m.p. 220–221°, no depression on admixture with authentic material. Acidification of the aqueous liquor furnished 1 g., m.p. 191–200°. Recrystallization of this second crop from acetic acid gave another 0.3 g. of 5-carbamoyl-1,3-dimethylbarbituric acid for a total yield of 73.5%.

The aqueous solution was concentrated to dryness and the residue suspended in acetone. The acetone-insoluble material was recrystallized from ethanol to furnish 0.2 g. of recovered 1,1-dimethylurea. The acetone liquor was concentrated. The residue furnished 0.3 g. (6.5%) of 1,3-dimethylbarbituric acid on recrystallization from benzene.

Fusion of 1,3 - dimethylbarbituric acid with biuret. A powdered mixture of 3.9 g. (0.025 mole) of 1,3-dimethylbarbituric acid and 3.09 g. (0.03 mole) of biuret was heated at 220° for 5 min. The vigorous reaction stopped after 4.5 min. of heating. The reaction mixture was suspended in 60 ml. of boiling glacial acetic acid and a little insoluble material removed with the aid of charcoal. The liquor was diluted to 300 ml. of water and cooled to furnish a white solid which was collected and recrystallized from 80 ml. of isopropyl alcohol to furnish 4.1 g. (83%) of 5-carbamoyl-1,3-dimethylbarbituric acid, m.p. 219–221°. The infrared spectra of this product and of material prepared by the reaction of urea with 1,3-dimethylbarbituric acid were identical. There was no depression in a mixed melting point determination.

Attempted reaction of tetramethylurea with 1,3-dimethylbarbituric acid. A solution of 3.9 g. (0.025 mole) of 1,3-dimethylbarbituric acid in 6.5 g. (0.05 mole) of tetramethylurea[15] was heated at 220–230° for 15 min. The internal reaction temperature was 200–205°. No apparent reaction occurred and the cooled mixture was dissolved in 50 ml. of hot benzene. Cooling gave 3.6 g. (92%) of unchanged 1,3-dimethylbarbituric acid.

Acknowledgment. The author is grateful to Dr. Richard T. Arnold for his suggestions regarding the mechanism proposed.

EVANSVILLE 21, IND.

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(15) W. Michler and C. Escherich, *Ber.*, 12, 1164 (1879). A sample of intermediate dimethylcarbamoyl chloride was supplied by the Ott Chemical Co., Muskegon, Mich.

[CONTRIBUTION FROM THE DEPARTMENT OF SYNTHETIC ORGANIC CHEMISTRY, MEAD JOHNSON RESEARCH CENTER, MEAD JOHNSON AND CO.]

The Reaction of Urea with Cyclic 1,3-Dicarbonyl and Other Active Hydrogen Compounds

HOMER C. SCARBOROUGH AND WILLIAM A. GOULD

Received March 1, 1961

A number of 2-carbamoyl cyclic 1,3-dicarbonyl compounds have been prepared by the reaction of urea and cyclic 1,3-dicarbonyl compounds. Other active methylene compounds failed to give simple carbamoyl derivatives.

The thermal reactions of some cyclic 1,3-dicarbonyl compounds with urea to form their 2-carbamoyl derivatives has been reported.[1] This work has been extended and some additional examples of the reaction are given. Urea was also heated with other active hydrogen compounds in an effort to prepare carbamoyl derivatives. While reactions did occur, simple carbamoyl derivatives could only be obtained from cyclic 1,3-dicarbonyl compounds.

The 2-carbamoyl cyclic 1,3-dicarbonyl compounds of Table I were prepared by heating one equivalent of the dicarbonyl compound with 1.5 to 2 equivalents of urea, either by simple fusion (Method F) or by refluxing in a suitable solvent (Method S).

In general, the fusion method was employed for those reactants giving a homogeneous melt at 132–150°. Fusion times varied from two to thirty minutes. Time-temperature relationships were determined experimentally for each reaction, but as a rule the lowest temperature yielding a homogeneous melt and evidence of interaction as determined visually and by evolution of acrid or ammoniacal gas was employed. The appearance of a precipitate when a sample in methanol was treated with methanolic cupric acetate was also useful in determining initiation of reaction.

