[Contribution from the George Herbert Jones Laboratory of the University of Chicago]

THE DETECTION OF FREE RADICALS IN SOLUTION. II. THE REACTION OF ALKYL AND ARYL HALIDES WITH MAGNESIUM IN THE PRESENCE OF ISOPRENE[1]

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In the previous publication (1) of this series, it was indicated that the reaction of phenoxyethyl bromide with magnesium, in the presence of isoprene and small amounts of ether, may be represented schematically as follows.

$$1.\quad C_6H_5OCH_2CH_2Br + Mg \xrightarrow{CH_2{=}C(CH_3)CH{=}CH_2}$$

$$\begin{array}{rl} C_6H_5OCH_2CH_2CH_2C(CH_3){=}CHCH_2\cdot & \\ \updownarrow & \quad \textbf{(A)} \\ C_6H_5OCH_2CH_2CH_2\underset{\bullet}{C}(CH_3)CH{=}CH_2 & \end{array}$$

$$2.\quad 2\ \textbf{A} \rightarrow C_6H_5OCH_2CH_2C_5H_8C_5H_8CH_2CH_2OC_6H_5$$

On the basis of these findings, it cannot be stated unequivocally whether magnesium acting on phenoxyethyl bromide forms the free phenoxyethyl radical

$$3.\qquad C_6H_5OCH_2CH_2Br + Mg \rightarrow C_6H_5OCH_2CH_2\cdot + (MgBr)\cdot$$

(which then adds in solution to isoprene), or whether the reaction is a "concerted" reaction in which the isoprene removes the ethyl radical at the same moment when the bromine atom is abstracted by the magnesium. In the latter case, no free phenoxyethyl radicals need be present in solution. However, the existence in solution of the free radical **A** seems plausible.[1]

The study indicated now has been extended to the products formed when other aryl and alkyl halides react with magnesium in the presence of isoprene and small amounts of ether. The following organic halides were studied: phenyl bromide, methyl iodide, *tert*-butyl bromide, benzyl bromide, *sec*-butyl bromide, β-diethylaminoethyl chloride. All of these halides react with magnesium[2] in the presence of isoprene to give products of the type:

$$4.\qquad RX + Mg \xrightarrow{C_5H_8} RC_5H_8C_5H_8R\quad \textbf{(B)}$$

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[1] The reactions cited in this paper proceed equally well with butadiene. For reasons fully discussed in a previous publication [Kharasch, Arimoto, and Nudenberg, *J. Org. Chem.*, **16,** 1557 (1951)], the interpretation of the mechanisms of these reactions with isoprene carry greater validity than the reactions with butadiene.

[2] As indicated in the experimental part of this paper, the reaction of β-diethylaminoethyl chloride with magnesium in the presence of isoprene and small amounts of ether, proceeds best when cobaltous bromide is present and the reaction is initiated with a small amount of a Grignard reagent.

However, in the case of *tert*-butyl, *sec*-butyl, and benzyl bromides, besides the adducts **B**, considerable quantities of the adducts **C** have been isolated.

5. $$RX + Mg \xrightarrow{C_5H_8} RC_5H_8R \quad (\mathbf{C})$$

Thus far, no attempt has been made to determine the optimum conditions for each of these reactions. In the preliminary experiments, the yields of the "dimers" ($RC_5H_8C_5H_8R$) varied from about 10% with methyl iodide to 20–25% with the *tert*-butyl bromide, phenyl bromide, and β-diethylaminoethyl chloride. With phenyl bromide, the yield of the "dimer" (on the basis of the phenyl bromide consumed in the reaction) rises to 44% when the reaction is carried out in the presence of three mole-% of cobaltous bromide. The amount of phenyl bromide accounted for varies from 65–86% depending upon the experimental conditions.[3] Careful study of these conditions[4] in the case of *sec*-butyl bromide resulted in substantial improvement in the yields of the reaction products $RC_5H_8C_5H_8R$ (47%) and RC_5H_8R (30%).

