temperature and added dropwise to the stirred *o*-nitrotoluene–sulfuric acid mixture during 6 minutes, while the temperature of the reaction mixture rose to about 70°. The reaction mixture was stirred an additional 16 minutes and then poured into 200 ml. of chipped ice and water. The precipitated crude dinitrotoluene was collected on a filter and dried; 2.51 g. To remove traces of occluded acids, it was dissolved in warm 95% ethanol and reprecipitated by the addition of excess cold 5% sulfuric acid solution; 2.48 g. (93%) of material was recovered, m.p. 45–50°. A 2.202-g. sample of this material was mixed with 2.024 g. of pure 2,3-dinitrotoluene, along with 8.4 g. of powdered iron and 7.1 ml. of 50% ethanol, and reduction was carried out by the addition of 0.8 ml. of concd. hydrochloric acid in 2.1 ml. of 50% ethanol, as described previously.[3] The toluenediamine sulfates were precipitated with 0.65 ml. of concd. sulfuric acid, collected on a filter and washed with ethanol; 4.21 g. (80%), m.p. 245–247°.

6-Methyl-1,2;3,4-dibenzophenazine was prepared by dissolving a 0.99-g. sample of the diamine sulfate in 48 ml. of a mixture of water and methanol (equal volumes) and adding this solution to a solution of 0.99 g. of *o*-phenanthrenequinone in 50 ml. of glacial acetic acid at 65°.[3] The crude phenazine which separated was, after cooling, collected on a filter, washed with methanol and dried; 0.93 g., m.p. 170–172°. One recrystallization from benzene (with *ca.* 40% loss of material) gave straw-colored crystals melting at 227–228°, and further recrystallization did not raise the m.p.

A sample of 6-methyl-1,2;3,4-dibenzophenazine prepared from pure 2,3-dinitrotoluene had the same properties.

Anal.[14] Calcd. for $C_{21}H_{14}N_2$: C, 85.69; H, 4.79; N, 9.52. Found: C, 85.62; H, 4.74; N, 9.56.

The phenazine from the isotope dilution experiment was radioassayed, recrystallized from benzene and reassayed. This was repeated until the radioassays were constant, within experimental error. The results are given in Table I.

Run 2.—The amounts of reactants are given in Table I. The sulfuric acid was divided between the *o*-nitrotoluene and the nitrating mixture as in run 1. The amount of nitric acid was 10% in excess of the theoretical; otherwise the experiment was identical to run 1. The yield of crude dinitrotoluenes was 96%. "Dilution," reduction and formation of the phenazine were carried out as before. Results of radioassays of the phenazine are given in Table I.

Run 3.—Amounts of reactants are given in Table I. Owing to the deficiency of nitric acid and, possibly, to the presence of additional water in this run, there was a considerable amount of unchanged *o*-nitrotoluene which had to be separated from the dinitrotoluenes. This was done by one recrystallization of the crude product from methanol. The recrystallized product, m.p. 42–50°, weighed 1.268 g.; the yield given in Table I is based on this material and ignores the unchanged *o*-nitrotoluene which was recovered from the fitrate. "Dilution" of the recrystallized product and further treatment were as in runs 1 and 2.

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AUSTIN 12, TEXAS

[CONTRIBUTION NO. 1033 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Phenylation of Ketones by Reaction with Phenyl Halides and Alkali Amides[1]

BY WILLIAM W. LEAKE[2] AND ROBERT LEVINE

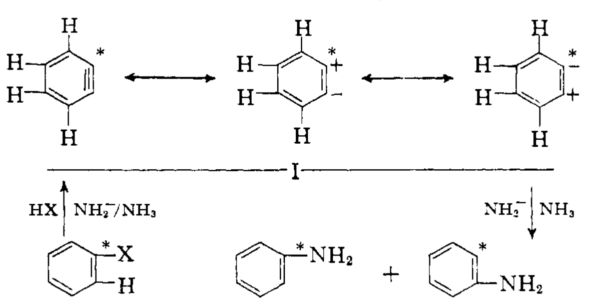
RECEIVED AUGUST 20, 1958

Four dialkyl ketones and one alkyl aryl ketone have been phenylated in fair to good yields by reaction with bromobenzene and excess sodium amide in liquid ammonia solution. In addition to the phenylated ketones, smaller amounts of aniline and diphenylamine are also formed. The products are believed to be formed from the addition of the ketone anions, amide ion and the anion of aniline to benzyne, the dehydrohalogenated derivative of bromobenzene.

