Anal. Calcd. for $C_{21}H_{22}N_2O_4S_2$: C, 58.6; H, 5.2; N, 6.5; S, 14.9. Found: C, 59.0; H, 5.3; N, 6.6; S, 15.0.

Hydrolysis of the dimethylsulfonamide with glacial acetic acid–concd. sulfuric acid gave a red oil which on distillation under nitrogen gave a 30% yield of N,N'-dimethyl-*o*-phenylenediamine as a colorless oil, b.p. 108.5–109° at 5 mm., $n^{25.5}$D 1.5914, m.p. 30.5–31°.

Anal. Calcd. for $C_8H_{12}N_2$: C, 70.5; H, 8.9; N, 20.6. Found: C, 70.6; H, 8.7; N, 20.5.

2-Pentylideneaniline.[27]—A mixture of 9.5 g. of freshly distilled aniline and 35 g. of methyl *n*-propyl ketone was refluxed in a nitrogen atmosphere in the usual apparatus[3] for four days during which 0.6 g. (33%) of water collected. The mixture was distilled under reduced pressure. After removal of excess ketone, unreacted aniline (4.0 g., 43%) and an intermediate fraction (2.5 g., b.p. 58–83° at 5 mm.), 3.5 g. (20%) of anil, b.p. 84° at 5 mm., $n^{25.5}$D 1.5190, d^{20}_4 0.939, was collected. It has a fishy odor and is readily hydrolyzed by dilute mineral acid.

Anal. Calcd. for $C_{11}H_{15}N$: C, 81.9; H, 9.4; N, 8.7. Found: C, 81.6; H, 9.4; N, 9.2, 9.0.

When toluene was used to aid in the removal of water, the yield was 30%.

The infrared spectrum shows a strong band at 6.1 μ which is not present in N-(2-pentyl)-aniline. There is no peak at 3.0 μ.

The anil (1.26 g.) absorbed the calculated amount of hydrogen over platinum oxide in alcohol solution at room temperature. The reduction product agreed in properties with the substance described below.

N-(2-Pentyl)-aniline.—Nitrobenzene (12.3 g.) and methyl *n*-propyl ketone (25.8 g.) was reduced in 10 ml. of glacial acetic acid and 150 ml. of 95% ethanol over platinum oxide at room temperature and 2 atm.[28] Distillation of the crude product under nitrogen after removal of the forerun gave 9.0 g. (55%) of the amine, b.p. 104.5–106.5° at 9 mm., 242° at atmospheric pressure, $n^{25.2}$D 1.523.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.9; H, 10.5; N, 8.6. Found: C, 80.7; H, 10.3; N, 8.6.

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[27] This anil is one of a series of aliphatic ketone anils reported by G. H. Reddelien [U. S. Patent 2,218,587; *C. A.*, **35**, 1065 (1941)] who used an excess of aniline in contrast to the procedure given here. He reported the b.p. of methyl-*n*-propylanil as 101° at 11 mm.

[28] W. S. Emerson and C. A. Uraneck, THIS JOURNAL, **63**, 749 (1941).

NEW YORK 27, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Reaction of 1-Methyl-2-(*t*-butyl)-benzimidazole with Organolithium Compounds[1]

BY ROBERT C. ELDERFIELD[2] AND VICTOR B. MEYER

RECEIVED DECEMBER 21, 1953

The reaction of 1-methyl-2-(*t*-butyl)-benzimidazole with methyllithium and with phenyllithium has been studied. The former reaction took an abnormal course and the product of the second reaction was unexpectedly labile to dilute acid.

When 2,2-dialkylbenzimidazolines or 1-methyl-2,2-dialkylbenzimidazolines are heated one of the substituents at the 2-position is lost in combination with the hydrogen at the 3-position as hydrocarbon[3] and a mechanism involving loss of the 2-substituent as an anion has been suggested.[3,4]

It was hoped that observation of the behavior of the products of addition of organolithium compounds to suitable 2-substituted benzimidazoles might provide additional evidence bearing on the suggested mechanism of the elimination reaction. If the postulated mechanism be correct the organolithium adduct may be considered analogous to the salt of the benzimidazoline. Although the reaction of organolithium compounds with benzimidazoles has not been studied, comparable reactions with similar types of compounds containing the azomethine linkage are well known.[5] In view of the unexpected outcome of these studies we should like to record our experience with the reaction.

