Experimental

Grignard Reagents.—Throughout this work purified n-butyl ether and alkyl halides were used, and all Grignard solutions were prepared and handled under an atmosphere of pure nitrogen or helium. They were filtered into storage flasks through a 1-cm. layer of ignited Celite on sintered glass. The filtered solutions were entirely colorless and clear.

It frequently is stated that high-purity sublimed magnesium must be used in work of this type to avoid the catalytic effect of impurities. Using carefully filtered water-clear solutions, we have noted no difference in the behavior of solutions prepared from fresh turnings of sublimed magnesium and those prepared from 99.9% commercial magnesium rod purchased from the Dow Chemical Co. Spectrographic analyses[11] of the rod indicated the percentages of impurities: Al, —; Si, —; Ca, 0.0004; Fe, —; Cu, 0.0002; Sn, 0.006; Pb, 0.01. Spectrographic analysis of a 99.99% rod of sublimed magnesium, available from Aluminum Company of America before 1936, gave the results: Al, 0.015; Si, 0.003; Ca, 0.001; Fe, 0.004; Cu, 0.0002; Sn, —; Pb, —.

The storage flasks were fitted with a Teflon stopcock, the outer end of which was covered by a rubber septum. Solutions were transferred by means of syringes fitted with long needles that could be passed through the septum and the bore of the stopcock into the solution. Grignard reagents were approximately 1 N and were standardized by titration with standard acid.

Catalyst Solutions.—To 3 equivalents of approximately 1 N Grignard reagent cooled in an ice bath was added 1 equivalent of metallic halide. The mixture darkened immediately. When allowed to warm to room temperature, gas was evolved and allowed to escape. After standing overnight, the mixture was filtered through Celite into the same type of reservoir used to store Grignard reagents. The copper, cobalt, and nickel solutions were standardized for metal content electrolytically. Iron was determined colorimetrically as the thiocyanate.

Infrared Spectra.—Infrared absorption was measured with a Perkin-Elmer 421 spectrograph fitted with the Perkin-Elmer mid-infrared interchange grating. Fixed thickness cesium bromide cells with Teflon spacers and plugs were used.

Electron paramagnetic resonance spectra were obtained with a Varian Model Y4501 spectrometer. Samples were observed at both room temperature and at the temperature of liquid nitrogen over a range of 500 gauss on either side of g = 2.

(11) Analyses by American Spectrographic Laboratories, San Francisco 3, Calif.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

The Catalyzed Reaction of Alkylmagnesium Halides with Alkyl Halides. III.[1] Course of the Reaction

BY V. D. PARKER[2] AND C. R. NOLLER

A reinvestigation of the products of the copper-catalyzed reaction of ethylmagnesium bromide with ethyl bromide has shown that butane, as well as ethane and ethylene, is a product of the reaction. An attempt to determine whether the alkene arises from the Grignard reagent or from the alkyl bromide by using different alkyl groups in the two reagents was inconclusive because the catalyst causes rapid functional exchange between the reagents. A study of the reaction of 1-C14-isopropyl bromide with isopropylmagnesium bromide and of 1-C14-isopropylmagnesium bromide with isopropyl bromide indicates that the alkene arises from the Grignard reagent and the alkane from the alkyl bromide. The results of the work as a whole support the view that the reaction proceeds by two pathways, one involving the intermediate formation of free radicals and the other a homolytic or heterolytic process that takes place by way of a transition state without the formation of free radicals.

Earlier work[3] showed that the copper-containing red solution formed by the reaction of ethylmagnesium bromide with cuprous chloride or cuprous bromide markedly catalyzes the reaction of ethylmagnesium bromide and ethyl bromide. The gaseous products were found to be ethane and ethylene in a ratio of 1.2 or less. No butane was detected. With the development of analysis by gas chromatography, it seemed desirable to repeat and extend this work.

Four series of reactions have been carried out in which all but one variable was held constant for each series, the variables being the amount of catalyst, the amount of ethyl bromide, the amount of ethylmagnesium bromide, and the total volume of the solution. The data are summarized in Tables I–IV. The amount of

TABLE I

EFFECT OF VARYING THE AMOUNT OF CATALYST

C₂H₅MgBr, 5.90 mmoles; C₂H₅Br, 2.68 mmoles; volume, 5.5 ml.

Catalyst, milliatom	C₂H₆, mmoles	C₂H₄, mmoles	C₄H₁₀, mmole	Yield, %	Abstrn. − combn. total
0.001	2.43	0.94	0.16	69	0.49
.002	2.74	1.36	.33	89	.43
.004	2.59	1.66	.39	94	.34
.008	2.68	1.82	.39	99	.31
.016	2.75	1.80	.33	97	.31
.024	2.39	1.71	.28	87	.27

(1) Paper II: V. D. Parker, L. H. Piette, R. M. Salinger, and C. R. Noller, J. Am. Chem. Soc., **86**, 1110 (1964).