In 1936, Bergstrom, *et al.*,[3] reported that the reactions of chloro-, bromo- and iodobenzene with excess potassium amide in liquid ammonia give mixtures of aniline, diphenylamine, triphenylamine and *p*-aminobiphenyl.

However, it was not until recently[4,5] that Roberts, *et al.*, elegantly demonstrated that the reactions of halobenzenes with alkali amides in liquid ammonia probably proceed by an elimination–addition mechanism which involves the transitory existence of an electrically neutral benzyne intermediate I. Thus, these workers found that the reactions of chloro- and iodobenzene-1-^{14}C gave essentially equal amounts of aniline-1-^{14}C and aniline-2-^{14}C.

Although alkali metal derivatives of ketones can be alkylated[6] by reaction with alkyl halides and acylated[7] by reaction with esters to give, respectively, high yields of the homologous ketones and β-diketones, the direct phenylation of these metallic derivatives by reaction with phenyl halides had apparently not been effected prior to the present study. Since the interaction of alkali amides with halobenzenes to give aniline (and its phenylated derivatives) may be regarded as involving the phenylation of the anion of ammonia, *i.e.*, amide ion, it was of interest to determine whether other anions, *e.g.*, ketone anions, could be phenylated.



Orienting experiments were performed with diethyl ketone. In Table I it may be seen that the interaction of the anion of this ketone (one equivalent), fluorobenzene (one equivalent) and one equivalent in excess of lithium or sodium amide (runs 1 and 2) gave only recovered starting materials.

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(1) For a preliminary communication on part of this work, see W. W. Leake and R. Levine, *Chemistry & Industry*, 1160 (1955).

(2) Monsanto Chemical Company Research Fellow.

(3) F. W. Bergstrom, R. E. Wright, C. Chandler and W. A. Gilkey, *J. Org. Chem.*, **1**, 170 (1936).

(4) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughan, THIS JOURNAL, **75**, 3290 (1953).

(5) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, **78**, 601 (1956).

(6) For pertinent references, see R. Levine and W. C. Fernelius, *Chem. Revs.*, **54**, 498 (1954).

(7) R. Levine and W. C. Fernelius, *ibid.*, pp. 490–497.

TABLE I

REACTIONS OF DIETHYL KETONE WITH HALOBENZENES AND ALKALI AMIDES

Run	Moles of reactants: MNH_2, M =	Moles of reactants: Ketone	Moles of reactants: C_6H_5X X =	Reacn. time, min.	Recovd., %, C_6H_5X	Yield of products, %: Phenylated ketone	Yield of products, %: Aniline	Yield of products, %: Diphenylamine
1	Li(0.4)[a]	0.2	F(0.2)	60	63	0	0	0
2	Na(0.4)[a]	.2	F(0.2)	60	60	0	0	0
3	Na(0.2)[b]	.2	Cl(0.2)	60	77	0	0	0
4	Na(0.2)[b]	.2	Br(0.2)	60	73	0	0	0
5	Na(0.4)[a]	.2	Cl(0.2)	60	58	26[c]	12	[d]
6	Na(0.8)[a]	.2	Cl(0.2)	60	7	25[c]	16	[d]
7	Na(0.8)[a]	.2	Cl(0.2)	10	0	54[c]	15	6
8	Na(0.4)[a]	.2	Br(0.2)	60	41	33[c]	9	[d]
9	Na(0.6)[a]	.2	Br(0.2)	60	3	43[c]	9	11
10	Na(0.6)[b]	.2	Br(0.2)	60	3	23[c]	15	22
11	Na(0.6)[a]	.2	Br(0.2)	10	30	46[c]	10	10
12	Na(0.8)[a]	.2	Br(0.2)	10	0	37[c]	16	11
13	Na(0.8)[a]	.4	Br(0.2)	10	0	62[c]	9	5

[a] This reaction was effected by the two-flask method. The ketone was converted to its anion by an equivalent of alkali amide. The mixture was stirred for 15 minutes. The halobenzene was added and then the excess alkali amide was siphoned into the reactor from a second flask. Finally, the reaction mixture was stirred for the period indicated in the column labeled "Reaction time." [b] This reaction was effected by the one-flask method, which is the same as the two-flask method except that all of the alkali amide is present in the reactor at the start of the reaction. [c] This is 2-phenyl-3-pentanone, b.p. 62–65° at 1.0 mm. (lit.[9] value 94–95° at 4.8 mm.); semicarbazone, m.p. 134.5–135.6° [J. Levy and P. Julien, *Bull. soc. chim.*, **45**, 941 (1929)]. [d] No attempt was made to isolate the diphenylamine.