The solvent method was generally used for those high melting 1,3-dicarbonyl compounds which did not give a homogeneous melt at fusion temperatures. The use of a solvent was preferred if the 1,3-dicarbonyl compound and formed product were stable to heat during the longer reaction time employed. The reaction time varied from one to twenty-four hours depending on the solvent, but was typically one to four hours using chlorobenzene as solvent. The solvents employed are given in Table I, chlorobenzene being particularly useful because of its solvent ability for urea and the 1,3-dicarbonyl compound at its boiling point which was sufficiently high to effect reaction. 1-Methyl-2-pyrrolidone could be employed for highly insoluble materials.

There appear to be two principal restrictions on the introduction of a carbamoyl moiety by this method. Since the reaction is run at elevated temperatures, thermal instability of the starting 1,3-dicarbonyl compound or of the formed carbamoyl compound is a serious preparative hindrance. Thus, 1,3-indandione gave anhydrobisdiketohydrinden when heated with urea, the latter also

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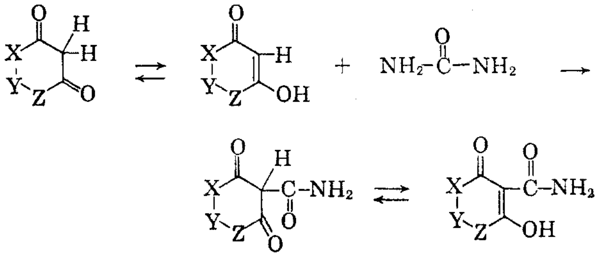
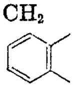
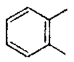
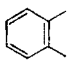
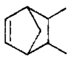
(1) H. C. Scarborough, *J. Org. Chem.*, 26, 2579 (1961).

TABLE I

CYCLIC 2-CARBAMOYL-1,3-DICARBONYL COMPOUNDS PREPARED BY THE REACTION OF UREA WITH 2-UNSUBSTITUTED CYCLIC 1,3-DICARBONYL COMPOUNDS



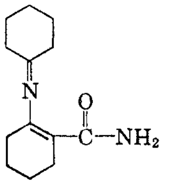
Compound	X	Y	Z	Method[a]	Yield, %[b]
I	CH_3N	C=O	CH_3N	F(135°)	70
II	NH	C=O	NH	S-4(145°)	96
III	CH—	CH_3C—	O	F(140°)	7
IV[c]	CH_2	$(CH_3)_2C$	CH_2	F(137°)	30
				S-1	20.5(36)
				S-5(135°)	19(14)
V	CH_2	C_6H_5CH	CH_2	F(140°)	20
VI[c]	C_6H_5N	NH	—	F(150°)	23
				S-2	18
VII[c]	C_6H_5N	C_6H_5N	—	F(145°)	59
VIII	CH_2	CH_2	—	F(143°)	[d]
IX	X + Y = 		O	F(145°)	45(54)
X	X + Y = 		S	S-2	47.5(28)
XI	X + Y = 		CH_3N	S-3	37.5(58)
XII	X + Y = 		—	F(132°)	9

[a] F, prepared by fusion of 1,3-dicarbonyl compound with urea (temperature). S, reaction using solvent: S-1, water (reflux); S-2, chlorobenzene (reflux); S-3, chlorobenzene plus 1-methyl-2-pyrrolidone (reflux); S-4, 1-methyl-2-pyrrolidone (temperature); S-5, dimethylformamide (temperature). [b] Yields are of pure material and could probably be improved in most instances (% starting material recovered). [c] Preparation of these compounds by this method are reported in ref. 1. [d] Characterized as the copper salt.

