Lithium cleavage of dibenzothiophene. Several runs, all resulting in the same products, proved 25° to be a very effective temperature. If the temperature were allowed above 50° a small amount of biphenyl was found in the neutral ether layer.

In a 500 ml. flask was placed 50 ml. of tetrahydrofuran, 9.2 g. (0.05 mole) of dibenzothiophene, and 2 g. (0.3 g. atom) of lithium. The reaction started immediately but was kept at 25° for 45 min. and then carbonated. Subsequent work-up yielded a trace of biphenyl (identified by method of mixture melting point) from the neutral layer and 4.7 g. (48%) of 3,4-benzothiocoumarin as white needles from ethanol-water, m.p. 131–133°.

Anal. Calcd. for $C_{13}H_8OS$: S, 15.09. Found: S, 15.12.

A small amount (0.4 g.) of the disulfide of 2-mercapto-2′-carboxybiphenyl was also obtained as white plates from ethanol, m.p. 264–266°.

Anal. Calcd. for $C_{26}H_{18}O_4S_2$: S, 13.97; neut. equiv., 229. Found: S, 13.97, 14.02; neut. equiv., 228.

Lithium cleavage of dibenzofuran. Fifty milliliters of tetrahydrofuran was added to 8.4 g. (0.05 mole) of dibenzofuran and 1 g. (0.15 g. atom) of lithium. The reaction was allowed to proceed for 45 min. without cooling and then carbonated to produce 1.5 g. (20%) of 3,4-benzocoumarin from methanol-water, m.p. 93.5–96° (reported[6] m.p. 94–95°).

The same reaction when terminated by hydrolysis yielded 2 g. (23%) of 2-hydroxybiphenyl (identified by method of mixture melting point) melting over the range of 54–58° from petroleum ether.

Lithium cleavage of thianthrene. This was carried out at 25° for 45 min. using 10.4 g. (0.05 mole) of thianthrene, 2 g. (0.3 g. atom) of lithium, and 50 ml. of tetrahydrofuran. The reaction was terminated by carbonation to produce 10 g. of unpleasant smelling, acidic oil which could not be identified. Only a trace of neutral material was recovered. An attempt to convert the acidic oil to a solid disulfide through a reaction with iodine in absolute ethanol was unsuccessful.

Lithium cleavage of N-ethylcarbazole. By refluxing 19.4 g. (0.1 mole) of *N*-ethylcarbazole, 2 g. (0.3 g. atom) of lithium, and 50 ml. of tetrahydrofuran for 1 hr., it was possible to obtain a positive Color Test I. However, carbonation, hydrolysis, or addition of this reaction mixture to benzophenone has not given an identifiable product. The usual recovery of starting material was about 75% with the remainder being presumably cleaved material.

Lithium cleavage of carbazole. The same conditions were used as with *N*-ethylcarbazole. No color change occurred and Color Test I was never positive. There was a 90% recovery of starting material.

Lithium cleavage of diphenyl ether. A mixture of 8.5 g. (0.05 mole) of diphenyl ether, 1 g. (0.15 g. atom) of lithium, and 50 ml. of tetrahydrofuran was allowed to react without cooling for 30 min. The reaction mixture gradually turned brown and Color Test I was positive after 10 min. After 30 min. the reaction mixture was carbonated. The products isolated consisted of phenol which was isolated as the 2,4,6-tribromophenol from ethanol, m.p. 93–96°; benzoic acid which was obtained by vacuum sublimation, m.p. 120–124°; and 2-carboxydiphenyl ether which remained as the residue after vacuum sublimation, m.p. 111–113°. All of the the products were verified by mixture melting points and infrared spectra.

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[6] R. Cahn, *J. Chem. Soc.*, 1400 (1933).

