completion of the addition, the mix was refluxed for 5.0 hr. The mix was then partially hydrolyzed by the cautious addition of 2.3 l. of 5% aqueous hydrochloric acid. At this point $MgCl_2 \cdot 6H_2O$ dropped out of suspension and the clear organic layer was separated. The salt was then dissolved by the addition of 2.0 l. of water. The very small organic layer that resulted was separated and combined with the major fraction.

The solution was fractionally distilled through a column of 8 theoretical plates to yield (*1*) 6800 ml. (85%) of pentane, b.p. 35–40° and (*2*) 3128 g. (85%) of tetrahydrofuran, b.p. 63–68°.

When the temperature of the distillate at the head of the column reached 129°, the column was by-passed and the product was distilled through a simple distillation head to yield (*3*) 417.5 g. (87.5%) of tetravinylsilane, b.p. 129–132°.

Dimethyldivinylsilane. In a 22.0-l. flask was placed 13.5 mole of vinylmagnesium chloride in 3100 g. of tetrahydrofuran. To this was added 725 g. (6.0 mole) of dimethyldichlorosilane in 8.0 l. of pentane; addition time 5.0 hr., reflux time 5.0 hr. The reaction mixture was then hydrolyzed and the organic layer separated.

The solution was fractionally distilled through a column of 8 theoretical plates to remove 7.0 l. (87.5%) of pentane, b.p. 36–40°. The residue was then fractionally distilled through a column of 75 theoretical plates to remove 2985 g. (96.4%) of tetrahydrofuran, b.p. 60–68°. When the temperature of the distillate at the head of the column reached 79°, the column was by-passed and the product was distilled through a simple distillation head to yield 396.7 g. (66.1%) of dimethyldivinylsilane, b.p. 79–82°.

Diphenyldivinylsilane. In a 22.0-l. flask was placed 9.2 mole of vinylmagnesium chloride in 2160 g. of tetrahydrofuran. To this was added 1042 g. (4.12 mole) of diphenyldichlorosilane in 8.0 l. of pentane at a rate to maintain reflux; addition time 3.0 hr., reflux time 8.0 hr. The reaction mixture was then hydrolyzed and the organic layer separated.

The solvents were then stripped using steam as the heat source and the residue was distilled under reduced pressure to yield 778.9 g. (80%) of diphenyldivinylsilane distilling at 130–131°/0.05 mm.

Triphenylvinylsilane. In a 22.0-l. flask was placed 10.8 mole of vinylmagnesium chloride in 2600 g. of tetrahydrofuran. To this was added 2659 g. (9.0 mole) of triphenylchlorosilane in 5.0 l. of tetrahydrofuran plus 3.0 l. of pentane; addition time 1.5 hr., reflux time 8.0 hr. The reaction mixture was then hydrolyzed and the organic layer separated. The solvents were then removed by distillation with the last traces distilling under reduced pressure (25 mm.). The residual oil was transferred to a crock and was solidified by cooling the crock in an ice bath. The solid was ground up, transferred to a 12.0 l. flask, and crystallized by dissolving in 3.0 l. of 90% ethanol plus 1.0 l. of benzene at reflux and cooling slowly to 15° with stirring. The solid was filtered by suction and thoroughly air-dried to give 1900 g. (73.5%) of triphenylvinylsilane melting at 57.5–59.5°. Concentration of the mother liquid led to the isolation of 350 g. (13.6%) of triphenylvinylsilane melting at 53–58°.

Acknowledgment: The authors would like to thank Dr. Marie Farnsworth and her coworkers in the Physical and Analytical Section of this laboratory for their assistance throughout this work.

RAHWAY, N. J.

[CONTRIBUTION FROM THE RAHWAY RESEARCH LABORATORY OF THE METAL & THERMIT CORP.]

Arylmagnesium Chlorides. Preparations and Characterizations[1]

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JOHN J. WALBURN, AND ROBERT CSERR

Received May 10, 1957

Substitution of tetrahydrofuran for ethyl ether allows conversion of aryl chlorides to arylmagnesium chlorides.

