were carried out in spectra grade cyclohexane with a Beckmann Model DU spectrophotometer.

The values for maxima and minima of the anthracenes are in good agreement with the proposed effects of groups.[11] The dimethyl and tetramethylanthracenes show a bathochromic effect with some loss of fine structure, with respect to anthracene. Dibenzylanthracene shows a fine structure effect, with a hyperchromic shift, no loss in fine structure and no bathochromic shift.

Acknowledgment. The work of Mr. Horn was supported by a grant from Research Corporation to whom the authors wish to express their gratitude.

PITTSBURG, KAN.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE PAINT DIVISION OF THE PITTSBURGH PLATE GLASS COMPANY]

N-Alkylation of Nitriles with Benzyl Alcohol, Related Alcohols, and Glycols[1]

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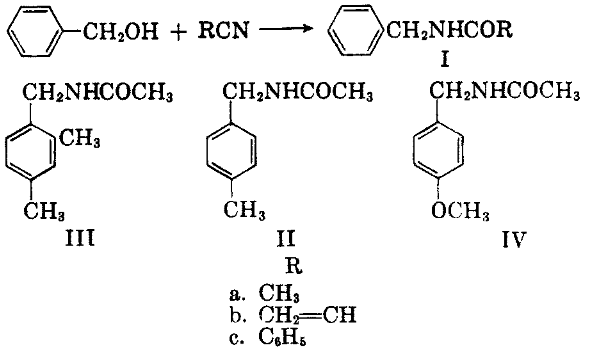
Nitriles are readily *N*-alkylated under mild conditions with primary alcohols related to benzyl alcohol and with glycols of the di(hydroxymethyl)benzene type to give good yields of *N*-aralkylamides and *N,N'*-bisaralkylamides, respectively.

In the reaction of nitriles with olefins and alcohols,[2,3] ethers,[4] esters,[5] and halides,[6] the alkylating compound is ordinarily restricted to those which can form a secondary or tertiary carbonium ion in an acidic medium.[7] An exception may be noted in the case of the primary halides which are known to form *N*-substituted nitrilium complexes with nitriles in the presence of Lewis acids.[8] Recently, Lora-Tamayo, Madronero, and Munoz reported that nitriles may be alkylated with β-phenylethyl chloride in the presence of stannic chloride to give derivatives of dihydroisoquinoline.[9] However, it has been asserted that primary alcohols are unreactive toward nitriles notwithstanding recourse to prolonged reaction times, elevated temperatures, and the use of fuming sulfuric acid as catalyst.[3c]

It was therefore noteworthy to observe in this laboratory that primary alcohols and glycols of the aralkyl type were condensed smoothly with nitriles under mild conditions to give *N*-aralklyamides and *N,N'*-bisaralkylamides in good yields. Thus, careful addition of benzyl alcohol to a large excess of acetonitrile containing substantial proportions of sulfuric acid resulted in a spontaneous reaction at 5–30° which afforded *N*-benzylacetamide[10] (Ia) in good yield. *N*-Benzylacrylamide[11] (Ib) was prepared from acrylonitrile, and, in similar manner, *N*-(4-methylbenzyl)acetamide[12] (II), *N*-(2,4-dimethylbenzyl)acetamide[13] (III), and *N*-(4-methoxybenzyl)acetamide[14] (IV) were prepared from the corresponding alcohols (Table I). The reaction was readily extended to glycols of the arenedimethanol type to produce several new difunctional amides. The reaction of 4,6-dimethyl-1,3-di(hydroxymethyl)-benzene with excess acetonitrile afforded *N,N'*-diacetyl-4,6-dimethyl-1,3-di(amino-



