methyl 3-cyclohexenecarboxylate, and the mixture was refluxed with stirring for 5.5 hr. Upon cooling, the solution was dried over anhydrous potassium carbonate and distilled. 3-Cyclohexene-1-methanol distilled at 93° 19 mm., n^{25}_{D} 1.4818, and had the expected infrared spectrum. The α-naphthylurethan, m.p. 106–106.5°, and the phenylurethan, m.p. 58.0–58.5°, derivatives were prepared and found to check with those reported[14]: α-naphthylurethan, m.p. 103°, and phenylurethan, m.p. 56–57°.

The aqueous saponification solution was acidified and washed with benzene. The benzene solution was dried with anhydrous magnesium sulfate and then evaporated to dryness under vacuum. The physical constants of the crude 3-cyclohexene-1-carboxylic acid, m.p. ~19°, n^{23}_{D} 1.4791, compare closely with those in the literature,[15] m.p. 17°, n^{20}_{D} 1.4812. The *p*-bromophenyl ester of the acid was also prepared and found to melt at 81.5–82.0° (lit.,[16] m.p. 83–84°).

Saponification of 4-Methyl-3-cyclohexenylmethyl 4-Methyl-3-cyclohexenecarboxylate.—To 0.6 g. (0.015 mole) of sodium hydroxide in 20 cc. of distilled water was added 2.42 g. (0.01 mole) of 4-methyl-3-cyclohexenylmethyl 4-methyl-3-cyclohexenecarboxylate, and the mixture was refluxed overnight. The aqueous solution was cooled, washed with benzene, and acidified. 4-Methyl-3-cyclohexenecarboxylic acid was collected by filtration and recrystallized from water. The acid melted at 98.5–99° (lit.,[17] m.p. 99°).

Test of Diels–Alder Reaction at High Dilution and Mild Temperature.—To 13.6 g. (0.2 mole) of isoprene in 500 cc. of pure, dry *n*-heptane, maintained at 32°, was added 14.4 g. (.26 mole) of acrolein in 100 cc. of *n*-heptane over a period of about 4.75 hr. Stirring was continued for an additional 1.5 hr. and then the solution was distilled. Nothing boiling higher than *n*-heptane was obtained.

Reaction of Acrolein with the Catalyst.—To 7.5 g. (0.066 mole) of triethyl aluminum in about 90 cc. of dry *n*-heptane was added with stirring 4.2 g. (0.022 mole) of titanium tetrachloride in about 10 cc. of dry *n*-heptane in a glove box as described above. The catalyst was removed from the glove box, and 11.2 g. (0.2 mole) of acrolein in 20 cc. of dry *n*-heptane was added over a period of about 2 hr. The addition was maintained at such a rate that the temperature of the reaction solution remained between 30–35°. After standing over the week end, the catalyst suspension was centrifuged and the *n*-heptane removed. *n*-Pentane was added, the insoluble catalyst was agitated, and then centrifuged again. This procedure was repeated four or five times to remove all but a trace of *n*-heptane from the catalyst.[18] The catalyst was then hydrolyzed with dilute sulfuric acid (6 cc. of concentrated H_2SO_4 in 40 cc. of distilled water). A brown precipitate resulted, and additional water was added. The brown precipitate was removed by filtration and washed several times with ether and *n*-pentane. The brown aqueous solution was also washed several times with ether and *n*-pentane, and the wash solutions were combined and dried over anhydrous potassium carbonate. After drying overnight, the ether *n*-pentane was stripped, and 0.5 g. of a cut distilling at 80–86°, n^{20}_{D} 1.3805, and 0.8 g. of a cut distilling at 87–70°, n^{20}_{D} 1.3898, were collected. A few drops of a liquid distilling at 69–120°/0.8–1 mm., $n^{20}_{\mathrm{D}} = 1.4681$,[19] and a very viscous orange pot residue were also obtained.