The uncertainty, whether free radicals are formed when magnesium reacts with organic halides and these add to isoprene, or whether the reaction is a "concerted" reaction in which the isoprene removes the radical at the moment when the bromine atom is abstracted by the magnesium, applies equally well to the formation of the products of the type RC_5H_8R. That is, it is questionable whether these products are formed by combination of the free radicals $RC_5H_8\cdot + R\cdot \rightarrow RC_5H_8R$ or whether the free radical $RC_5H_8\cdot$ removes the radical R at the same moment when the bromine atom is abstracted by the magnesium ("concerted reaction"). It is noteworthy that no products of the type $C_6H_5C_5H_8C_6H_5$ have been isolated from phenyl bromide (in spite of a careful search for such a product), although the yield of the "dimeric" product ($C_6H_5C_5H_8C_5H_8C_6H_5$) is rather high (44%). However, because of the uncertainties here mentioned, it is futile to speculate on collateral problems based on the yields of the adducts ($RC_5H_8C_5H_8R$ and RC_5H_8R) with different organic halides. It is hoped that the results of the work now underway on the reaction of optically active *sec*-butyl bromide with magnesium in the presence of isoprene will resolve some of these uncertainties as to mechanism of the reaction, and thus permit reasonable conclusions to be drawn from these and other pertinent data which it is hoped to accumulate.

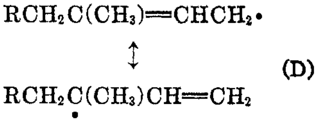
The structures of the "dimeric" products, $RC_5H_8C_5H_8R$ and the products RC_5H_8R, were derived from molecular weight determinations, analyses, and the product formed by ozonolysis.

Insofar as the "dimeric" products ($RC_5H_8C_5H_8R$) are concerned, they are

[3] The effect of other metal halides ($NiBr_2$, $FeCl_2$, $CuCl_2$, $MnCl_2$, etc.) has not been determined as yet.

[4] The reaction of magnesium with *sec*-butyl bromide in the presence of isoprene was investigated more thoroughly than with any other alkyl halide, since a similar reaction of optically active *sec*-butyl bromide was contemplated, and obviously good yields of the "adducts" were, therefore, desired.

probably mixtures of the types resulting from the dimerization of the resonance-hybrid **D**.

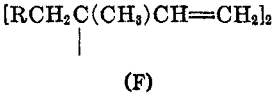


$$\mathrm{RCH_2C(CH_3){=}CHCH_2\cdot} \updownarrow \mathrm{RC H_2\overset{}{\underset{\bullet}{C}}(CH_3)CH{=}CH_2}$$

(D)

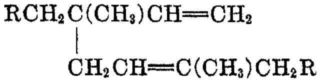
$[\mathrm{RCH_2C(CH_3){=}CHCH_2{-}}]_2$

(E)



$$[\mathrm{RCH_2C(CH_3)CH{=}CH_2}]_2$$

(F)



$$\mathrm{RCH_2C(CH_3)CH{=}CH_2} \;|\; \mathrm{CH_2CH{=}C(CH_3)CH_2R}$$

$[\mathrm{R} = \mathrm{C_6H_5};\ \mathrm{C(CH_3)_3};\ \mathrm{CH_3};\ \mathrm{C_6H_5CH_2};\ \text{etc.}]$

(G)

From the amount of succinic acid isolated upon oxonolysis, the "dimer" **E** probably accounts for at least 80–85% of the total "dimeric" products.

Similarly, the adducts **C** are mixtures of the types $\mathrm{RCH_2C(CH_3){=}CCH_2R}$ and $\mathrm{RCH_2C(CH_3)RCH{=}CH_2}$, in which the former product predominates (80–85%).

EXPERIMENTAL

β-Diethylaminoethyl chloride. β-Diethylamino chloride hydrochloride was treated with a saturated sodium carbonate solution, and the oil which separated was extracted with ether. The ether solution was dried with a mixture of potassium carbonate and sodium sulfate. The ether solution was separated, and the ether removed. β-Diethylaminoethyl chloride thus was obtained (b.p. 47–48.5°/21 mm., 66.4 g., 78% of calculated amount) as a colorless liquid.