(2) American Chemical Society Fellow, 1961–1963.

(3) C. B. Linn and C. R. Noller, J. Am. Chem. Soc., **58**, 816 (1936).

TABLE II

EFFECT OF VARYING THE AMOUNT OF ETHYL BROMIDE

C₂H₅MgBr, 6.78 mmoles; catalyst, 0.004 milliatom; volume, 5.5 ml.

C₂H₅Br, mmoles	C₂H₆, mmoles	C₂H₄, mmoles	C₄H₁₀, mmoles	Yield, %	Abstrn. + combn. total
1.34	1.70	0.65	0.18	101	0.52
2.68	2.91	1.61	.40	99	.40
5.36	4.58	3.33	.87	90	.31
6.70	5.09	3.69	1.07	82	.32
8.03	5.28	3.47	1.11	81	.37

TABLE III

EFFECT OF VARYING THE AMOUNT OF GRIGNARD REAGENT

C₂H₅Br, 6.70 mmoles; catalyst, 0.004 milliatom; volume, 5.5 ml.

C₂H₅MgBr, mmoles	C₂H₆, mmoles	C₂H₄, mmoles	C₄H₁₀, moles	Yield, %	Abstrn. + combn. total
2.04	1.39	1.14	0.22	73	0.23
3.16	2.45	1.88	.43	82	.28
4.28	3.27	2.66	.62	84	.26
5.40	4.07	3.34	.85	84	.27
6.52	4.95	3.77	1.05	83	.30

catalyst always is expressed in terms of milliatoms of metallic copper. All amounts of reagents and of products are given in millimoles. The yields are calculated from the sum of the amounts of ethane, ethylene, and twice the butane, and are based on the limiting reagent. The solvent in all of this work was n-butyl ether.

TABLE IV

EFFECT OF VARYING THE VOLUME OF SOLUTION

C_2H_5MgBr, 3.16 mmoles; C_2H_5Br, 6.70 mmoles; catalyst, 0.004 milliatom

Vol., ml.	C_2H_6, mmoles	C_2H_4, mmoles	C_4H_{10}, mmoles	Yield, %	Abstrn. + combn. total
2.5	2.17	1.77	0.55	80	0.30
3.5	2.25	1.79	.53	81	.30
4.5	2.36	1.81	.51	82	.30
5.5	2.46	1.95	.46	85	.27
6.5	2.37	1.71	.38	77	.30
7.5	2.38	1.76	.37	77	.28

In general, the ratio of ethane to ethylene is somewhat higher than reported earlier.[3] Contrary to the previous report, butane always is one of the products. When the amounts of products are plotted against the variable, reasonably smooth curves are obtained. The mechanism commonly proposed in the past for this type of reaction is that free radicals are formed, which disproportionate to alkene and alkane and also combine to the alkane with twice the number of carbon atoms. It now is known, however, that in the gas phase[4] the ratio of disproportionation to combination for ethyl radicals is about 0.14 and that in a solvent cage the ratio is around 0.14 in "isooctane" and 0.18 in 2-propanol.[5] On this basis the low yields of butane in the present work indicate that the amount of ethylene formed by disproportionation is negligible and may be disregarded within the accuracy obtained. Practically all of the ethylene, along with an equal amount of ethane, must result from a process that does not involve free radicals. Accordingly, we wish to propose that the reaction follows two courses. In one, free ethyl radicals are formed, which combine to give butane and abstract hydrogen from the solvent to give ethane, the latter to the extent that ethane exceeds the ethylene. The sum of the ethane formed by abstraction of hydrogen and twice the amount of butane then is approximately the extent to which free radicals are formed. The remaining ethylene and ethane result from a process not involving free radicals. The last column of each table gives the ratio of the sum of abstraction and combination to the total hydrocarbons formed, [(ethane − ethylene) + 2 × butane]/(ethane + ethylene + 2 × butane). These ratios are reasonably constant and indicate that approximately 30% of the reaction goes by way of free radicals.

Further evidence that free radicals are formed is that a rapidly reacting solution in n-butyl ether, when frozen in liquid nitrogen, gives a much stronger electron paramagnetic resonance signal than either the frozen catalyst solution or the frozen Grignard reagent alone. This signal is in the region of $g = 2$ where signals from alkyl radicals occur.

