

A possible mechanism for this reaction, in which the formation of dibenzoselenophene proceeds through the intermediate, *o*-biphenylselenenyl bromide, (IV), is shown below. The presence of the selenenyl bromide is indicated by the dark violet color of the solution, a color typical of compounds of this type. This color disappears as the reaction progresses. When very pure diselenide is used, the completion of the reaction is indicated by almost complete disappearance of the monobromide and by cessation of hydrogen bromide evolution.

Experimental

***o*-Selenocyanobiphenyl.**—Eighty-six grams of technical grade *o*-aminobiphenyl was dissolved in 75 cc. of warm concentrated sulfuric acid. This solution was added to 2.5 liters of ice-water in a large enamelware pail, mechanical stirring was initiated and 36 g. of solid sodium nitrite was added in small portions, keeping the temperature below 7°. Solid sodium acetate was added to the diazonium solution until the solution no longer turned congo red paper blue. A solution of 0.5 mole of sodium selenocyanate⁶ was slowly added to the buffered solution while thorough stirring was maintained. The mixture was allowed to decompose for an hour, after which the brown oil produced was extracted with 1500 ml. of benzene. The benzene extractions were dried with anhydrous sodium sulfate and the benzene stripped off. Distillation at 157–160° (1.1 mm.), using a short-path distilling flask with a built in spray-trap, yielded 95 g. (71%) of an orange oil, the crude selenocyanate.

Di-(*o*-biphenyl) Diselenide (III).⁴—To a solution of 60 g. of potassium hydroxide in 240 g. of methanol was added 86 g. of *o*-selenocyanobiphenyl. The mixture was swirled vigorously, allowed to stand for 30 minutes, then added to a separatory funnel containing 2 liters of saturated aqueous boric acid and one liter of benzene. After vigorous shaking, the aqueous layer was discarded and the benzene layer washed twice with 1500-ml. portions of distilled water. The benzene solution was then dried with anhydrous magnesium sulfate, the solvent removed by evaporation on a steam-bath and the residue was recrystallized twice from 250-ml. portions of acetone. The diselenide forms large, canary-yellow crystals, m. p. 100–101°. The yield was 62 g. (80%).

Anal. Calcd. for C₂₄H₁₈Se₂: Se, 34.0; equiv. wt., 77.4. Found: Se, 34.0; equiv. wt.,⁵ 76.8.

Behagel and Hofmann report a m. p. of 77–78°. The identity of our compound was substantiated both by analysis and by oxidation to *o*-biphenylseleninic acid⁷ which was shown to be non-identical to both the meta and para isomers. The latter two compounds are described in another communication.

Dibenzoselenophene.—To a solution of 62 g. of twice recrystallized di-(*o*-biphenyl) diselenide in 250 ml. of redistilled carbon tetrachloride was added 23 g. of bromine. The solution was allowed to stand on a sand-bath at 78–80° for 36 hours, at the end of which time the intense color had almost completely disappeared, the evolution of hydrogen bromide gas had ceased and the total volume of solution had been reduced to about 170 ml. The solution was decolorized once, the carbon tetrachloride removed by evaporation on a steam-bath, and the almost colorless residue purified either by recrystallization from a mixture of 25 ml. of carbon tetrachloride and 400 ml. of methanol or by vacuum distillation (136–139° at 1.5–2.0 mm.). The yield was 60 g. (97%). When less pure diselenide was used, the reaction was severely retarded, for the reaction mixture did not fade, even after standing on the sand-bath for 48 hours. In such cases, the reaction was accelerated by evaporating off the solvent and keeping the dark-colored residue at 120–130° until evolution of hydrogen bromide

has ceased. Subsequent vacuum distillation produced a water-white product, m. p. 73°.

Anal. Calcd. for C₁₂H₈Se: Se, 34.2. Found: Se, 34.1.

Dibenzoselenophene Oxide.—To 4 g. of dibenzoselenophene was added dropwise a 40% solution of peracetic acid in glacial acetic acid.⁸ The solution immediately became hot, and the solid disappeared. The mixture was then allowed to cool to room temperature and 5 ml. of concentrated ammonium hydroxide was added, precipitating the selenoxide as a white solid. The oxide was recrystallized from 100 ml. of water and dried for one hour in an Abderhalden pistol at 90° over phosphoric anhydride. The product melted at 229–230° (dec.). The yield was 1.9 g. (48%).

Anal. Calcd. for C₁₂H₈SeO: Se, 32.0; equiv. wt., 123.6. Found: Se, 32.1; equiv. wt. (iodometric), 123.7.

(8) Obtained from the Buffalo Electrochemical Co., Buffalo, N. Y.