Reaction between β-diethylaminoethyl chloride and magnesium in the presence of isoprene. Magnesium (2.7 g., 0.11 g-atom) was covered with ether (10 ml.), and β-diethylaminoethyl chloride (13.4 g., 0.1 mole) dissolved in isoprene (17.0 g., 0.25 mole) was added. No reaction occurred, even on prolonged heating. Cobaltous bromide (0.4 g.) and isopropylmagnesium bromide (0.5 ml. of a 2 *N* ethereal solution) were added. A slow reaction commenced which was barely self-sustaining.

The whole was gently heated for five hours and the reaction mixture then was diluted with ether (100 ml.) and poured onto crushed ice. The reaction products were separated in the usual way. About 1.1 g. of the unreacted β-diethylaminoethyl chloride was recovered.

The residue (5.5 g.) on molecular distillation (bath temp. 100°) gave 4.0 g. of a colorless oil, n_D^{20} 1.4721.

Anal. Calc'd for $[\mathrm{(C_2H_5)_2NCH_2CH_2C_5H_8{-}}]_2$, $\mathrm{C_{22}H_{44}N_2}$: C, 78.50; H, 13.18; Mol. wt., 336; Hydrogenation eq., 168.

Found: C, 78.97; H, 13.19; Mol. wt., 320; Hydrogenation eq., 174.7.

Reaction between bromobenzene and magnesium in the presence of isoprene. A 500-ml. three-necked flask, equipped with a stirrer, dropping-funnel, and reflux condenser, was flushed with dry nitrogen and into it were placed magnesium (3.9 g., 0.16 g-atom, sublimed) and dry ether (10 ml.). A small amount of bromobenzene was added and when the reaction commenced, the mixture of isoprene (51 g.) and bromobenzene (total 47 g.) was introduced through a dropping-funnel. The rate of addition of this mixture was regulated to maintain vigorous refluxing. When the reaction rate slackened, the mixture was gently heated for five hours longer.

The reaction mixture was cooled, diluted with dry ether (100 ml.), and poured onto solid carbon dioxide (300 g., powdered). About 0.2 g. of unreacted magnesium remained in the flask. The carbon dioxide ether mixture was allowed to come to 0° and dilute sulfuric acid (5 *N*, 50 ml.) was added. The organic material was separated, the aqueous layer extracted with ether (2 × 50 ml.), and the combined ethereal extracts shaken with sodium carbonate solution (20%). The alkaline solution was extracted with a further 50 ml. of ether and this was combined with the main ether fraction.

The alkaline solution was acidified with 10% hydrochloric acid and extracted with methylene chloride. The organic material was dried (calcium sulfate) and the solvent was evaporated. Crude benzoic acid, m.p. 117–119° (7.5 g.; 22.3% yield), thus was obtained.

The ethereal solution containing the neutral products was dried (calcium sulfate) and the ether was removed.

The residue on distillation gave bromobenzene (17 g., b.p. 50–53°/20 mm.; 37% recovery), biphenyl (0.6 g., b.p. 63–72°/0.2 mm., m.p. 70–71°; 2.6% yield), and a residue of 13.9 g.

The residue on molecular distillation gave the following fractions: Fraction 1, bath temp. 100–110°, 0.7 g.; n_D^{21} 1.5583; Fraction 2, bath temp. 110–115°, 7.7 g., n_D^{21} 1.5547; Fraction 3, bath temp. 115–117°, 2.2 g., n_D^{21} 1.5549; Fraction 4, bath temp. 117–140°, 0.6 g., n_D^{21} 1.5548; Fraction 5, Residue, 2.4 g.

Fractions 2 (mol. wt. 284), 3 (mol. wt. 293), and 4 (mol. wt. 294) are presumably the adducts $C_6H_5C_5H_8C_5H_8C_6H_5$ (Calc'd mol. wt. 290). The weight of these fractions was 10.4 g. (24% on the basis of the phenyl bromide charged).

The hydrogenation equivalent of Fraction 2: $C_{22}H_{26}$. Calc'd, 145. Found, 137.5.