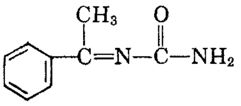
being formed[2] when 1,3-indandione is warmed with water. The desired 2-carbamoyl-1,3-indandione has been prepared[3] by another method. The other principal failure was with compounds containing functional groups in addition to the 1,3-dicarbonyl system. The reaction of cyclopentene-3,5-dione[4] with urea gave a polymeric material apparently similar to that reported[4] by treatment of cyclopentene-3,5-dione with traces of base. 2-Methyl-1,3,5-cyclopentanetrione[5] gave an ureido derivative when heated with urea.

The possible significance of failure of reaction with 2-methyl-1,3-cyclopentanedione, 2,5,5-trimethyl-1,3-cyclohexanedione and 1,3,5-trimethylbarbituric acid will be discussed in a separate publication.[6]

When cyclohexanone and urea were heated at 140° for one hour there was obtained an 81% yield of product melting at 200–202° and with analysis corresponding to $C_{13}H_{20}N_2O$. The same product was obtained in 82% yield from the reaction of 1-morpholinocyclohexane with urea. The identity of this product as cyclohexylidene 2-carbamoylcyclohex-1-enylamine, XIII, which has recently been reported in 28.5% yield by the reaction of cyclohexanone with urea in an alkaline medium[7] was suspected on the basis of the similarity of melting points (reported 224–225°, evacuated capillary) and infrared spectra. Confirmatory evidence was obtained by catalytical reduction of XIII to cyclohexyl 2-carbamoylcyclohexylamine.[7]



XIII



XIV

The reaction of urea with acetophenone furnished *N*-(α-methylbenzylidene)urea, XIV.[8]

Urea decomposed rapidly (as evidenced by boiling and gas evolution) when heated with benzenesulfonamide, but the latter was recovered unchanged in quantitative yield. Urea appeared to decompose when heated with phenol or resorcinol, but the alkali soluble portion of the reaction product contained no nitrogen.[9]

Succinimide furnishes an urea addition compound when heated with urea. Attempts to convert the addition compound to *N*-carbamoylsuccinimide by heat were unsuccessful. *N*-Carbamoylmaleimide and *N*-carbamoylsuccinimide have been reported by another method.[10] The former is reported to be hydrolytically and thermally unstable.[10]

No discrete products (such as materials giving precipitates with methanolic cupric acetate) could be isolated from the reactions of cyclopentanone, nitromethane, and 2-acetylcyclohexanone with urea.

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[2] W. Wislicenus and A. Kötzle, *Ann.*, **252**, 72 (1889); *J. Chem. Soc.*, Abstracts, **56**, 1067 (1889).

[3] R. L. Horton and K. C. Murdock, *J. Org. Chem.*, **25**, 938 (1960).

[4] C. H. De Puy and E. F. Zaweski, *J. Am. Chem. Soc.*, **81**, 4920 (1959).

[5] M. Orchin and L. W. Butz, *J. Am. Chem. Soc.*, **65**, 2296 (1943).

[6] H. C. Scarborough, *J. Org. Chem.*, **26**, 3717 (1961).

[7] A. F. McKay, E. J. Tarlton, and C. Podesva, *J. Org. Chem.*, **26**, 76 (1961).

[8] J. M. Das-Gupta, *J. Indian Chem. Soc.*, **10**, 111 (1933); *Chem. Abstr.*, **27**, 4218 (1933).

[9] K. Birnbaum and G. Lucie in *Ber.*, **13**, 1619 (1880), describe the fusion of urea with phenol in a retort at 250°. The complex product obtained ($C_{30}H_{32}N_{16}O_{14}$) does not melt at the boiling point of mercury.

[10] (a) P. O. Tawney *et al.*, *J. Org. Chem.*, **25**, 56 (1960). (b) R. H. Snyder, U. S. Pat. 2,788,349 (1957).