Although phenylmagnesium chloride has been known for a number of years, no general procedure has been forthcoming for the preparation of other arylmagnesium chlorides. The preparations of phenylmagnesium chloride in chlorobenzene in the absence of solvent under pressure,[2] using freshly prepared magnesium,[3] catalytic quantities of metal salts,[4] a special magnesium-copper alloy and ethyl ether and allowing an initiating period of 4–11 days[5] or using the diethyl ether of ethylene glycol[6] do not seem to be general enough for preparing other arylmagnesium chlorides. Usually for these compounds it is necessary to use molar quantities of ethyl bromide as an entrainment carrier for the aryl chloride.[7] Compounds made in this way include phenylmagnesium chloride and *p*-chlorophenylmagnesium chloride. Pentamethylphenyl-

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(1) Parts of this paper were presented at the 130th National Meeting of the AMERICAN CHEMICAL SOCIETY, Atlantic City, Sept., 1956.

(2) H. Gilman and R. Brown, *J. Am. Chem. Soc.*, **52**, 3330–2 (1930); P. Shornigin, *et al.*, *Ber.*, **64B**, 2584 (1931); E. Britton and Slagh, U. S. Patents **1,996,746** [*Chem. Abstr.*, **29**, 3352 (1935)] and **2,056,822** [*Chem. Abstr.*, **30**, 8246 (1936)].

(3) R. Manske and A. Ledingham, *Can. J. Research*, **27B**, 158 (1949); A. Weissenborn, Ger. Patent **697,420** (1940) [*Chem. Abstr.*, **35**, 6600^4 (1941)]; and U. S. Patent **2,058,373** [*Chem. Abstr.*, **31**, 118^2 (1937)].

(4) A. Weissenborn, Ger. Patent **660,075** (1938) [*Chem. Abstr.*, **32**, 5857^1 (1938)].

(5) H. Gilman and N. St. John, *Rec. trav. chim.*, **49**, 717 (1930).

(6) J. Hill, U. S. Patent **2,552,676** (1951) [*Chem. Abstr.*, **45**, 9079f (1951)].

(7) W. V. Evans and E. M. Diepenhorst, *J. Am. Chem. Soc.*, **48**, 715 (1926); R. T. Dufford, S. Calvert, and D. Nightingale, *J. Am. Chem. Soc.*, **45**, 2068 (1923); T. Jezierski, *Roczniki Chem.*, **20**, 47 (1946) [*Chem. Abstr.*, **42**, 1910 (1948)].

TABLE I

PREPARATION OF GRIGNARD REAGENTS

Aryl Chloride	Heating	Addition, Time/Hr.	Time to Complete,[a] Hr.	Yield[b]	Remarks
Chlorobenzene	None	1.0	2.0	95	
o-Chlorotoluene	Throughout	1.5	2.25	98.5	
p-Chlorotoluene	Throughout	1.0	1.3	93	
m-Chlorotoluene	Throughout	1.0	2.5	96	The *m*-chlorotoluene must be freshly distilled
2-Chloro-*p*-xylene	Throughout	3.5	0.5	92.5	Difficult initiation
p-Ethylchlorobenzene	Throughout	1.5	6.0	97	Magnesium used, 96.7%
p-Chloroanisole	To initiate[c]	3.0	5.0 at 45° C.	77	
o-Chlorophenetole	Throughout	1.75	2.5	98.5	
p-Dichlorobenzene	None	1.0	2.0	96	[d]
o-Dichlorobenzene[e]	Throughout	8.75	22.5	19	
Hexachlorobenzene[f]	Throughout	7.0	0.5	77.5	
p-Chlorodiethylaniline	Throughout	1.25	10.0	95.5	Magnesium used, 91.7%
p-Chlorodimethylaniline				88	
2,4-Dichlorotoluene	To initiate			83	
2,4-Dichlorophenetole	To initiate			90	Magnesium used, 92.1%
o-Trifluoromethylchlorobenzene	Throughout			62	
m-Trifluoromethylchlorobenzene[g]	Throughout			5.7	
p-Trifluoromethylchlorobenzene[g]	Throughout			9.1	
Ethylpentachlorobenzene	None			49	Strongly exothermic
m-Fluorochlorobenzene	Throughout		3	50	Magnesium used, 89.2%
Monochlorobiphenyl[h]	Throughout	14.3	8.0	22.6	
α-Chloronaphthalene	Throughout	2.0	6.0	40	