For the purpose at hand 1-methyl-2-(*t*-butyl)-benzimidazole (I) was chosen. This would not be expected to be amphoteric since a hydrogen is lacking at the 1-position; the absence of an α-hydrogen located in the 2-substituent would minimize competitive metalation reactions; finally, inasmuch as the *t*-butyl group should be eliminated more readily than other alkyl groups it would provide a direct test of whether the elimination reaction proceeds in accordance with the predicted course when, for example, methyllithium is the reagent. However, the reactions took a different course.

When an ether solution of I was added to excess methyllithium in ether at −5°, a white precipitate formed which did not dissolve on refluxing in either ether or benzene. It consisted of I and lithium iodide (from the preparation of the reagent) in a molar ratio of approximately 1:2. Since the filtrate from this solid contained 90% of the original methyllithium (by titration) it was obvious that formation of the insoluble complex removed most of the benzimidazole from solution and thereby effectively prevented it from reacting with the methyllithium.

When I was allowed to react with phenyllithium in ether again a white precipitate appeared. However, in this instance the precipitate dissolved after stirring for two hours at room temperature. After acid hydrolysis of the reaction mixture 15% each of N-methyl-*o*-phenylenediamine and trimethylacetophenone together with unreacted I was obtained. This indicated that phenyllithium had added slowly to the azomethine linkage of I but that the adduct was unstable in the presence of acid used in working up the product.

The anomalous results noted raise the questions of whether the benzimidazole azomethine linkage *per se* represents an exception to the generally observed course of reaction of other heterocycles containing a similar linkage with organolithium

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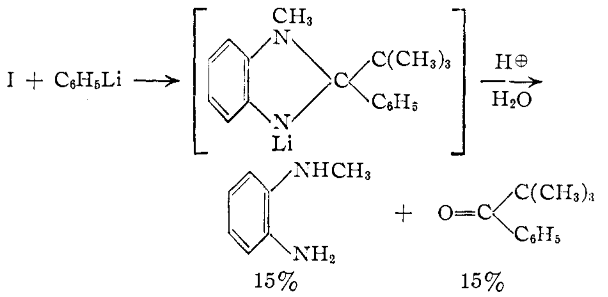
[1] The material here presented is taken from a dissertation submitted by Victor B. Meyer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Columbia University.

[2] University of Michigan, Ann Arbor, Michigan.

[3] R. C. Elderfield and J. R. McCarthy, THIS JOURNAL, **73**, 975 (1951).

[4] R. C. Elderfield and V. B. Meyer, *ibid.*, **76**, 1887 (1954).

[5] H. Gilman and J. A. Beel, *ibid.*, **71**, 2328 (1951), *inter alia*.



compounds or whether the *t*-butyl group is exhibiting an unpredicted effect. These reactions are under further investigation.

Experimental[6,7]

1-Methyl-2-(*t*-butyl)-benzimidazole (I).—N-Methyl-*o*-phenylenediamine was prepared in 48% over-all yield by heating a methanol solution of *o*-chloronitrobenzene and excess methylamine in a bomb for six hours at 150°[8] and catalytically reducing the *o*-nitro-N-methylaniline thus formed in ethanol over Raney nickel at 70° and 300 lb. pressure. The diamine was finally distilled under nitrogen through a 65-cm. helix-packed column; b.p. 123–124° at 10 mm., $n^{25.8}$D 1.6111, d^{25}_4 1.0749, m.p.'s, 7.5–7.9° and 21–23° (prisms, two crystalline forms); reported b.p. 136–139° at 16 mm.[3]

To a stirred solution of 92.5 g. (0.76 mole) of the above diamine in 400 ml. of dry pyridine under nitrogen 95 ml. (92 g., 0.76 mole) of trimethylacetyl chloride, b.p. 104.5–106°[9] was added dropwise over 50 minutes during which the temperature was held below 50° by external cooling. After warming on the steam-bath for one hour, the cooled mixture was poured into 3 l. of water. After addition of 250 ml. of 20% sodium hydroxide solution, the black oil which separated was extracted with ether. After washing with water and drying over anhydrous sodium sulfate the residue after removal of the ether was distilled under nitrogen yielding a forerun of unreacted diamine and 101 g. of higher-boiling pale yellow oil which was redistilled through a 20-cm. helix-packed column. The forerun, 7 g., b.p. 67–87° at 0.1 mm., n^{25}D 1.587, was largely diamine. The next fraction, 10.5 g., b.p. 87–88° at 0.1 mm., $n^{25.3}$D 1.5669, was also rejected. The final fraction, b.p. 88–89° at 0.1 mm., $n^{25.3}$D 1.5654, d^{25}_4 1.0360, was nearly water-white and weighed 71.5 g. (50%). The benzimidazole crystallized readily as square deliquescent plates, m.p. 38–39.5°.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 76.5; H, 8.6; N, 14.9. Found: C, 76.3; H, 8.7; N, 14.5.

