absolute ethanol as the solvent. The compounds examined were purified by fractional distillation immediately before determination of the spectra. In the case of mesityl methyl ether, the original sample was redistilled and the spectrum redetermined; identical results were obtained with both samples. The wave lengths and logarithms of the molar extinction coefficients at the absorption maxima and at prominent points of inflection are listed in Table I.

TABLE I

ULTRAVIOLET ABSORPTION DATA

Compound	Source[a]	Maxima[b] λ, (mμ)	Log ε
Mesityl methyl ether	1	315	1.50
		278	2.88
		274	2.83
		270	2.80
		215	3.90
p-Tolyl methyl ether	2	286	3.21
		279	3.27
		223	3.88
Mesitylene[c]	2	272	2.26
		268	2.26
		265	2.34
		(262)	2.24
		259	2.21
		(256)	2.17
		215	3.87

[a] Source references: (1) Biedermann and Ledoux, *Ber.*, 8, 57 (1875); (2) Eastman Kodak Co., redistilled. [b] The wave lengths in parentheses refer to inflection points. [c] *Cf.* Conrad-Billroth, *Z. physik. Chem.*, B29, 170 (1935); Pickett, Walter and France, THIS JOURNAL, 58, 2296 (1936).

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UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PA.
AND SWARTHMORE COLLEGE, SWARTHMORE, PA.
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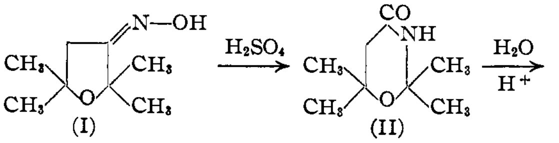
Beckmann Rearrangement of 2,2,5,5-Tetramethyltetrahydro-3-furanone Oxime

BY G. F. HENNION AND JOSEPH L. O'BRIEN

Previous work made available a liberal sample of 2,2,5,5-tetramethyltetrahydro-3-furanone.[1] It was thought that the Beckmann rearrangement of its oxime[2] (I) would prove of interest because the anticipated lactam (II) should undergo ring cleavage in the process, leading ultimately to acetone, ammonia and β,β-dimethylacrylic acid. These are indeed the products of the reaction with moderately strong sulfuric acid.



$$CH_3COCH_3 + (CH_3)_2C{=}CH{-}COOH + NH_3$$

This confirms the instability of (II) and indicates that the oxime (I) has the *trans* structure, perhaps on account of the steric effect of the neighboring *gem*-dimethyl group.

Experimental

A solution of 5 g. of the oxime (m. p. 122–123°)[3] in 10 ml. of approximately 77% sulfuric acid in a Claisen flask was heated while nitrogen was bubbled through it. Vigorous reaction occurred and about 3 ml. of distillate was recovered in the receiver cooled in a salt–ice mixture. After drying with calcium chloride (0.95 g. recovered), the boiling point (micro) was 62° and the n^{25}D 1.381. Qualitative tests indicated that it was chiefly acetone. In a duplicate run the distillate was treated with 2,4-dinitrophenylhydrazine; the derivative was obtained in 64% yield based on the oxime used and melted at 123–124°.

Ammonia liberated from one of the above sulfuric acid solutions, collected and titrated in the usual way, showed a 55% yield.

The alkaline residue from the ammonia distillation was filtered from a small amount of tar and extracted with ether (discarded). The aqueous solution was then acidified with sulfuric acid and extracted twice with 20-ml. portions of ether. The ether extract was dried with calcium chloride and the ether evaporated, leaving 0.75 g. of residue which soon crystallized. This material was purified by solution with potassium carbonate, reprecipitation with hydrochloric acid and crystallization from petroleum ether. Small needles melting at 66–67° were thus obtained. The bromine addition product melted at 105–106°. Ustinoff[4] gives 69.5–70° and 105–106° as the melting points of β,β-dimethylacrylic acid and its dibromide, respectively.

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[1] Froning and Hennion, THIS JOURNAL, **62**, 653 (1940).

[2] Dupont, *Ann. chim.*, [8] **30**, 536 (1913).

[3] Dupont[2] gives 128°.

[4] Ustinoff, *J. prakt. Chem.*, [2] **34**, 478 (1886).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA
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Halogen–Metal Interconversions with Halogenated Anilines and Anilides

BY HENRY GILMAN AND C. G. STUCKWISCH[1]

In connection with studies concerned with the introduction of variously substituted aryl groups into organolead compounds, it was desirable to prepare organolithium compounds containing functional groups such as amino or alkylamino. A method of choice for the synthesis of such types is the halogen–metal interconversion reaction.[2]

$$RX + R'Li \longrightarrow RLi + R'X.$$

The halogen compounds studied in the present investigation are *o*-bromoaniline, *p*-bromoaniline, *p*-bromo-N-methylaniline and N-(*p*-iodophenyl)-phthalimide. In each instance a diethyl ether solution of *n*-butyllithium was added to the halogen compound dissolved in diethyl ether. The reaction mixture was carbonated and the resulting acid isolated as such or as the benzenesulfonamide. Details are given in the experimental section.

The previously reported reaction of *n*-butyl-

[1] Present address: Department of Chemistry, University of Wichita, Wichita, Kansas.

[2] (a) Gilman and Stuckwisch, THIS JOURNAL, **64**, 1007 (1942); (b) Gilman and Arntzen, *ibid.*, **69**, 1537 (1947); (c) Gilman and Melstrom, *ibid.*, **70**, 4177 (1948); (d) for general references, see pp. 538–539 of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943.