That the ketone anion was not phenylated by fluorobenzene even in the presence of excess alkali amide is in agreement with the results of Bergstrom, *et al.*,[3] who found that fluorobenzene is not aminated in liquid ammonia by reaction with potassium amide. It may further be seen (runs 3 and 4) that from the interaction of equivalents of the ketone anion (prepared from equivalents of the ketone and sodium amide) and chloro- or bromobenzene again only the recovered halobenzenes and none of the phenylated derivative of the ketone were obtained. A number of experiments was then performed (runs 5–13) in which the ketone, chloro- or bromobenzene and excess sodium amide were allowed to react. It can be seen that the highest yield (62%, run 13) of the phenylated derivative of diethyl ketone, 2-phenyl-3-pentanone, was obtained by the interaction of bromobenzene (one equivalent), diethyl ketone (two equivalents) and sodium amide (four equivalents) by the two-flask method.[8]

From these results it is apparent that amide ion in excess of that which is needed to convert the ketone to its anion must be present in order to phenylate the ketone with chloro- or bromobenzene. If phenylation occurred by a simple displacement process, then equivalents of the ketone anion (prepared from equivalents of the ketone and alkali amide) and chloro- or bromobenzene should give phenylated product. However, the results of runs 3 and 4 indicate that phenylation does not occur under these conditions.

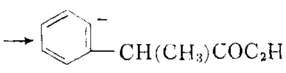
$$(C_2H_5COCHCH_3)^-Na^+ + C_6H_5Br \not\xrightarrow{NH_3} C_2H_5COCH(C_6H_5)CH_3 + NaBr$$

The fact that phenylation does occur when amide ion (from sodium amide) is present in excess of that which is necessary to produce the ketone anion (runs 5–13) may be rationalized by assuming that the excess base dehydrohalogenates the halobenzene to benzyne, II, to which the ketone anion adds as shown in the scheme

$$C_2H_5COC_2H_5 + NH_2^- \xrightarrow{NH_3} \underset{\text{II}}{(C_2H_5COCHCH_3)^-} + NH_3$$

$$C_6H_5X + NH_2^- \xrightarrow{NH_3} X^- + \text{I (benzyne)} + NH_3$$

I (benzyne) + II →



III

$$\text{III} \xrightarrow{NH_4Cl} C_2H_5COCH(C_6H_5)CH_3$$

X = Cl or Br

The formation of aniline and diphenylamine in runs 5–13 may also be explained as involving the addition of amide ion and the anion of aniline, respectively, to benzyne.[5]

It should be pointed out that apparently the anion of diethyl ketone II is not a sufficiently strong base to appreciably dehydrohalogenate a halobenzene to benzyne. Otherwise, the interaction of equivalents of the ketone, sodium amide and chloro- or bromobenzene (runs 3 and 4) should have given some phenylated ketone. However, this was not the case.

Several other ketones were also phenylated and the results are found in Table II. Acetone gave a 35% yield of methyl benzyl ketone and the best yield of 3-phenyl-4-heptanone, which was obtained by phenylating di-*n*-propyl ketone, was 56% of theory. It is interesting to note that the phenylation of di-*n*-propyl ketone using sodium amide as the base gave only a 35% yield of product. Since the sodium derivative of the ketone is very insoluble in liquid ammonia, the reaction was repeated using potassium amide to form the potassium derivative of the ketone. Then, bromobenzene was added and the reaction was completed by the addition of sodium amide. Under these conditions the higher yield (56%) of product was obtained.