[a] After addition. [b] Titration.[20] [c] At 79° C. a rapid exothermic reaction began. [d] On hydrolysis, no benzene was found. In further work, some benzene has been obtained, as well as higher boiling residues. [e] Illustration of the *ortho* chlorine effect. Some 65–70% of the magnesium was consumed. [f] Hexachlorobenzene required a cyclic process and 7.0 moles of tetrahydrofuran. A second run adding solid hexachlorobenzene was exothermic after initiation.[18] [g] The *m*- and *p*-trifluoromethylchlorobenzenes reacted vigorously at first, but coated the magnesium badly. [h] Arochlor 1221, an impure monochlorobiphenyl.

magnesium chloride has been prepared, but no details of its preparation are available.[8]

Normant recently reported the successful preparation of phenylmagnesium chloride and *p*-chlorophenylmagnesium chloride using tetrahydrofuran as solvent.[9] Although he gives no details of procedure, these preparations are easily carried out. In an extensive study of the preparation of arylmagnesium chlorides carried out in this laboratory and independently of Normant,[10] it has been determined that every aryl chloride or heterocyclic chloride[11] tried reacts with magnesium in tetrahydrofuran. With most aryl chlorides results have been excellent in forming Grignard reagents, except where ortho chlorine atoms are present or more than two chlorine atoms are on the same aromatic ring, in which case considerable coupling occurs. Hexachlorobenzene is an exception and does not display this behavior. Yields as summarized in Table I, show, this reaction to be very much more general than Normant states.

In a further study of the scope of this reaction, ethers other than tetrahydrofuran were investigated as suitable solvents. No simple ethers of the open chain type R-O-R′ were found to be effective for aryl chlorides other than chlorobenzene. However, with the cyclic ethers a limitation was found. Tetrahydropyran[12a] 2-methyltetrahydrofuran, tet-

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[8] H. Clement and J. Savard, *Compt. rend.*, **204**, 1724 (1937).

[9] H. Normant, *Compt. rend.*, **239**, 1510 (1954).

[10] Our work was carried out within a few months of that by Normant (as determined by private communications with Prof. Normant, of the Sorbonne, Paris, France, during 1955).

[11] H. E. Ramsden and A. E. Balint, unpublished results.

[12a] As contrasted to the discouraging results obtained by H. Hepworth, *J. Chem. Soc.*, 119, 1249–52 (1921). (b) In further reactions where excess acidic reagents are present these two solvents are unstable.

rahydrofurfuryl ethyl ether, 2-ethoxytetrahydropyran,[12b] and dihydropyran[12b] were all found to be good solvents for the preparation. *N*-Methylmorpholine has shown some use as a solvent in this reaction. Pentamethylene sulfide, tetramethylene sulfide, and furan do not seem to be suitable solvents, although 4-thiapentamethylene oxide does function to some extent. Reaction does not occur in 2,5-dimethyltetrahydrofuran or 2,2,5,5-tetramethyltetrahydrofuran as solvent; not even chlorobenzene could be induced to react in these two solvents.

These facts may suggest that a possible mechanism is tied in with the availability of the oxygen *p* electrons. The configuration of the ring is such as to make these electrons more available for coordination than is true with ethyl ether or any of the R-O-R types and the coordination may serve to drive the reaction to completion, either by the simple matter of dissolving reagent off the surface of the magnesium, by free energy relationships, or by an ill-defined solvation of the aryl chloride. Anything which renders the electrons less available, such as the resonance in furan or the steric influence which seems to operate in 2,5-dimethyltetrahydrofuran or 2,2,5,5-tetramethyltetrahydrofuran also stops the reaction.