EXPERIMENTAL[11]

5-Carbamoyl-1,3-dimethylbarbituric acid (I). A mixture of 7.8 g. (0.05 mole) of 1,3-dimethylbarbituric acid[12] and 6 g. (0.1 mole) of urea was heated at 135° for 12 min. to furnish a solid reaction mass. The solid was dissolved in 75 ml. of glacial acetic acid and the solution diluted with water and chilled to furnish a white solid which was recrystallized from 150 ml. of 1-propanol. There was obtained 7 g. (70%), m.p. 218–221°. A pale blue solid was obtained with methanolic cupric acetate. $\lambda_{\max}^{0.1N\ \mathrm{NaOH}}$ 254 mμ (ϵ 18,500).

Anal. Calcd. for $C_7H_9N_3O_4$: C, 42.21; H, 4.55; N, 21.10. Found: C, 42.24; H, 4.71; N, 21.28.

5-Carbamoylbarbituric acid (II). A powdered mixture of 6.4 g. (0.05 mole) of barbituric acid and 6 g. (0.1 mole) of urea in 10 ml. of 1-methyl-2-pyrrolidone was heated at 145° for 10 min. The reaction mixture was leached with water and then with 125 ml. of hot dimethylformamide to furnish 8.2 g. (96%) of a white solid, melting point above 360°. A suspension in methanol was treated with methanolic cupric acetate to furnish a pale blue-green solid. $\lambda_{\max}^{0.1N\ \mathrm{NaOH}}$ 315 and 258 mμ (ϵ 2460 and 16,350).

Anal. Calcd. for $C_5H_5N_3O_4$: N, 24.56. Found: N, 24.66.

3-Carbamoyl-6-methylpyronone (III). A mixture of 6.3 g. (0.05 mole) of 6-pyronone[13] and 6.0 g. (0.1 mole) of urea was heated at 140° for 30 min. The gummy mass obtained upon cooling was triturated with aqueous methanol to yield a solid which was collected. The solid did not yield a precipitate with methanolic cupric acetate and was discarded. The aqueous methanol liquor was treated with methanolic cupric acetate to precipitate a brown solid which was separated by filtration with the aid of Celite. The solid materials were stirred with a mixture of 10% aqueous sulfuric acid and 100 ml. of ether at room temperature for 6 hr. The ethereal portion was separated and evaporated to dryness to furnish an orange residue which was recrystallized twice from 2-propanol to give 0.6 g. (7%), m.p. 207–209°.

Anal. Calcd. for $C_7H_7NO_4$: C, 49.71; H, 4.17; N, 8.28. Found: C, 50.17; H, 4.27; N, 8.64.

2-Carbamoyl-5,5-dimethyl-1,3-cyclohexanedione (IV). A solution of 5.6 g. (0.04 mole) of 5,5-dimethyl-1,3-cyclohexanedione and 3.15 g. (0.06 mole) of urea in 125 ml. of water was refluxed for 7 hr. Cooling gave 1.5 g. (20.5%), m.p. 141–145.5°, no depression with the product obtained by fusion.[1] Acidification of the reaction liquor (*p*H 8) with dilute hydrochloric acid gave a solid which was recrystallized from ethyl acetate to furnish 2 g. (36%) of unchanged 5,5-dimethyl-1,3-cyclohexanedione.

A solution of 14 g. (0.1 mole) of 5,5-dimethyl-1,3-cyclohexanedione and 12 g. (0.2 mole) of urea in 20 ml. of dimethylformamide was heated at 135° for 15 min. The reaction solution was cooled, diluted with 100 ml. of water, and acidified with dilute hydrochloric acid. The solution was diluted to 400 ml. with water and chilled to furnish an off-white solid which was recrystallized from methanol and from ethyl acetate to furnish 3.5 g. (19%) of the carbamoyl compound, m.p. 145–146°, no depression on admixture of melting point with product prepared by fusion. Further cooling of the aqueous-dimethylformamide liquor deposited 2 g. (14%) of starting 5,5-dimethyl-1,3-cyclohexanedione.

