and were kindly provided by Dr. Thomas L. McMeekin of the Eastern Regional Laboratory. One-ml. samples containing 5 mg. of protein in veronal acetate buffer of *p*H 6.4 were incubated with 0.05 mg. of prostate phosphatase for 6 and 24 hours, respectively. Preliminary to the estimation of the inorganic phosphate that is released by the enzyme, one ml. of 20% trichloroacetic acid was added and the protein precipitate removed by centrifugation. The results with the three preparations are summarized in Table I.

Table I

Action of Prostate Phosphatase on Casein Fractions

Protein	Phosphorus content, %	Time of incubation at 37° in hours	Phosphorus released by enzyme, % of total phosphorus
"Unfractionated"	0.8	6	0
casein		24	12.5
α-Casein	1.0	6	24.0
		24	42.0
β-Casein	0.6	6	0
		24	0

During the dephosphorylation of α-casein the solubility of the protein decreases. Simultaneously several new components appear in the electrophoretic pattern, as is shown in Fig. 1. Here the full curve is the tracing of the pattern of α-casein whereas the dashed line is that of the protein after 20% of the phosphorus had been liberated.

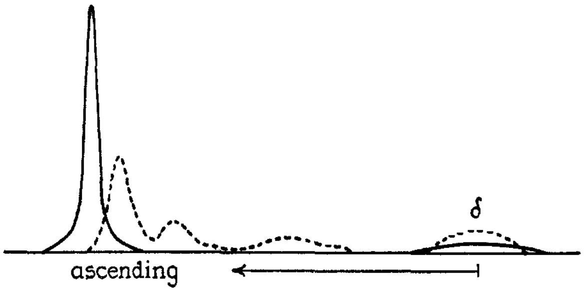

Fig. 1.—Superimposed tracings of electrophoretic patterns of α-casein, ——, and partially dephosphorylated α-casein, - - - - -. Patterns recorded after electrophoresis of 0.5% protein solutions in 0.1 ionic strength sodium phosphate buffer of *p*H 6.8 at a potential gradient of 6 volts per cm. for 8200 seconds.

In experiments in which α-casein and β-casein are remixed in different proportions, if the total concentration of the β-component exceeds 30%, the enzyme reaction is partially inhibited, the degree of inhibition being proportional to the concentration of the β-casein. From these results it emerges that the failure of previous investigators to dephosphorylate crude casein without a preceding transformation to phosphopeptone may be due to the inhibiting action of β-casein on the dephosphorylation of the α-form.

I wish to express my sincere thanks to Dr. Gerhard Schmidt of the Boston Dispensary for a generous sample of prostate phosphatase.

The Rockefeller Institute
for Medical Research
New York, N. Y.

Reduction of N-Nitrosodiphenylamine to *unsym*-Diphenylhydrazine by Lithium Aluminum Hydride[1]

By R. H. Poirier and F. Benington

Received February 11, 1952

The reduction of nitrosodimethylamine to *unsym*-dimethylhydrazine by adding the nitrosamine to an excess of lithium aluminum hydride has recently been described by Schueler and Hanna.[2] Their attempt to apply this procedure to the preparation of *unsym*-diphenylhydrazine by the reduction of N-nitrosodiphenylamine yielded only diphenylamine. We have found, however, that by using equimolar quantities of the reactants, *unsym*-diphenylhydrazine is obtained in 73% yield, along with approximately 20% of diphenylamine. Moreover, the yield of hydrazine is increased to more than 90% by an "inverse" order of addition, that is, by adding a solution of lithium aluminum hydride to N-nitrosodiphenylamine. The course of reaction is best expressed by the equation

$$2Ph_2NNO + 2LiAlH_4 \longrightarrow (Ph_2NN)_2AlLi + LiAlO_2 + 2H_2$$
$$\Big\downarrow 2H_2O$$
$$2Ph_2NNH_2 + LiAlO_2$$