Gas chromatographic (g.c.) analysis, using 150 ft. of R′ capillary column at 100°, showed that the first cut (80–86°) contained 0.8% allyl alcohol and 3.5% 1-penten-3-ol in an *n*-pentane-*n*-heptane mixture, and the second cut (87–70°) contained a trace of allyl alcohol and 4.6% 1-penten-3-ol in *n*-heptane. Each g.c. peak was identified by spiking the distilled fractions with authentic samples. The 1-penten-3-ol was further identified by comparison of the infrared spectrum of the second cut with that of an authentic sample and found to be superimposible between 9 and 11 μ.[20]

A small portion of the original *n*-heptane solution, from which the insoluble catalyst had been removed, was evaporated to dryness, leaving a slightly yellow colored powder. X-ray fluorescence spectra showed that this compound contained titanium and chlorine with no more than a trace of aluminum. The remainder of the *n*-heptane solution was shaken with dilute hydrochloric acid, evaporated, and dried over anhydrous potassium carbonate. The acid solution was washed with both *n*-heptane and ether which were then added to the previously recovered *n*-heptane. After concentration of the solution by fractionation through a short column, gas chromatography and infrared spectra showed that no more than a trace of penten-3-ol was formed by hydrolysis of *n*-heptane soluble catalyst.

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[14] E. G. E. Hawkins, D. J. G. Long, and F. W. Major, *J. Chem. Soc.*, 1465 (1955).

[15] I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1953, p. 433.

[16] Ref. 14, p. 1466.

[17] Ref. 15, p. 449.

[18] The *n*-heptane was removed so that the alcohol(s) expected on catalyst hydrolysis could be more easily recovered and identified.

[19] The infrared spectrum showed a carbonyl band, and it is assumed that this is a small amount of allyl acrylate.

[20] Since the second cut was at least 95% *n*-heptane, only a region where 1-penten-3-ol absorbs very strongly could be used for comparison.

3-Substituted Thiophenes. XI. Abnormal Products from 3-Thenyl Grignard Reagents[1]

E. CAMPAIGNE AND O. E. YOKLEY[2]

Contribution No. 1104 from the Chemistry Laboratories of Indiana University, Bloomington, Indiana

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A modified cyclic reactor, giving Grignard reagents from active halides in high yield, was used to prepare 3-thenylmagnesium bromide. Carbon dioxide reacts with this reagent to produce 3-thienylacetic acid (the normal product) and 3-methyl-2-thenoic acid (the abnormal product) in a ratio of 2:3, thus confirming the hypothesis that abnormal products are formed more readily when the reaction site is activated toward electrophilic substitution. 3-Thenylmagnesium bromide reacts with ethyl chlorocarbonate, acetyl chloride, and formaldehyde to give the abnormal products, as shown by comparison to authentic samples.

In an attempt to prepare 3-thienylacetic acid by carbonation of 3-thenylmagnesium bromide, Campaigne and Le Suer[3] found that the principal acidic product was 3-methyl-2-thenoic acid. This observation led to the suggestion that this substance might have been formed as the abnormal carbonation product of the 3-thenyl Grignard reagent, although such abnormal products from Grignard reagents and carbon dioxide were then unknown. It was further suggested that the high activity of the alpha position of thiophene at which carbonation had occurred, may have been responsible for the observed result. Subsequently, abnormal carbonation was found to be the rule, rather than the exception, in reactions with Grignards derived from

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[1] Taken from a thesis submitted by O. E. Yokley for the degree Doctor of Philosophy at Indiana University, June 1954. For the previous paper in the series, see E. Campaigne and R. L. Patrick, *J. Am. Chem. Soc.*, **77**, 5425 (1955).