I

III

II

IV

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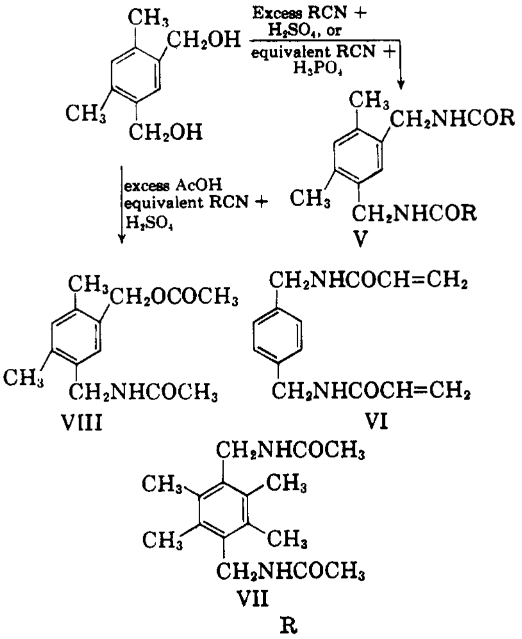
TABLE I

N-ARALKYLAMIDES FROM BENZYL-TYPE ALCOHOLS WITH NITRILES AND SULFURIC ACID

Compound	Formula	Yield, %	Melting Point °C.	Melting Point Lit., °C. (ref.)		Analyses C	Analyses H	Analyses N
Ia	$C_9H_{11}NO$	48	64.5–66.5	60–61[a]	Calcd.	72.45	7.43	9.40
				60.4–61.4[b]	Found	72.30	7.64	9.35
						72.52	7.64	
Ib	$C_{10}H_{11}NO$	50	70–72	69[c]	Calcd.	74.50	6.88	8.70
					Found	74.86	6.81	8.60
						74.69	6.84	
II	$C_{11}H_{15}NO$	40	110.5–111.5	109[d]	Calcd.	74.54	8.53	7.90
					Found	74.81	8.53	7.77
						74.90	8.55	
III	$C_{10}H_{13}NO$	87	111–112	106.5[e]	Calcd.	73.59	8.03	8.58
				107–108[f]	Found	73.61	7.70	8.76
						73.57	7.79	
IV	$C_{10}H_{13}NO_2$	60	94.5–96	96[g]	Calcd.	67.02	7.31	7.82
				97[h]	Found	67.30	7.16	7.68
						67.28	7.09	

[a] Ref. (10) (c). [b] Ref. (10) (d). [c] Ref. (11). [d] Ref. (13). [e] Ref. (12) (a). [f] Ref. (12) (b). [g] Ref. (14) (a). [h] Ref. (14) (b).

methyl)-benzene (Va) in 62% yield. A variation in technique consisted in treating the glycol with a slight molar excess of nitrile in a large volume of sirupy phosphoric acid. In similar manner the diamides Vb–e, VI, and VII were prepared from the corresponding glycols. The properties of these compounds are summarized in Table II.



R
a. CH_3
b. $CH_2{=}CH$
c. C_6H_5
d. $ClCH_2$
e. $ClCH_2CH_2$

When the reaction was carried out in the presence of acetic acid both alkylation and esterification occurred in some instances. Thus 2,4-dimethylbenzyl alcohol with acetonitrile in acetic and sulfuric acids afforded 28% of 2,4-dimethylbenzyl acetate together with 33% of the amide III. Under the same conditions 4,6-dimethyl-*m*-xylene-α,α'-diol afforded only an 8% yield of the diamide Va. The main product, melting at 114–115°, displayed both ester and monosubstituted amide bands in the infrared spectrum, and had the correct analysis for the mixed ester-amide VIII.

EXPERIMENTAL[15]

Benzyl alcohol and 4-methoxybenzyl alcohol were obtained from commercial sources and used without further purification. p-Xylene-α,α'-diol, m.p. 117.3–118.5°, was obtained from the Columbia-Southern Chemical Company. 2,3,5,6-Tetramethyl-p-xylene-α,α'-diol, m.p. 250–251°, was obtained from the Shell Development Company. 4-Methylbenzyl alcohol, m.p. 57.5–59°, was prepared from the corresponding bromide.[16] 2,4-Dimethylbenzyl alcohol, b.p. 108–110° (5 mm.) and 4,6-dimethyl-*m*-xylene-α,α'-diol, m.p. 152–154°, were prepared similarly from the corresponding chlorides.[17] Commercial acetonitrile and acrylonitrile were redistilled before use; other nitriles were not purified further.

