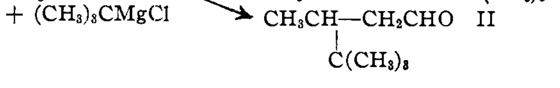
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 120]

The Action of Organomagnesium Halides on α,β-Unsaturated Aldehydes

BY PHILIP G. STEVENS

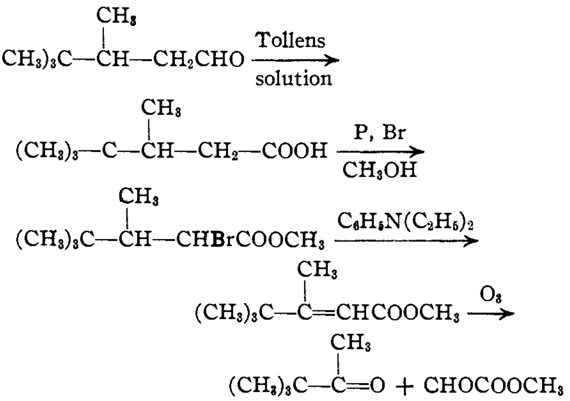
The action of organomagnesium halides on α,β-unsaturated aldehydes has been the subject of many investigations. Grignard,[1] the pioneer in this field, obtained only secondary carbinols. Thereafter came a host of investigators who likewise obtained only secondary carbinols or degradation products derived from them. Very few, however, attempted to detect any product other than that formed by 1,2 addition. Kohler,[2] the first of these, treated cinnamic and α-bromocinnamic aldehydes with phenylmagnesium bromide. A careful search, however, revealed no trace of a 1,4 addition product. Three years later Kohler[3] found that similarly acrolein formed no 1,4 addition products with either ethyl- or phenylmagnesium bromides. The following year Wohl and Losanitch[4] treated acrolein with methylmagnesium iodide and obtained a product which they believed did not contain any 1,4-addition product because it failed to reduce ammoniacal silver nitrate. From this time on, therefore, it has been generally accepted that α,β-unsaturated aldehydes, because of their highly reactive carbonyl group, react with organomagnesium halides solely through the carbonyl group, that is 1,2 addition.

The work described in this paper is the result of an attempt to prepare propenyl-*t*-butylcarbinol I from crotonic aldehyde and *t*-butylmagnesium chloride. According to the past behavior of α,β-unsaturated aldehydes, only 1,2 addition (exclusive of possible reduction products) should take place. However, such was not the case, for over 20% of the total product was a saturated aldehyde II, as shown by its reduction of cold Tollens solution and Schiff reagent, formation of a semicarbazone, and oxidation to an acid with the same number of carbon atoms.



$$\begin{matrix} CH_3CH{=}CHCHO \\ + (CH_3)_3CMgCl \end{matrix} \begin{matrix} \longrightarrow CH_3CH{=}CHCHOHC(CH_3)_3 \quad I \\ \searrow CH_3\underset{\underset{C(CH_3)_3}{|}}{CH}{-}CH_2CHO \quad II \end{matrix}$$

Since the formation of this aldehyde by 1,4 addition was quite unexpected, it was necessary to prove its structure conclusively. This was accomplished by the following series of reactions



$$(CH_3)_3C{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_2CHO \xrightarrow[\text{solution}]{\text{Tollens}}$$
$$(CH_3)_3{-}C{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_2{-}COOH \xrightarrow[CH_3OH]{P,\ Br}$$
$$(CH_3)_3C{-}\overset{\overset{CH_3}{|}}{C}H{-}CHBrCOOCH_3 \xrightarrow{C_6H_5N(C_2H_5)_2}$$
$$(CH_3)_3C{-}\overset{\overset{CH_3}{|}}{C}{=}CHCOOCH_3 \xrightarrow{O_3}$$
$$(CH_3)_3C{-}\overset{\overset{CH_3}{|}}{C}{=}O + CHOCOOCH_3$$

In view of the anomalous behavior of this tertiary Grignard reagent, a reinvestigation of the action of other Grignard reagents on crotonic aldehyde was made in order to see whether or not previous investigators had overlooked small amounts of 1,4-addition products; and to find out if progressive branching of the carbon chain affected the mode of addition. The reactions were carried out by a standard procedure, and the carbinols were determined as phthalates, the aldehydes as semicarbazones. The results are shown in Table I.

