EXPERIMENTAL

N-(2′-Hydroxyethyl)-2-oxazolidone. To 472 g. (4.0 moles) of diethyl carbonate under agitation 420 g. (4.0 moles) diethanolamine was slowly added. The resulting reaction mixture was then heated to reflux and ethanol taken off using a 10-in. column packed with refractory material and fitted with a variable take-off head. In this way, 84% of the ethanol was stripped out with a pot temperature mainly between 110°–120°, and gradually rising to 135°. The remaining ethanol was separated using reduced (aspirator) pressure. The crude product was treated with finely divided decolorizing carbon and filtered hot to yield 513 g. (98.0%) of clear, light-colored *N*-(2′-hydroxyethyl)-2-oxazolidone.

This product was quite suitable for use in subsequent reactions. Initial batches readily distilled at 162°/1.0 mm., n_D^{25} 1.4823; but later runs demonstrated a tendency to decompose during distillation. These data compare favorably with those reported in the patent literature.[8,9]

Anal. Calcd. for $C_5H_9O_3N$: C, 45.79; H, 6.92; N, 10.68; Hydroxyl value, 429. Found: C, 45.81; H, 6.89; N, 10.84; Hydroxyl value 428.7.

N-(2′-Chloroethyl)-2-Oxazolidone. A total of 238 g. (2.0 moles) thionyl chloride was gradually added to 262 g. (2.0 moles) *N*-(2′-hydroxyethyl)-2-oxazolidone in 200 ml. dry benzene over a 3-hr. period at 30 ± 5°. The use of an efficient Friedrichs condenser throughout the reaction period is strongly recommended since any thionyl chloride losses give an incomplete reaction and amplify isolation problems. The clear, amber-colored solution resulting from an originally cloudy dispersion was strongly acidic. Even though a slow stream of nitrogen was passed through the reaction mixture overnight, almost a full equivalent of sodium bicarbonate was required for complete neutralization (HCl complex with oxazolidone heterocycle?). The filtrate resulting from the products of this neutralization was combined with additional benzene washings of the sodium chloride salt, clarified with finely divided decolorizing carbon, and stripped of solvent to yield 241 g. (80.6%) of a light amber-colored liquid *N*-(2′-chloroethyl)-2-oxazolidone. This material was readily distilled, b.p. 100°/0.1 mm., n_D^{25} 1.4900.

Anal. Calcd. for $C_5H_8O_2NCl$: C, 40.15; H, 5.39; N, 9.37; Cl, 23.70. Found: C, 39.48; H, 5.45; N, 9.46; Cl, 24.65. Excess Cl equivalent to 1.39% (combined?) HCl.

N-Vinyl-2-oxazolidone. To a previously prepared solution of potassium *tert*-butoxide[10] in *tert*-butanol, made by reacting 40 g. (1.02 moles) potassium metal with 700 ml. dry *tert*-butanol, 150 g. (1.002 moles) *N*-(2′-chloroethyl)-oxazolidone was added slowly over a 2.5-hr. period. The initial exothermic reaction carried the temperature from 60° to 85° (reflux), and this latter temperature was maintained during most of the addition period. Reflux was then continued for an additional 20 hr. when a titration indicated the reaction to be 88% complete. The reaction slurry was then filtered and the solid potassium chloride thoroughly washed with additional solvent. Combined washings and filtrate were then treated with finely divided decolorizing carbon, and stripped of solvent to yield 90 g. (79.6%) of crude, amber-colored *N*-vinyl-2-oxazolidone. This liquid readily distilled at 70°/0.1 mm., n_D^{25} 1.4939. A cooling bath indicated the m.p. of this distilled product to be approximately −15°. An infrared curve showed strong absorption at 1620 cm.$^{-1}$ characteristic of the $CH_2{=}CH{-}$ group.

Anal. Calcd. for $C_5H_7O_2N$: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.54; H, 6.46; N, 12.42.

Homopolymerization of N-vinyl-2-oxazolidone. To a solution of 20 g. of *N*-vinyl-2-oxazolidone in 80 g. of xylene was added 0.60 g. (3% on weight of monomer) of α,α′-azobisisobutyronitrile (catalyst). The resulting clear solution was heated on a steam bath (95°) under a reflux condenser for 3 hr. The white solid polymer which precipitated from solution during the heating period was filtered and washed thoroughly with fresh xylene. After drying under reduced pressure, the poly(*N*-vinyl-2-oxazolidone) weighed 14.1 g. (70.5%). The dried material was found to be water soluble. The molecular weight of this polymer was about 1250 by microisopiestic measurements. Infrared confirmed the structure as that of poly(*N*-vinyl-2-oxazolidone).

Additional *N*-vinyl-2-oxazolidone polymerizations have indicated that homopolymers with molecular weights ranging from 450 to over 100,000 can be formed. All of the products were water soluble, white solids.