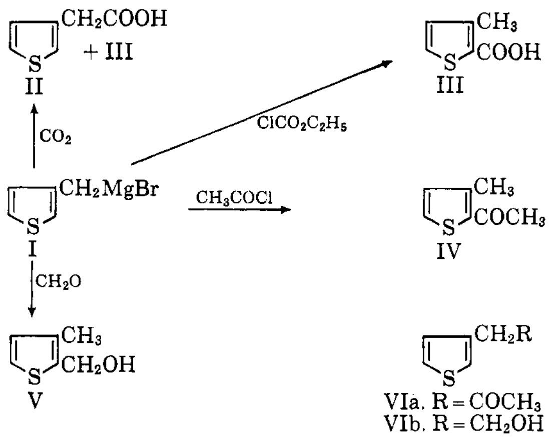
[2] Sterling-Winthrop Fellow in Chemistry, 1952–1953.

[3] E. Campaigne and W. M. Le Seur, *J. Am. Chem. Soc.*, **70**, 1555 (1948).

halomethyl heterocycles. The principal product of carbonation of 3-furylmagnesium chloride was shown to be 3-methyl-2-furoic acid.[4] Gaertner[5] made a thorough study of the 2-thenyl Grignard, and showed that reagents which usually gave a mixture of normal and abnormal products with benzyl Grignards, such as formaldehyde, ethyl chlorocarbonate and acetyl chloride,[6] gave exclusively abnormal 2-methyl-3-substituted thiophenes. With carbon dioxide, a mixture of normal 2-thienylacetic acid and abnormal 2-methyl-3-thenoic acid, in a ratio of 2:1, was obtained, thus emphasizing the greater tendency to form abnormal products in the heterocyclic series. Gaertner then compared the isomeric benzothiophene derivatives.[7] He found that 2-benzothenylmagnesium chloride gave exclusively abnormal carbonation, while 3-benzothenylmagnesium chloride gave a mixture of normal and abnormal products in a ratio of 1:3.6 ± 0.2. Gaertner pointed out that this behavior was "in agreement with the hypothesis that rearrangement[8] will occur more extensively into a position which is attacked preferentially in electrophilic substitution."[7]

It would be of great interest to compare other pairs of isomers in their tendency to produce normal and abnormal Grignard adducts, in order to determine whether they behave in agreement with this hypothesis. The failure of 2-chloromethylfuran to form a Grignard[4,9] has so far prevented such a comparison in the furan series. The very complete work by Gaertner on 2-thenylmagnesium chloride,[5] plus the extensive experience in 3-substituted thiophenes in our laboratories,[10] suggested a study of the behavior of 3-thenylmagnesium bromide with various reagents.

A repetition of the earlier carbonation of 3-thenylmagnesium bromide (I),[3] prepared in the ordinary way on a larger scale, gave an acidic product which could be fractionally crystallized to produce 3-methyl-2-thenoic acid (III) and 3-thienylacetic acid (II) in a ratio of 10:1. However, the major product was di-3-thienylethane. Using the modified cyclic reactor, described in the experimental part, I could be prepared in yields higher than 90%. Carbonation of this solution produced 71% of crude acids, which could be fractionally crystallized to yield 34% of III and 23% of II. Thus abnormal carbonation is favored over normal carbonation by 3:2 with 3-thenyl Grignards. This is quite in agreement with the hypothesis of enhanced abnormal substitution at a more reactive position, since only about 33% of the product was abnormal when it required reaction at the β-position in thiophene,[5] while 60% was abnormal when the same reaction involved an α-position of thiophene.



Reagents shown by Gaertner[5] to produce principally abnormal products with 2-thenylmagnesium chloride, also gave abnormal products with I. Thus ethyl chlorocarbonate gave a product which on saponification gave III. No other acidic products were found. Reaction of I with acetyl chloride gave an oil which was principally 3-methyl-2-acetothienone (IV) as shown by conversion to derivatives and comparison to authentic samples. None of the normal product, 3-thienylacetone (VIa) previously reported,[11] could be identified in the distillation products, or was apparent as impurities in the preparation of derivatives.