Because of the known complex character of the Grignard reagent[13] and its preparation,[14] any attempt at posing a well-defined mechanism for this process requires more data.

More evidence of the solubility effect is given by sodium *p*-chlorophenoxide, a compound fairly soluble in tetrahydrofuran. On addition of a tetrahydrofuran solution of sodium *p*-chlorophenoxide to activated magnesium, we obtained evidence of an extremely vigorous reaction. However it was short-lived and a gelatinous precipitate appeared on the magnesium. Apparently, as expected, the effect of the charge on the oxygen atom was transmitted through the ring and a very much activated carbon to chlorine bond resulted. However the reagent, *p*-sodio oxyphenylmagnesium chloride, was not soluble in the tetrahydrofuran. This resulted in an impenetrable coating on the magnesium, thus ending attack on the magnesium. A similar type of inhibition by rapid initial attack and insolubility of product is shown by Mihailescu and Caragea in the case of diiodobenzene[15] where use of a different solvent allowed the reaction to go to completion. The greater energy of formation of alkylmagnesium chloride complexes with tetrahydrofuran over that of the corresponding complexes with ethyl ether[9] (and of boron trifluoride etherates[16]) is inherently shown by Normant in his quantitative replacement of the ethyl ether of these complexes.

Concentration seems to have little effect in this reaction, at least in the preparation of phenylmagnesium chloride. In studies of the ratio of moles of tetrahydrofuran to moles of chlorobenzene needed for optimum reaction, the ratio has been varied from as low as 0.5 to as high as 4.0. At the lower ratios, however the resulting solution has been found to be too viscous for efficient stirring and a ratio of 2:1 was found to be about the lowest for ease of handling. At this ratio, if the solution is allowed to cool and stand overnight, the complex crystallizes and the solution solidifies into a mass of fine long white needles of relatively low melting point. Little success has been obtained in attempts to free these crystals of mother liquor as they appear to be pressure sensitive. However, there is actually very little mother liquor present.

With solid aryl chlorides the amount of tetrahydrofuran necessary is governed by the solubility of the aryl chloride. The Grignard reagents themselves are very soluble and, by a cyclic process of distilling a portion of the tetrahydrofuran off, dissolving more aryl chloride in this solvent, and adding the resulting solution to the reaction mass, the amount necessary can be kept to a minimum.

In their reactions, the reagents are similar to the more common Grignard reagents. The reactivity of the simpler less substituted types is at least as great as that of phenylmagnesium bromide. Many of these reagents were characterized by further reactions with aldehydes, ketones, and esters, metal and metalloid halides (such as those of tin,[17] phosphorus, silicon,[18] and antimony), and other reactive compounds. They react with carbon dioxide as expected and also give Gilman and Schultz' Color Test I[19] with the exception of some of those containing *ortho* or two or more chlorine atoms on the ring. Pentachlorophenylmagnesium chloride did not carbonate nor did it give a strongly positive Color Test, although it reacted with silicon tetrachloride.[18] Addition of the tetrahydrofuran solutions to Dry Ice (or bubbling dry carbon dioxide into the Grignard at 10°) and a subsequent recovery of the acids served to help in structure determination. One preparation of phenylmagnesium chloride was intentionally carried out in an atmosphere of dry carbon dioxide to ascertain if this would hinder the reaction. No inhibition of reaction was noted.

Conversion of the arylmagnesium chlorides to arylethanols by use of ethylene oxide has been

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(13) See, in particular, M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, pp. 99–115.

(14) See, in particular, M. S. Kharasch and A. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, pp. 44–45.

(15) M. A. Mihailescu and St. P. Caragea, *Bull. Soc. Sci., Acad. Roumaine*, **12**, No. 4/5, 7–18 (1929) [*Chem. Abstr.*, **24**, 2116 (1930)]; also A. Bourgom, *Bull. soc. chim. Belg.*, **33**, 101 (1924) for another analogy.

(16) H. Normant, *Bull. soc. chim. France*, 739 (1950).

(17) S. D. Rosenberg and H. E. Ramsden, unpublished results.

(18) S. D. Rosenberg, J. J. Walburn, and H. E. Ramsden, unpublished results.