2-Carbamoyl-5-phenyl-1,3-cyclohexanedione (V). A mixture of 4.5 g. (0.025 mole) of 5-phenyl-1,3-cyclohexanedione[14] and 3.0 g. (0.05 mole) of urea was heated at 140° for 30 min. Upon cooling the solidified melt was recrystallized from 2-propanol and from methanol to furnish 1.0 g. (20%), m.p. 163–165°. A blue precipitate was obtained with methanolic cupric acetate. $\lambda_{\max}^{0.1N\ \mathrm{NaOH}}$ 274 mμ (ϵ 18,800).

Anal. Calcd. for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.82; H, 5.89; N, 6.38.

2-Carbamoylcyclopentane-1,3-dione, copper salt (VIII). A powdered mixture of 92 mg. (0.94 mmole) of 1,3-cyclopentanedione[4,15,16] and 110 mg. (100% excess) of urea was heated at 143° for 2 min. (brisk reaction). The copper salt was obtained by the addition of methanolic cupric acetate to a solution of the reaction mixture in methanol. The salt decomposed to a black powder at 310°.

Anal. Calcd. for $C_6H_6NO_3\cdot 1/2Cu$: N, 8.15; Cu, 18.4. Found: N, 7.99; Cu, 17.9.

3-Carbamoyl-4-hydroxycoumarin (IX). A powdered mixture of 6.5 g. (0.04 mole) of 4-hydroxycoumarin and 4.8 g. (0.08 mole) of urea was heated at 140–145° for 20 min. The cooled melt was dissolved in 500 ml. of hot methanol, the solution treated with activated charcoal and then concentrated to 300 ml. Cooling furnished a white crystalline product which was recrystallized from ethyl acetate and from methanol to furnish 3.7 g. (45%), m.p. 215–216°. A precipitate was obtained with methanolic cupric acetate. $\lambda_{\max}^{0.1N\ \mathrm{NaOH}}$ 290 and 230 mμ (ϵ 16,000 and 24,750). Lit.[17] m.p. 219° by a total synthesis.

Anal. Calcd. for $C_{10}H_7NO_4$: N, 6.83. Found: N, 7.00.

3-Carbamoyl-4-hydroxy-1-thiacoumarin (X). A mixture of 3.55 g. (0.02 mole) of 4-hydroxy-1-thiacoumarin[18,19] and 1.8 g. (0.03 mole) of urea in 40 ml. of chlorobenzene was stirred under reflux for 6 hr., an additional 1.8 g. of urea being added after 2 hr. After standing overnight the solid was broken up and the entire reaction mixture shaken with ether and 150 ml. of dilute ammonium hydroxide. The insoluble material was collected and recrystallized from 50 ml. of glacial acetic acid to furnish 1.3 g., m.p. 185–191° dec. The aqueous phase was separated and the organic layer washed with dilute ammonium hydroxide. The combined aqueous solutions were washed with ether and acidified to *p*H 7.5 to precipitate a solid which was recrystallized from glacial acetic acid to furnish an off-white solid, m.p. 188–191°. The products obtained from glacial acetic acid were combined and recrystallized from ethanol to give 2.1 g. or 47.5% of white needles, m.p. 188–191°. $\lambda_{\max}^{0.1N\ \mathrm{NaOH}}$ 315 and 231 mμ (ϵ 13,500 and 33,200).

Anal. Calcd. for $C_{10}H_7NSO_3$: C, 54.30; H, 3.19; S, 14.49. Found: C, 54.33; H, 3.39; S, 14.64.

Acidification of the aqueous solution to *p*H 4 precipitated 1.0 g. or 28% of 4-hydroxy-1-thiacoumarin.

