homogeneous, (6) and (7), mechanisms will account for the data obtained. There is some indication to favor the heterogeneous reaction in which chains are started and broken on the surface of the reactor it being implied that the surface in all of our reactions was such that it was not a limiting factor.

It might be of interest to point out that the surface reaction which we have suggested as one of the possible mechanisms is the same as the one found by Morris and Pease[11] for the thermal hydrogen–chlorine reaction.

Acknowledgment.—The authors wish to acknowledge the suggestion of this problem by Dr. Paul M. Gross.

Summary

1. The kinetics of the gas phase thermal chlorination of benzal chloride at 169, 195 and 230° have been studied with carefully purified materials.

2. The reaction is predominantly a side-chain substitution, a maximum of 5% ring chlorination having been observed.

3. No change in over-all rate with varying pressure or surface–volume ratio was observed.

4. Some discussion of the rate law and possible reaction mechanisms has been presented.

5. A rough calculation indicates that the reaction involves a long chain length.

(11) J. C. Morris and R. N. Pease, *ibid.*, **61**, 391, 396 (1939).

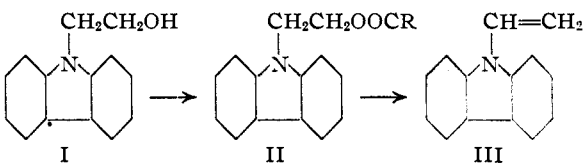
DURHAM, NORTH CAROLINA RECEIVED FEBRUARY 19, 1948

[CONTRIBUTION FROM THE PITTSFIELD LABORATORY, APPARATUS DEPARTMENT, GENERAL ELECTRIC COMPANY]

Some Reactions of N-(β-Hydroxyalkyl)-carbazoles

BY RALPH G. FLOWERS, HARRY F. MILLER AND LEOLA W. FLOWERS

In the preparation of N-vinylcarbazole (III) by decomposition of the N-acyloxyethyl derivatives, according to the scheme[1]



we have had the occasion to prepare N-(β-hydroxyethyl)-carbazole (I) and several of its esters (II). The esterification of (I) proceeded normally with good yields in all cases tried, except in the attempted preparation of a phthalate, where no reaction was observed. The use of small quantities of sulfuric acid to catalyze the reactions gave only tarry products.

(1) Miller and Flowers, U. S. Patent 2,426,465; *C. A.*, **42**, 224 (1948).

The N-vinylcarbazole was best prepared by the decomposition of N-(β-acetoxyethyl)-carbazole, although many attempts were made to convert (I) directly into the vinyl derivative by various dehydration methods. These trials included treatment of (I) with phosphorus pentoxide and vapor phase treatment with alumina over a wide range of temperatures. Unreacted (I), carbazole and a small amount of polymer was obtained from these trials. Better conversion of N-(β-acetoxyethyl)-carbazole to (III) over that previously reported[1] is obtained when the reaction is carried out at reduced pressures in the presence of an inert vapor and a copper borate catalyst.

A similar program was carried out in an attempt to prepare N-propenylcarbazole (VI) from the de-