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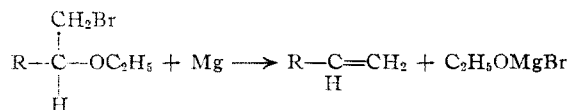
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The Alpha Elimination in Grignard Preparations

By L. S. MOODY

When β -chloroethoxytrimethylsilane reacts with magnesium in diethyl ether, the expected Grignard reagent is not obtained. Instead a gas, non-condensable at Dry Ice-toluene temperature, is steadily evolved during the course of the reaction. The gas will readily decolorize bromine dissolved in glacial acetic acid and is presumed to be ethylene. A heavy precipitate of the magnesium salt of trimethylsilanol is formed during the reaction. No products from the expected Grignard reagent have been found.

The elimination of the trimethylsiloxy group from the molecule is analogous to known eliminations. Thus Grignard¹ reported that β -chlorophenetole and magnesium gave ethylene and phenoxymagnesium bromide. Swallen and Boord² reported that β -bromo alkyl ethers underwent a similar elimination



Likewise, it has been shown³ that from magnesium and ethylene dibromide, only ethylene and magnesium bromide are obtained as products.

(1) Grignard, *Compt. rend.*, **138**, 1048 (1904).

(2) L. C. Swallen and C. E. Boord, *THIS JOURNAL*, **52**, 651 (1930).

(3) Chao-Lun Tseng and Fu-Min. Fam, *Science Quart. Nat. University Peking*, **4**, 1–8 (1934); *C. A.*, **28**, 4376^a (1934).

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Furanization and Cleavage of 1,4-Diketones by Use of Polyphosphoric Acid

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The present paper reports the effectiveness of polyphosphoric acid, originally used for cyclodehy-

(1) du Pont Postdoctoral Fellow 1949–1950. Research and Development, Phillips Petroleum Company, Bartlesville, Oklahoma.

(6) T. W. Campbell and J. D. McCullough, *THIS JOURNAL*, **67**, 1965 (1945).

(7) J. D. McCullough and E. S. Gould, *ibid.*, **71**, 674 (1949).

TABLE I
 FURANIZATION OF 1,4-DIKETONES

1,4-Diketone	Reacn. temp., °C.	Time, min.	Derivative	Yield, %	M. p., °C.	M. p., °C. (lit.)	Method of purif. ^a
1,2-Dibenzoyl ethane	130-140	90	2,5-Diphenyl- ^b	95	88-89	88-90 ⁷	S
1,2-Bis-(<i>p</i> -bromobenzoyl)-ethane	145-150	90	2,5-Bis-(<i>p</i> -bromophenyl)- ^b	91	201-202	201-202 ⁸	R
1,2-Bis-(<i>p</i> -chlorobenzoyl)-ethane	130-140	90	2,5-Bis-(<i>p</i> -chlorophenyl)- ^c	97	168-169		R
1,2-Bis-(<i>p</i> -toluyl)-ethane	145-150	20	2,5-Bis-(<i>p</i> -tolyl)- ^b	61	165-166	165-166 ⁹	S
1,2-Bis-(<i>p</i> -bromobenzoyl)-1,2-dibromo-ethane	150-155	90	2,5-Bis-(<i>p</i> -bromophenyl)-3,4-dibromo- ^b	43	190-191	190-191 ¹⁰	S, R
1,2-Dibenzoylcyclohexane	140-150	30	^d	62	97-98	97-98 ¹¹	S, R
1,2-Dibenzoyl-4,5-dibromocyclohexane	140-150	30	^e	26	149-150	149-150 ¹²	S, R
Acetylacetone	Tars; no acetylacetone could be recovered						

^a S = sublimation at 0.5 mm.; R = recrystallization from ethanol. ^b Identified by a mixed melting point determination with an authentic sample. ^c *Anal.* Calcd. for C₁₈H₁₀Cl₂O: C, 66.69; H, 3.50; Cl, 24.61. Found: C, 66.41; H, 3.64; Cl, 24.48. ^d Product = 1,3-diphenyl-4,5,6,7-tetrahydroisobenzofuran. ^e Product = 5,6-dibromo-1,3-diphenyl-4,5,6,7-tetrahydroisobenzofuran.

 TABLE II
 CLEAVAGE OF HINDERED KETONE GROUPS

Reactant	Reacn. temp., °C.	Time, min.	Product	B. p., °C.	Yield, %	n _D ²⁰
1,2-Dimesitylolethane	170-175	35	Mesitylene ^a	162-164	80 ^b	1.4921
1,2-Dimesitylolethane	170-180	45	Mesitylene ^a	162-163 ^{1/2}	52 ^b	1.4923
Benzoylmesitylene	180-185	30	Mesitylene ^a	163-164	63	1.4919
			Benzoic acid		57	
1,2-Bis-(2,4,6-triisopropylbenzoyl)-ethane	200-210	180	No reacn.; 95% recovery of reactant			

^a Identified as the trinitro derivative, m. p. 222-223°. ^b Yield is based on formation of two moles of mesitylene per mole of diketone.

dration reactions by Snyder and Werber,² for the conversion of 1,2-diaroyl ethanes (1,4-diaryl-1,4-butanediones) to the corresponding 2,5-diarylfurans. In Table I is listed a series of 1,4-diketones which have been furanized successfully. In general, 2,5-diarylfurans can be prepared in high yields by this method whereas 1,3-diarylisobenzofuran derivatives can be prepared only in low yields.