The results in Tables I–IV were obtained by analyzing the total gases evolved from the beginning to the end of the reaction. In order to determine whether the composition of the gases changed during the course of the reaction, a run was made in which the evolved gases were collected in two parts and analyzed separately. The results given in Table V indicate that no change occurs

It was noted previously[3] that the rate of the reaction initially is of zero order using a tenfold excess of ethyl bromide. Either solid cuprous chloride or the red solution was used as the catalyst. The zero order was interpreted as indicating that the reaction is hetero-

(4) (a) H. Cerfontain and K. O. Kutsche, Can. J. Chem., 36, 344 (1958); (b) J. C. J. Thynne, Trans. Faraday Soc., 58, 676 (1962).

(5) M. Matsuoka, P. S. Dixon, A. P. Stefani, and M. Swarc, Proc. Chem. Soc., 304 (1962).

TABLE V

COMPOSITION OF GASES FROM EARLY AND LATE PORTIONS OF THE REACTION

C_2H_5MgBr, 11.1 mmoles; C_2H_5Br, 13.4 mmoles; catalyst, 0.004 milliatom; volume, 11.5 ml.

	C_2H_6	C_2H_4	C_4H_{10}	Ratios
First portion	3.78	2.12	0.34	1.78:1:0.16
Second portion	3.02	1.75	0.26	1.73:1:0.15

geneous. An extension of this work in which the concentration of the catalyst in the form of the red solution was varied, showed that the reaction is first order with respect to the catalyst. The rates and calculated first-order rate constants are given in Table VI.

TABLE VI

VARIATION OF RATE WITH CONCENTRATION OF CATALYST AT $18.2 \pm 0.1°$

Catalyst, mole/l. × 10^{-4}	Rate, mole/l. sec.$^{-1}$	k, sec.$^{-1}$
2.63	8.50 × 10^{-5}	0.32
5.26	1.49 × 10^{-4}	.28
7.89	2.25 × 10^{-4}	.29
10.52	3.06 × 10^{-4}	.29

Although the rate measurements do not eliminate the possibility of heterogeneous catalysis, they are equally consistent with a rate dependent on the decomposition of an intermediate complex involving reagents and catalyst.

A qualitative comparison of the rates of reaction of ethylmagnesium bromide with ethyl chloride, ethyl bromide, and ethyl iodide under the same conditions showed that whereas reaction with ethyl bromide is complete in 3.5 min., gas evolution with ethyl chloride is slow and still incomplete after 3 days. Reaction with ethyl iodide also is slow and stops after about 3 hr. without going to completion. Examination of the solution showed that the catalyst had been flocculated by the addition of ethyl iodide with disappearance of the red color.

A series of reactions of n-propylmagnesium bromide with n-propyl bromide was run, using a copper-containing catalyst prepared in n-propylmagnesium bromide solution. The results are given in Table VII. The amount of hexane was not determined, but the excess of propane over propylene indicates that the course of the reaction is analogous to that of the reaction of ethylmagnesium bromide with ethyl bromide.
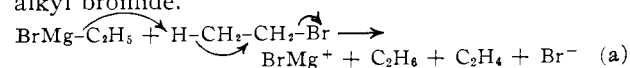
TABLE VII

CATALYZED REACTION OF n-PROPYLMAGNESIUM BROMIDE WITH n-PROPYL BROMIDE

n-C_3H_7Br, 5.50 mmoles; catalyst, 0.004 milliatom; volume, 5.5 ml.

n-C_3H_7MgBr, mmoles	C_3H_8, mmoles	C_3H_6, mmoles	C_3H_8/C_3H_6	Yield, %
2.04	1.47	1.19	1.23	65
3.16	2.70	2.21	1.22	78
4.28	3.58	2.91	1.23	76
5.40	4.90	4.00	1.23	82
6.52	5.29	4.07	1.30	85

Table VIII gives the results of a series of runs of isopropylmagnesium bromide with isopropyl bromide.

The portion of the reaction that yields equal amounts of alkane and alkene could take place in two ways. In one, process a, alkide ion from the Grignard reagent could cause elimination of hydrogen bromide from the alkyl bromide.

$$BrMg\!-\!C_2H_5 + H\!-\!CH_2\!-\!CH_2\!-\!Br \longrightarrow$$
$$BrMg^+ + C_2H_6 + C_2H_4 + Br^- \quad (a)$$

In the other, process b, the Grignard reagent could re-

TABLE VIII

CATALYZED REACTION OF ISOPROPYLMAGNESIUM BROMIDE
WITH ISOPROPYL BROMIDE

i-C_3H_7Br, 5.33 mmoles; catalyst, 0.011 milliatom; volume, 5.5 ml.