A quantity of this material (1.2 g.) was hydrogenated (PtO_2/ethanol), and the resulting product was distilled in a molecular still: Fraction 1, bath temp. 100–105°, 0.2 g., n_D^{21} 1.5273; Fraction 2, bath temp. 105–110°, 0.8 g., n_D^{21} 1.5303.

Anal. Calc'd for $C_{22}H_{30}$: C, 89.72; H, 10.27.
Found: C, 89.20; H, 10.58.

Other experiments with magnesium, bromobenzene, isoprene, and small amounts of ether were carried out. Substantially the same results were obtained, except when small amounts of cobaltous bromide (3 mole-%) were added to the reaction mixture. In those instances, the yield of the "dimers" ($C_6H_5C_5H_8C_5H_8C_6H_5$) was over 40% on the basis of the phenyl bromide consumed in the reaction.

Ozonolysis of $C_6H_5C_5H_8C_5H_8C_6H_5$. The compound $C_6H_5C_5H_8C_5H_8C_6H_5$ (4.3 g.) was dissolved in pure ethyl acetate (300 ml.), cooled to −50°, and ozonized in the usual way. The solvent was removed at reduced pressure (room temperature), and 10% hydrogen peroxide solution (60 ml.) was added to the residue of ozonide (a viscous yellow oil). The mixture was allowed to stand (0.5 hr.), then gently warmed, and finally heated to 100° (4 hr.).

Platinum oxide (0.4 g.) and then 10% sodium carbonate solution were added (to decompose residual hydrogen peroxide) and the neutral product was extracted with ether (2 × 50 ml.). The combined ethereal extracts were washed with sodium carbonate solution (10%; 2 × 50 ml.), dried (calcium sulfate), and the ether was removed. The residue upon distillation gave exclusively benzyl methyl ketone (1.6 g.; b.p. 50°/1 mm., n_D^{20} 1.5210). The product was identified by conversion to the *semicarbazone* (m.p. 188–190°). The *2,4-dinitrophenylhydrazone* of the benzyl methyl ketone thus obtained melted at 153–154° and did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of benzyl methyl ketone.

Acidification of the alkaline extract gave a little tarry acidic material. This may have been impure phenylacetic acid, resulting from oxidation of benzyl methyl ketone (Sapon. equiv. found. 154, 158; $C_8H_8O_2$ requires 136).

The aqueous layer was evaporated to dryness at reduced pressure, and the solid material was extracted with ethyl acetate. Upon evaporation of the ethyl acetate a solid was obtained which melted at 185–187°, and which did not depress the melting point of an authentic sample of succinic acid.

Reaction between tert-butyl bromide and magnesium in the presence of isoprene. Magnesium (6.1 g.) and dry ether (5 ml.) were placed in the usual apparatus, and the flask (500 cc.) was flushed with dry nitrogen. *tert*-Butyl bromide (b.p. 72°; 45 g.) and isoprene (51 g.) were weighed out, and a little of the halide was added. When the reaction commenced isoprene (10 ml.) was added. The mixture was stirred and the remainder of the halide, dissolved in the remainder of the isoprene to which 10 ml. of ether was added, was introduced dropwise. The reaction was vigorous throughout the time of addition. The whole was then gently heated for three hours. A gas (assumed to be isobutene) was evolved during the reaction.

The mixture was cooled, diluted with dry ether (100 ml.), decanted from the unreacted magnesium, and poured onto crushed ice. No noticeable reaction occurred. The reaction mixture was worked up in the usual way.

Ether was removed by distillation at ordinary pressure. The final traces of ether and the unreacted alkyl halide were removed at 10 mm. pressure, and collected in the cold-trap (condensate 1). The residue 1 weighed 24.2 g.

The condensate 1 upon fractionation gave 4.5 g. of *tert*-butyl bromide (10% recovery) and a small amount of an unidentified material (1 g.) which boiled at 80–90°.