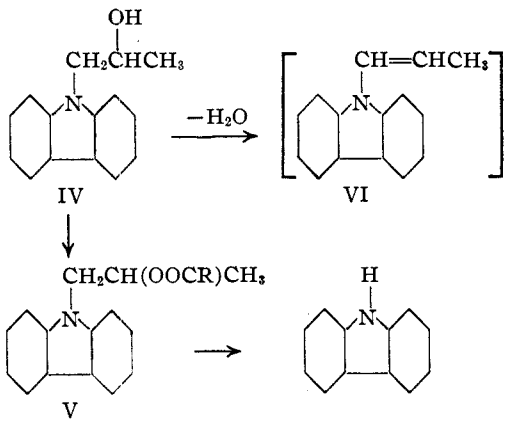
TABLE I

N-CARBAZOLE DERIVATIVES

Compound	M. p., °C.[a]	Reac. time, hr.[b]	Esterifying reagent	Yield, %	Molecular formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
β-Hydroxyethyl-	83–83.5	26	.....	40	$C_{14}H_{13}NO$	79.59	79.81	6.26	6.31	6.63	6.52
β-Acetoxyethyl-	74–74.5	64	Anhydride	74	$C_{16}H_{15}NO_2$	75.89	75.84	5.98	6.04	5.54	5.59
β-Propionoxyethyl-	74–75	27	Anhydride	95	$C_{17}H_{17}NO_2$	76.40	76.05	6.38	6.47	5.25	5.24
β-Butyroxyethyl-	48–49	21	Anhydride	60	$C_{18}H_{19}NO_2$	76.86	76.83	6.81	6.95	4.98	5.09
β-Phenylacetoxyethyl-	70–71	94	Acid	26	$C_{22}H_{19}NO_2$	80.30	79.94	5.83	5.80	4.39	4.35
β-Benzoxylethyl-	142–143	A	Acid chloride	98	$C_{21}H_{17}NO_2$	80.00	79.59	5.40	5.44	4.44	4.54
β-3,5-Dinitrobenoxyethyl-	261–262	B	Acid chloride	98	$C_{21}H_{15}N_3O_6$	62.30	62.33	3.71	3.79	10.38	10.24
β-Hydroxypropyl-	120–121	31	.....	90	$C_{15}H_{15}NO$	79.56	79.78	6.90	6.81	6.40	6.28
β-Acetoxypropyl-	104–104.5	1	Acid chloride	95	$C_{17}H_{17}NO_2$	76.36	76.57	6.42	6.58	5.24	5.35
β-Propionoxypropyl-	64–64.5	46	Anhydride	80	$C_{18}H_{19}NO_2$	76.83	76.85	6.81	6.84	4.98	5.13
β-Butyroxypropyl-	42–43	A	Acid chloride	61	$C_{19}H_{21}NO_2$	76.24	76.86	7.18	7.27	4.75	4.76
β-Phenylacetoxypropyl-	50–50.5	120	Acid	20	$C_{23}H_{21}NO_2$	80.47	80.63	6.17	6.23	4.08	4.10
β-Benzoxypropyl-	89.5–90	A	Acid chloride	77	$C_{22}H_{19}NO_2$	80.21	80.12	5.82	5.86	4.26	4.31
β-3,5-Dinitrobenzoxypropyl-	167.5–168	B	Acid chloride	65	$C_{22}H_{17}N_3O_6$	63.01	62.84	4.10	3.86	10.02	9.38

[a] All melting points corrected. [b] A = 1 min.; B = 5 min. Analyses were performed by Dr. Carl Tiedcke, Mrs. B. Sicard and Miss F. Durkee.

hydration of N-(β-hydroxypropyl)-carbazole (IV) or from the decomposition of esters (V) of N-(β-hydroxypropyl)-carbazole.



The attempt to obtain VI by dehydration of the alcohol resulted only in a product having the properties of a low molecular weight polymer. As indicated in the above diagram, pyrolysis of the esters (V) gave only carbazole.

Experimental

N-(β-Hydroxyethyl)-carbazole (I).—This new compound was prepared by a modification of the method used by Stevens and Tucker[2] for certain other carbazole derivatives. Eighty grams (0.48 mole) of carbazole, recrystallized from acetone, was dissolved in 400 cc. of ethyl methyl ketone in a 3-liter, 3-necked flask, equipped with an efficient stirrer, a reflux condenser and a dropping funnel. This solution was heated on a sand-bath until refluxing began, at which time a solution of 70.4 g. (1.76 mole) of sodium hydroxide in 36 cc. of water was added. After refluxing for thirty minutes to allow a reaction to take place between the carbazole and sodium hydroxide, 64 cc. (0.954 mole) of ethylene chlorohydrin was added dropwise to the green caustic solution over a period of one hour. The reaction mixture was stirred with refluxing for three hours and then an additional 40 g. of sodium hydroxide was added and 64 cc. of ethylene chlorohydrin was introduced dropwise. After refluxing for twenty-six hours, the contents of the reaction flask were poured into three liters of water. The ethyl methyl ketone solution was extracted from the aqueous layer with ethyl ether. The ether was then evaporated on the steam-bath and the residue filtered to remove the bulk of unreacted carbazole.