Some indication of the presence of a small amount of impurity, possibly normal product, was found in the product of the reaction of I with formaldehyde. The product, a liquid alcohol, formed an α-naphthylurethane which melted sharply at 139° after several recrystallizations. Comparison was made with authentic samples of 3-methyl-2-thenyl alcohol (V) and β-3-thienylethanol (VIb). V had approximately the same boiling point and refractive index, and formed an α-naphthylurethane which melted sharply at 144°. A mixture melting point was 140–142°. VIb had a different boiling point and refractive index, and formed an α-naphthylurethane melting at 108–109°, depressed to 95–105° when mixed with that melting at 139°. Experiments with mixing small amounts of the α-naphthylurethane of VIb with that from V did not lead to the formation of a eutechtic melting at 139°, as hoped. However, only trace amounts of the derivative of VIb lowered the melting point below 139°, showing that the product of the reaction of formaldehyde with I was principally, if not exclusively, the abnormal product, V.

These results show that there is a greater tendency for abnormal products to be formed in the 3-thenyl Grignard reactions, where the reaction leading to abnormal product occurs at a center activated toward electrophilic substitution, than in the reactions with the isomeric 2-thenyl Grignards, where the reaction leading to abnormal products would occur at a less activated position.

Experimental

The Modified Cyclic Reactor.—Rowlands, Greenlee, and Boord[12] have described the details of a device for preparing Grignard reagents in high yield from halides—such as benzyl and allyl halides—which tend to produce coupled products. This cyclic reactor recycles the solvent, with the effect of carrying out the reaction at high dilution. In the apparatus described, there are six ball joints and two standard taper joints over which ether must flow. In order to cut down on the number of potential leaks in the apparatus, and also to make it more compact, we

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[4] E. Sherman and E. D. Amstutz, *J. Am. Chem. Soc.*, **72**, 2195 (1950).

[5] R. Gaertner, *ibid.*, **73**, 3934 (1951).

[6] *Cf.* P. R. Austin and J. R. Johnson, *ibid.*, **54**, 647 (1932).

[7] R. Gaertner, *ibid.*, **74**, 766, 2185 (1952).

[8] Since no rearrangements occur, but the products result from two different sites of reaction, we prefer the ambiguous but less misleading terms, "normal" and "abnormal" for these products.

[9] R. Gaertner, *J. Am. Chem. Soc.*, **73**, 4400 (1951).

[10] For this work, see previous papers in this series.

[11] E. Campaigne and W. McCarthy, *J. Am. Chem. Soc.*, **76**, 4466 (1954).

[12] D. C. Rowlands, K. W. Greenlee, and C. Boord, Abstracts of Papers, 117th National Meeting of the American Chemical Society, April, 1950, p. 8L. A detailed description of the apparatus was kindly supplied by K. W. Greenlee.

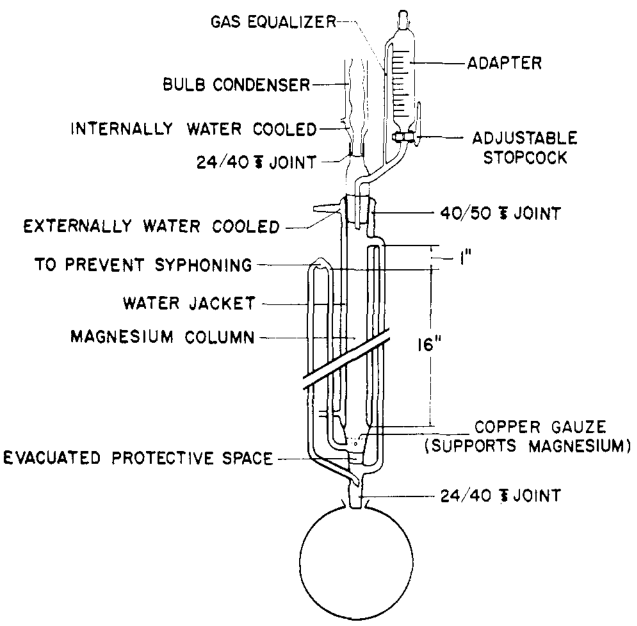

Fig. 1.—Modified cyclic reactor.

have designed the modification of the cyclic reactor shown in Fig. 1.