TABLE I

PERCENTAGE YIELDS WITH CROTONIC ALDEHYDE

Grignard reagent	Carbinol	Aldehyde	Complex products	Ratio aldehyde/± carbinol
Phenyl	90[5]	0.1	7.1	0.0011
Ethyl[6,7]	70.3	0.1	11.4	.0014
Propyl[6]	78.3	Trace	7.6	.001
Allyl[8]	..	Trace	..	.001
Isopropyl[6]	46.5	0.3	34.1	.007
t-Butyl	30.6	20.3	39.3	.6
t-Amyl	16.3	22.6	45.7	1.4

These results show that with crotonic aldehyde, both 1,2- and 1,4-addition reactions take place, the relative amounts varying with the reagent. The amounts of 1,4 addition with phenyl-, ethyl-, propyl-, allyl- and isopropylmagnesium bromides

---

[1] Grignard, *Ann. chim. phys.*, [7] **24**, 433 (1901).

[2] Kohler, *Am. Chem. J.*, **31**, 642 (1904).

[3] Kohler, *ibid.*, **38**, 511 (1907).

[4] Wohl and Losanitsch, *Ber.*, **41**, 3621 (1908).

[5] Partly diphenyl, see text.

[6] Compare Reif, *Ber.*, **41**, 2739 (1908).

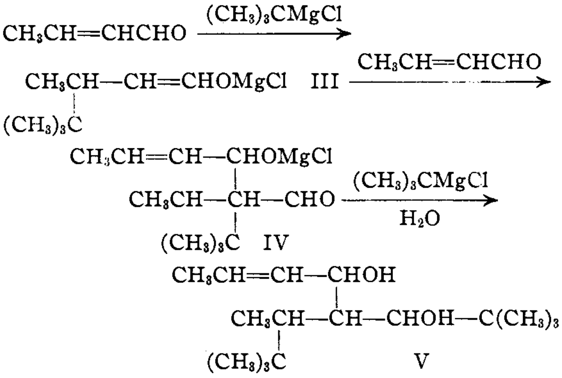
[7] Compare Kyriakides, THIS JOURNAL, **36**, 657 (1914).

[8] Compare Enklaar, *Ber.*, **49**, 211 (1916).

are so small, however, that at present it is not possible to compare them with each other; but there is no doubt that *t*-butyl- and *t*-amylmagnesium chlorides do react enormously differently and distinctly favor 1,4 addition.

The reason for this abnormal mode of addition is undoubtedly a difference in the reaction velocities of 1,2 and 1,4 addition, but the underlying causes for these different reaction velocities is not clear. The effects of temperature, stirring, etc., can be eliminated, however, as all these reactions were carried out in essentially the same way. A difference in halogen is probably not of major importance because *t*-butylmagnesium bromide gave an 11% yield of 1,4 addition. Furthermore, the composition of the Grignard reagent itself can be disregarded as a factor, for the amounts of R_2Mg and RMgX in phenylmagnesium bromide and *t*-butylmagnesium chloride seem too nearly the same (75–81 and 62–75% R_2Mg, respectively)[9] to account for the striking difference in their behavior noted here toward crotonic aldehyde. Steric hindrance likewise seems to be an inadequate explanation as it fails to show why phenylmagnesium bromide, which contains a group that ordinarily presents more steric hindrance to addition to the carbonyl group than the methyl or ethyl group, always gives more 1,2 addition to α,β-unsaturated ketones than methyl- or ethylmagnesium bromides.[2,3,10] The best answer at present is that these differences in reaction velocity of 1,2 and 1,4 addition are due mainly to the differences in the individual chemical character or polarity of the organic radical of the Grignard reagent. This is the view already suggested by Kohler and Burnley for α,β-unsaturated ketones.[11] It is in no way strange that the differences in reactivity between aryl, primary, secondary and tertiary alkyl carbinols and halides, particularly the first and last named, should reappear when these radicals are part of the Grignard reagent. That some differences in the polarity of these radicals do exist is shown by their electrolysis potentials as determined by Evans, Lee and Lee;[12] but whether or not these potentials influence the mode of addition to α,β-unsaturated aldehydes is as yet problematical, for allylmagnesium bromide, which has an even lower potential than *t*-butylmagnesium bromide, reacts with crotonic aldehyde just like phenylmagnesium bromide and gives only a trace of 1,4 addition.