Methyl ethyl ketone and methyl *n*-propyl ketone have been phenylated to give 3-phenyl-2-butanone and 3-phenyl-2-pentanone in yields of 75 and 65%, respectively. Apparently both ketones were phenylated exclusively at their methylene carbon atoms.

$$CH_3COCH_2CH_3 + C_6H_5Br \xrightarrow{NaNH_2/NH_3} CH_3COCH(C_6H_5)CH_3$$

$$CH_3COCH_2CH_2CH_3 + C_6H_5Br \xrightarrow{NaNH_2/NH_3} CH_3COCH(C_6H_5)CH_2CH_3$$

The structures of both products were established in the same way. Thus, that the product derived from methyl *n*-propyl ketone is indeed 3-phenyl-2-pentanone was shown by a mixed melting point determination between its semicarbazone (made in 98% yield) and that of an authentic sample. The authentic sample of the ketone[9] was prepared from

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(8) For the meaning of the term, two-flask method see footnote *a* of Table I.

(9) K. Mislow and C. L. Hamermesh, THIS JOURNAL, **77**, 1590 (1955).

the reaction of methyllithium and α-phenylbutyric acid.

TABLE II

THE PHENYLATION OF CERTAIN KETONES BY BROMOBENZENE AND SODIUM AMIDE[a]

Ketone	Yield of products, % Phenylated ketone	Aniline	Diphenylamine
CH_3COCH_3	$CH_3COCH_2C_6H_5$,[b] 35 B.p. 105–108° (23 mm.)[c]	18	4
$CH_3COC_2H_5$	$CH_3COCH(C_6H_5)CH_3$[d] 75 B.p. 55–58° (1.8 mm.)[e]	5	4
$CH_3COC_3H_7$-*n*	$CH_3COCH(C_6H_5)C_2H_5$[f] 65 B.p. 81–85 (4 mm.)[e]	9	5
$C_2H_5COC_2H_5$	$C_2H_5COCH(C_2H_5)CH_3$, 62 B.p. 62–65° (1.0 mm.)[g]	9	5
n-$C_3H_7COC_3H_7$-*n*	*n*-$C_3H_7COCH(C_6H_5)C_2H_5$, $35^{h,i}(56^{i,j})$ B.p. 87–90° (2 mm.)[e]	$18^{h}(15^{j})$	$14^{h}(6^{j})$
$CH_3COC_6H_5$	$C_6H_5CH_2COC_6H_5$, $28^{k}(14^{l})$ M.p. 55.4–56.4[m]	$4^{k}(10^{l})$	$0^{k}(0^{l})$

[a] In all runs, except where noted, the molar ratio of bromobenzene:ketone:sodium amide was 1:2:4, the two-flask method was used and a reaction time of 10 minutes was employed (see footnote *a* of Table I). [b] Semicarbazone, m.p. 185–185.8° [G. G. Smith, THIS JOURNAL, **75**, 1134 (1953)]. [c] R. M. Herbst and R. H. Manske, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 389. [d] Semicarbazone, m.p. 169.4–170.4° [A. Favorsky and A. Tchilingaren, *Compt. rend.*, **182**, 221 (1926)] alone and when mixed with an authentic sample (see ref. 9)]. [e] See ref. 9. [f] Semicarbazone, m.p. 189.4–190° (see ref. 11) alone and when mixed with an authentic sample. [g] See footnote *c* of Table I. [h] These yields were obtained using sodium amide. In addition 3% of triphenylamine was isolated. [i] Semicarbazone, m.p. 105.2–106° [J. Levy and P. Jullien, *Bull. soc. chim.*, **45**, 941 (1929)]. [j] These yields were obtained by converting the ketone (two equivalents) to its anion by potassium amide (two equivalents) followed by the addition of bromobenzene (one equivalent) and sodium amide (two equivalents). [k] The ketone formed a 2,4-dinitrophenylhydrazone, m.p. 202–203° alone and when mixed with an authentic sample. In addition 4% of benzanilide, m.p. 160–161.2° alone and when mixed with an authentic sample, was obtained. The benzanilide was further identified by hydrolysis to a mixture of benzoic acid, m.p. 120–121°, and aniline, b.p. 87–89° at 30 mm., N-benzoyl derivative, m.p. 160–161° alone and when mixed with an authentic sample. [l] These yields as well as 12% of benzanilide and 6.0% of phenyl benzlhydryl ketone, m.p. 135–135.8° alone and when mixed with an authentic sample (see ref. 13), were obtained from the reaction of a 1:2:2 molar ratio of chlorobenzene: acetophenone:sodium amide by the two-flask method. [m] C. F. H. Allen and W. E. Barker, note *c*, p. 156.