(19) H. Gilman and F. Schultz, *J. Am. Chem. Soc.*, **47**, 2022 (1925).

TABLE IV

Arylethanol	Boiling Point	Yield[a]	n_D^{25}	Lit.
β-*o*-Tolylethanol	95° at 6 mm.	91	1.5324	1.5347[b]
β-*m*-Tolylethanol	96° at 6 mm.	77	1.5254	1.5231[b]
β-*p*-Tolylethanol	94° at 6 mm.	74.5	1.5253	1.5271[b]
β-*p*-Anisylethanol	124° at 7 mm.[c]	75.6	1.5351	
β-*p*-Phenethylethanol	123° at 3 mm.[d]	69.5	1.5213	
β-2-*p*-Xylylethanol	98° at 4 mm.	70.8	1.5290	

[a] Based on ethylene oxide. [b] K. K. Ling, *Anzeuger Akad. Wiss. Krakau*, 632 (1908), [*Chem. Z.*, 1863 (1908II)]. [c] M.p. 20–22°. Grignard, *Compt. rend.*, **141**, 45 (1905) gives 22–24°. [d] M.p. 39°.

found an excellent device for a rough check on yields and products. Contrasted to Manske *et al.*,[3] who found that phenylmagnesium chloride in excess chlorobenzene gave moderate yields of phenylethanol, we have consistently obtained good yields (based on Grignard reagent) in tetrahydrofuran. This is true when ethylene oxide equivalent to the reagent is added. If excess ethylene oxide is added, the yield of arylethanol is lowered proportionately to the excess. A higher-boiling residue, presumably made up of arylethoxyethanols, is formed.

EXPERIMENTAL

All of the preparations were carried out under dry nitrogen (commercial low-oxygen grade) and were stirred by means of an anchor stirrer (which swept the bottom fairly closely) at 100–200 r.p.m.

The trifluoromethylchlorobenzenes were supplied by the Hooker Electrochemical Co. Arochlor 1221 was supplied by the Monsanto Chemical Co.

Tetrahydrofuran as supplied by the Du Pont Company was found to be quite suitable for use. Its content of water was below 0.1% (frequently below 0.05%) and peroxide content was so low that analysis showed none present. This material is stabilized by 0.1% hydroquinone and remained free of peroxides for some months. If the material were colored it was distilled with the usual precautions to prevent possible build-up of peroxides. Purified tetrahydrofuran and purified recovered tetrahydrofuran were found suitable but of no advantage over the commercial material. If stored over sodium, the tetrahydrofuran should be distilled before use, as the sodium seems to cause some decomposition after a few weeks.

Magnesium turnings as supplied by the Dow Chemical Co. were used.

Grignard preparations. In general, the aryl chlorides (1 mole) were dissolved in three moles of tetrahydrofuran. Initiation was made by adding 2–4 ml. of ethyl bromide to one g.-atom of magnesium turnings and 15 to 20 ml. of the aryl chloride–tetrahydrofuran solution, and the stirrer was started. Initiation frequently was immediate, although occasionally it was necessary to heat the reaction mass to reflux in order to get the initiation reaction going well. Once the reaction was going, the solution was added at a rapid dropwise rate and the reaction allowed to proceed at reflux. (Sometimes no external heating was necessary after initiation.) After completion of addition, the reaction was heated at reflux for 0.5 to 2.0 hr., until the magnesium was nearly consumed.

In determining yields by titration, the solution was diluted with tetrahydrofuran to 1000 ml. in a volumetric flask, 20 ml. aliquots were pipetted into 50 ml. of 0.5*N* sulfuric acid and 50 ml. of water, heated on a steam bath for 30 min., and back-titrated with 0.2*N* sodium hydroxide (with phenolphthalein or bromcresol purple as indicator).[20]