Experimental

To 9.9 g. (0.05 mole) of N-nitrosodiphenylamine[3] in 50 ml. of dry ether at 10° was slowly added 57 ml. of a 0.97 molar solution of lithium aluminum hydride (0.055 mole) in ether. A precipitate, presumably $LiAlO_2$, appeared during the addition of the hydride to the nitrosamine. After standing at 10° for one hour, excess hydride and the product complex were decomposed by adding 25 ml. of wet ether followed by 100 ml. of a 30% solution of potassium sodium tartrate. The aqueous phase was separated and extracted with four 100-ml. portions of ether. Upon treating the combined ether solutions successively with water, brine solution, and ether previously equilibrated with concentrated hydrochloric acid, 10.85 g. of crude *unsym*-diphenylhydrazine hydrochloride precipitated. The crude product decomposed at 140–145°. Recrystallization from absolute ethanol gave 9.9 g. (90%) of silvery gray needles which began to decompose at 140°.[4]

Anal. Calcd. for $C_{12}H_{13}N_2Cl$: N, 12.7. Found: N, 12.2.

This product gave a mono-acetyl derivative which, after recrystallization from ethanol, melted at 188.5°,[5] and did not depress the melting point of an authentic sample.

Anal. Calcd. for $C_{14}H_{14}N_2O$: N, 12.4. Found: N, 11.9.

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[1] This is a part of the research supported by the United States Air Force under Contract AF 33(038)-12656.

[2] F. W. Schueler and C. Hanna, This Journal, **73**, 4996 (1951).

[3] S. Wexman, *Farm. Chilena*, **20**, 299 (1946).

[4] All decomposition and melting points are uncorrected.

[5] D. Vorländer and G. Bittins, *Ber.*, **68B**, 2269 (1935), reported 186° as the melting point for N-monoacetyldiphenylhydrazine, and 125° for N,N-diacetyldiphenylhydrazine.

Battelle Memorial Institute
Columbus 1, Ohio

Infrared Spectrum of Cyclobutene. A Correction

By John D. Roberts and C. W. Sauer

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Reëxamination of the infrared spectra reported for cyclobutene[1] has revealed that the samples were heavily contaminated with carbon dioxide (strong absorption at 2350 cm.$^{-1}$). The infrared spectrum of carbon dioxide-free cyclobutene pre-

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[1] J. D. Roberts and C. W. Sauer, This Journal, **71**, 3925 (1949).

pared by the decomposition of cyclobutyldimethylamine oxide[1] is shown in Fig. 1.

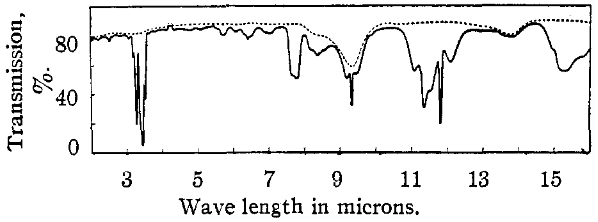

Fig. 1.—Infrared spectrum of cyclobutene at about 100 mm. pressure in 5-cm. cell with NaCl windows determined with Baird Spectrograph with NaCl prism. The solid line is the sample curve and the dashed line is the curve for the empty cell. The reference cell compartment contained a NaCl slab.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

The Structure of Methylenedihydrofuran

BY HAROLD L. RICE[1]

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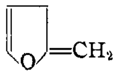
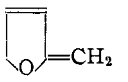
In the course of studies on the decomposition of hydrazones Kishner found[2] that furfural hydrazone half hydrate, when decomposed with heat in small portions over platinized clay plate and potassium hydroxide, gave, in addition to 2-methylfuran, a product which boiled at 78–80°. Two possible structures, I and II, were proposed for this material



I



II

on the basis of its conversion by a trace of acid into methylfuran and by analogy to the isomerization of methylenecyclohexane to methylcyclohexene.[3] Structure I, in which the exo- and endocyclic double bonds are not conjugated, was preferred by Kishner because the molecular refraction was in better agreement, and because a normal condensation product with maleic anhydride was not formed.[4] Levulinic anhydride and pentene-2-ol-1-one-4 were formed when the methylenedihydrofuran was hydrated, and this suggested that the material could be a mixture of I and II.

The present spectral investigation has, on the other hand, led to the conclusion that structure II is more likely. Non-aromatic conjugation is indicated by the strength and position of the absorption maximum; λ_{max}, 239 mμ; ϵ_{max}, 6300 mμ.