The residue 1 (22 g.) was distilled on a molecular still and the following fractions were collected: Fraction 1, bath temp. 80–84°, 14.5 g. n_D^{20} 1.4603; Fraction 2, in the cold-trap, 4 g. n_D^{20} 1.4540; Residue, 3 g. Fractions 1 and 2 were combined (18.5 g.) and fractionated at reduced pressure. The following fractions were collected: Fractions 3–7, b.p. 44°/0.7 mm. 1.6 g. The index of refraction of these fractions varied from n_D^{20} 1.4442 to 1.4453. Fractions 8 and 9, b.p. 71–98°/1.6 mm. n_D^{20} 1.4475 to 1.4526 (total 0.9 g.). Fractions 9–14, b.p. 102–107°/1.6 mm. n_D^{20} 1.4618 to 1.4615 (total 8 g.) and a cold-trap condensate (2) of 3.5 g.

Fractions 9–14 comprise the "dimeric" compounds $(CH_3)_3CC_5H_8C_5H_8C(CH_3)_3$ (31% calculated on the basis of *tert*-butyl bromide consumed in the reaction). The molecular weight of these fractions varied from 250 to 243 (Calc'd 250). The hydrogenation equivalent of fraction 9 was 116. (Calc'd for $C_{18}H_{34}$, 125.)

The fractions 9–14 were combined and part of it, dissolved in ethanol, was hydrogenated in the presence of PtO_2. The residue obtained after removal of the alcohol was distilled in a molecular still, and the following fractions were collected: Fraction 9a, bath temp. 60–65°, n_D^{21} 1.4545; Fraction 9b, bath temp. 65–68°, n_D^{21} 1.4525.

Anal. Fraction 9a. Calc'd for $C_{18}H_{38}$: C, 84.95; H, 15.05.
Found: C, 84.99; H, 14.99.
Fraction 9b. Calc'd for $C_{18}H_{38}$: C, 84.95; H, 15.05.
Found: C, 85.01; H, 14.74.

Fractions 3–7 (8% on the basis of the *tert*-butyl bromide consumed in the reaction) appear to be a mixture of the adducts $(CH_3)_3CC_5H_8C(CH_3)_3$. The hydrogenation equivalent calculated for $C_{13}H_{26}$ is 182, the value obtained was 173. The analysis was performed on the hydrogenated material (b.p. 83°/18 mm.; n_D^{22} 1.4350).

Anal. Calc'd for $C_{13}H_{28}$: C, 84.56; H, 15.30.
Found: C, 84.70; H, 15.5.

Ozonolysis of $(CH_3)_3CC_5H_8C_5H_8C(CH_3)_3$. The suspected "dimer" (mixture of fractions 9–14, n_D^{20} 1.4615; 2.07 g.) was dissolved in dry pure ethyl acetate (300 ml.) and cooled to −50°, and ozonized in the usual way. Ethyl acetate was removed at reduced pressure, and hydrogen peroxide solution (5%; 80 ml.) was added to the residue. The reaction mixture was allowed to stand at room temperature (0.5 hr.), and was then warmed slowly (1 hr.), and finally heated at 100° (2 hr.). The hydrogen peroxide was decomposed by the addition of platinum oxide, and 10% sodium carbonate solution (50 ml.), and ether (40 ml.) added to the cooled solution. The organic material was separated and shaken with sodium carbonate solution (10%; 3 × 50 ml.). The combined alkaline extract was extracted with ether (3 × 40 ml.) and the combined ethereal extract was dried (sodium sulfate). The ether was removed by distillation through a Fenske column, and the residue (1.05 g.; 60% theoretical) was distilled. The following fractions were obtained: Fraction A, b.p. 80–110°, 0.3 g., n_D^{20} 1.4010; Fraction B, b.p. 110–112°, 0.5 g.; Fraction C, a small residue. Fraction A (micro boiling point) boiled at 123–124°. Fractions A and B gave a *2,4-dinitrophenylhydrazone* (orange-yellow plates) which when crystallized from aqueous ethanol melted at 98–99°. The melting point of the 2,4-dinitrophenylhydrazone of 4,4-dimethylpentanone-2 is in agreement with this value (2).

