## The Condensation of Active Methylene Compounds with Hydroxybenzaldehydes by Ammonium Acetate

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Hydroxybenzaldehydes are condensed with active methylene compounds such as benzoylacetonitrile, ethyl cvanoacetate, and ethyl acetoacetate in the presence of ammonium acetate to give benzoquinazolines, dihydrobenzoquinazolines, and dihydrobenzoquinoline.

In previous papers, syntheses of various nitrogen-containing heterocyclic compounds by condensation of active methylene compounds such as ethyl cyanoacetate,<sup>1</sup> ethyl acetoacetate,<sup>2</sup> malononitrile,<sup>3</sup> and benzoylacetonitrile<sup>4</sup> with ketones in the presence of ammonium acetate were reported.

The present paper deals with syntheses of 10-oxa-5Hbenzo[g]quinazoline,6-oxadihydrobenzo[h]quinazoline, 6-oxadihydrobenzo [h]quinoline, 1,2-dihydropyridine, and pyridine derivatives by condensation of active methylene compounds with such substituted benzaldehydes, e.g., o- and p-hydroxybenzaldehydes, o- and p-methoxybenzaldehydes, 2-hydroxy-3-methoxybenzaldehyde, 5-nitrosalicylaldehyde, and 3,5-dibromosalicylaldehyde in the presence of ammonium acetate.

The reaction of benzoylacetonitrile with salicylaldehyde and C-substituted salicylaldehydes was carried out by heating a mixture of nitrile, aldehyde, and ammonium acetate (molar ratio 1:1:1.2) in ethanol. Benzoylacetonitrile reacted with 2 mol of aldehydeto give 2-substituted 4-phenyl-10-oxa-5H-benzo[g]quinazoline (1) with elimination of 3 mol of water as indicated in Scheme I.

When a mixture of benzoylacetonitrile, 3,5-dibromosalicylaldehyde, and ammonium acetate (1:1:0.7 molar)ratio) was refluxed in a large volume of benzene,  $\alpha$ -(3,-5-dibromo-2-hydroxyphenyl) -  $\beta$  - benzoyl -  $\beta$  - cyanoeth-

ylene (2), resulting from a Knoevenagel reaction, and 3-benzoyl-6,8-dibromocoumarin were isolated. Furthermore, when compound 2 was heated with 3,5-dibromosalicylaldehyde and ammonium acetate in ethanol, 7,9-dibromo-2-(3',5'-dibromo-2'- hydroxyphenyl)-4-phenyl-10-oxa-5H-benzo [g] quinazoline (1c) was obtained. These facts indicated that in the reaction of benzoylacetonitrile with o-hydroxybenzaldehyde or its derivatives, Knoevenagel condensation first takes place and the resulting compound (type 2) further condenses with aldehyde to give 10-0xa-5H-benzo[g] quinazolines (1) (see Table I). Condensation of benzoylacetonitrile with p-hydroxybenzaldehyde or p-methoxybenzaldegave 3,5-dicyano-4-(p-hydroxyphenyl)-2,6-dihvde phenylpyridine (3a) and 3,5-dicyano-4-(p-methoxyphenyl)-2,6-diphenylpyridine (3b), respectively (Scheme III). In these cases, 2 mol of benzoylacetonitrile react with 1 mol each of aldehyde and ammonia to give **3a** and **3b**. When o-methoxybenzaldehyde was used instead of *p*-methoxybenzaldehyde, the condensation afforded 3,5-dicyano-4-(o-methoxyphenyl)-2,6diphenyl-1,4-dihydropyridine (4) with elimination of 3 mol of water. In this case, oxidation of the dihydropyridine ring to the pyridine ring did not occur. The

SCHEME II

CHO



(1) A. Sakurai and H. Midorikawa, Bull. Chem. Soc. Jap., 40, 1680 (1967).

(2) A. Sakurai and H. Midorikawa, ibid., 41, 165 (1968). (3) A. Sakurai and H. Midorikawa, ibid., 41, 430 (1968).

(4) A. Sakurai and H. Midorikawa, ibid., 42, 220 (1969).