The solvent was removed by distillation at 2.5 mm. pressure. All material distilling below 135° was discarded. The residue was recrystallized several times from a 50–50 benzene–ligroin mixture, as long, fine, colorless needles (see Table I).

N-(β-Hydroxypropyl)-carbazole (IV).—The procedure for the preparation of (IV) from carbazole and propylene chlorohydrin was similar to that used for (I) except that very little carbazole remained unreacted and was not filtered. Some of the solvent, ethyl methyl ketone, was removed before the reaction mixture was poured into water. The solid was filtered and washed, until neutral. It was recrystallized from small amounts of acetone and finally from benzene, to give small, colorless needles, melting at 120–121° (see Table I).

Esters of N-(β-Hydroxyethyl)-carbazole (I) and N-(β-Hydroxypropyl)-carbazole (IV).—The esterifications of (I) and (IV) were carried out by refluxing the hydroxy compound with an excess of the acid, acid chloride or acid anhydride. The reagent used and time required is indicated in Table I for the respective derivatives. The products were recrystallized from ethyl alcohol. All the esters crystallized out as colorless needles, except the derivatives prepared with the 3,5-dinitrobenzoyl chloride, which came down as fine, yellow needles.

N-Vinylcarbazole (III).—Forty grams (0.158 mole) of N-(β-acetoxyethyl)-carbazole was dissolved in 200 cc. of benzene and added dropwise into a vertical, 24-inch reaction column packed with copper borate–alumina pellets.[3] The temperature was maintained at about 540°. The reaction was carried out at pressures of 3–20 mm. The product contained 5 g. of carbazole and 7 g. of N-vinylcarbazole (23% yield).

(2) Stevens and Tucker, *Chem. Soc. Trans.*, **123**, 2140 (1923).

(3) Catalysts in pellet form were obtained from Harshaw Chemical Company, Cleveland, Ohio.

Dehydration of N-(β-Hydroxypropyl)-carbazole (IV).— In a typical experiment, 29 cc. of dry benzene, 29 g. of phosphorus pentoxide and 0.2 g. of *p-t*-butylcatechol were heated to refluxing in a 125-cc., 3-necked flask, equipped with condenser, stirrer and dropping funnel. Five and eight-tenths grams (0.022 mole) of (IV) in 27 cc. of dry benzene was added over a period of fifteen minutes. After fifteen minutes more of refluxing, the contents of the flask were diluted with a large volume of water and neutralized with sodium carbonate. The solid was filtered, washed and air-dried. The product contained no monomer, but 4 g. (88% yield) of a solid which was precipitated as a white powder from its benzene solution with methyl alcohol. This powder had a softening point of 180°. Viscosity measurements at several concentrations indicate that this material is a polymer having a molecular weight between 20,000 and 40,000.

Summary

A method is described for preparing N-vinylcarbazole and the polymer of N-propenylcarbazole. The synthesis and properties are given for N-(β-hydroxyethyl)-carbazole and N-(β-hydroxypropyl)-carbazole and several esters of each.