The alkaline extract was acidified with diluted hydrochloric acid. No organic material separated. The solution was extracted continuously with ether (60 hr.), and the ethereal extract was dried (calcium sulfate) and the solvent was removed by distillation. The residue (*ca.* 0.5 g.) was set aside for three days, during which time the material crystallized. These crystals melted at 179–184°. After drying the specimen at reduced pressure, the melting point was 187–189°, and it was not depressed when mixed with an authentic specimen of succinic acid.

Reaction between sec-butyl bromide and magnesium in the presence of isoprene. Magnesium (6.1 g.) and dry ether (5 ml.) were placed in the usual apparatus, and the air in the flask was displaced by nitrogen. *sec*-Butyl bromide (45 g., b.p. 90°) and isoprene (51 g.) were weighed out and a little of the halide was added to the reaction mixture. When the reaction commenced isoprene (10 ml.) was immediately added. The remainder of the *sec*-butyl bromide and the isoprene were combined and 15 ml. of dry ether was added to the mixture. The whole then was added dropwise to the stirred reaction mixture, and finally the mixture was heated gently for five hours. At the end of that time, the mixture was cooled and poured on ice to which hydrochloric acid had been added. The organic layer was separated and the aqueous layer was extracted twice with 50 ml. of ether. The organic materials were combined and dried.

The ether and isoprene were removed by distillation at reduced pressure. The residue was distilled at reduced pressure and the following fractions were collected: Fractions 1–4, b.p. 50–53°/0.2 mm. The indices of refraction of these fractions varied from $n_{\rm D}^{25}$ 1.4429 to 1.4431. Total weight 5.6 g. Fractions 5–7, b.p. 57–89°/0.2 mm. The indices of refraction of these fractions varied from $n_{\rm D}^{25}$ 1.4450 to 1.4563. Total weight 5 g. Fractions 8–10, b.p. 92–108°/0.2 mm. The indices of refraction varied from $n_{\rm D}^{25}$ 1.4606 to 1.4621. Total weight 15.1 g. The residue weighed 5 g. About one gram of material was collected in the cold-trap.

Fractions 8–10 correspond to the adduct $C_4H_9C_5H_8C_5H_8C_4H_9$. Calc'd mol. wt. 250. Found 254. Hydrogenation equiv. Calc'd 125. Found 136. The yield of this material is about 17.5 g. (47% of calc'd, on the amount of halide consumed) if one allows for the amount of this material present in the intermediate fractions 5–7.

Hydrogenation of fractions 8–10 gave a material which when subjected to distillation in a molecular still boiled at 67° (bath temp. 67°) and had an index of refraction of 1.4441 at 22°.

Anal. Calc'd for $C_{18}H_{38}$: C, 84.96; H, 15.05.
Found: C, 85.10; H, 15.02.

Fractions 1–4 appear to be the adduct $C_4H_9C_5H_8C_4H_9$. Total yield 8 g. (30% on the basis of *sec*-butyl bromide used) allowing for the material present in the intermediate fractions 5–7. The molecular weight of these fractions was 182 (calc'd 182). The hydrogenation equivalent was 170 (calc'd 182).

For analyses the material was hydrogenated in the usual way. The solvent was removed. The residue was fractionated. Three fractions were obtained which boiled in the range of 95–98°/17 mm. and varied in refractive index $n_{\rm D}^{20}$ from 1.4319 to 1.4322.

Anal. Calc'd for $C_{13}H_{28}$: C, 84.70; H, 15.30.
Found: C, 84.77; H, 15.23.