Cyclization Products Obtained by the Reaction of Benzoylacetonitrile and Aldehydes												
	Reaction			Crystn	Yield,					Found, %		
Aldehyde	Produc	Product time, hr		solvent	%	Formula	С	н	N	С	H	Ν
Salicyl	1a	1	228 - 230	Acetic acid	<b>25</b>	$C_{23}H_{16}N_2O_2$	78.39	4.58	7.95	78.29	4.69	7.92
3-Methoxysalicyl	1b	3	210-211	Acetic acid	<b>23</b>	$C_{25}H_{20}N_2O_4$	72.80	4.89	6.79	72.72	4.75	6.95
3,5-Dibromosalicyl	1c	3	321-323	Pyridine	38	$C_{23}H_{12}N_2O_2Br_4$	41.32	1.79	4.19	41.09	1.85	4.35
5-Nitrosalicyl	1d	0.5	>350	Pyridine	15	$\mathrm{C}_{23}\mathrm{H}_{14}\mathrm{N}_{4}\mathrm{O}_{6}$	62.44	3.19	12.67	62.69	3.38	12.87

TABLE 1

## SCHEME III



infrared spectra of type 1 compounds exhibit no characteristic bands for cyano, carbonyl, imino, or amino groups. On the other hand, compound 4 exhibited absorption peaks at 2200 and at 3240 cm<sup>-1</sup> attributed to a cyano and imino group, respectively. Compounds **3a** and **3b** have bands at about 2220 cm<sup>-1</sup> due to the cyano group, but no characteristic bands due to the imino stretching vibration. Nmr spectra of type 1 compounds (in trifluoroacetic acid) revealed signals at 4.3 ppm (singlet, 2 H) due to the presence of a methylene group. When heated with acetic anhydride and pyridine, type 1 compounds were converted to their corresponding monoacetylated derivatives.

Condensation of ethyl cyanoacetate with o-hydroxybenzaldehyde and 2-hydroxy-3-methoxybenzaldehyde was carried out by heating a mixture of ester, aldehyde, and ammonium acetate (molar ratio 1:1:1:3) in ethanol for 0.5 hr. In this case, cyclization occurred between 2 mol of both ethyl cyanoacetate and the aldehyde to form 4-amino-2-(3'-coumarinyl)-5-oxo-6oxa-5,6-dihydrobenzo[h]quinazolines (5) with elimination of 2 mol of both ethanol and water, and 1 mol of hydrogen, as indicated in Scheme IV. A mixture of ethyl cyanoacetate, o-hydroxybenzaldehyde, and ammonium acetate in ethanol gave 5a as the main product after standing at room temperature for 7 hr (Scheme V). On the other hand, when glacial acetic acid was used as the solvent, this mixture gave 3-ethoxycarbonylcoumarin as the main product under the same reaction conditions.

The infrared spectrum of 5a revealed absorption bands for a primary amino group at 3400, 3300, and



3200 cm<sup>-1</sup> and at 1750 and 1730 cm<sup>-1</sup> for a coumarintype carbonyl group. Nmr spectrum showed signals at 7.5–8.6 (coumarin ring) and 9.55–9.95 ppm (NH<sub>2</sub>). Acetylation of compound **5a** with acetic anhydride in pyridine gave 4-acetamido-(3'-coumarinyl)-5-oxo-6oxa-5,6-dihydrobenzo [h]quinazoline.

Condensation between ethyl acetoacetate and salicylaldehyde was carried out in a 1:1 molar ratio in the presence of ammonium acetate (slight excess). This reaction occurred between 2 mol of both the ester and aldehyde, as in the case of ethyl cyanoacetate affording 2-(3' - coumarinyl) -4-methyl-5-oxo-6-oxa-5,6-dihydrobenzo [h]quinoline (6) (Scheme VI). Formation of a com-



pound of this type occurred only when salicylaldehyde was employed as the aldehyde reactant.

The infrared spectrum of 6 showed absorptions at 1740 and 1725  $cm^{-1}$  due to a coumarin-type carbonyl group. In addition, the nmr spectrum showed signals for a methyl group at 3.50 ppm corresponding to three protons and olefinic methine signals at 7.50-8.50, 9.13, and 9.40 ppm. The integrated areas of the peaks are compatible with structure 6.

## **Experimental Section**

All melting points are uncorrected. The infrared spectra were determined by means of potassium bromide pellets. Nmr spectra were determined in trifluoroacetic acid or deuteriochloroform at 60 Mc, using tetramethylsilane as the internal standard. Chemical shifts are reported as parts per million downfield from TMS.