A picrate prepared from equimolar amounts of picric acid and the benzimidazole in ethanol formed yellow needles, m.p. 178–179°.

Anal. Calcd. for $C_{18}H_{19}N_5O_7$: C, 51.8; H, 4.6; N, 16.8. Found: C, 51.9; H, 4.6; N, 16.7.

A second **picrate** was obtained when more than two moles of picric acid was used. It formed yellow hexagonal plates, m.p. 178–179°. The m.p. was depressed on admixture with the first picrate. The analytical data correspond best to a compound consisting of three picric acid and two benzimidazole molecules.

Anal. Calcd. for $C_{42}H_{41}N_{13}O_{21}$: C, 47.4; H, 3.9; N, 17.1. Found: C, 47.8; H, 3.9; N, 16.9.

A 3,5-dinitrobenzoate which formed white crystals, m.p. 166.5–167.5°, from acetone was obtained from equimolar quantities of the benzimidazole and 3,5-dinitrobenzoic acid in ethanol.

Anal. Calcd. for $C_{19}H_{20}N_4O_6$: C, 57.0; H, 5.0; N, 14.0. Found: C, 56.9; H, 5.1; N, 14.1.

What appeared to be a molecular compound of the above 3,5-dinitrobenzoate and 3,5-dinitrobenzoic acid was formed when more than two moles of the acid was used. It formed white crystals, m.p. 158–159°, from acetone.

Anal. Calcd. for $C_{26}H_{24}N_6O_{12}$: C, 51.0; H, 3.9; N, 13.7. Found: C, 51.4; H, 3.8; N, 13.9.

A picrylsulfonate, m.p. 213.5–214° from acetone, was obtained from the benzimidazole and excess picrylsulfonic acid in ethanol.

Anal. Calcd. for $C_{18}H_{19}N_5O_9S$: C, 44.9; H, 4.0; N, 14.6; S, 6.7. Found: C, 44.8; H, 4.1; N, 14.7; S, 6.3.

When the trimethylacetyl chloride was added to the pyridine solution of the diamine at room temperature and the mixture was poured into water, a white crystalline monoamide separated in 52% yield. It was readily soluble in cold, dilute hydrochloric acid and formed white needles, m.p. 141.5–142.5°, from benzene.

Anal. Calcd. for $C_{12}H_{18}N_2O$: C, 69.9; H, 8.8; N, 13.6. Found: C, 69.8; H, 8.7; N, 13.8.

Treatment of the amide with nitrous acid followed by an alkaline solution of β-naphthol did not give a dye. Rather the nitrous acid quantitatively precipitated white crystals, m.p. 102–103.5°, which were not investigated further. We conclude that the primary amino group of the diamine was acylated.

The amide hydrochloride (neut. equiv. calcd., 243; found, 241) was formed when dry hydrogen chloride was passed into an ethereal solution of the amide. It melts with ebullition at about 130° and then resolidifies to form the benzimidazole hydrochloride, m.p. 230–233° dec., (neut. equiv. calcd., 225; found, 225).