In Table II, it may also be seen that the phenylation of acetophenone with chloro- or bromobenzene gave all or some of the following products: desoxybenzoin, IV; phenyl benzhydryl ketone, V; aniline, VI; and benzanilide, VII.

$$\begin{array}{lll} CH_3COC_6H_5 \xrightarrow{NaNH_2/NH_3} & & \\ \quad + & C_6H_5CH_2COC_6H_5 + & (C_6H_5)_2CHCOC_6H_5 \\ C_6H_5X & \quad\text{IV} & \quad\quad\text{V} \\ & \quad + C_6H_5NH_2 + & C_6H_5CONHC_6H_5 \\ & \quad\quad\text{VI} & \quad\quad\text{VII} \\ & X = \text{Cl or Br} & \end{array}$$

While the origin of IV, V and VI may be readily explained *via* a benzyne intermediate, the source of the benzanilide (VII), is not clear at the present time. It was believed that the benzanilide might possibly have been formed by a number of routes such as: (1) the cleavage of desoxybenzoin (IV) by sodioaniline to give toluene and benzanilide (VII); (2) the cleavage of phenyl benzhydryl ketone (V) to give diphenylmethane and benzamide; or (3) the cleavage of phenyl trityl ketone (the triphenylated derivative of acetophenone) by sodium amide to give triphenylmethane and benzamide. If any benzamide were formed by routes 2 and/or 3, it might conceivably be phenylated to give benzanilide (VII).

Therefore, the following experiments were performed. From the reaction of desoxybenzoin with sodium amide or sodioaniline 92–95% of the ketone was recovered and neither benzamide nor benzanilide was isolated. The reaction of phenyl benzhydryl ketone with sodium amide gave a 91% recovery of the ketone and no cleavage products. It was also found that phenyl trityl ketone, on treatment with sodium amide in liquid ammonia, resulted in 38% recovery of the ketone and the formation of the cleavage products triphenylmethane (26%) and benzamide (34%).

However, it should be pointed out that no triphenylmethane was isolated from the phenylation of acetophenone by chloro- or bromobenzene. Furthermore, no benzanilide was obtained in the attempted phenylation of benzamide with bromobenzene in the presence of sodium amide. Instead, recovered benzamide (98.5%), aniline (18%), diphenylamine (30%) and triphenylamine (20%) were obtained. Therefore, for the present, the origin of the benzanilide in the reaction of acetophenone, chloro- or bromobenzene and sodium amide remains obscure.

This study is being extended to the phenylation of other active hydrogen compounds.

Experimental

Preparation of 3 Phenyl-2-pentanone by the Phenylation of Methyl *n*-Propyl Ketone Using the Two-flask Method.— Two batches (0.5 mole each) of sodium amide were prepared by the previously described[10] method. In flask A, a 2000-ml., three-neck, round-bottom flask, the sodium amide was present as a suspension in 750–800 ml. of anhydrous ammonia, and in flask B the alkali amide was contained in 350–400 ml. of ammonia. Methyl *n*-propyl ketone (0.5 mole, 43.0 g.) was added to flask A over a 15-minute period and then the mixture was stirred for an additional 15 minutes to ensure complete anion formation. Bromobenzene (0.25 mole, 39.3 g.) was added. The sodium amide suspension from flask B was siphoned into flask A over a period of 20–30 minutes and the mixture was stirred for an additional 10-minute period. The reaction was quenched by the addition of solid ammonium chloride (1.25 moles, 70.0 g.), 150 ml. of ether was added and the ammonia was removed by heating the reactor on a water-bath. More ether was added periodically and heating was continued until all the liquid ammonia had been removed and the ether began to reflux. The reaction mixture was poured onto crushed ice, was made strongly acidic with concentrated hydrochloric acid, was extracted with several portions of ether and the combined extracts (extract 1) were dried over anhydrous sodium sulfate. The residual aqueous phase was made basic with solid sodium carbonate, was extracted with several portions of ether and the combined extracts (extract 2) were dried over anhydrous sodium sulfate. Extract 1 was distilled to give 12.9 g. of recovered methyl *n*-propyl ketone, b.p. 34–38° at 41.0 mm., and 26.4 g. (65%) of 3-phenyl-2-pentanone, b.p. 81–85° at 4.0 mm.[9]; the semicarbazone,[11] m.p. 189.4–190° alone and when mixed with the semicarbazone of an authentic sample, prepared as described below, was obtained in 98% yield. The residue was dissolved in anhydrous ether and saturated with anhy-

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[10] R. Levine and C. R. Hauser, THIS JOURNAL, **66**, 1768 (1944).