3-Carbamoyl-4-hydroxy-1-methyl-2-quinolone (XI). A mixture of 4.3 g. (0.0245 mole) of 4-hydroxy-1-methyl-2-quinolone[20] 2.2 g. (0.037 mole) of urea, 5 ml. of 1-methyl-2-pyrrolidone, and 40 ml. of chlorobenzene was stirred under reflux for a 8.5 hr., an additional 2.2 g. of urea being added after 4 hr. The mixture was diluted with ether and shaken with dilute ammonium hydroxide to precipitate an insoluble solid which was separated. The aqueous ammonium hydroxide layer was separated and acidified to *p*H 8 to precipitate a solid which was collected and combined with the first solid. Recrystallization from glacial acetic acid furnished 2 g., 37.5%, m.p. 209–211°. The melting point was unchanged upon recrystallization from acetonitrile. $\lambda_{\max}^{0.1N\ \mathrm{NaOH}}$ 300 and 225 mμ (ϵ 12,180 and 37,900).

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[11] All melting points are uncorrected. Microanalyses were determined by Spang Microanalytical Laboratory, Ann Arbor, Mich.

[12] H. Biltz and H. Wittek, *Ber.*, **54**, 1035 (1921).

[13] J. N. Collie, *J. Chem. Soc.*, **59**, 607 (1891).

[14] D. Vorländer, *Ber.*, **27**, 2053 (1894).

[15] J. H. Boothe *et al.*, *J. Am. Chem. Soc.*, **75**, 1732 (1953).

[16] C. H. De Puy and E. F. Zaweski, *J. Am. Chem. Soc.*, **79**, 3923 (1957).

[17] (a) C. Ukita and K. Arakawa, *Pharm. Bull.* (*Japan*), **1**, 255 (1953); *Chem. Abstr.*, **49**, 8269 (1955). (b) R. Anschütz, *Ann.*, **367**, 169; *Chem. Abstr.*, **3**, 2976 (1909).

[18] E. Ziegler and H. Janek, *Monatsh. Chem.*, **86**, 29 (1955).

[19] The authors are grateful to Mr. Joseph L. Minielli for preparation of these intermediates.

[20] R. E. Lutz *et al.*, *J. Am. Chem. Soc.*, **68**, 1810 (1946).

Anal. Calcd. for $C_{11}H_{10}N_2O_3$: C, 60.54; H, 4.62; N, 12.84. Found: C, 60.15; H, 4.62; N, 12.69.

The aqueous liquor was acidified to *p*H 3 to precipitate a solid which was collected, dried and extracted with chloroform to furnish 2.5 g. or 58% of recovered 4-hydroxy-1-methyl-2-quinolone.

2-Carbamoyl-4,7,8,9-tetrahydro-4,7-methyleneindane-1,3-dione (XII). A powdered mixture of 4.51 g. (0.0275 mole) of 4,7,8,9-tetrahydro-4,7-methyleneindane-1,3-dione[4] and 3.3 g. (0.055 mole) of urea was heated under nitrogen at 132–135° for 20 min. The melt was cooled and dissolved in 60 ml. of water. The orange solid which separated upon slow cooling was collected and dried. This portion (3.2 g.) did not give a precipitate with methanolic cupric acetate and was discarded. The aqueous liquor was acidified and chilled for 30 hr. to give 1 g. of separated solid, m.p. 132–144°. The product was suspended in 50 ml. of a solution of equal parts of benzene and heptane and the insoluble material removed with Norite activated charcoal. Dilution of the liquor with 100 ml. of *n*-heptane and strong chilling furnished needles which were recrystallized from 25 ml. of 30% aqueous methanol. There was obtained 0.5 g. (9%) of buff needles, m.p. 158–161°. The product gives a precipitate with methanolic cupric acetate. $\lambda_{\max}^{0.1N\ \mathrm{NaOH}}$ 256 mμ (ε 19,610); $\lambda_{\max}^{0.1N\ \mathrm{HCl\ in\ CH_3OH}}$ 251 mμ (ε 11,880).

Anal. Calcd. for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.94; H, 5.52; N, 6.71.