Additional polymerization characteristics of N-vinyl-2-oxazolidone. Exposure of N-vinyl-2-oxazolidone monomer droplets to air gave clear, solid, orange-colored beads after several days' exposure. *N*-vinyl-2-oxazolidone when heated to 80° in the presence of benzoyl peroxide gave dark viscous liquids. Using the same conditions, α,α′-azobisisobutyronitrile gave clear, tough, orange-colored, water soluble glasses.

When a solution of one part *N*-vinyl-2-oxazolidone in four parts acrylonitrile was heated to 80° in the presence of α,α′-azobisisobutyronitrile, a vigorous evolution of heat resulted. The product, in part, was a rubbery, colorless, translucent mass which was water insoluble.

NEW PRODUCT DEVELOPMENT DEPARTMENT
AMERICAN CYANAMID CO.
30 ROCKEFELLER PLAZA
NEW YORK 20, N. Y.

---

[8] J. R. Caldwell, U. S. Patent **2,656,328** Ex. 3 (1953); *Chem. Abstr.*, **48**, 2415 (1954).

[9] J. B. Bell, and J. D. Malkemus, U. S. Patent **2,755,286** Ex. IV & V (1956).

[10] S. M. McElvain and A. N. Bolstad, *J. Am. Chem Soc.*, **73**, 1988 (1951).

Lithium Cleavages of Some Heterocycles in Tetrahydrofuran

HENRY GILMAN AND JOSEPH J. DIETRICH

Received December 13, 1956

Cleavages of heterocycles using various media and cleaving agents has often proved to be a valuable tool in synthesis and structure proof.

Using lithium in refluxing ether over a period of 22 hr., there were obtained excellent yields of 3,4-benzocoumarin from dibenzofuran when the reaction was terminated by carbonation. When refluxing dioxane was used as the solvent, only 2-hydroxybiphenyl was obtained upon hydrolysis or carbonation after 12 hr.[1]

Dibenzo-*p*-dioxin has been cleaved by lithium in refluxing ether after 24 hr. to yield upon carbonation 23% of 2-hydroxy-2′-carboxydiphenyl ether.[2] This molecule could presumably be cleaved in refluxing dioxane.

In refluxing ether lithium does not cause the cleavage of dibenzothiophene even after 36 hr. However, dibenzothiophene can be cleaved by lithium in refluxing dioxane over a period of 12 hr. to yield biphenyl and 2-mercaptobiphenyl

---

[1] H. Gilman and D. Esmay, *J. Am. Chem. Soc.*, **75**, 2947 (1953).

[2] Unpublished studies.

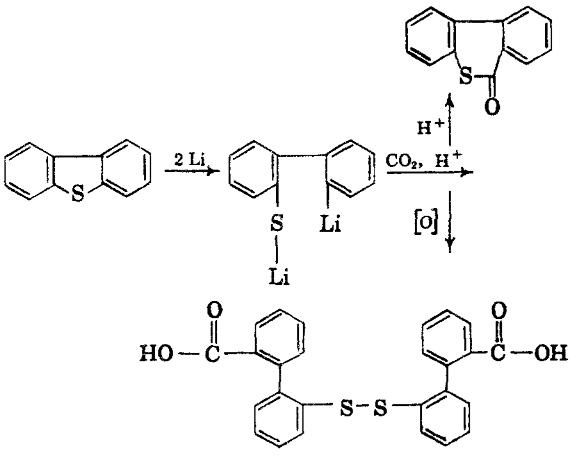
after hydrolysis or carbonation.[1] This again demonstrates the destructive nature of refluxing dioxane on organometallic compounds.

Attempts to cleave *N*-ethylcarbazole with lithium in refluxing dioxane have resulted in essentially quantitative recovery of starting material after 24 hr.[3] The cleavage was not attempted in ether, but a negative result may be a fairly safe assumption. Carbazole gave the same results under identical conditions.[3]

Using purified tetrahydrofuran all of the aforementioned compounds have undergone cleavage with significant ease. In all cases the reactions were exothermic giving rise to a dark blue-green color. Color Test I[4] was usually positive within 2 min. after the reactants were mixed. In many instances, the dark blue-green color gradually turned to a dark brown. For comparison purposes, the reactions were all run for 45 min. and then either hydrolyzed or carbonated.

Dibenzothiophene and dibenzo-*p*-dioxin reacted completely during the alloted time. Both reactions approached the reflux temperature of tetrahydrofuran if they were not controlled.

Dibenzo-*p*-dioxin gave the normal products upon carbonation in better yield than the corresponding diethyl ether cleavage, but dibenzothiophene produced 3,4-benzothiocoumarin and the disulfide of 2-mercapto-2′-carboxybiphenyl. These are probably formed from the 2-mercapto-2′-carboxybiphenyl during the work-up. A small amount of biphenyl was also obtained from the uncontrolled reactions of dibenzothiophene. A postulated reaction sequence for dibenzothiophene is as follows:[1]



A maximum yield of cleavage products was realized at 25° for dibenzothiophene and dibenzo-*p*-dioxin, using an ice bath to moderate the reactions.