i-C_3H_7MgBr, mmoles	C_3H_8, mmoles	C_3H_6, mmoles	C_3H_8/C_3H_6	Yield, %
2.08	1.53	1.49	1.03	73
2.28	1.53	1.53	1.00	67
3.38	2.49	2.04	1.22	67
5.38	3.21	2.64	1.22	54

duce the alkyl halide to alkane by transfer of a hydride ion.

$$BrMg\text{-}CH_2\text{-}CH_2\text{-}H + CH_2CH_3 \longrightarrow$$
$$\underset{Br}{\mid}$$
$$BrMg^+ + C_2H_4 + C_2H_6 + Br^- \quad (b)$$
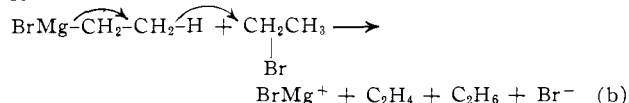
The latter reaction does not seem likely for a simple bimolecular reaction, although intervention of the catalyst conceivably could make it possible.

It has been shown, using a different alkyl group in the organometallic compound from that in the alkyl halide, that the so-called disproportionation products formed in the Wurtz reaction do not result from free radicals, which should yield a mixture of both alkanes and both alkenes, but that the alkylsodium removes halogen acid from the halide, thus converting the alkyl group of the halide to alkene and that of the alkylsodium to alkane.[6] On the other hand, it has been reported[7] that when an alkyllithium reacts with an alkyl halide in hexane, the alkane arises by reduction of the alkyl halide.

It was expected that by using different alkyl groups it would be possible not only to distinguish between process a and process b in the catalyzed Grignard reactions, but also between the view that free radicals are intermediates and the view that alkene and an equivalent amount of alkane arise chiefly by a process not involving free radicals.

Table IX lists the results of a series of reactions of ethylmagnesium bromide with n-propyl bromide and Table X those for the reaction of n-propylmagnesium bromide with ethyl bromide. The yields of pentane and hexane were not determined.

TABLE IX

PRODUCTS OF THE REACTION OF n-PROPYL BROMIDE WITH
VARIOUS AMOUNTS OF ETHYLMAGNESIUM BROMIDE

n-C_3H_7Br, 5.50 mmoles; catalyst, 0.004 milliatom; volume, 6.0 ml.

C_2H_5MgBr, mmoles	C_2H_6, mmoles	C_2H_4, mmoles	C_4H_{10}, mmole	C_3H_8, mmoles	C_3H_6, mmoles
2.04	0.87	0.63	0.06	0.53	0.54
3.16	1.71	0.94	.16	0.92	0.85
4.28	2.00	1.28	.28	1.22	1.27
5.40	2.35	1.53	.35	1.41	1.47

TABLE X

PRODUCTS OF THE REACTION OF ETHYL BROMIDE WITH
VARIOUS AMOUNTS OF n-PROPYLMAGNESIUM BROMIDE

C_2H_5Br, 6.70 mmoles; catalyst, 0.004 milliatom; volume, 6.0 ml.

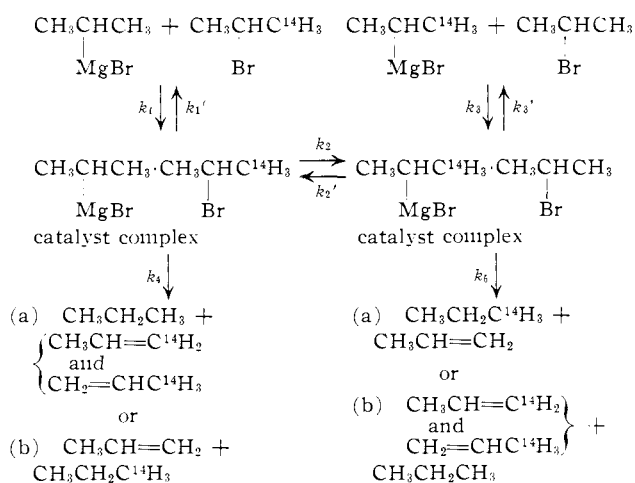| C_3H_7MgBr, mmoles	C_2H_6, mmoles	C_2H_4, mmoles	C_4H_{10}, mmole	C_3H_8, mmoles	C_3H_6, mmoles
2.04	1.22	0.56	. . .	0.76	1.06
3.16	1.61	0.80	0.16	0.91	1.03
4.28	2.34	1.19	.17	1.54	1.75
5.40	3.05	1.53	.25	2.16	2.37
6.52	2.77	1.33	.22	2.31	2.15

(6) (a) F. C. Whitmore and H. D. Zook, J. Am. Chem. Soc., 64, 1783 (1942); (b) A. A. Morton, J. B. Davidson, and B. L. Hakan, ibid., 64, 2242 (1942).