Chemistry of Unsaturated Lactones. I. Reaction of Oxazolones with Phenylmagnesium Bromide

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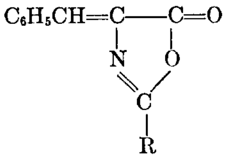
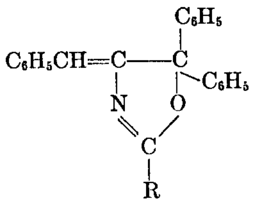
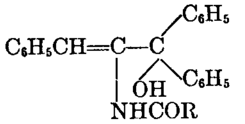
It has been shown[1] that 2-phenyl-4-methyl-5(4*H*)oxazolone reacts with excess phenylmagnesium bromide to form 1,1-diphenyl-2-benzamido-1-propanol. Recently, Pourrat[2] and Mustafa and Harhash[3] reported the reaction of unsaturated azlactones with this Grignard reagent. The results of these investigators differed in several instances. Thus Pourrat[2] found that 2-phenyl-4-benzylidene-5(4H)-oxazolone (I) reacted with excess phenylmagnesium bromide to give a mixture of 2,5,5-triphenyl-4-benzylidene-2-oxazoline (II) and 1,1-diphenyl-2-benzamidocinnamyl alcohol (III) in the ratio of 3:1.


I, R = C_6H_5
V, R = CH_3


II, R = C_6H_5
VI, R = CH_3


III, R = C_6H_5
VII, R = CH_3

II and III were separated by means of elution chromatography on alumina. Mustafa and Harhash found, however, that III was the exclusive product of this reaction. III was converted by acetic acid-hydrochloric acid into a substance whose structure was tentatively assigned that of the oxazoline II. However the melting points of II and III differed markedly from those given by Pourrat. The structure proposed for II was based on elemental analysis and its yellow color, while the structure of III was inferred by its analysis and by the fact that it contained two active hydrogens.

We have studied this reaction in detail and have observed that the nature of the products is dependent upon the reaction conditions. When I was treated with phenylmagnesium bromide in a 1:1 molar ratio, using inverse addition, the reaction was very sluggish and most of the azlactone

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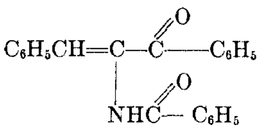
[1] Cornforth in *The Chemistry of Penicillin*, Princeton University Press, Princeton, N. J., 1949, p. 738.

[2] Pourrat, *Bull. soc. chim. France*, 828 (1955).

[3] Mustafa and Harhash, *J. Org. Chem.*, 21, 575 (1956).

was recovered unchanged. However, a small amount of a colorless substance IV was isolated. IV is believed to be α-benzamidobenzalacetophenone. The structural assignment is based on elemental analysis, and its ultraviolet and infrared spectra.



$C_6H_5CH{=}\underset{\underset{NH\overset{O}{\overset{\|}{C}}{-}C_6H_5}{|}}{C}{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5$

IV

IV exhibits three maxima in the ultraviolet. The short wave length, high intensity K band of the conjugated system is found at 229 mμ (ε20,400), in close agreement with the value predicted by Woodward's rule.[4] The longest wave-length band at 296–299 mμ (ε15,700) may be attributed to the cinnamoyl system.[5a] The middle band maximum at 257 mμ (ε15,700) is probably due to the benzoyl or acrylophenone groups[5a] which behave as independent chromophores due to steric interference toward coplanarity brought about by the presence of the α-benzamido group. The styrylamine system may also make an important contribution.[5b] The infrared spectrum of IV shows absorption at 1660 cm.$^{-1}$ (probably due to C=O stretching in an α,β-unsaturated diaryl ketone),[6] 3250 cm.$^{-1}$ (due to —NH— stretching) and 1645 cm.$^{-1}$ and 1525 cm.$^{-1}$ (the amide I and II bands).[6] It is not possible with the available data definitely to assign the geometric configuration to IV. However, if based on the tentative assignment of configuration for the oxazolone,[7] the phenyl and benzoyl groups would be *trans* to each other.

When a suspension of I in ether or benzene was added to excess (3:1 molar ratio) phenylmagnesium bromide, the product isolated appeared to be primarily determined by a dilution factor. When we were unable to get consistent results and noted the conflicting reports of the other investigators, we examined the possibilities of temperature, solvent, and concentration factors. The course of the reaction was independent of the temperature or whether the azlactone was suspended in ether or benzene, but was markedly influenced by the total volume of solvent used. At relatively high dilution (as also used by Mustafa) the predominant product was III, in yields of 65 - 70%, m.p. 163–164°. This melting point is somewhat higher than that given by Mustafa (156°), but lower than the 174° reported by Pourrat. A small amount of gummy brown product was also isolated, but not identified. This may have been the oxazoline II. When the volume of solvent was considerably reduced, II, containing a small quantity of III, was obtained in over 80% yield. It was difficult to remove the last traces of III by fractional crystallization and elution chromatography on alumina was employed as mentioned earlier. The melting point was raised above that reported by Pourrat, but differed significantly from the product obtained by Mustafa and Harhash. We were unable to repeat their work, but we did obtain a mixture of II and III by heating II with acetic anhydride.