The modified cyclic reactor consists of four parts joined by only three standard taper joints. The flask at the bottom and reflux condenser at the top are standard pieces. Leakage of ether vapor past the reflux condenser joint was greatly reduced by using a condenser with an internally water-cooled male joint. A special graduated adapter was constructed which introduced the halide directly onto the top of the magnesium column. By counting the ether drops from the reflux condenser and the adapter, and knowing the concentration of halide in the dropping adapter, it was possible to have some quantitative control of the dilution used. The gas-pressure equalizer on the adapter was important, since frequently it was desirable to pass an inert gas through the system from bottom to top, to prevent oxidation of the Grignard when very high dilution required very slow addition of the halide.

The reactor itself consisted of a single piece of wide diameter (38-mm. i.d.) tubing having an externally cooled wide female joint (40/50 Ŧ) at the top, and water-jacketed for external cooling. This was necessary to prevent boiling of the ether on the magnesium column, since such mixing tended to increase the amount of coupled product. The rest of the column was made up like a Soxhlet extractor, as shown in Fig. 1, with some changes. Three indentations at the base of the water jacket, just above the over-flow exit, provided support for a copper gauze screen which supports the magnesium column and prevents blocking of the exit. Since a steady flow of solvent through the system is desired, the apparatus must not siphon and fill alternately, as does a Soxhlet extractor. Siphoning was prevented by blowing a bulb at the top turn of the over-flow exit. Flow resistance in the magnesium column required a small head of ether, which was provided by placing the vapor inlet at the top of the column at least one inch above the level of the top of the over-flow exit. In order to prevent boiling in the column caused by heat exchange between the rising solvent vapors and solvent in the column, it was necessary to insulate the column at the bottom by an evacuated compartment.

When the column was in operation, ether was refluxed from the boiling flask and percolated back through the column at a steady rate. The column was filled with magnesium turnings to the level of the top of the over-flow exit. Such a column has been operated continuously for 24 hr. with very little loss of ether. If the same Grignard reagent was prepared several times in succession it was possible simply to replace the dissolved magnesium at the top of the column each time. However, when a different halide was used, best results were obtained when the column was cleaned and dried in an oven, and a fresh fill of magnesium provided. Such a column produced a water white solution of benzylmagnesium bromide in 99% yield.

Carbonation of 3-Thenylmagnesium Bromide (I). A.—A 500-ml. three-neck flask was fitted with dropping funnel, stirrer, and condenser equipped with drying tube, and 3 g. (0.125 g.-atom) of magnesium turnings and 40 ml. of dry ether were placed therein. A small crystal of iodine was added, and then 19.5 g. (0.11 mole) of freshly distilled 3-thenyl bromide[13] dissolved in 50 ml. of ether was added dropwise with stirring. When the addition was complete, refluxing was maintained for 30 min., and the reaction mixture cooled in an ice bath. The mixture was then poured into a sludge of 20 g. of solid carbon dioxide in 50 ml. of ether. This mixture was stirred for several minutes and then poured into 200 ml. of 25% sulfuric acid. The mixture finally separated into two layers. The ether layer was removed and washed with three 15-ml. portions of 10% sodium hydroxide. Acidification of the alkaline extracts produced a crude solid which was separated and dissolved in 10 ml. of hot 10% acetic acid. On cooling, the white needles which formed weighed 3.2 g. (20%) and melted at 143–144° after one more recrystallization from water. The melting point was not depressed when the sample was mixed with an authentic sample of III, prepared by the Grignard method from 2-bromo-3-methylthiophene.[14]