(7) J. E. Eastham and G. W. Gibson, J. Org. Chem., 28, 280 (1963).

Contrary to expectations, the alkene does not arise predominantly from the alkyl bromide in either series. Actually the amount from the Grignard reagent exceeds that from the halide slightly in the first instance, and markedly in the second instance. It is clear, however, that the reactions do not take place solely by way of free radicals, since such a process should yield a gaseous mixture having the same composition in both series.

It soon was found that these reactions are complicated by the rapid functional exchange brought about by the catalyst, a factor that was of minor consequence in the reaction of an alkylsodium with an alkyl halide.[6] Thus after 7.2 mmoles of n-propylmagnesium bromide had reacted with methyl bromide in the presence of the copper-containing catalyst and after the gaseous products had been removed, alcoholysis of the residue gave 2.93 mmoles of methane and only 0.21 mmole of propane. Similarly, when an excess of n-amylmagnesium bromide was allowed to react with 1.73 mmoles of methyl bromide followed by alcoholysis, 0.43 mmole of methane was the sole gaseous product. Repetition of the experiment in the absence of catalyst gave no methane on alcoholysis after evacuation.

The comparison of the reaction of ethylmagnesium bromide and n-propyl bromide with the reaction of n-propylmagnesium bromide and ethyl bromide is complicated not only by the exchange itself, but also because the two rates of exchange may be different as well as the rates of the disproportionation reactions. It was thought that the latter difficulties could be overcome and the system simplified by the use of isotopically labeled reagents. Accordingly, the catalyzed reactions of isopropylmagnesium bromide with 1-C^{14}-isopropyl bromide and of 1-C^{14}-isopropylmagnesium bromide with isopropyl bromide were investigated. Since the catalyst is necessary for all reactions, they must go through intermediate molecular complexes. Hence the reactions involved may be represented as

$$CH_3CHCH_3 + CH_3CHC^{14}H_3 \qquad CH_3CHC^{14}H_3 + CH_3CHCH_3$$
$$\underset{MgBr}{\mid} \qquad \underset{Br}{\mid} \qquad\qquad \underset{MgBr}{\mid} \qquad \underset{Br}{\mid}$$
$$k_1 \Big\downarrow\Big\uparrow k_1' \qquad\qquad\qquad k_3 \Big\downarrow\Big\uparrow k_3'$$
$$CH_3CHCH_3 \cdot CH_3CHC^{14}H_3 \underset{k_2'}{\overset{k_2}{\rightleftarrows}} CH_3CHC^{14}H_3 \cdot CH_3CHCH_3$$
$$\underset{MgBr}{\mid} \quad \underset{Br}{\mid} \qquad\qquad\qquad \underset{MgBr}{\mid} \quad \underset{Br}{\mid}$$
$$\text{catalyst complex} \qquad\qquad \text{catalyst complex}$$
$$k_4 \Big\downarrow \qquad\qquad\qquad\qquad k_6 \Big\downarrow$$

(a) $CH_3CH_2CH_3 +$
$\begin{cases} CH_3CH\text{=}C^{14}H_2 \\ \text{and} \\ CH_2\text{=}CHC^{14}H_3 \end{cases}$
or
(b) $CH_3CH\text{=}CH_2 +$
$CH_3CH_2C^{14}H_3$

(a) $CH_3CH_2C^{14}H_3 +$
$CH_3CH\text{=}CH_2$
or
(b) $\begin{rcases} CH_3CH\text{=}C^{14}H_2 \\ \text{and} \\ CH_2\text{=}CHC^{14}H_3 \end{rcases} +$
$CH_3CH_2CH_3$

Processes a and b are alternative possibilities. In process a the alkene comes from the alkyl halide, whereas in process b it comes from the Grignard reagent. The rate constants k_1, k_2, k_3, k_4(b), and k_5(a) should not be subject to primary isotope effects because the labeled carbon is not involved. Hence $k_1 = k_3$, $k_1' = k_3'$, and $k_2 = k_2'$. The maximum isotope effect expected for $k_{C^{12}H}$ $k_{C^{14}H}$ is approximately 1.04.[8] For k_4(a) and k_5(b) the maximum effect should be approximately 1.02 because hydrogen may be removed from either methyl group. If exchange is so much more rapid than disproportionation that equilibrium essentially is established before reaction takes place, the activity of the pro-

(8) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1962, p. 72.

pane should exceed that of the propylene regardless of which reagent is labeled but should be at most only 1.02 times greater. The same conclusions hold if the alkene and alkane arise solely from the formation of free radicals followed by disproportionation and hydrogen abstraction. If the rate of exchange is slower or not much faster than the rate of decomposition of the complex and if process a takes place, the activity of the propane should be less than that of the propylene starting with labeled bromide and greater than that of propylene starting with labeled Grignard. If process b takes place the reverse is expected. The results obtained are listed in Table XI. Runs using catalyst solutions prepared from cobaltous bromide, nickel bromide, and ferric chloride[1] also are included.