Reaction of Benzoylacetonitrile with Salicylaldehyde and C-Substituted Salicylaldehydes .--- A mixture of benzoylacetonitrile (0.014 mol), aldehyde (0.014 mol), and ammonium acetate (0.015 mol) in ethanol (3 ml) was refluxed for 1-3 hr. After the solution was cooled at room temperature, deposited crystals were collected and washed with methanol and then with water. Experimental results are summarized in Table I. The molecular weight of 1a was determined to be 352 (calcd for C23H16N2O2, 352.37) by means of high resolution mass spectrometry. Nmr spectra (CF<sub>3</sub>CO<sub>2</sub>H) of 1a and 1b exhibited the following peaks: 1a, 4.30 (CH<sub>2</sub>, singlet, 2 H), 7.0-7.65, 8.45, and 8.6 (substituted benzene and hetero ring, multiplet, 8 H), 7.8 ppm (phenyl, singlet, 5 H); 1b, a doublet centered at 3.97 (OCH<sub>2</sub>, 6 H), 4.30 (CH<sub>2</sub>, singlet, 2 H), 6.7-7.4 and 7.9-8.15 (substituted benzene and hetero ring, multiplet, 6 H), 7.7 ppm (phenyl, singlet, 5 H).

Reaction of 2-(o-Hydroxyphenyl)-4-phenyl-10-oxa-5H-benzo-[g] quinazoline (1a) and Acetic Anhydride.—To a solution of 1a (0.1 g) dissolved in pyridine (5 ml), acetic anhydride (8 ml) was added and refluxed for 4 hr. After being cooled, the solution was poured into ice water. The deposited precipitate was collected and recrystallized from glacial acetic acid-water to give 0.1 g of  $2 - (o \cdot acetyloxyphenyl)-4-phenyl-10-oxa-5H-benzo[g] quinazoline:$ mp 206-208°; nmr (CDCl<sub>3</sub>) peaks at 2.1 (CH<sub>3</sub>, singlet, 3 H), 4.1 (CH<sub>2</sub>, singlet, 2 H), 7.0-7.7 and 8.35-8.5 ppm (hetero ringand phenyl, multiplet, 13 H). Anal. Calcd for C<sub>25</sub>H<sub>18</sub>N<sub>2</sub>O<sub>8</sub>: C, 76.13; H, 4.60; N, 7.10.

Found: C, 75.65; H, 4.45; N, 7.21.

Reaction of 2-(2'-Hydroxy-3'-methoxyphenyl)-9-methoxy-4phenyl-10-oxa-5H-benzo[g] quinazoline (1b) and Acetic Anhydride.—Acetic anhydride (9 ml) was added to a solution of 1b (0.4 g) dissolved in pyridine (5 ml). After refluxing for 4 hr, the reaction mixture gave 0.3 g of 2-(2'-acetyloxy-3'-methoxyphenyl)-9-methoxy-4-phenyl-10-oxa-5H-benzo[g]quinazoline, mp 203-205°, when treated as above. The nmr spectrum  $(CDCl_3)$  exhibited bands at 2.1 (CH<sub>3</sub>, singlet, 3 H), 3.85 (OCH<sub>3</sub>, doublet, 6 H), 4.1 (CH<sub>2</sub>, singlet, 2 H), 6.55-7.7 and 7.9-8.1 ppm (hetero ring and phenyl, multiplet, 11 H).

Anal. Caled for  $C_{27}H_{22}N_2O_5$ : C, 71.35; H, 4.88; N, 6.16. bund: C, 71.44; H, 4.90; N, 6.25. Found:

Reaction of Benzoylacetonitrile and 3,5-Dibromosalicylaldehyde in Benzene.--A mixture of benzoylacetonitrile (1.45 g, 0.01 mol), 3,5-dibromosalicylaldehyde (2.8 g, 0.01 mol), and ammonium acetate (0.54 g, 0.007 mol) in benzene (20 ml) was refluxed for 1 hr. The cooled mixture was washed with water and extracted with benzene. The extract was dried over anhydrous sodium sulfate and allowed to stand at room temperature. After the resulting crystals (A) had been filtered off, ligroin was added to the filtrate affording a pale yellow precipitate. The precipitate was collected and washed with a small amount of cold dilute methanol and dried. Recrystallization from ethanolwater afforded 1 g of  $\alpha$ -(3,5-dibromo-2-hydroxyphenyl)- $\beta$ benzoyl- $\beta$ -cyanoethylene (2): mp 172–174°;  $\nu_{\text{max}}^{\text{KBr}}$  3390 (OH), 2190 (conjugated C=N), and 1640 cm<sup>-1</sup> ( $\alpha,\beta$ -unsaturated C=O). Anal. Calcd for C16H9NO2Br2: C, 47.17; H, 2.21; N, 3.44.