Polyphosphoric acid is superior to dehydration reagents such as sulfuric acid,³ acetic anhydride,⁴ hydrochloric acid,⁵ zinc chloride,⁶ phosphorus pentoxide⁶ and many others used for similar furanization reactions.

In contrast to the above results hindered 1,2-diaroyl ethanes are not cyclized by polyphosphoric acid, but they may be cleaved to yield an aromatic hydrocarbon and an acid fraction. This effect is not unexpected since Lutz, Johnson and Wood¹³ have found that 1,2-dimesitylolethane is cleaved by 85% phosphoric acid at elevated temperatures to give mesitylene and succinic acid. Similarly mesi-

tyl phenyl ketone is cleaved to give mesitylene and benzoic acid. In the case of the very hindered 1,2-bis-(2,4,6-triisopropylbenzoyl)-ethane neither cleavage nor furanization occurs at temperatures up to 210°. Results obtained with hindered diketones are listed in Table II.

Experimental¹⁴

Furanization of 1,4-Diketones.—A mixture of 2 g. of the diketone and 8-10 g. of polyphosphoric acid in a 50-ml. flask was stirred and heated in an oil-bath at the temperature indicated in Table I. The colored complex which formed was decomposed by pouring it into 100 g. of crushed ice. The crystalline furan which separated was recovered by filtration and purified by sublimation and/or recrystallization. Identification was aided by mixed melting point determinations with authentic samples when indicated.

Cleavage of Hindered 1,4-Diketones.—The procedure for the cleavage of hindered 1,4-diketones was essentially the same as that described for the furanizations. In a 2-necked 100-ml. flask, fitted with a rubber sealed stirrer and a water condenser set for downward distillation, a mixture of 10 g. of the diketone and 50 g. of polyphosphoric acid was stirred and heated in an oil-bath at the temperature indicated in Table II. The pressure was maintained at 25-30 mm. by means of a water aspirator to facilitate removal of the liquid aromatic hydrocarbon fraction as it formed. The hydrocarbon, mesitylene, was purified by distillation and identified by its refractive index and conversion to its trinitro derivative.¹⁵ The polyphosphoric acid residue was hydrolyzed with ice and water, but only in the run with mesityl phenyl ketone could an acid fraction be isolated. In this case benzoic acid precipitated during the hydrolysis and

(14) All melting and boiling points are uncorrected.

(15) Shriner and Fuson, "Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 163.

- (2) Snyder and Werber, *THIS JOURNAL*, **72**, 2962 (1950).
- (3) Smith, *J. Chem. Soc.*, **87**, 643 (1890).
- (4) Paal, *Ber.*, **17**, 2559 (1884).
- (5) Borsche and Fels, *ibid.*, **39**, 1925 (1906).
- (6) Dietrich and Paal, *ibid.*, **20**, 1085 (1887).
- (7) Paal, *ibid.*, **21**, 1491 (1888).
- (8) Thiele and Rossner, *Ann.*, **306**, 214 (1899).
- (9) Holleman, *Rec. trav. chim.*, **6**, 72 (1887).
- (10) Perkins and Schlosser, *J. Chem. Soc.*, **57**, 954 (1890).
- (11) Fuson, Speck and Hatchard, *J. Org. Chem.*, **10**, 55 (1945).
- (12) Adams and Gold, *THIS JOURNAL*, **62**, 61 (1940).
- (13) Lutz, Johnson and Wood, *ibid.*, **60**, 716 (1938).

was collected by filtration; it was purified by sublimation and identified by melting point, 121–122°, and by a mixed melting point with an authentic sample.

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Some Factors Influencing the Activity of Raney Nickel Catalyst. I. Preparation of Raney Nickel from Nickel–Magnesium Alloy¹

BY JOHN N. PATTISON AND ED. F. DEGERING²

The preparation of Raney nickel from nickel–magnesium alloys has been the subject of three patents.^{3,4,5} None of these give details of the preparation or the activity of the catalysts thus prepared. Organic acids, such as acetic, in concentrations of 20% or less were recommended by Zeltner.⁴

We have studied the preparation of Raney nickel from nickel–magnesium alloys and found that a catalyst comparable in activity to that of Pavlic and Adkin W-4⁶ can be produced. The activity comparisons were based on the rate of reduction of styrene at ambient temperature in an Adams reductor. In order to eliminate induction effects, only the time for the middle 64% of the reduction was used. Thus we found W-4 to be 2.12 times as active as W-2⁷ and the catalyst described in detail below to be 2.02 times as active as W-2.