TABLE XI

RELATIVE ACTIVITIES OF PRODUCTS FROM THE CATALYZED REACTION OF ISOPROPYLMAGNESIUM BROMIDE WITH ISOPROPYL BROMIDE USING C^{14}-LABELED REAGENTS

Run	Metal in catalyst	Labeled reagent	$C_3{}^{14}H_8/$ $C_3{}^{14}H_6$	—% activity in—— Propane	Propylene
1	Copper	Halide	1.31	57	43
2	Copper	Halide	1.20	55	45
3	Copper	Halide	1.29	56	44
4	Copper	Halide	1.13	53	47
5	Copper	Grignard	0.70	41	59
6	Copper	Grignard	0.76	43	57
7	Cobalt	Halide	1.27	56	44
8	Cobalt	Halide	1.21	55	45
9	Nickel	Halide	1.20	55	45
10	Nickel	Halide	1.28	56	44
11	Iron	Halide	1.56	61	39
12	Iron	Halide	1.49	60	40

Triplicate analyses on the gas obtained in run 1 and duplicate analyses on the gas from run 6 gave perfect checks indicating excellent reproducibility of the analyses. The variation between runs is larger than desired, but the deviation from the average is a maximum of 4% in runs 1 to 4 and 1% or less in the other pairs of runs. Moreover none of the runs crossed from one side of a 1:1 ratio to the other.

The excess of propane over propylene indicates that about 23% of the propane arises from free radicals that abstract hydrogen. Since only half of this propane arises from active reagents, it has a leveling effect on the difference between the activity of the propane and that of the propylene. Thus in process b it decreases the activity of the propane starting with labeled bromide and increases the activity starting with labeled Grignard.

Contrary to original expectations, but in line with the mixed reactions involving both ethyl and n-propyl groups, the results indicate that process b rather than process a is involved; that is, the alkane results from reduction of the alkyl halide, and the alkene arises from the Grignard reagent. It is possible that both processes a and b occur but that b predominates over a. In view of the fact that exchange is rapid, however, it seems more likely that only process b is involved and that the rate of the disproportionation reaction is of the same order of magnitude as that of the exchange reaction.

Experimental

General.—The preparation and handling of reagents was the same as that described in paper II.[1] The apparatus used to run the reaction and collect the products is sketched and described in Fig. 1. In operation, reservoir B and buret E are filled with mercury. With stopcock L closed to A, reaction flask A is evacuated through H. Nitrogen then is admitted to A, and the evacuation and filling repeated five times to free the flask of air. Next, the Grignard reagent and catalyst are introduced into A through septum K and stopcock J by means of syringes fitted with long needles. With J closed, evacuation
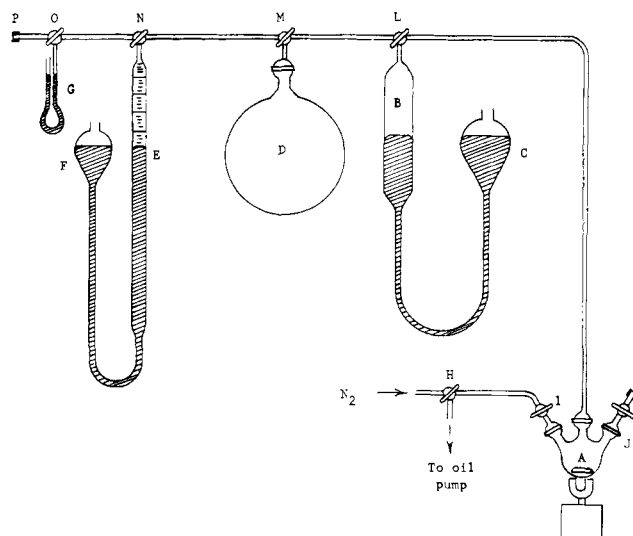

Fig. 1.—A, 50-ml. reaction flask containing a Teflon-coated magnetic stirring bar; B, 300-ml. gas reservoir with leveling bulb, C, containing mercury; D, 2-l. gas reservoir; E, 100-ml. gas buret with leveling bulb; F, containing mercury; G, open-end mercury manometer; H, L, M, N, and O, three-way stopcocks; I and J, two-way stopcocks; K and P, rubber septums over flanged ends of glass tubing.