Carbonation of phenylmagnesium chloride during preparation. Two g.-atoms (48.6 g.) of magnesium turnings were activated by 2 ml. of ethyl bromide, a small iodine crystal, and 20 ml. of a solution of 225.2 g. (2 moles) of chlorobenzene, and 433 g. (6 moles) of tetrahydrofuran. An atmosphere of carbon dioxide was maintained during this entire preparation. As soon as the initiation reaction began, the solution of chlorobenzene–tetrahydrofuran was added dropwise to the mixture, heated to reflux. The addition required 8.5 hr. Heating under carbon dioxide was continued for an additional 2 hr., the mixture was cooled, hydrolyzed by the addition of 330 ml. of concentrated hydrochloric acid, diluted to 2000 ml. with water. The two layers were separated, the aqueous layer was extracted with two 200-ml. portions of ether and discarded. The extracts and the organic layer were combined and extracted with one liter of 10% sodium hydroxide. This extract on acidification yielded solid acid, which, recrystallized from 95% ethanol, yielded a small amount of benzoic acid, m.p. 120–121°, and 14.0 g. of triphenylacetic acid, m.p. 263–267° (lit.[21] 267°); neut. equiv. 286.8 (calcd. 288.3).

The *amide*, m.p. 244° (sublimes) (lit.[21] 246–247°) and the *anilide*, m.p. 166–168° (lit.[21] 167–168°, 173.5–174.5°) were prepared.

The organic layer was evaporated to yield 90 g. of residue which was fractionated to yield 23 g. benzophenone, b.p. 142–189° at 28 mm., and 19 g. triphenylcarbinol, b.p. 176–180° at 0.3 mm.

Carbonation of phenylmagnesium chloride. Phenylmagnesium chloride (from 1.0 g.-atom of magnesium and 1.0 mole of chlorobenzene) was carbonated by bubbling dry carbon dioxide gas in at 10–20°. Crude benzoic acid, 82.0 g. (67.2%) m.p. 117–118° was obtained. Recrystallization from water yielded material, m.p. 122° (corrected).

Carbonation of p-tolylmagnesium chloride. *p*-Tolylmagnesium chloride [from 126 g. (1 mole) *p*-chlorotoluene, 24.3 g. (1 g.-atom) magnesium turnings and 216 g. (3 moles) tetrahydrofuran] was added to an ethyl ether slurry of Dry Ice and allowed to stand overnight. The dark supernatant liquid was decanted; the remaining solid was dissolved in 300 ml. of water; a second organic liquid layer was decanted, the water solution was acidified with concentrated hydrochloric acid to yield (after chilling and standing) 102.3 g. (76%) of crude *p*-toluic acid melting at 164–165.5°.

β-Phenylethanol. General procedure. A solution of 2.0 moles (88 g.) of ethylene oxide in 2 moles (144 g.) of tetrahydrofuran was added slowly to a solution of phenylmagnesium chloride (from 225 g. chlorobenzene, 48.6 g. magnesium turnings, and 432 g. tetrahydrofuran) cooled by means of an ice bath to keep the temperature below 50°. As soon

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(20) H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1929).

(21) I. Heilbron, *Dictionary of Organic Compounds*, Vol. IV, Oxford University Press, New York, 1953, p. 628.

as the addition was completed, the mixture was heated to reflux until the clear solution became a grey slurry[22] (about 1 hr.). The mixture was hydrolyzed by addition of 186 ml. of 37% hydrochloric acid in 500 ml. of water and the two layers were separated. The aqueous layer was extracted with two 50-ml. portions of toluene. The organic layer and the extracts were combined and distilled through a 4-inch Vigreux head at atmospheric pressure to remove tetrahydrofuran and toluene, and finally at 3–5 mm. where phenylethanol boiling at 84–86° came over. Yield, 215.5 g., 88.4% (based on original Mg and ethylene oxide). n_D^{19} 1.5332 (Beilstein: n_D^{20} 1.5337).

Acknowledgments. The authors would like to thank Dr. S. D. Rosenberg for his helpful and critical advice in the later phases of this work. We are also indebted to Dr. C. K. Banks for his constant encouragement, throughout. We also thank the management of the Metal & Thermit Corp. for permission to publish as well as for its continuous support during the work.

RAHWAY, N. J.