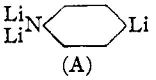
TABLE I

REACTIONS OF RX COMPOUNDS WITH n-C_4H_9Li

RX	RX, mole	Ether, cc.	n-C_4H_9Li, mole	Ether, cc.	Reaction time, min.	Product[a]	Yield, %
o-$BrC_6H_4NH_2$	0.042	25	0.128	125	45	Sulfonamide	40
p-$BrC_6H_4NH_2$	.033	25	.10	100	60	Sulfonamide	65
p-$BrC_6H_4NHCH_3$[b]	.063	25	.13	150	60	Acid[c]	27
N-p-$IC_6H_4(CO)_2C_6H_4$[d]	.03	0[e]	.03	250	60	Acid	37

[a] See general procedure. [b] Prepared in essential accordance with the procedure of Chowdhury, Desai and Hunter, *J. Indian Chem. Soc.*, 10, 637 (1933). [c] Identified by mixed melting point with an authentic specimen. Houben and Shottmueller, *Ber.*, 42, 3739 (1909). [d] Prepared by the method of Gabriel, *Ber.*, 11, 2260 (1878). [e] RX was added in the solid state to the solution of n-C_4H_9Li.

lithium with p-bromoaniline[2a] has now been more carefully examined. In this reaction there is formed a bright yellow precipitate which has been isolated and analyzed. It appears to be p-N,N-trilithioaniline (A).



(A)

This product, when dry, is highly explosive in contact with air. When less than two equivalents of n-butyllithium were used, or when the reaction mixture was extremely dilute, no precipitate formed and no p-aminobenzoic acid could be isolated after carbonation of the reaction mixture.

Experimental

General Procedure.—An ether solution of n-butyllithium, standardized by the indirect procedure,[3] was added to the RX compound dissolved in ether. In the experiments with o- and p-bromoaniline, approximately one-third of the RLi solution was added at such a rate that gentle refluxing was maintained. The heat of reaction then subsided and the remainder of the solution was added rapidly. With p-bromo-N-methylaniline one-half of the solution was added dropwise and the remainder rapidly. All of the interconversions were carried out at room temperature with the exception of the one with N-(p-iodophenyl)-phthalimide. The latter was run at −50°. The reaction times given in the accompanying table apply to the period of time after the addition of RLi solution was completed. All reaction mixtures were poured on a suspension of crushed, dry carbon dioxide in ether and then hydrolyzed with water. The acid produced was isolated by acidifying the aqueous alkaline layer of the hydrolyzed mixture or by treating the aqueous alkaline layer with benzenesulfonyl chloride and then precipitating the benzenesulfonamide of the amino acid with dilute hydrochloric acid. Details are given in Table I.

p-N,N-Trilithioaniline.—An ether solution of n-butyllithium was added to p-bromoaniline as described in the preceding section. The yellow precipitate was collected under nitrogen, on a sintered-glass disc sealed into a previously tared weighing bulb. The weighing tube was swept with a warm current of nitrogen until it came to constant weight. The dried precipitate was slowly hydrolyzed with moist ether and finally with water. The ether layer was separated and dried over anhydrous sodium sulfate and fractionated. The aniline fraction was identified as acetanilide. The aqueous layer was titrated with 0.5 *N* hydrochloric acid. Aniline and lithium hydroxide were present in a 1 to 3 molar ratio. The yield of dry p-N,N-trilithioaniline was 70%.[4]

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(3) Gilman and Haubein, THIS JOURNAL, 66, 1515 (1944).

(4) The authors are grateful to R. K. Abbott for assistance.

The Influence of the Walls of the Autoclaves Upon the Hydrogenation of p-Cymene

BY V. N. IPATIEFF, HERMAN PINES AND E. E. MEISINGER

During the study of hydrogenolysis of polycyclic compounds in the presence of a copper–alumina catalyst[1] (67% CuO, 33% Al_2O_3) it was noticed that the degree of hydrogenolysis depended upon the autoclave used; a stainless steel autoclave caused much more hydrogen to be absorbed than an ordinary steel autoclave. In order to investigate the effect of ordinary and stainless steel autoclaves upon hydrogenation, p-cymene was subjected to the treatment with hydrogen in the presence of a copper–alumina catalyst.

The reaction was carried out in rotating autoclaves of 450-cc. capacity charged with 60 g. of p-cymene and with 6 g. of the above-mentioned CuO–Al_2O_3 catalyst which were heated at 325° for five hours in the presence of hydrogen at an initial pressure of 100 atmospheres. The percentage of p-cymene in the product was determined by ultraviolet absorption based on the band at 273.5 mμ equivalent.

In the absence of the catalyst no reaction took place irrespective of the material with which the autoclave was lined. In the presence of the catalyst there was formed (a) in the steel autoclave 2% of p-menthane; (b) in the stainless steel autoclave[2] 48% of p-menthane and 10% of lower boiling aromatics; (c) in the steel autoclave with a new stainless steel liner 21% of p-menthane and 2% of lower boiling aromatics.

The results with the newly machined stainless steel liner showed that the promoting effect could have only been in part due to any contamination present in the old stainless steel autoclave where the largest percentage of p-menthane was formed. The most probable explanation of these results is that the stainless steel is responsible for all of the promoting effect, the greater activity of the old stainless steel autoclave as compared with the autoclave with the new steel liner being due to

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(1) V. N. Ipatieff and V. Haensel, THIS JOURNAL, 64, 520 (1942).

(2) The following is the composition of the steel as recorded by the manufacturer: The ordinary steel bomb was made of 1020 steel which contained carbon, 0.15–0.25%; manganese, 0.30–0.60%; phosphorus, 0.045% max.; sulfur, 0.50% min. The stainless steel bomb was made of type 304 grade 18-8 which contained carbon, 0.08%; manganese, 2.00%; silicon, 0.5% max.: chromium, 18–20%; nickel, 8–10%.