Experimental

To a 2-liter erlenmeyer flask, equipped with a Hershberg stirrer, add 230 ml. of glacial acetic acid and 500 ml. of water. The temperature of this solution is brought to 50 ± 2° and 100 g. of finely powdered NiMg alloy (50% Ni by weight) is added in small portions over a period of 20 to 30 minutes. Cooling is provided by an external ice-bath in order to maintain the temperature between 48 and 52° during the addition. After all of the alloy has been added, the mixture is digested for 50 minutes at 50° with continued stirring. The catalyst is allowed to settle and the solution decanted. Approximately 500 ml. of 1% acetic acid is added, the mixture is swirled and allowed to settle before decanting again. The mixture is rinsed twice more in this fashion and then transferred to a 75 × 500 mm. Pyrex tube equipped with a side arm 1 inch below the top and a coarse porosity sintered disc at the bottom for the admission of the wash solution. A stainless steel stirrer is placed just above the disc and a baffle is provided near the top to aid in settling. About 10 liters of 1% acetic acid is passed upward through the catalyst which is suspended to a height of about 250 mm. by regulation of the stirring speed. Following this, the catalyst is similarly washed with about 15 liters of distilled water. The rate of flow of the wash solutions is 150 ml. per minute. After the washing is complete, the water is drawn off through the sintered disc and replaced by a suitable solvent such as absolute alcohol or dioxane for future storage. Fresh portions of the solvent are stirred up with the catalyst and withdrawn through the

sintered disc four to six times to remove the water. The catalyst should be stored in a tightly closed bottle completely filled with liquid in order to exclude contact with oxygen.

Discussion.—Variation of the mesh size of the alloy and amount of acid used in the activation step had very little effect on the activity of the catalyst produced. However, the amount of nickel in the alloy and the method of washing are very important. A catalyst prepared from a 30% nickel (by weight) alloy was only one-half as active as one prepared from a 50 weight per cent. alloy of nickel. If the acetic acid wash is omitted, the resulting preparation will not reduce styrene at all under these conditions.

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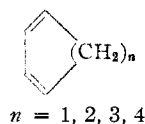
THE PURDUE RESEARCH FOUNDATION AND
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Ultraviolet Absorption Spectrum of 1,3-Cycloheptadiene

BY E. PESCH AND S. L. FRIESS

In connection with a study of conjugated unsaturation in cyclic systems, it was of interest to prepare a sample of 1,3-cycloheptadiene (I) to be used for determination of its ultraviolet absorption spectrum. Although the compound has been prepared previously by several workers,^{1,2} no mention was made of its absorption characteristics. Further, since the ultraviolet spectra of cyclopentadiene,³ 1,3-cyclohexadiene^{4a,b} and 1,3-cyclooctadiene⁵ in suitable solvents are available in the literature, the evaluation of the wave length of maximum absorption for I in the present study fills the blank for the seven-membered diene, and makes possible a correlation of λ_{\max} values with ring size in the series of conjugated cyclic dienes



Experimental⁶

The cyclic diene I was prepared by experimental procedures exactly paralleling those used by Cope⁶ for the synthesis of 1,3-cyclooctadiene. The synthetic sequence is outlined below. With the exception of II, all members of the sequence were previously known and characterized.

- (1) From the Ph. D. Thesis of John N. Pattison, Purdue University, June, 1948; Battelle Memorial Institute, Columbus, Ohio.
- (2) Miner Laboratories, Chicago, Illinois.
- (3) French Patent 844,783, May 1, 1939.
- (4) J. Zeltner, U. S. Patent 2,326,275, August 10, 1943.
- (5) J. H. Hahn, U. S. Patent 2,328,140, August 31, 1943.
- (6) Pavlic and Adkins, *THIS JOURNAL*, **68**, 1471 (1946).
- (7) Moringo, *Organic Syntheses*, **31**, 15 (1941).

- (1) Willstätter, *Ann.*, **317**, 204 (1901).
- (2) Kohler, Tishler, Potter and Thompson, *THIS JOURNAL*, **61**, 1057 (1939).
- (3) Scheibe, *Ber.*, **59**, 1333 (1926).
- (4) (a) Allsopp, *Proc. Roy. Soc. (London)*, **143A**, 618 (1934); (b) Henri and Pickett, *J. Chem. Phys.*, **7**, 439 (1939).
- (5) Cope and Estes, *THIS JOURNAL*, **73**, 1128 (1950).
- (6) Melting points are corrected. Analyses by Mrs. G. L. Sauvage.