The favoring of an open chain compound at high dilution in the reaction of a Grignard reagent with a lactone has been previously described by Kohn.[8,9] Thus, α,γ-dihydroxy-α,γ-dimethylvaleric acid γ-lactone reacted with three equivalents of phenylmagnesium bromide to give the tetrahydrofuran derivative whereas the trihydroxy, open-chain product, was isolated at very high dilution.

The structure previously proposed for III is supported by its infrared spectrum which exhibited absorption at 1667 cm.$^{-1}$ and 1525 cm.$^{-1}$ (amide I and II bands), 3270 cm.$^{-1}$ (—NH— stretching) and 3475 cm.$^{-1}$ (OH stretching).[6] The conversion of III to a mixture of II and III also tends to favor this structure. There was no indication of the formation of a 1,4-addition product as might have been expected when one considers the normal preference of the reagent towards this mode of addition.[10,11a] Lutz[11a] has shown that phenylmagnesium bromide forms 1,4 addition products with both *cis* and *trans* α- phenylchalcones. The effect of an α-benzamido group on addition reactions to α,β-unsaturated systems has not been evaluated, though ethyl α-benzamido cinnamate reacted with the phenyl Grignard reagent to give only III.[3] While it is possible in the reaction we have studied that the geometric isomerism may be such as to offer steric resistance to 1,4-addition, a more important factor operating against such addition may be the electron-donating effect of the nitrogen atom.[11b]

The suggested structure for II is given support by the formation of a methochloride, by the presence of a medium intensity band at 1660 cm.$^{-1}$ (probably due to >C=N—)[6] and the absence of —OH, —NH, and amide absorptions, and by its ultraviolet spectrum. Two maxima were observed. The first, at 341 mμ (ε 15,200), may be attributed to the $C_6H_5CH{=}\overset{|}{C}{-}N{=}\overset{/}{C}$ chromophore.[12] The oxazolone I, which bears the same chromophore, exhibits a maximum at 361 mμ, but this bathochromic shift is enhanced by cross-

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(4) Woodward, *J. Am. Chem. Soc.*, **63**, 1123 (1941); **64**, 72, 76 (1942).

(5a) Black and Lutz, *J. Am. Chem. Soc.*, **77**, 5134 (1955).

(5b) The possible contribution of the styrylamine system was cited by one of the referees.

(6) Bellamy, *The Infrared Spectra of Complex Molecules*, J. Wiley and Sons, Inc., New York, N. Y. (1954).

(7) Buckles, Filler, and Hilfman, *J. Org. Chem.*, **17**, 233 (1952).

(8) Kohn, *Monatsh.*, **34**, 1729 (1913).

(9) Kohn and Ostersetzer, *Monatsh.*, **37**, 37 (1916).

(10) Kohler, *Am. Chem. J.*, **36**, 177, 511 (1906).

(11a) Lutz and Rinker, *J. Am. Chem. Soc.*, **77**, 366 (1955).

(11b) This suggestion was made by one of the referees.

conjugation, which is absent in I. The second maximum at 241 mμ (ε 22,800) may be due to partial chromophores such as $C_6H_5CH{=}C<$ and $C_6H_5\underset{|}{C}{=}N{-}$.[12]

We are unable at this time to resolve the differences between our results and those of Mustafa[3] with regard to II. Geometric isomerism may be involved. A number of such isomeric pairs in similar compounds[13–15] have been isolated. Further work toward elucidating the structures of these compounds is in progress.

2-methyl-4-benzylidene-5(4*H*)oxazolone (V) reacted with excess phenylmagnesium bromide to give the tertiary alcohol VII as previously reported by Pourrat,[2] though no structure proof was presented. However, we found that its infrared spectrum and its quantitative conversion by acetic anhydride to VI, substantiated this assignment. The structure of VI was inferred by its color, elemental analysis and infrared spectrum.