Found: C, 47.57; H, 2.91; N, 3.84. Recrystallization of A from glacial acetic acid-water gave 1.2 g

of 3-benzoyl-6,8-dibromocoumarin, mp 201-203° (lit.<sup>5</sup> mp 196°). Reaction of Compound 2 and 3,5-Dibromosalicylaldehyde.— To a mixture of 2 (0.1 g) and 3,5-dibromosalicylaldehyde (0.08 g) in ethanol (2 ml), ammonium acetate (0.1 g) was added and heated for 1 hr. A pale yellow solid crystallized. Recrystallization from pyridine-water gave 0.05 g of white crystals, mp 318-320°. This compound was identical with 1c by a study of infrared spectra.

Anal. Caled for C23H12N2O2Br4: N, 4.19. Found: N, 4.24

3,5-Dicyano-4-(p-hydroxyphenyl)-2,6-diphenylpyridine (3a).-A mixture of benzoylacetonitrile (2 g, 0.014 mol), p-hydroxybenzaldehyde (1.7 g, 0.014 mol), and ammonium acetate (1.2 g, 0.015 mol) in glacial acetic acid (2 ml) was heated for 5 hr. Pale vellow crystals began to separate from the solution. The crystals were collected and washed with methanol and then with water. Recrystallization from glacial acetic acid gave 1.9 g of white needles, mp 283-285°

Anal. Calcd for C25H15N3O: C, 80.41; H, 4.05; N, 11.25. Found: C, 80.05; H, 4.24; N, 11.32.

3,5-Dicyano-4-(p-methoxyphenyl)-2,6-diphenylpyridine (3b).-Ammonium acetate (1.2 g, 0.015 mol) was added to a mixture of benzoylacetonitrile (2 g, 0.014 mol) and *p*-methoxybenzaldehyde (1.9 g, 0.014 mol) and heated for 7 hr. After cooling, a crystalline matter precipitated. It was recrystallized from glacial acetic acid to afford 1 g of colorless needles, mp  $250-253^{\circ}$ . Anal. Calcd for  $C_{26}H_{17}N_{3}O$ : C, 80.60; H, 4.42; N, 10.85.

C, 80.44; H, 4.19; N, 10.85. Found:

3,5-Dicyano-4-(o-methoxyphenyl)-2,6-diphenyl-1,2-dihydropyridine (4).--A mixture of benzoylacetonitrile (2 g, 0.014 mol), o-methoxybenzaldehyde (1.9 g, 0.014 mol), and ammonium acetate (1.2 g, 0.015 mol) was heated for 6 hr. When the reaction mixture was left to stand overnight, an oily product was obtained. The solid which crystallized upon the addition of ether (8 ml) was collected, washed with ether-methanol, and recrystallized from ethanol-glacial acetic acid to give 1.2 g of pale yellow

needles, mp 242-245° (lit.<sup>6</sup> mp 242.5°). Anal. Calcd for  $C_{26}H_{19}N_3O$ : C, 80.18; H, 4.92; N, 10.79. Found: C, 80.09; H, 4.75; N, 10.81.

4-Amino-2-(3'-coumarinyl)-5-oxo-6-oxa-5,6-dihydrobenzo-[h]quinazoline (5a).-To a solution of ethyl cyanoacetate (3.39 g, 0.03 mol) and salicylaldehyde (3.66 g, 0.03 mol) in ethanol (5 ml), ammonium acetate (3.08 g, 0.04 mol) was added and refluxed for 0.5 hr. After cooling, the resulting precipitate was collected and recrystallized from pyridine-water to give 1.5 g (28%) of pale yellow crystals: mp 274–276°;  $\nu_{max}^{KB}$ , 3400, 3300, 3200 (NH<sub>2</sub>), 1750, 1730 (C=O), and 1650 cm<sup>-1</sup> ( $\delta$  NH<sub>2</sub>); nmr (CE CO H) 7.5 8.6 (cm<sup>-1</sup>) (CF\_3CO\_2H), 7.5-8.6 (coumarin ring, multiplet, 9 H), 9.55-9.95

<sup>(5)</sup> R. K. Pandva and K. C. Pandva. Agra Univ. J. Res., 4, 345 (1955).