Reactions in excess of nitrile. Preparation of N-benzylacrylamide (Ib). To 200 g. (3.8 mole) of freshly distilled acrylonitrile contained in a 1 l. three-necked flask equipped with a Hershberg stirrer, thermometer, and dropping funnel was added dropwise 75 ml. concentrated sulfuric acid at 0–10° over a period of 1 hr. A clean dropping funnel was substituted and then 108.0 g. (1 mole) benzyl alcohol was added slowly at the same temperature in 1 hr. After 2 hr. longer the yellow solution was allowed to warm slowly to 25–30°, then stirred for 2 days. The mixture was poured into ice water and the resulting oil was separated. The aqueous phase was extracted with three 200-ml. portions of ethyl acetate. The combined organic phases were washed successively with three 200-ml. portions of saturated salt solution, saturated sodium bicarbonate solution, and again with salt solution. The neutral extract was concentrated and the oily residue was distilled. The product was a light yellow

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[15] All melting and boiling points are uncorrected. Kjeldahl analyses by Dr. James B. Lear and staff of these laboratories. Infrared spectra by Miss Ruth M. Johnston. Carbon and hydrogen analyses by Galbraith Laboratories, Knoxville, Tenn.

[16] C. K. Ingold and E. Rothstein, *J. Chem. Soc.*, 1278 (1928).

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TABLE II

N,N'-Bisaralkylamides Prepared from Arenedimethanols and Nitriles

Nitrile, mol/mol of Glycol, Acid[a]	Product	Formula	Melting Point, °C.	Yield, %		Analyses		
						C	H	N
CH_3CN, 29/1, S	VII	$C_{18}H_{24}N_2O_2$	over 300	88	Calcd.	69.53	8.75	10.14
					Found	69.45	8.69	10.07
$CH_2{=}CHCN$, 23/1, S	VI	$C_{14}H_{16}N_2O_2$	polym. 230	65	Calcd.	68.83	6.60	11.47
					Found	68.93	6.44	11.25
						68.71	6.45	
CH_3CN, 30/1, S	Va	$C_{14}H_{20}N_2O_2$	245–246.5	62	Calcd.	67.71	8.12	11.28
					Found	67.70	8.01	11.16
						67.46	8.06	
CH_3CN, 1.1/1, P	Va		244–245.5	74				
$CH_2{=}CHCN$, 1.1/1, P	Vb	$C_{16}H_{20}N_2O_2$	polym. 250	98	Calcd.	70.56	7.40	10.29
					Found	70.79	7.50	10.32
						70.70	7.41	
C_6H_5CN, 1.1/1, P	Vc	$C_{24}H_{24}N_2O_2$	263.5–264.5	98	Calcd.	77.18	6.48	7.50
					Found	76.96	6.60	7.45
						77.17	6.55	
$ClCH_2CN$, 1.1/1, P	Vd	$C_{14}H_{18}Cl_2N_2O_2$	231–232	98	Calcd.	53.01	5.72	8.83
					Found	53.21	5.51	8.61
						53.39	5.60	
$ClCH_2CH_2CN$, 1.1/1, P	Ve	$C_{16}H_{22}Cl_2N_2O_2$	206 (dec.)	98	Calcd.	55.65	6.42	8.11
					Found	55.49	6.63	8.29
						55.45	6.62	

[a] S, concentrated sulfuric acid; P, sirupy phosphoric acid.

oil, b.p. 120–124° (0.02 mm.), that crystallized in the cold receiver. The yield of solid distillate was 97–99 g. (60–61%). The product was dissolved in a mixture of 50 ml. benzene and an equal volume of Skellysolve B on the steam bath. The solution was transferred quantitatively to a 500-ml. erlenmeyer flask with the aid of a little more benzene and was then concentrated to about two thirds of its volume. The product crystallized upon refrigeration. After filtration and drying there was recovered 95–98 g. of amide, m.p. 65–67.5°. The analytical sample melted at 70–72° after repeated recrystallization from benzene. The compounds reported in Table I were prepared in similar fashion from the corresponding alcohols and nitriles.