[11] E. M. Schultz, J. B. Bicking, S. Mickey and F. S. Crossley, *ibid.*, **75**, 1072 (1953).

drous hydrogen chloride to give 1.2 g. (5.0%) of diphenylamine hydrochloride, m.p. 169–172° with decomposition; m.p. of the free base, 55–56° alone and when mixed with an authentic sample. Distillation of extract 2 gave 2.1 g. (9.0%) of aniline, b.p. 87–89° at 30 mm., N-benzoyl derivative, m.p. 160–161° (from 95% ethanol) alone and when mixed with an authentic sample.

In those reactions which were performed by the one-flask method all of the sodium amide was prepared in one flask and then the reactions were effected as described above.

Preparation of an Authentic Sample of 3-Phenyl-2-pentanone. (a) **Synthesis of α-Phenylbutyronitrile.**—Phenylacetonitrile (1.5 moles, 176.0 g.) was added over a period of 2.5 hours to sodium amide (1.5 moles) suspended in 1500 ml. of liquid ammonia. The ammonia was replaced by anhydrous ether. Then diethyl sulfate (1.5 moles, 231.5 g.) was added over a 2-hour period and the mixture was allowed to stand overnight. It was then poured onto ice and was extracted with several portions of ether. The combined extracts were dried over anhydrous sodium sulfate and distilled to give 37.6 g. of recovered phenylacetonitrile, b.p. 86–93° at 5.6 mm., and 152.5 g. (70.0%) of α-phenylbutyronitrile, b.p. 103–105° at 6.4 mm. (lit. value 88–93° at 5.0 mm.).[12]

(b) **Hydrolysis of α-Phenylbutyronitrile to α-Phenylbutyric Acid.**—The nitrile was hydrolyzed in 53.0% yield to α-phenylbutyric acid, b.p. 124–126.5° at 1.7 mm. (lit.[9] value 138° at 4 mm.) using the method described in the literature[9] for the hydrolysis of similar nitriles.

(c) **Conversion of α-Phenylbutyric Acid to 3-Phenyl-2-pentanone.**—α-Phenylbutyric acid (0.1 mole, 16.4 g.), dissolved in an equal volume of anhydrous ether, was added over a period of 1.5 hours to methyllithium (0.3 mole) in 300 ml. of anhydrous ether. The mixture was refluxed for 0.5 hour, poured onto ice, extracted with ether and the basic ether extracts discarded. The reaction mixture was then acidified with dilute hydrochloric acid and extracted with several portions of ether. The combined extracts were dried over anhydrous sodium sulfate and distilled to give 13.5 g. (83.0%) of 3-phenyl-2-pentanone, b.p. 81–85° at 4 mm.[9]; semicarbazone,[11] m.p. 188.8–189.8°.

Attempted Cleavage of Desoxybenzoin. (a) **By Sodioaniline.**—Desoxybenzoin (0.06 mole, 11.8 g.) was added as the solid to sodioaniline (0.12 mole), which was prepared from sodium amide (0.12 mole) and aniline (0.12 mole, 11.2 g.) in 300 ml. of liquid ammonia. The reaction mixture was stirred for 10 minutes and then processed in the regular manner to give 10.9 g. (92.0%) of recovered desoxybenzoin, m.p. 56.5–57.5°, and 9.3 g. (83.0%) of recovered aniline, b.p. 94–96° at 39.1 mm.; N-benzoyl derivative, m.p. 160–161° alone and when mixed with an authentic sample.

(b) **By Sodium Amide.**—When the last reaction was repeated except that desoxybenzoin (0.1 mole, 19.6 g.) was added to sodium amide (0.2 mole) in 400 ml. of liquid ammonia there was obtained 18.5 g. (94.5%) of recovered desoxybenzoin, m.p. 56.8–57.4°.