The intermediate cyclopentene-3,5-dione was readily obtained[19] as reported by DePuy[4] except that the crude material was conveniently purified by recrystallization from diisopropyl ether instead of by vacuum sublimation prior to reaction with cyclopentadiene.[21]

Ureido derivative of 2-methyl-1,3,5-cyclopentanetrione. A powdered mixture of 1.43 g. (0.01 mole) of 2-methyl-1,3,5-cyclopentanetrione[5] and 1.2 g. (0.02 mole) of urea was heated at 110–120° for 4 min. to furnish a clear red solution which solidified during the latter stages of heating. The mixture was recrystallized from water and from ethanol to furnish 1 g. (60%), m.p. 215°. $\lambda_{\max}^{0.1N\ \mathrm{NaOH}}$ 320 and 228 mμ (ε 9850 and 8310); $\lambda_{\max}^{0.1N\ \mathrm{HCl}}$ 290 mμ (ε 14,500).

Anal. Calcd. for $C_7H_5N_2O_3$: N, 16.66. Found: N, 16.51.

Cyclohexylidene 2-carbamoylcyclohex-1-enylamine (XIII). A mixture of 9.8 g. (0.1 mole) of cyclohexanone and 12.0 g. (0.2 mole) of urea was heated at 140° for 1 hr. The mixture which completely solidified upon cooling was recrystallized several times from aqueous methanol to furnish 8.9 g. (81%), m.p. 200–202°. Lit.[7]: m.p. 224–225° (evac. capil.). The same product was obtained by heating 8.4 g. (0.05 mole) of 1-(*N*-morpholino)cyclohexene[22] and 6 g. (0.1 mole) of urea in 20 ml. of 1-methyl-2-pyrrolidone at 140° for 30 min. The yield was 4.5 g. (82%).

Anal. Calcd. for $C_{13}H_{20}N_2O$: C, 70.87; H, 9.15; N, 12.72. Found: C, 71.13; H, 9.35; N, 12.97.

The product was characterized by reduction in ethanol containing hydrochloric acid to cyclohexyl-2-carbamoylcyclohexylamine hydrochloride, m.p. 270–273°. Lit.[7]: m.p. 276°. The addition of aqueous sodium hydroxide to a solution of the hydrochloride in water furnished the free base, m.p. 127°. Lit.[7] m.p. 128°.

N-(α-Methylbenzylidene)urea (XIV). This material was obtained from the reaction of 12 g. (0.1 mole) of acetophenone and 12 g. (0.1 mole) of urea as above, m.p. 175–179°. There was no precipitate with methanolic cupric acetate. Lit.[8]: m.p. 176.°

Succinimide-urea addition compound. A mixture of 9.9 g. (0.1 mole) of succinimide and 12 g. (0.2 mole) of urea was heated at 132–138° for 30 min. during which ammonia was evolved and a clear solution was obtained. The reaction product which solidified on cooling was recrystallized from methanol, extracted with cold water and finally recrystallized from methanol to furnish 10 g. (63%), m.p. 124–128°, good depression on admixture with urea.

Anal. Calcd. for $C_4H_5NO_2 \cdot CH_4NO$: N, 26.41. Found: N, 26.43.

Acknowledgment. The authors are indebted to Dr. Coy W. Waller and to Dr. Rolland F. Feldkamp for their suggestions during the course of this work.

EVANSVILLE 21, IND.

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(21) A generous sample of intermediate dicyclopentadiene was furnished by Enjay Co., Inc.

(22) S. Hunig, E. Benzing, and E. Lücke, *Ber.*, **90**, 2833 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Direct Preparation of Benzyllithium and α-Methylbenzyllithium in Tetrahydrofuran

HENRY GILMAN AND HERBERT A. McNINCH

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Benzyllithium has been prepared by the lithium cleavage of ethers of the type $C_6H_5CH_2OR$, where R is methyl, ethyl, phenyl, and benzyl. Benzyltriphenylsilane has also been cleaved by lithium. Bis(α-methylbenzyl) ether was cleaved to give α-methylbenzyllithium.

Benzyllithium has been prepared by a number of indirect methods.[1] In each instance, the organometallic compound had at least a transitory existence. However, these methods were not satis-

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