Preparation of N,N'-diacrylyl-1,4-di(aminomethyl)benzene (VI). To a cold solution of 75 ml. sulfuric acid in 600 g. (11.3 mole) acrylonitrile was added 69.0 g. (0.5 mole) *p*-xylene-α,α'-diol in small portions at 0–10°. After 2 hr. the temperature was allowed to rise slowly to 30° and the resulting two-phase mixture was then stirred overnight. The upper layer was decanted and discarded. The residue formed a voluminous precipitate upon neutralization with dilute ammonium hydroxide. After filtration and drying there was obtained 80 g. (64%) of diamide which polymerized at about 230°. The analytical sample was prepared by three recrystallizations from methanol. The diamides Va and VII were prepared similarly (Table II).

Reactions in 85% phosphoric acid. Preparation of N,N'-diacetyl-4,6-dimethyl-1,3-di(aminomethyl)benzene (Va). To a mixture of 16.6 g. (0.1 mole) of 4,6-dimethyl-*m*-xylene-α,α'-diol and 9.1 g. (0.22 mole) of acetonitrile was added 100 ml. sirupy phosphoric acid. The temperature was allowed to rise spontaneously to 55° accompanied by changes in color from pink to yellow. After 18 hr. the mixture was poured into ice water. The resulting granular solid was filtered, washed, and dried to give 19 g. (72%) of crude diamide, m.p. 225–240°. The analytical sample was prepared by three recrystallizations from methanol. In similar manner the diamides Vb–e (Table II) were prepared from the corresponding glycols and nitriles.

Reactions in acetic acid-sulfuric acid mixture. Reaction of 2,4-dimethylbenzyl alcohol. From the reaction of 13.6 g. (0.1 mole) of 2,4-dimethylbenzyl alcohol and 4.5 g. (0.11 mole) of acetonitrile in 175 ml. acetic acid with 5.5 ml. of sulfuric acid there were obtained two products. The first fraction consisted of 5.0 g. (28%) of colorless oil, b.p. 65–72° (0.1 mm.), n^{25}_{D} 1.5040, identified by the infrared spectrum as 2,4-dimethylbenzyl acetate. A fraction obtained at 130–140° (0.1 mm.) weighed 6.1 g. and solidified in the receiver. After recrystallization from a mixture of benzene and hexane the melting point was 112–113° and did not depress the melting point of *N*-(2,4-dimethylbenzyl)acetamide (III) prepared by the method of Nightingale and Shanholzer,[13] m.p. 110–112°.

Reaction of 4,6-dimethyl-1,3-di(hydroxymethyl)benzene. To a mixture of 16.6 g. (0.1 mole) of glycol and 9.1 g. (0.22 mole) of acetonitrile was added a cold solution of 15 ml. sulfuric acid in 175 ml. acetic acid with cooling below 30°. After 18 hr. at room temperature the mixture was treated with water and dilute ammonium hydroxide. The resulting oily semisolid weighed 18 g. and melted at 80–130°. Recrystallization from a mixture of benzene and hexane gave 2.0 g. of solid, m.p. 197–237°. The mother liquor was retained. A second recrystallization of the solid raised the melting point to 244–247°. By mixture melting point and infrared spectrum this fraction was shown to be the diacetyl derivative of 4,6-dimethyl-*m*-xylene-α,α'-diamine (Va) described above.