through H with stirring removes any dissolved gases. Nitrogen then is admitted, stopcock I is closed, and A is connected to reservoir B. The alkyl bromide then is injected through K and J, and bulb C is lowered to allow the gases produced to pass into B under slightly reduced pressure. After the reaction has gone to completion, flask D is evacuated to a pressure of 1 mm. of mercury through P (cap removed). A is connected to D to remove most of the dissolved gases, and the content of B is transferred to D. A long syringe needle connected through a stopcock to the nitrogen source is inserted through K and J into the reaction mixture. A slow stream of nitrogen is passed through the reaction mixture with stirring and into B until reservoir B is filled. The flow of nitrogen is stopped temporarily while the content of B is transferred to D. Filling of B and transferral to D is repeated until D reaches atmospheric pressure. It had previously been determined that the passage of 1400 ml. of nitrogen is sufficient to remove all butane from the reaction mixture.

Stopcocks L, M, and N are adjusted so that the buret E is connected to flask A with reservoirs B and D closed. Sufficient nitrogen is admitted for the buret to contain 50 ml. at atmospheric pressure. Stopcock L is closed to D, and D is connected to buret E. The gases are mixed by raising and lowering bulb F five times. With stopcock N open, the contents of E and D are brought to atmospheric pressure by means of the leveling bulb F and the manometer G. Aliquots of the gaseous mixture are removed through the septum P. The volume of gas removed is determined from the buret after the pressure is returned to 1 atmosphere. The measured volume of the system from L to P with 50 ml. of gas in buret E is 2140 ml.

Gas Analysis.—The gaseous mixtures were analyzed by means of an Aerograph A-90-C gas chromatograph. The 6-m. column was packed with silica gel containing 2% of 2-ethylhexyl sebacate. Samples were transferred by means of a 30-ml. gas-tight polystyrene syringe. The procedure was calibrated by means of synthetic gas mixtures and by alcoholizing known amounts of standardized ethylmagnesium bromide solution in the reaction apparatus. Results could be duplicated within ±1%.

Rate Measurements.—The reaction flask containing a Teflon-coated magnetic stirring bar and fitted with a three-way stopcock for evacuation, admission of nitrogen, and release of gases, and with a second stopcock and rubber septum for the introduction of reagents and removal of samples, was immersed in a constant temperature bath at 18.2 ± 0.1°. Approximately 1 N ethylmagnesium bromide in n-butyl ether and containing the desired amount of copper catalyst was introduced into the reaction flask, and a flask containing ethyl bromide in n-butyl ether was placed in the bath. Both solutions were allowed to stand for 1 hr. to reach temperature equilibrium. The stirrer then was started and 0.5 equivalent of the ethyl bromide solution added to the reaction flask. Samples of the reaction mixture were withdrawn at timed intervals, the time at which the first sample was taken being recorded as zero time. The samples were immediately injected into standard hydrochloric acid solutions to quench the reaction. Upon completion of the sampling, the samples were

titrated with standard sodium hydroxide solution. Plots of the amount of Grignard reagent consumed against time gave straight lines, the slope of which gave the rate.

C[14]-Labeling Experiments.—1-C[14]-Isopropyl bromide was prepared by the series of reactions $C^{14}H_3OH \rightarrow C^{14}H_3I \rightarrow C^{14}H_3MgI \rightarrow C^{14}H_3CHOHCH_3 \rightarrow C^{14}H_3CHBrCH_3$. In each run 4.30 mmoles of Grignard reagent was allowed to react with 4.25 mmoles of halide in the presence of 0.011 mmole of catalyst for copper, 0.033 mmole for cobalt, 0.035 mmole for nickel, and 0.063 mmole for iron. In order to avoid dilution of the products, the gases were collected directly in a 300-ml. reservoir. From the reservoir, 30 ml. of the gas mixture was transferred to the gas chromatograph column. At the instant the propane peak began to appear, the emergent gases were collected in a gas bag, which was left attached to the Aerograph for exactly 5 min. This time was more than sufficient to collect all of the propane. When the propylene appeared on the recorder, a second bag was attached to the Aerograph and the propylene collected for a period of exactly 5 min. The ratio of propane to propylene was determined from the areas under the respective peaks on the chart of the recorder.