<sup>(6)</sup> A. Courts and V. Petrow, J. Chem. Soc., 334 (1952).

ppm (NH<sub>2</sub>, broad, 2 H). The molecular weight was determined to be 357 (calcd for  $C_{2c}H_{11}N_3O_4$ , 357.31) by means of high resolution mass spectrometry.

Anal. Calcd for  $C_{23}H_{11}N_3O_4$ : C, 67.22; H, 3.10; N, 11.76. Found: C, 66.50; H, 3.16; N, 11.86.

Reaction of Compound 5a and Acetic Anhydride.—Acetic anhydride (9 ml) was added to a solution of 5a (0.2 g) dissolved in pyridine (5 ml) and refluxed for 4 hr. After cooling, water (3 ml) was added to the reaction mixture; a crystalline precipitate was formed. Recrystallization from glacial acetic acid gave 0.15 g of 4-acetamido-2-(3'-coumarinyl)-5-oxo-6-oxa-5,6-dihydrobenzo[h]quinazoline, mp 312-313°.

Anal. Calcd for  $C_{22}H_{13}N_3O_5$ : C, 66.16; H, 3.28; N, 10.52. Found: C, 65.93; H, 2.99; N, 10.65. 4-Amino-2-(8'-methoxy-3'-coumarinyl)-7-methoxy-5-oxo-6-

4-Amino-2-(8'-methoxy-3'-coumarinyl)-7-methoxy-5-oxo-6oxa-5,6-dihydrobenzo[ $\hbar$ ]quinazoline (5b).—To a solution of ethyl cyanoacetate (3.39 g, 0.03 mol) and 2-hydroxy-3-methoxybenzaldehyde (4.56 g, 0.03 mol) dissolved in ethanol (8 ml), ammonium acetate (3.08 g, 0.04 mol) was added and refluxed for 20 min. A pale yellow crystalline matter precipitated out during the reaction; this was collected and washed with ethanol and then with water. Recrystallization from pyridine-water afforded 2.2 g (35%) of pale yellow crystals: mp 303-306°;  $\nu_{max}^{RB}$  3410, 3300, 3210 (NH<sub>2</sub>), 1735, 1700 (C=O), and 1640 cm<sup>-1</sup> ( $\delta$  NH<sub>2</sub>); nmr spectrum (CF<sub>3</sub>CO<sub>2</sub>H) gave signals at 4.15 (OCH<sub>3</sub>, singlet, 6 H), 7.5-8.0 and 8.2-8.6 (coumarin ring, 7 H), 9.5-10.1 ppm (NH<sub>2</sub>, broad, 2 H).

Anal. Calcd for  $C_{22}H_{15}N_3O_6$ : C, 63.31; H, 3.62; N, 10.07. Found: C, 63.21; H, 3.85; N, 9.85.

Reaction of Ethyl Cyanoacetate and Salicylaldehyde in Glacial Acetic Acid at Room Temperature.—To a solution of ethyl cyanoacetate (2.26 g, 0.02 mol) and salicylaldehyde (2.44 g, 0.02 mol) in glacial acetic acid (5 ml), ammonium acetate (2.31 g, 0.03 mol) was added and allowed to stand at room temperature. After 7 hr, a crystalline compound (B) separated; B was filtered off and water was added to the filtrate; the deposited crystals were then collected and recrystallized from ethanol-water to give 4.6 g of 3-ethoxycarbonylcoumarin, mp  $92-94^{\circ}$  (lit.<sup>7</sup> mp  $94^{\circ}$ ). The

(7) E. Knoevenagel, Chem. Ber., 31, 2593 (1898).

compound B was recrystallized from glacial acetic acid to afford 0.3 g of 5a, mp 275-277°.