The mother liquor from the initial recrystallization was extracted with ether, the extract dried, and the ether evaporated, leaving an oily residue. This was recrystallized twice from *n*-hexane to give 0.30 g. of white plates, (1.9%) m.p. 79–80°, undepressed when mixed with an authentic sample of II.[3]

The original ether solution which had been carbonated was dried and evaporated, and the residue recrystallized from methanol to yield 8 g. (75%) of *sym*-3,3′-dithienylethane, m.p. 64–65°, undepressed when mixed with an authentic sample.[3]

3-Thenylmagnesium Bromide (I).—The inner tube of the modified cyclic reactor was filled with clean dry magnesium turnings, and these were covered with a saturated ethereal solution of mercuric chloride. The color of the magnesium changed to blue-gray after about 12 hr. The amalgamated magnesium was washed by refluxing ether over the column for several hours, after which a fresh dry two-necked boiling flask, calibrated to hold 250 ml. of ether, was attached, and a stream of dry nitrogen was slowly passed through the system. About 150 ml. of dry ether was added through the adapter after which 26.5 g. (0.15 mole) of freshly distilled 3-thenyl bromide dissolved in 50 ml. of dry ether was placed in the adapter. A few drops of this solution were admitted to the column. After a few minutes, Grignard reagent began to form at the top of the column, as evidenced by cloudiness and agitation of the solution. Refluxing of the ether in the boiling flask was begun, and the 3-thenyl bromide solution was added very slowly (about 2 drops per min.). About 10 hr. were required for complete addition, after which refluxing was continued for 1 hr. longer to remove all the Grignard solution from the reactor. After about 15 ml. of the halide solution had been added, it was necessary to keep a slow stream of water moving through the water jacket of the cyclic reactor unit to prevent boiling and mixing in the reactor tube.

The solution in the boiling flask was made up to 250 ml. volume by adding dry ether to the mark, and the flask removed and stoppered. A 10-ml. aliquot, titrated with standard sulfuric acid,[15] was 0.546 molar (91%). More rapid addition of the 3-thenyl bromide solution resulted in lower yields of Grignard reagent.

Carbonation of I. B.—A solution (220 ml. 0.546 molar) of 3-thenylmagnesium bromide containing 0.120 mole of reagent was poured over a slurry of 200 g. of solid carbon dioxide in ether. After warming to room temperature, 100 ml. of 25% sulfuric acid was added, and the ethereal layer separated and extracted with four 30-ml. portions of 10% sodium hydroxide. Adidification of the cold alkaline solution produced 12.2 g. (71%) of crude acids. The crude mixture was dissolved in 250 ml. of hot 10% acetic acid, and then cooled. The pale yellow needles were collected and recrystallized once more from 10% acetic acid to yield 5.8 g. (34%) of white needles melting at 144–145°. The melting point was not depressed by mixing with an authentic sample of III.

The mother liquors of the above recrystallizations were combined, and extracted several times with ether, and the ether extracts were dried. After removing the solvent in a stream of dry air, the residue was twice recrystallized from *n*-hexane, to give 4.0 g. (23.4%) of glistening white plates, melting at 79–80°, undepressed when mixed an authentic sample of II.

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[13] E. Campaigne and B. F. Tullar, *Org. Syn.*, **33**, 96 (1953).

[14] W. Steinkopf and H. Jacob, *Ann.*, **515**, 273 (1935).

[15] H. Gilman, P. D. Wilkerson, W. P. Fishel, and C. H. Meyer, *J. Am. Chem. Soc.*, **45**, 150 (1923).

A second experiment, conducted in the same manner, except that the Grignard was used directly without titration, assuming 100% conversion, resulted in a 57% yield of crude acids. Fractional crystallization gave 27.2% of III and 20.1% of II.