Ozonolysis of $C_4H_9C_5H_8C_5H_8C_4H_9$ *adduct.* The adduct (mixture of Fractions 8–10) (1.7 g.) was dissolved in ethyl acetate, cooled to −70° and ozonized oxygen was passed through the solution until a pale blue color developed. The slight excess of ozone was removed by the passage of oxygen through the solution, and the solvent was removed at reduced pressure. To the residue hydrogen peroxide (10%, 80 ml.) was added and the whole gently was warmed on the steam-bath for four hours. Platinum oxide (50 mg.) and 10% sodium carbonate (30 ml.) then were added, and the whole was warmed until oxygen evolution ceased. The whole then was extracted with ether (2 × 50 ml.). The ether extract was washed with 10% sodium carbonate, the layers separated, the ether solution dried, and the ether removed. The residue upon distillation gave 4-methylhexanone-2 (0.5 g.; b.p. 58–60°/42 mm. $n_{\rm D}^{20}$ 1.4082). The following indices of refraction are recorded in the literature for 4-methylhexanone-2: Davies, Dixon, and Jones [*J. Chem. Soc.*, 468 (1930)]$n_{\rm D}^{25}$ 1.4050; Chang [*J. Chinese Chem. Soc.*, **18,** 65 (1951)] $n_{\rm D}^{20}$ 1.4081. The *semicarbazone* of the 4-methylhexanone-2 prepared by us melted at 125°, while the British and Chinese investigators report that the *semicarbazone* melts at 120–121° and 126–127°, respectively.

The alkaline extract was acidified with dilute hydrochloric acid, and extracted in a continuous extractor with ether. Upon evaporation of the ether, a residue remained (0.6 g.) which upon standing deposited large crystals of succinic acid. The acid thus obtained did not depress the melting point of an authentic sample of succinic acid.

Ozonolysis of $C_4H_9C_5H_8C_4H_9$ *adduct.* Fractions 1–4 were combined and a quantity (4.9 g.), was dissolved in ethyl acetate (300 ml.) and subjected to the action of ozonized oxygen at −70°. The ozonide was isolated and decomposed in the manner previously described and the neutral and acidic products were separated.

The neutral material (2.1 g.) gave on distillation about 0.5 g. of 4-methylhexanone-2 (b.p. 68–70°/50 mm.) and a material (1.4 g.; b.p. 114–130°/20 mm.; n_D^{20} 1.4349) which was not identified. The *semicarbazone* of the 4-methylhexanone-2 melted at 125–126°.

The acidic material (1.8 g.) was 2-methylvaleric acid (b.p. 97–100°/18 mm.). The *anilide* of this acid melted at 86° [Hannalen, *Bull. soc. chim. Belg.*, **42**, 243 (1933) reports that the anilide of 4-methylvaleric acid melts at 87°].

Reaction between benzyl bromide and magnesium in the presence of isoprene. Magnesium (4.9 g.; 0.2 g.) and dry ether (5 ml.) were placed in the usual apparatus (300 cc.). Benzyl bromide (42.75 g., 0.25 mole) and isoprene (42.5 g., 0.625 mole) were weighed out. The apparatus was swept out with dry nitrogen and a little of the halide added to the reaction mixture. When the reaction commenced, slow stirring was started and isoprene (15 ml.) was added. The remainder of the mixture of benzyl bromide in isoprene then was added slowly. The reaction started readily and was well-sustained throughout. The mixture was finally heated for five hours longer, cooled, and the reaction mixture decanted from the residual magnesium (<2.4 g.) onto crushed ice and worked up in the usual way.

Upon removal of the ether, the residue was distilled at reduced pressure and the following fractions were collected: Fraction 1, b.p. 34–65°/0.1 mm., 3.2 g.; Fraction 2, b.p. 65–73°/0.1 mm., 2.0 g.; Fraction 3, b.p. 73–77°/0.1 mm., 8.34 g.; Fraction 4, residue, 11 g. A small amount of benzyl bromide (2 g.) was recovered from the cold trap. Fraction 1 was a mixture of benzyl bromide and dibenzyl. Fractions 2 and 3 solidified, and when crystallized from ethanol melted at 52–54°. The yield of dibenzyl was 10 g. (45% calculated on the amount of benzyl bromide used.

Fraction 4 (the residue, 11 g.) on molecular distillation gave the following fractions: Fraction 4a, bath temp. 105–110°, 0.8 g., n_D^{20} 1.5472; Fraction 4b, bath temp. 110–140°, 2.45 g., n_D^{20} 1.5472; Fraction 4c, bath temp. 140–145°, 2.5 g., n_D^{20} 1.5485. Residue (5.2 g.).