In the case of dibenzofuran, it was best to use a higher temperature since a 75% recovery of starting material resulted at 25°. The uncontrolled reactions which warmed up to 40–50° gave a 20% yield of 3,4-benzocoumarin after carbonation.

Cleavage of thianthrene at 25° with lithium yielded no identifiable products, but most of the starting material was in the form of an unpleasant smelling, acidic oil after carbonation. This evidence plus the fact that Color Test I was positive can only be reconcilable with cleavage of this heterocycle. Using refluxing diethyl ether as the solvent, 72% of thianthrene was recovered even though Color Test I was positive after 1 hr.

No products have been identified from the lithium cleavage of *N*-ethylcarbazole in tetrahydrofuran. Some cleavage was certain though, since only 75% of the starting material was recovered after 45 min. of refluxing and Color Test I was positive. Some of the recovered oils showed an N—H band on their infrared spectra. Lithium in refluxing tetrahydrofuran for 45 min. failed to cleave carbazole, giving a 90% recovery of starting material.

It is interesting to note that while dibenzofuran cleaved rather easily in ether, dibenzothiophene resisted cleavage under these conditions. However, in tetrahydrofuran, dibenzothiophene gave the best yield of cleavage product at 25° whereas dibenzofuran was appreciably cleaved only at higher temperatures.

A noteworthy deviation from heterocycles was the cleavage of diphenyl ether to yield phenol, benzoic acid, and 2-carboxydiphenyl ether after carbonation. The last product may be accounted for by assuming metalation of the diphenyl ether by phenyllithium obtained by cleavage of the diphenyl ether.

EXPERIMENTAL[5]

The tetrahydrofuran used in all the experiments was purified by shaking with sodium hydroxide, drying over sodium metal, and finally distilling from lithium aluminum hydride prior to every reaction. A nitrogen atmosphere was always used.

Lithium cleavage of dibenzo-p-dioxin. Run I. To 50 ml. of tetrahydrofuran in a 500 ml. flask was added 9.2 g. (0.05 mole) of dibenzo-*p*-dioxin and 1 g. (0.15 g. atom) of lithium ($^1/_8''$ pieces of wire) at room temperature. A brown color immediately appeared and Color Test I was positive after 2 mins. The reaction was allowed to proceed without cooling for 45 min. at which time the reaction mixture was carbonated by pouring into a dry ice–ether slurry. Work-up resulted in 3.7 g. (32%) of 2-hydroxy-2′-carboxydiphenyl ether as white needles, m.p. 127–129° from petroleum ether-benzene; 0.4 g. of unidentified phenolic material, m.p. 192–195° from ethanol; and 0.5 g. of crude neutral material.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 67.82; H, 4.35; neut. equiv., 230. Found: C, 67.87, 67.86; H, 4.45, 4.46; neut. equiv., 228.

Run II. This time the temperature was controlled at 25°. Work-up, after carbonation, gave 6 g. (56%) of 2-hydroxy-2′-carboxydiphenyl ether and 0.5 g. of unidentified phenolic material.

---

(3) H. Gilman, J. B. Honeycutt, Jr., and R. Ingham, *J. Org. Chem.*, **22**, 338 (1957).

(4) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(5) All melting points are uncorrected. The petroleum ether used had b.p. 60–70°.

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.

Acknowledgment. The authors are indebted to E. M. Layton, Jr., of the Institute of Atomic Research for infrared spectra. This work was supported in part by the United States Atomic Energy Commission under Contract No. AT(11-1)-59.

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

---

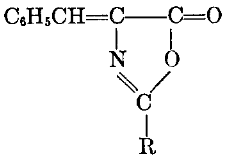
[6] R. Cahn, *J. Chem. Soc.*, 1400 (1933).

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

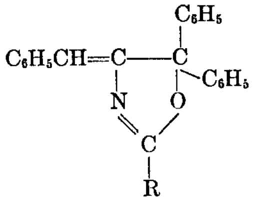
ROBERT FILLER AND JAMES D. WISMAR

Received November 14, 1956

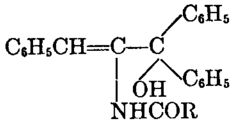
It has been shown[1] that 2-phenyl-4-methyl-5 (4*H*)oxazolone reacts with excess phenylmagnesium bromide to form 1,1-diphenyl-2-benzamido-1-propanol. Recently, Pourrat[2] and Mustafa and Harhash[3] reported the reaction of unsaturated azlactones with this Grignard reagent. The results of these investigators 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

---

[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).