Concentration of the original mother liquors gave 10 g. of solid, m.p. 106–110°. Recrystallization from benzene, distillation, and another recrystallization from benzene-hexane raised the melting point to 114–115°. The infrared spectrum showed a typical strong ester band at 5.8 μ and the usual bands at 6.1 μ and 6.5 μ characteristic of a monosubstituted amide,[18] suggesting the structure to be the ester-amide VIII.

Anal. Calcd. for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.21, 67.20; H, 7.50, 7.60; N, 5.82.

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SPRINGDALE, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Consecutive Ortho Substitution Rearrangements Starting with 2- and 4-Substituted Benzyltrimethylammonium Ions[1]

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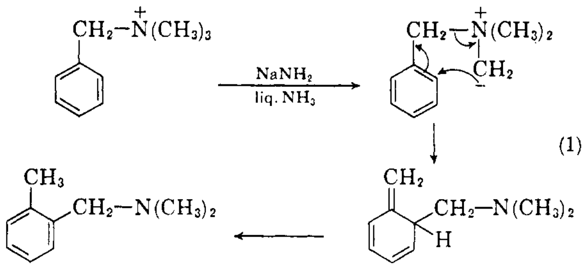
Ortho substitution rearrangements of 2-substituted benzyltrimethylammonium ions and of the methiodides of the products were found to take place not only when the substituent was methyl or ethyl as reported previously, but also when the substituent was methoxy or chlorine. Similar consecutive rearrangements were realized starting with 4-substituted benzyltrimethylammonium ions where the substituent was methyl, isopropyl, methoxy, or chlorine, but not when the substituent was cyano. The yields were generally good to excellent, but they were very low in the second rearrangement when the substituent was chlorine. The structures of the rearranged amines were established in several ways. These results extend considerably the usefulness of the ortho substitution rearrangement in synthesis. Infrared data for a number of benzyldimethylamines are presented.

It has previously been shown that the benzyltrimethylammonium ion undergoes the ortho substitution rearrangement with sodium amide in liquid ammonia to form 2-methylbenzyldimethylamine in 96% yield[3,4] The mechanism has been represented by Equation 1.[3] The methiodide of the product was further rearranged, and the process was repeated until the aromatic ring was completely substituted.[3]



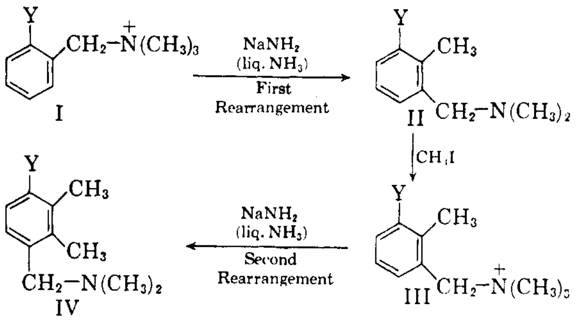
(1)

The α-methylbenzyltrimethylammonium ion also has been rearranged and the resulting 2-ethylbenzyldimethylamine rearranged through its methiodide.[5] This process was repeated once more.[5]

In the present investigation a study was made of the generality of this type of rearrangement starting with 2- and 4-substituted benzyltrimethylammonium ions.

Results with 2 - substituted benzyltrimethylammonium ions. The general reactions for two consecutive rearrangements starting with quaternary ammonium ions of this type may be represented by Scheme A.

Scheme A



Y = CH_3, C_2H_5, CH_3O, Cl

As indicated above, these two consecutive rearrangements have previously been observed when Y is methyl and ethyl. They have now been realized when Y is methoxy and chlorine. The yields, including those from the earlier examples for comparison, are summarized in Table I. The yields for the methylations of type II amines to form type III quaternary ions, which are not included in this table, were almost quantitative.

The structures of the two new amines IIc and IId from the first rearrangement in Scheme A were established by oxidations to known acids and anhydrides (Scheme B).

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(1) Supported in part by the National Science Foundation.

(2) Union Carbide Chemicals Co. Fellow, 1956–58.

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