Fractions 4a (mol. wt. 246) and 4b (mol. wt. 249) (3.3 g., 10%) were substantially the pure adduct $C_6H_5CH_2C_5H_8CH_2C_6H_5$ (mol. wt. 250). Hydrogenation equivalent: Calc'd for $C_{19}H_{22}$, 250. Found: 237.

The analyses were performed on the hydrogenated material. Unfortunately, the sample was allowed to stand in air for a considerable period prior to analysis, and the low value for carbon is undoubtedly due to oxygen absorption by the sample.

Anal. Calc'd for $C_{19}H_{24}$: C, 90.40; H, 9.58.
Found: C, 89.04; H, 9.69.

Fraction 4c (mol. wt. 322) was substantially pure adduct $C_6H_5CH_2C_5H_8C_5H_8CH_2C_6H_5$ (mol. wt. 318).

Hydrogenation equivalent found 153. $C_{24}H_{30}$ requires 159. The weight of this product was 2.5 g. (6.2% of calculated on the basis of benzyl bromide used).

The following results were obtained on the hydrogenated material (n_D^{20} 1.5235) which was distilled in a molecular still prior to analysis.

Anal. Calc'd for $C_6H_5CH_2C_5H_{10}C_5H_{10}CH_2C_6H_5$ ($C_{24}H_{34}$): C, 89.36; H, 10.63.
Found: C, 89.20; H, 10.23.

Substantially the same results were obtained when benzyl chloride was substituted in the above described experiment for benzyl bromide.

Reaction between methyl iodide and magnesium in the presence of isoprene. Magnesium

(4.9 g.; 0.2 g.a.) and dry ether (10 ml.) were placed in the usual apparatus. The reaction flask (500 cc.) was flushed with dry nitrogen. Methyl iodide (36.0 g., 0.25 mole) and isoprene (42.5 g., 0.625 mole) were weighed out. Reaction was started with a small amount of methyl iodide, isoprene (10 ml.) was added immediately, followed by the remainder of the methyl iodide dissolved in isoprene. The reaction mixture was heated under reflux and stirred (4 hr.). The Grignard reagent formed a viscous layer on the bottom of the reaction flask. The reaction mixture was cooled, diluted with ether (50 ml.), and decanted from the residual magnesium (1.7 g.) onto crushed ice. A vigorous reaction occurred.

The mixture was worked up in the usual way. Ether was removed by fractionation, leaving a residue of 3.0 g. On distillation this gave a material which boiled at 123–126°/85 mm. (n_D^{20} 1.4586). Distillation of this material at reduced pressure gave the following fractions: Fraction 1, b.p. 75–77.5°/14 mm., n_D^{20} 1.4542; Fraction 2, b.p. 77.5–80°/14 mm., n_D^{20} 1.4542; Fraction 3, b.p. 80°/14 mm., n_D^{20} 1.4545.

Thus, Fractions 1, 2, and 3 are substantially the same product, $CH_3C_5H_8C_5H_8CH_3$. The molecular weight of a sample from the combined fractions was 165. Calculated for $C_{12}H_{22}$, 166.

The hydrogenation equivalent was 89. Calculated for $C_{12}H_{22}$, 83.

Anal. Calc'd for $CH_3C_5H_8C_5H_8CH_3$; $C_{12}H_{22}$: C, 86.6; H, 13.34.
Found: C, 86.1; H, 13.71.

The hydrogenated product boiled at 79–81°/14 mm. (n_D^{21} 1.4285).

Anal. Calc'd for $C_{12}H_{26}$: C, 84.63; H, 15.39.
Found: C, 84.66; H, 15.75.

SUMMARY

1. It has been established that aryl and alkyl halides react with magnesium in the presence of isoprene (and small amounts of ether) to give products of the type $RC_5H_8C_5H_8R$ [R = C_6H_5, CH_3, $(CH_3)_3C$—, $C_6H_5CH_2$, $C_2H_5CHCH_3$, $(C_2H_5)_2NCH_2CH_2$—].

2. With benzyl, *tert*-butyl and *sec*-butyl halides, in addition to the products cited in 1, compounds of the type RC_5H_8R are also formed.

3. A mechanism for the formation of the products cited in 1 and 2 is suggested.

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