Action of Methyllithium on 1-Methyl-2-(*t*-butyl)-benzimidazole.—Into a 100-ml. three-necked Morton flask[10] equipped with a thermometer, mechanical stirrer and addition funnel was placed a freshly prepared solution (62 ml.) of methyllithium in absolute ether[11] containing 0.055 mole of methyllithium (determined by titrating an aliquot with standard acid against phenolphthalein). Under a nitrogen atmosphere and at a temperature of −5° (ice-salt-bath) a solution of 5.2 g. (0.028 mole) of the benzimidazole in 15 ml. of absolute ether was added dropwise over 20 minutes. An insoluble white solid separated. After cooling and stirring for an additional 20 minutes the suspension was filtered under nitrogen pressure through a sintered glass stick and the solid was washed with two 25-ml. portions of ether. The filtrate contained 0.050 mole (90% of the amount used) of methyllithium by titration. The white powder (7.5 g.) melted to a dark red liquid at 250–254°. It gave a positive test for iodide ion with alcoholic silver nitrate and the ash remaining on ignition gave the characteristic crimson flame test for lithium. When suspended in water a viscous yellow oil separated which showed $n^{25.7}$D 1.5626 after extraction with ether and removal of the solvent. The oil was identified as **1-methyl-2-(*t*-butyl)-benzimidazole** by m.p.'s and mixed m.p.'s of its picrate, 3,5-dinitrobenzoate and picrylsulfonate. The somewhat impure oil comprised between 43 and 46% of the weight of the powder; calcd. for a compound of two molecules of lithium iodide and one molecule of the benzimidazole, 41.3%.

In a second experiment, the thermometer was replaced by a reflux condenser and, after addition of the benzimidazole, the mixture was refluxed for 16 hours with no apparent reaction. The ether was replaced with 50 ml. of dry benzene and, after refluxing the suspension for five hours, hydrolysis gave quantitative recovery of the starting benzimidazole.

Reaction of 1-Methyl-2-(*t*-butyl)-benzimidazole with Phenyllithium.—Into a 200-ml. three-necked Morton flask[10] equipped with a reflux condenser, mechanical stirrer and addition funnel was placed a freshly prepared solution (72 ml.) of phenyllithium in absolute ether[11] containing 0.084 mole of reagent. Under a nitrogen atmosphere a solution of 7.85 g. (0.042 mole) of the benzimidazole in 25 ml. of absolute ether was added dropwise over ten minutes at room temperature. A white crystalline solid separated from the orange solution during the addition. On continual stirring the precipitate slowly dissolved and after two hours the reaction mixture was a clear, wine-red solution. After stirring for another hour, the cooled reaction mixture was hydrolyzed by dropwise addition of 20 ml. of water. The clear layers were separated, the aqueous layer was extracted with two 10-ml. portions of ether. After washing the com-

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[6] All melting points and boiling points are corrected.

[7] Microanalyses by Schwarzkopf Microanalytical Laboratory, Middle Village 79, New York.

[8] J. J. Blanksma, *Rec. trav. chim.*, **21**, 269 (1902).

[9] H. C. Brown, THIS JOURNAL, **60**, 1325 (1938).

[10] A. A. Morton, *Ind. Eng. Chem., Anal. Ed.*, **11**, 170 (1939).

[11] H. Gilman, E. A. Zoellner and W. M. Selby, THIS JOURNAL, **55**, 1252 (1933).

bined ether solution and extracts with water and drying over anhydrous sodium sulfate, removal of the solvent left 10 g. of light orange oil. This was treated with 40 ml. of 5% hydrochloric acid in which it partially dissolved. After standing for two hours the mixture was extracted with ether which yielded 2.0 g. of a brown oil from which 1.05 g. (15%) of nearly pure trimethylacetophenone was isolated by use of Girard Reagent "T."[12] The recovered redistilled ketone was a colorless oil, b.p. 219–223°, $n^{26}\text{D}$ 1.5058; reported b.p. 219–221°, $n^{19.2}\text{D}$ 1.5086. The 2,4-dinitrophenylhydrazone melted at 192.5–193.5° (reported 194–195°[13]), the oxime melted at 164.5–165° (reported 165°[14]), and the semicarbazone melted at 160–160.5° (reported 159°[15]).

When the acidic aqueous solution from the above ether extraction was made basic 6.1 g. of red oil separated. On distillation this gave 0.80 g. (15%) of N-methyl-*o*-phenylenediamine along with unreacted benzimidazole. The diamine was identified by conversion to 1,2-dimethylbenzimidazole with acetic anhydride. The m.p. and mixture m.p. with a known sample was 111–112°.[16]

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[12] A. Girard and G. Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

[13] J. H. Ford, C. D. Thompson and C. S. Marvel, THIS JOURNAL, **57**, 2619 (1935).

[14] J. U. Nef, *Ann.*, **310**, 316 (1899).

[15] P. Lucas, *Compt. rend.*, **152**, 1771 (1911).