The propane fraction was transferred to a reservoir and diluted to a definite volume with nitrogen. The reservoir was connected to an evacuated ionization chamber, and the ionization chamber filled with the gas mixture under atmospheric pressure. The C[14] assay was made with a Model 31 Cary vibrating-reed electrometer.[9] The activity of the propylene fraction was determined

(9) V. F. Raaen and G. A. Ropp, *Anal. Chem.*, **25**, 174 (1953).

in the same way. The relative activities per mole were calculated from the ratio of the propane to propylene and from the ratio of the activity of propane to the activity of propylene using the equation

$$\text{propane*/propylene*} = \frac{\text{activity of propane}}{\text{activity of propylene}} \times \frac{\text{propylene}}{\text{propane}}$$

Electron Paramagnetic Resonance Spectra.—Ethyl bromide was added to a solution of catalyst in excess ethylmagnesium bromide in the spectrometer sample tube at room temperature. Evolution of gas took place at once and the tube was plunged into liquid nitrogen. The frozen sample was scanned with a Varian Model 4501 e.p.r. spectrometer in the range of 500 gauss on either side of $g = 2$.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, N. J.]

# A Study of the Decomposition of 3,3,3-Triphenylpropanoyl Peroxide

BY DONALD B. DENNEY,[1] ROBERT L. ELLSWORTH, AND DOROTHY Z. DENNEY

The decomposition of 3,3,3-triphenylpropanoyl peroxide has been studied in the absence of solvent, in carbon tetrachloride, and in a mixture of carbon tetrachloride, iodine, and water. In all cases 3,3,3-triphenylpropanoic acid, 1,1,2-triphenylethylene, 1,1,2-triphenylethane, 1,1,1,4,4,4-hexaphenylbutane, phenyl 3,3-diphenylpropenoate, and carbon dioxide were formed. The relative yields of these substances were considerably affected by the changes in reaction conditions. An oxygen-18 tracer study of the formation of phenyl 3,3-diphenylpropenoate showed that 65% of the original carbonyl label becomes the ether oxygen of the ester. Essentially all of the remaining label was found in the carbonyl group. The formation of 1,1,1,4,4,4-hexaphenylbutane indicates that 2,2,2-triphenylethyl radicals have some stability under the conditions used for their generation. Several novel features of the decomposition are discussed and compared to other diacyl peroxide decompositions.

It seems well recognized that most free radical rearrangements proceed in a stepwise manner which involves generation of the radical followed by rearrangement.[2] This behavior is to be contrasted to many carbonium ion rearrangements in which migration occurs as the electron deficient center is being formed.[3]

Decarbonylation of aldehydes which would have been expected to give the highly substituted radicals (Ia,b)

$$R = H, CH_3$$
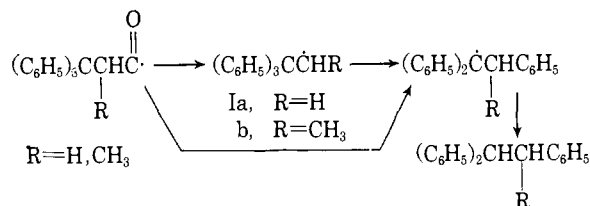
yielded rearranged products exclusively.[4] This could be due to a simultaneous migration of phenyl as carbon monoxide is lost or simply to the fact that the intermediate radicals (Ia,b) rearrange faster than they abstract hydrogen from an aldehydo group of another molecule.

Of the open chain radicals it seems clear that highly arylated systems such as Ia,b will be the most prone

to rearrange. A clear-cut demonstration that such rearrangements are or are not synchronous with generation of the radical seems desirable. In principle there are several ways of attacking such a problem. In the case now being reported, trapping of the radical before rearrangement could occur was selected as the method to be used. The trap was to be another radical generated at the same or essentially the same time and in close proximity to the radical under study. It was believed that decomposition of a diacyl peroxide would provide radicals generated in juxtaposition which could undergo some combination before diffusion.[5] The peroxide chosen was 3,3,3-triphenylpropanoyl peroxide (II) which on decomposition would

$$[(C_6H_5)_3C-CH_2-CO_2]_2 \quad (C_6H_5)_3C-CH_2-CH_2-C(C_6H_5)_3$$
$$\text{II} \qquad\qquad\qquad \text{III}$$
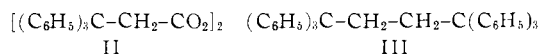
give 1,1,1,4,4,4-hexaphenylbutane (III) if rearrangement of a phenyl group was not synchronous with decomposition and if "cage combination" could occur before diffusion or rearrangement of Ia. It was of interest to study the decomposition of II in its own right and several novel features of this decomposition have been found.

Results

The synthesis of 3,3,3-triphenylpropanoyl peroxide was accomplished from the acid chloride by reaction with sodium peroxide in aqueous acetone[6] or by re-

(1) Rutgers Research Council Faculty Fellow, 1963–1964.

(2) C. Walling, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 7.

(3) D. J. Cram, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 5.

(4) D. Y. Curtin and M. F. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952)

(5) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961)

(6) S. Gambarajan, *Ber.*, **42**, 4003 (1909)