Comparison of the position of this maximum with those of β-phellandrene (232 mμ), 7-methylenecholesterol (236 mμ), $\Delta^{4,6}$-cholestadienol (238 mμ), and 9-oxycholestadienol (248 mμ) would indicate that there is conjugation.[5] That this conjugation is not aromatic can be seen from Fig. 1

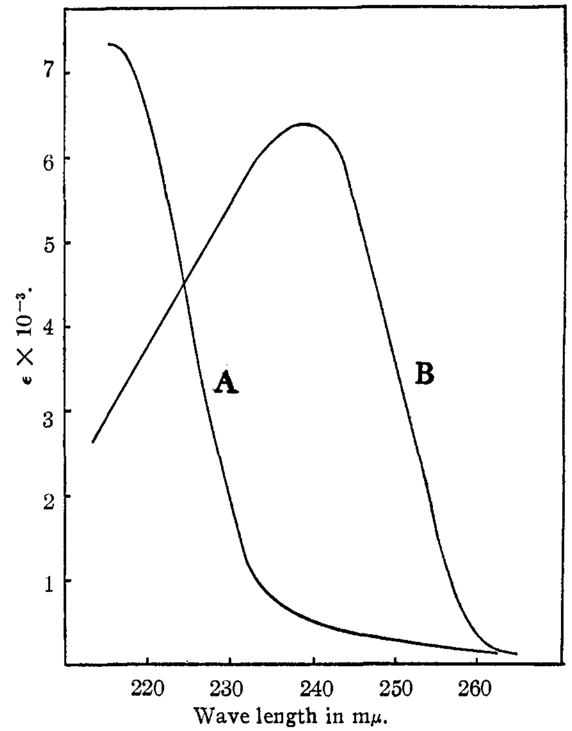


Fig. 1.—Absorption spectrum of 2-methylfuran (A) and 2-methylene-2,5-dihydrofuran (B) in absolute methanol.

wherein the maximum for methylfuran is at about 217 mμ The strength of the maximum in B is of the expected order of magnitude[6] when compared to those of vinylcyclohexene (8500) and cyclopentadiene (2,500).

The procedure which was reported by Kishner for the preparation of methylenedihydrofuran was followed closely here, but with somewhat variable results. The ratio of methylenedihydrofuran to methylfuran varied from 1.7 down to 0.43 in different preparations; ratios of about 1.0 were the most common. In order to improve the yield of methylenedihydrofuran and to decrease variability in the ratio of the isomers obtained, several different procedures were tried. The amount of hydrazone, of potassium hydroxide, and of platinized clay plate was changed independently with either no improvement in the constancy of the ratio of isomers or adverse effect on the yield. The time for each decomposition also was varied, again with no constant effect. The best yield of the unstable isomer was 29%, which was comparable to that reported by Kishner[2] (32%).

Experimental

Furfural Hydrazone Half Hydrate.—This compound was prepared in 89% yield by the method of Kishner.[2]

2-Methylene-2,5-dihydrofuran.—Furfural hydrazone half hydrate (530 g.) was added in 10–15-ml. portions to a mixture of 1.5 g. of potassium hydroxide pellets and 1.5 g. of platinized clay chips.[7] After each portion was added, the mixture was heated gently until the decomposition became self-sustaining. Because reaction was vigorous, a long and

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[1] du Pont Post-doctoral Fellow, University of Illinois, 1949. Present address, E. I. du Pont de Nemours & Co., Inc., Electrochemicals Department, Niagara Falls, New York.

[2] N. Kishner, *J. Gen. Chem.* (*U.S.S.R.*), **1**, 1212 (1931).

[3] A. Favorskii and I. Borgmann, *Ber.*, **40**, 4871 (1907).

[4] N. Kishner, *J. Gen. Chem.* (*U.S.S.R.*), **3**, 198 (1933).

[5] R. B. Woodward, THIS JOURNAL, **64**, 72 (1942).

[6] E. A. Braude, *Ann. Reports, Chem. Soc.*, 111 (1946).

[7] In the preparation of the catalyst 15 g. of clay chips was soaked in 15 ml. of 5% chloroplatinic acid, the water evaporated on a steam-bath and the material was reduced in a stream of hydrogen. The temperature was raised to 150° over a two-hour period. After cooling the system, the hydrogen was displaced by carbon dioxide and the chips were stored, for later use, under an atmosphere of carbon dioxide.