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[22] If heating is stopped just before this point, the reaction mass sets up to a hard gel, which may be dispersed on addition of more tetrahydrofuran.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Formation of Dieckmann Reaction Products under Acyloin Conditions. Competition of the Two Reactions

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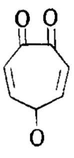
Received May 6, 1957

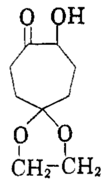
The acyloin reaction, under conditions which effected the condensation of ethyl sebacate satisfactorily, has been shown to give Dieckmann products from the lactone of ethyl γ-hydroxypimelate (IX) and ethyl γ,γ-ethylenedioxypimelate (III). It is suggested that the anomaly resulted from an intramolecular interaction of functions producing an enhanced polarization of the carbonyl group(s). The preparation of pimeloin has been re-examined and found to be as reported. When stabilized dispersion is used, however, products derived from the Dieckmann reaction were also obtained. Interesting derivatives of compounds in this series were obtained, two of which appear to have resulted from oxidation by phenylhydrazine.

The experimental conditions required for the cyclic acyloin reaction are in many respects similar to those used in the Dieckmann reaction. Major differences between the two are (*a*) particle size of the sodium, the acyloin reaction requiring colloidal dispersions,[1,2] and (*b*) concentration, acyloin (intramolecular) conditions being most satisfactory when the ester is added at high dilution.[3]

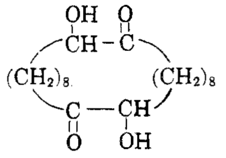
The work herein described resulted from an attempt to synthesize tropoquinone (I). The proposed synthesis required the formation of 2-hydroxy-5,5-ethylenedioxycycloheptanone (II) (or the corresponding dione) by the acyloin condensation of ethyl γ,γ-ethylenedioxypimelate (III).[4] The approach appeared to be sound in that pimeloin itself has been prepared in this manner[5,6] and substances possessing the dioxolane linkage have been shown to cyclize normally without destruction of the ketal linkage.[7]



I



II



IV

To avoid the use of high-speed stirring, a prepared (stabilized with 1% of sodium oleate) dispersion of sodium in xylene[8] was employed in early experiments. It was found to be quite satisfactory for the well-known cyclization of sebacic ester[2] from which there was obtained sebacoin and a by-product, tentatively formulated as cyclododecane-2,12-diol-1,11-dione or the isomeric 2,11-diol-1,12-dione (IV). No Dieckmann products were detected. When III was submitted to reaction under the same conditions, however, the only products isolated were the Dieckmann product, 2-carbethoxy-4,4-ethylenedioxycyclohexanone (V) and its decarbethoxylation product 4,4-ethylenedioxycyclohexanone (VI). The appearance of the latter substance in later fractions from the distillation of the reaction mixture, and the occurrence of gas evolution during the entire operation, suggested that VI formed thermally from the corresponding β-keto acid. That any of the β-keto ester (V) survived the reaction conditions is somewhat surprising since

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(1) V. L. Hansley, U. S. Patent **2,228,268**; *Chem. Abstr.*, **35**, 2534 (1941).

(2) N. L. Allinger, *Org. Syntheses*, **36**, 79 (1956).

(3) Compare, for example, ref. (2) with M. Stoll and J. Hulstkamp, *Helv. Chim. Acta*, **30**, 1815 (1947).

(4) During the preparation of this manuscript, a paper appeared containing mention of an attempted acyloin reaction with this substance. N. J. Leonard, L. A. Miller, and J. W. Berry, *J. Am. Chem. Soc.*, **79**, 1482 (1957).

(5) J. D. Knight and D. J. Cram, *J. Am. Chem. Soc.*, **73**, 4136 (1951).

(6) N. J. Leonard and G. C. Robinson, *J. Am. Chem. Soc.*, **75**, 2143 (1953).

(7) M. Stoll, J. Hulstkamp, and A. Rouve, *Helv. Chim. Acta*, **31**, 543 (1948).

(8) We are grateful to E. I. du Pont de Nemours and Co., Inc., for a most generous gift of this dispersion.