Reaction of I with Ethyl Chlorocarbonate.—The general procedure employed by Gaertner[5] for the isomeric thenyl Grignard was used. I, prepared in the cyclic reactor from 17.7 g. (0.1 mole) of 3-thenyl bromide, was allowed to react with 53 ml. (0.56 mole) of resistilled ethyl chlorocarbonate, and 8.1 g. (57%) of crude acid was obtained. Two crystallizations from 10% acetic acid yielded 7.5 g. (52.8%) of pure III melting at 145–146°.

Extraction of the mother liquors of recrystallization with ether and evaporation produced only a trace of crude solid acid melting above 90°, which was discarded.

Reaction of I with Acetyl Chloride.—Following the procedure of Gaertner[5] for the isomer, the 3-thenyl Grignard prepared in the cyclic reactor from 45 g. (0.25 mole) of 3-thenyl bromide was allowed to react with 71.5 ml. (1.0 mole) of redistilled acetyl chloride, and the product, a pink oil (32 g.), was distilled under reduced pressure. A fore-fraction, b.p. 28–52°/0.5 mm., weighed 7.3 g. but gave a negative ketone test with 2,4-dinitrophenylhydrazine reagent, and a negative iodoform test. The major fraction, weighing 19.3 g. (55%), was collected between 57° and 90°/0.5 mm., n^{26}D 1.5650. Hartough and Conley[16] report 3-methyl-2-acetothienone (IV), b.p. 72–73°/2 mm., n^{20}D 1.5618. About 5 ml. of dark viscous residue remained in the distillation flask. The middle fraction was redistilled, giving 15 g. of colorless oil boiling from 52–57° at 0.3 mm., n^{26}D 1.5637.

A semicarbazone was prepared and found to melt at 207–208°, as previously reported[16] for the semicarbazone of IV. A mixed melting point with a semicarbazone prepared from an authentic sample[17] of IV, prepared by the method of Hartough and Kosak,[18] was not depressed.

Oxidation of 3.5 g. (0.025 mole) of the ketone with sodium hypochlorite solution, as described by Hartough and Conley,[16] gave 2.7 g. (77%) of III, m.p. 146°, after two recrystallizations from 10% acetic acid. Extraction of the mother liquors with ether and concentration under vacuum left only a trace of non-acidic oil.

Reaction of I with Formaldehyde.—Following the Gaertner procedure,[5] a solution of I prepared from 36.8 g. (0.21 mole) of 3-thenyl bromide in the cyclic reactor, was treated with gaseous formaldehyde generated from 50 g. of paraformaldehyde and swept into the reaction mixture with a slow stream of nitrogen, as described by Gilman and Catlin.[19] It was necessary to dry the nitrogen by passing it through an alkaline drying train of calcium chloride, calcium sulfate, and sodium hydroxide pellets, since the sulfuric acid drying tower described[19] caused polymerization of the products in the reaction.

The reaction produced a yellow oil from which a colorless distillate, b.p. 80–83°/3 mm., n^{25}D 1.5520, weighing 10.3 g. (40%) was obtained. One gram of the fresh distillate was treated with α-naphthyl isocyanate, and the α-naphthylurethane which crystallized was recrystallized from carbon tetrachloride twice. It melted sharply at 139°.

Anal. Calcd. for $C_{17}H_{15}NO_2S$: C, 68.64; H, 5.08; N, 4.71. Found: C, 68.58; H, 5.02; N, 4.75.

3-Methyl-2-thenyl alcohol (V).—A Grignard reagent was prepared from 17.7 g. (0.1 mole) of 2-bromo-3-methylthiophene, and excess gaseous formaldehyde passed through the reaction mixture under nitrogen. The mixture was then treated as previously described and the colorless distillate, b.p. 70–74°/1.5 mm., n^{25}D 1.5524, weighed 9.0 g. (70%).