Attempted Cleavage of Phenyl Benzhydryl Ketone by Sodium Amide.—Phenyl benzhydryl ketone (0.02 mole, 5.4 g.), prepared by the method of Yost and Hauser,[13] was added to sodium amide (0.04 mole) in 300 ml. of liquid ammonia. The mixture was stirred for 25 minutes and processed to give 4.9 g. (91.0%) of recovered phenyl benzhydryl ketone, m.p. 135.0–135.8°.[13]

Cleavage of Phenyl Trityl Ketone by Sodium Amide.—Phenyl trityl ketone (0.017 mole, 6.0 g.) was added to sodium amide (0.035 mole) in 300 ml. of liquid ammonia. The mixture was stirred for 25 minutes and processed to give 2.3 g. (38.3%) of recovered phenyl trityl ketone, m.p. 177–178°[14]; 1.1 g. (25.8%) of triphenylmethane, m.p. 92.6–93.6° alone and when mixed with an authentic sample; and 0.7 g. (34.0%) of benzamide, m.p. 126–127.4° alone and when mixed with an authentic sample.

Attempted Phenylation of Benzamide with Bromobenzene.—Benzamide (0.5 mole, 60.6 g.) was added to sodium amide (0.5 mole) in 1000 ml. of liquid ammonia. The mixture was stirred for 15 minutes. Then, bromobenzene (0.25 mole, 39.3 g.) was added and stirring was continued for an additional 5 minutes. Finally, sodium amide (0.5 mole in 350 ml. of liquid ammonia) was siphoned into the mixture from a second flask, stirring was continued for an additional 10 minutes and then the reaction mixture was processed to give: 59.7 g. (98.5%) of recovered benzamide, m.p. 126–127°; 4.2 g. (18.0%) of aniline, b.p. 103–105° at 60.7 mm.; 6.3 g. (30.0%) of diphenylamine, m.p. 55–56° alone and when mixed with an authentic sample; and 4.1 g. (20.0%) of triphenylamine, m.p. 126–127° alone and when mixed with an authentic sample.

PITTSBURGH 13, PENNA.

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[12] J. V. Murray and J. B. Cloke, THIS JOURNAL, **68**, 126 (1946).

[13] R. S. Yost and C. R. Hauser, *ibid.*, **69**, 2325 (1947).

[14] W. E. Bachmann, *Org. Syntheses*, **14**, 12 (1934).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Epoxyethers. XVIII. Reactions of α-Hydroxyacylals with Amines

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An α-hydroxyacylal II was isolated in good yield from the reaction of 1,2-epoxy-1-methoxy-2-methylpropane with 9-fluorenecarboxylic acid. This α-hydroxyacylal II reacted with triethylamine and piperidine to give a β-hydroxy-γ-lactone IV, with cyclohexylamine to give a β-(N-cyclohexyl)-amino-γ-lactone VI, and with ammonia to give 9-fluorenecarboxylic acid amide. The β-hydroxy-γ-lactone IV could be converted to the β-(N-cyclohexyl)-amino-γ-lactone VI.

The reactions of organic acids with isobutyraldehyde epoxyether have been shown previously to give relatively stable α-hydroxyacylals. These acylals readily underwent O-to-O acyl migrations in the presence of triethylamine catalyst with the loss of alcohol to give esters of α-hydroxyisobutyraldehyde.[3] Since the acylals are potential acylating agents, the object of the present work was to investigate the reaction of an α-hydroxyacylal with ammonia, a primary and a secondary amine. An α-hydroxyacylal from 9-fluorenecarboxylic acid was chosen so that the various products would be crystalline and the results indicated that the acylal would acylate only ammonia. The primary amine was incorporated into the product VI and the secondary amine gave the same product as a tertiary amine. In this instance product IV was not an ester of an α-hydroxyaldehyde III, resulting from O→O acyl migration, but rather the result of an additional internal aldol reaction.

When 9-fluorenecarboxylic acid was allowed to react with the epoxyether from isobutyraldehyde I at 0°, a solid acylal II resulted in over 90% yield.

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[2] Abstracted from the dissertation submitted by Bradley L. Winch in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Wayne State University, 1958.

[3] C. L. Stevens and B. T. Gillis, THIS JOURNAL, **79**, 3448 (1957).