EXPERIMENTAL[16]

Reaction of 2-Phenyl-4-benzylidene-5(4H)-oxazolone with excess phenylmagnesium bromide. (a) High dilution. To 3.65 g. (0.15 g. atom) of magnesium turnings in 50 ml. anhydrous ether was added dropwise 23.6 g. (0.15 mole) of bromobenzene in 65 ml. of dry ether. To this Grignard reagent was added in portions over a period of 1 hr., 12.5 g. (0.05 mole) of 2-phenyl-4-benzylidene-5(4*H*)-oxazolone suspended in 250 ml. of ether. The reaction mixture was heated under reflux with stirring for an additional 1.5 hours and then decomposed with either a 10% solution of sulfuric acid or a saturated solution of ammonium chloride. The yellow-white product was insoluble in both ether and water and precipitated. The yellow-white product was insoluble in both ether and water and precipitated. The crude product was recrystallized twice from benzene to give 12.2 g. (66% yield) of small white needles, m.p. 163–164°. On evaporation of the ether layer about 5 g. of a brown amorphous material was obtained which could not be readily crystallized.

Anal. Calcd. for $C_{28}H_{23}NO_2$: C, 82.94; H, 5.72; N, 3.45. Found: C, 82.87; H, 5.60; N, 3.31.

When the material was heated with acetic anhydride and sodium acetate, a yellow-brown product, melting range 140–160°, was obtained.

(*b*) *Lower dilution.* When this Grignard reaction was carried out using a total solvent volume of about 150 ml., a bright yellow product was obtained, which was soluble in benzene and fairly soluble in ether. This material was crystallized from a 70–30 volume % mixture of ethanol and water to give small yellow plates, m.p. 141–144°. This melting point could not be raised by repeated crystallization. Elution chromatography on alumina using ether as eluant, raised the melting point of most of the crystals to 161–163° but some lower melting crystals were also obtained. The crude yield of oxazoline was 83%.

Anal. Calcd. for $C_{28}H_{21}NO$: C, 86.79; H, 5.46; N, 3.62. Found: C, 86.83; H, 5.73; N, 3.55.

Heating of the oxazoline with dimethyl sulfate and treatment of the resulting solution with 6*N* HCl yielded the *methochloride* as a gray precipitate which was crystallized from glacial acetic acid to give a white product, m.p. 108–111°.

Anal. Calcd. for $C_{29}H_{24}ClNO$: C, 79.53; H, 5.52. Found: C, 80.07; H, 5.30.

Reaction of the oxazolone with phenylmagnesium bromide in a 1:1 molar ratio using inverse addition. In a 500-ml., 3-necked flask was placed 12.5 g. (0.05 mole) of oxazolone suspended in 50 ml. dry ether. An ether solution of phenylmagnesium bromide, prepared from 1.22 g. (0.05 g. atom) magnesium turnings and 7.9 g. (0.05 mole) bromobenzene was then added dropwise with stirring. After addition was complete, the mixture was decomposed with dilute sulfuric acid. The ether was removed and the solid residue dissolved in hot ethanol. About 200 ml. of water was added and the oxazolone precipitated. The milky suspension was digested by heating and the product collected. After crystallization from benzene, about 1 g. of white product, m.p. 144–145°, was obtained.

Anal. Calcd. for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23. Found: C, 80.45; H, 5.21.

2-Methyl-4-benzylidene-5(4H)oxazolone with excess phenylmagnesium bromide. Using a procedure similar to that described for the 2-phenyl analog at high dilution, a white product, m. 144–146°, was obtained.[17]

Anal. Calcd. for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.39; H, 6.09; N, 4.09.

When this compound was heated with acetic anhydride and sodium acetate, light yellow needles, m.p. 95–96°, were isolated.

Anal. Calcd. for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 84.33; H, 5.70; N, 4.24.

Spectral measurements. The infrared spectra were obtained on a Baird Associates infrared double beam recording spectrophotometer equipped with a rock-salt prism. The samples were examined either as Nujol mulls or by use of a KBr disk.

The ultraviolet spectra were determined with a Beckman DU spectrophotometer. 95% ethanol was used as solvent.

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[12] Bassi, Deulofeu, and Ortega, *J. Am. Chem. Soc.*, **75**, 171 (1953).

[13] Carter and Risser, *J. Biol. Chem.*, **139**, 255 (1941).

[14] Larsen and Bernstein, *J. Am. Chem. Soc.*, **72**, 4447 (1950).

[15] Gagnon and Charette, *Can. J. Research*, **19B**, 275 (1941).

[16] All m.p.'s were determined on a Fisher-Johns block and are corrected.

[17] Pourrat[2] reported m.p. 149° (uncorr.) for this compound.