Anal. Calcd. for C_6H_8OS: C, 56.22; H, 6.29. Found: C, 56.55; H, 6.55.

This oil formed glistening plates of an α-naphthylurethane melting sharply at 144°. A mixture melting point with the urethane previously prepared was 140–142°.

β-(3-Thienylethanol (VIb).—Following the procedure of Nystrom and Brown[20] for the reduction of carboxylic acids, a solution of 8.4 g. (0.059 mole) of 3-thienylacetic acid[3] in 100 ml. of absolute ether was added dropwise to 4.6 g. (0.12 mole) of lithium aluminum hydride in 200 ml. of dry ether at such a rate as to maintain gentle refluxing of the solution. After addition was complete and refluxing had subsided, water was slowly added followed by 10% sulfuric acid until a clear aqueous layer was formed. This was separated and washed with two 50-ml. portions of ether. The combined ether layers were dried over anhydrous magnesium sulfate, concentrated, and the residual oil distilled. The product was a colorless oil boiling at 67°/0.5 mm. It weighed 6.0 g. (79%).

Anal. Calcd. for C_6H_8OS: C, 56.22; H, 6.29. Found: C, 55.69; H, 6.50.

The compound formed an α-naphthylurethane having a melting point at 108–109°, which was depressed to 95–105° when mixed with the urethane melting at 139°, obtained from the product of I and formaldehyde.

Anal. Calcd. for $C_{17}H_{15}NO_2S$: N, 4.71. Found: N, 4.83.

A 3,5-dinitrobenzoate was also prepared from VIb. It melted at 110° after two recrystallizations from ethanol and water.

Anal. Calcd. for $C_{13}H_{10}N_2O_6S$: N, 8.69. Found: N, 8.68.

Acknowledgment.—The authors are indebted to the Sterling-Winthrop Research Institute for the Fellowship in support of this research.

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[16] H. D. Hartough and L. G. Conley, *J. Am. Chem. Soc.*, **69**, 3096 (1947).

[17] We are indebted to Dr. R. L. Patrick for this preparation. See R. L. Patrick, Ph.D. thesis, Indiana University, 1949.

[18] H. D. Hartough and A. Kosak, *J. Am. Chem. Soc.*, **69**, 3093 (1947).

[19] H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 188.

[20] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

Reactions of Mercuric Carboxylates with Trivalent Phosphorus Compounds

TERUAKI MUKAIYAMA, HIROHIKO NAMBU, AND ISAO KUWAJIMA

Laboratory of Organic Chemistry, Tokyo Institute of Technology, Tokyo, Japan

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Reactions of mercuric carboxylates with triethyl phosphite or with tertiary phosphines have been studied. When mercuric acetate was treated with triethyl phosphite, acetic anhydride was obtained in good yield along with mercury and triethyl phosphate. Similarly, the reaction of mercuric acetate with tri-*n*-butylphosphine resulted in the formation of acetic anhydride, mercury, and tri-*n*-butylphosphine oxide. In addition, it was found that, when mercurous propionate was treated with triethyl phosphite or with tri-*n*-butylphosphine, propionic anhydride was formed in good yield along with mercury, and triethyl phosphate or tri-*n*-butylphosphine oxide, respectively. Mechanisms of these reactions are discussed.

Deoxygenation reactions of diphenylfuroxane, isocyanates, and diphenyl ketene into diphenylfurazan, isonitriles, and tolane, by means of tertiary phosphites have been described in a previous paper.[1]

In the present study, the deoxygenation by tertiary phosphites was tested on ethylene carbonate under the assumption that it would, when deoxygenated, yield ethylene and carbon dioxide.[2] But it was found

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[1] T. Mukaiyama, H. Nambu, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).

[2] It was reported that ethylene carbonate was deoxygenated by tertiary phosphine to yield ethylene and carbon dioxide. P. T. Keough and M. Grayson, *ibid.*, **27**, 1817 (1962).