Reaction of Ethyl Acetoacetate and Salicylaldehyde.—To a solution of ethyl acetoacetate (5.2 g, 0.04 mol) and salicylaldehyde (4.9 g, 0.04 mol) in ethanol (7 ml), ammonium acetate (3.08 g, 0.05 mol) was added. After the reaction mixture was refluxed for 1 hr, a crystalline precipitate was formed. The crystals were collected and washed with methanol and dried. Recrystallization from pyridine gave 2.2 g (31%) of 2-(3'-coumarinyl)-4-methyl-5-oxo-6-oxa-5,6-dihydrobenzo[h]quinoline (6): mp 291-292°; nmr spectrum (CF<sub>4</sub>CO<sub>2</sub>H) revealed signals at 3.50 (CH<sub>3</sub>, singlet, 3 H), 7.5-8.5 (hetero ring, multiplet, 8 H), 9.13 and 9.4 ppm (hetero ring, singlet, 2 H). The molecular weight determined by mass spectrometry was 356 (calcd for C<sub>22</sub>H<sub>14</sub>NO<sub>4</sub>, 355.33).

Anal. Caled for  $C_{22}H_{13}NO_4$ : C, 74.36; H, 3.69; N, 3.94. Found: C, 74.59; H, 3.72; N, 4.00.

**Registry No.**—1a, 21537-68-8; 1b, 21537-69-9; 1c, 21537-70-2; 1d, 21537-71-3; 2, 21545-00-6; 3a, 21545-01-7; 3b, 21545-02-8; 5a, 21545-03-9; 5b, 21537-66-6; 6, 21537-67-7; ammonium acetate, 1066-32-6; 2-(o-acetyloxyphenyl)-4-phenyl-10-oxa-5Hbenzo[g]quinazoline, 21545-04-0; 2-(2'-acetyloxy-3'methoxyphenyl)-9-methoxy-4-phenyl-10-oxa-5H-benzo-[g]quinazoline, 21545-05-1; 4-acetamido-2-(3'-coumarinyl)-5-oxo-6-oxa-5,6-dihydrobenzo[h]quinazoline, 21545-06-2.

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## Conjugate Addition Reactions with Lithium Diallylcuprate<sup>1a</sup>

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Although the conjugate addition of an allyl group from lithium diallylcuprate to 2-cyclohexenone (1) was successful, the more hindered ketone, 3,5,5-trimethylcyclohexenone (2), underwent 1,2 addition with the same reagent. Attempts to effect or to catalyze the conjugate addition of acetylide anions or enolate anions to unsaturated ketones by the presence of copper(I) derivatives were not successful.

The pronounced tendency of metal organocuprate derivatives, e.g., LiCuR<sub>2</sub> where R = alkyl, vinyl, or aryl, to add in a conjugate fashion to  $\alpha,\beta$ -unsaturated carbonyl compounds<sup>2</sup> raises the question whether the conjugate addition of more stable carbanionic intermediates could be catalyzed by copper(I) derivatives. The answer to the question is of particular interest for the allylic, acetylide, and enolate anions since the conjugate addition of these systems has substantial synthetic utility (e.g., the Michael reaction<sup>3</sup>). A previous study of the reaction of 2-cyclohexenone (1) with  $\beta$ methylallylmagnesium chloride indicated that addition

(2) See (a) H. O. House and W. F. Fischer, Jr., J. Org. Chem., 33, 949
(1968); (b) H. O. House, W. L. Respess, and G. M. Whitesides, *ibid.*, 31, 3128 (1966); (c) H. O. House, R. A. Latham, and C. D. Slater, *ibid.*, 31, 2667 (1966); and references cited in these papers.

(3) E. D. Bergmann, D. Ginsburg, and R. Pappo, Org. Reactions, 10, 179 (1959).

of catalytic amounts of the ether-insoluble copper(I) chloride did not yield a conjugate addition product; only the alcohol from 1,2 addition was isolated.<sup>4</sup> In this study we have synthesized allylic and acetylenic copper(I) derivatives and have examined their behavior as potential reagents for conjugate addition. Also, we have examined one possible route to copper(I) enolates.

Reaction of cyclohexenone (1) with lithium diallylcuprate (3) in ether solution at  $-70^{\circ}$  did indeed produce the conjugate addition product 4 in 90-94% yield. The phosphine complex 8 of allylcopper(I) also produced the adduct 4, but in very poor yield (10-15%) accompanied by high molecular weight by-products. This problem of high molecular weight by-products was encountered earlier<sup>2a</sup> when phosphine and phosphite complexes of methylcopper(I) were allowed to react with cyclohexenone derivatives. Thus, the lithium cuprate reagents are generally more satisfactory

(4) L. Mandell and J. M. Brodmann, J. Org. Chem., 31, 591 (1966).

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