[16] M. A. Phillips, *J. Chem. Soc.*, 2820 (1929).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reductive Coupling and Polymerization of Unsaturated Amides. II. Effect of Substituents[1]

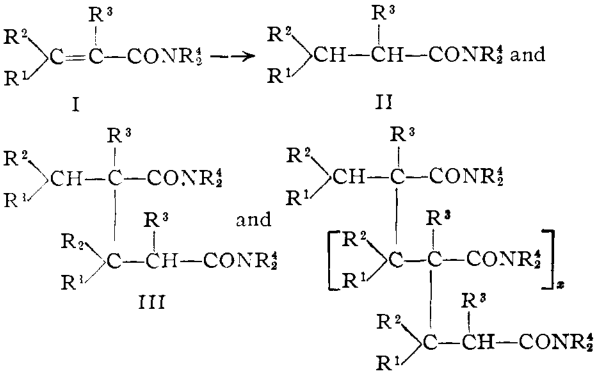
BY H. R. SNYDER AND ROBERT E. PUTNAM[2]

RECEIVED OCTOBER 24, 1953

The reduction of a series of N,N-disubstituted *α,β*-unsaturated amides with lithium aluminum hydride has been investigated. In nearly every case the major product was formed by reaction at the carbon–carbon double bond. However, the nature of this product depended on the sizes of the substituent groups. A mechanism to account for observed differences in reaction course has been postulated. Evidence for a stereospecific formation of reductively coupled products from N,N-diethylcinnamamide, N,N-diethylcrotonamide, N-methyl-N-phenylcinnamamide and cinnamic piperidide was obtained.

In the preceding paper[1] the reduction of N,N-diethylcrotonamide with lithium aluminum hydride was reported. Inverse addition of the hydride was shown to give a mixture of reductively coupled amide, N,N,N′,N′-tetraethyl-*α*-ethyl-*β*-methylglutaramide, a polymer of N,N-diethylcrotonamide and several amines. The relative amounts of these products could be controlled within limits by variation of the quantity of hydride added. Investigation of the behavior of a series of substituted acrylamides in the presence of lithium aluminum hydride now has been completed. The results indicate that the nature of the major product in each case is strongly dependent on the size of the substituent groups.

All of the successful reductions led to a major product of one of three types (II, III, IV). That the sizes of R^1, R^2 and R^3 in the *α,β*-unsaturated amide I should influence the course of the reaction is not at all surprising. However, the observation that the nature of R^4 is perhaps even more critical was not anticipated. It will be shown that effects of both types can be explained satisfactorily by consideration of the steric requirements of the groups involved.



I

II

III

IV ($x > 0$)

Table I lists the yields of the saturated amide II, the dimeric amide III and the polymer IV obtained when R^1, R^2 and R^3 are varied in size through the series R = hydrogen, methyl, *α*-furyl and phenyl, while R^4 is maintained constant at ethyl. A consideration of these data shows the strong dependence of reaction product type on the nature of the substituent group. Thus as the size of R^1 is increased ($R^2 = R^3 = $ H) the degree of polymerization decreases. N,N-Diethylacrylamide (V) gives a high molecular weight polymer in nearly 100% yield. N,N-Diethylcrotonamide (VI) yields an

TABLE I

REDUCTIVE COUPLING OF SOME UNSATURATED DIETHYL AMIDES BY LITHIUM ALUMINUM HYDRIDE

Amide[a] structure	R^1	R^2	R^3	Molar ratio, hydride/amide	Yield,[b] % II	III	IV
V	H	H	H	0.25[c]	0	0	90–100
VI	CH_3	H	H	.19[d]	0	29.3	37
				.5[d]	0	10.6	17.7
VII	CH_3	CH_3	H	.26	47	12	0
VIII	CH_3	H	CH_3	.31	0	0	0
IX	*α*-C_4H_3O	H	H	.5	0	43–53	0
X	C_6H_5	H	H	.56	0	45–53	0

[a] For the significance of R^1 and R^2, etc., see accompanying equation. [b] For the significance of the Roman numerals, see accompanying equation. [c] This figure is based on the amount of hydride placed in the extractor thimble. Because of the rapidity of the polymerization the solution soon became very viscous and the reaction was stopped at about one-sixth of the usual reaction time; undoubtedly extraction of the hydride into the reaction solution was incomplete. [d] For results at other molar ratios see ref. 1.

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[1] For the preceding paper in this series see H. R. Snyder and Robert E. Putnam, THIS JOURNAL, **76**, 31 (1954).

[2] National Science Foundation Fellow, 1952-1953.