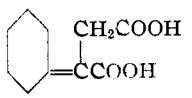
PITTSFIELD, MASS. RECEIVED APRIL 10, 1948

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

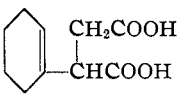
The Stobbe Condensation with Cyclohexanone

BY WILLIAM S. JOHNSON, CHESTER E. DAVIS,[1] RICHARD H. HUNT AND GILBERT STORK[2]

The first report of this condensation was made in 1941 by Robinson and Seijo[3] who used equimolar quantities of cyclohexanone, dimethyl succinate and sodium methoxide. The product (yield unspecified) gave on hydrolysis an acid melting at 186–187° which was presumed by them to be cyclohexylidenesuccinic acid, I.[4] A product also presumed to have this structure had been previously reported by Ingold, Seeley and Thorpe[5] as melting at 175°, the evidence for the position of the double bond being based on the odor of the oxidation product.[6] More recently Alder, Pascher and Schmitz[7] described the sodium ethoxide-catalyzed Stobbe condensation of cyclohexanone with diethyl succinate. The crude saponified product was obtained in "over 40%" yield and on purification gave a dibasic acid melting at 146°, also presumed to be cyclohexylidenesuccinic acid, I. An acid of the same description has since been similarly prepared in 37% yield (after a reaction period of more than two weeks) by Swain, Todd and Waring[8] who suggested that the 146° acid was not I, but cyclohexenylsuccinic acid, II. That this conclusion was correct is demonstrated below.



I



II

The probable nature of the other products is also elucidated.

The modified procedure for the Stobbe condensation involving the use of potassium *t*-butoxide[9] was employed with striking success, the distilled half-ester III being obtained in 84% yield after a reaction period of only ten minutes. Saponification of the half-ester with barium hydroxide gave a mixture from which two pure acids were isolated, one melting at 179–180° with evolution of gas and the other at 145–146° without decomposition. According to Stobbe's generalization[10] that all itaconic acids melt around 170–185° with elimination of water (anhydride formation) and that alkylidene pyrotartaric acids melt around 140–155° with very slow decomposition it would be concluded that the 180° acid is I and the 146° acid II. The opposite conclusion is reached, however, on the basis of the generalizations regarding the behavior of such acids with acetyl chloride at room temperature, since the lower melting acid reacted more rapidly than the 180° acid.

The structures of the two acids were shown by oxidation with cold alkaline permanganate: the 180° acid gave cyclohexanone isolated in 28% yield as the semicarbazone, while the 146° acid under identical reaction conditions gave no detectable cyclohexanone. The former therefore is undoubtedly cyclohexylidenesuccinic acid, I, and the latter the 3-carbon tautomer II. When the half-ester was similarly oxidized no cyclohexanone could be detected and the position of the double bond is therefore formulated in the endocyclic position (formula III). Although exclusion from the liquid half-ester of all traces of the isomeric cyclohexylidene derivative could not be established by the oxidation tests, the appreciable quantities of the derivative obtained on saponification of the

(1) Present address: Chemical Research Division, National Cash Register Corp., Dayton, Ohio.

(2) Present address: Department of Chemistry, Harvard University, Cambridge, Massachusetts.

(3) Robinson and Seijo, *J. Chem. Soc.*, 582 (1941).

(4) Robinson and Seijo (ref. 3) state that, "All the substances mentioned in this section afforded cyclohexanone on oxidation with alkaline permanganate." This observation is not incompatible with the premise set forth in the present communication that their material was actually the paraconic acid IV.

(5) Ingold, Seeley and Thorpe, *ibid.*, 853 (1923).

(6) The authors (ref. 5) state that "It instantly decolorizes cold alkaline permanganate, and gives an odour of *cyclo*hexane . . ." (undoubtedly they meant cyclohexanone).

(7) Alder, Pascher and Schmitz, *Ber.*, **76B**, 27 (1943).

(8) Swain, Todd and Waring, *J. Chem. Soc.*, 548 (1944).

(9) (a) Johnson, Petersen and Schneider, THIS JOURNAL, **69**, 74 (1947); (b) Johnson, Goldman and Schneider, *ibid.*, **67**, 1357 (1945); (c) Johnson, Johnson and Petersen, *ibid.*, **67**, 1360 (1945); (d) Johnson and Petersen, *ibid.*, **67**, 1366 (1945).

(10) Stobbe, *Ann.*, **308**, 67 (1899).