Mention should be made of the complex products formed from *t*-butylmagnesium chloride and crotonic aldehyde. One of them is a solid melting at 128–129°. Its composition is represented by $2C_4H_6O + 2C_4H_{10}$. It has two active hydrogen atoms, has no carbonyl group, is actively unsaturated and is insoluble in petroleum ether. The most probable formula is represented by V. This formula is consistent with its properties and with the work of Kohler and Peterson,[13] who recently showed that the primary products of 1,4 addition could, as enolates, add to the original α,β-unsaturated ketone, or to an aldehyde. In this case, also, the original 1,4-addition product III adds 1,2 to another molecule of crotonic aldehyde, thus forming IV with a new aldehyde group which then further condenses with the Grignard reagent. The final product, V, is therefore an unsaturated glycol.



$$CH_3CH{=}CHCHO \xrightarrow{(CH_3)_3CMgCl} CH_3\underset{(CH_3)_3C}{\underset{|}{CH}}{-}CH{=}CHOMgCl \quad \text{III} \xrightarrow{CH_3CH=CHCHO}$$

$$CH_3\underset{(CH_3)_3C}{\underset{|}{CH}}{-}\overset{CH_3CH=CH-CHOMgCl}{\overset{|}{CH}}{-}CHO \quad \text{IV} \xrightarrow[H_2O]{(CH_3)_3CMgCl}$$

$$CH_3\underset{(CH_3)_3C}{\underset{|}{CH}}{-}\overset{CH_3CH=CH-CHOH}{\overset{|}{CH}}{-}CHOH{-}C(CH_3)_3 \quad \text{V}$$

These reactions show that the actual amount of original 1,4 addition must be greater than indicated in Table I. The large amounts of complex products formed with isopropyl- and *t*-amylmagnesium halides are doubtless of a similar nature, suggesting that here, too, the amounts of original 1,4 addition are considerably greater than shown in Table I.

α,β-Unsaturated ketones were next studied in order to see if the same effect with *t*-butylmagnesium chloride could be observed. The ketones used were ethylidene acetone and mesityl oxide. The latter gave no 1,4-addition product with *t*-butylmagnesium chloride, the same result as found by Kohler with ethyl- and phenylmagnesium bromides. The former, according to Kohler, gave both 1,4- and 1,2-addition products with ethylmagnesium bromide in the ratio of 3 to 1.

---

[9] Johnson and Adkins, THIS JOURNAL, **54**, 1944 (1932).

[10] Kohler, *Am. Chem. J.*, **37**, 369 (1907); **42**, 375 (1909).

[11] Kohler and Burnley, *ibid.*, **43**, 412 (1910).

[12] Evans, Lee and Lee, THIS JOURNAL, **57**, 489 (1935).

[13] Kohler and Peterson, *ibid.*, **55**, 1073 (1933).

Gry,[14] however, reported that no ketonic products could be detected. It was necessary, therefore, to carry out this reaction again, and under exactly the same conditions as used with *t*-butylmagnesium chloride.

TABLE II

PERCENTAGE YIELDS

		Ethylidene acetone		Mesityl oxide	
		This paper	Kohler	This paper	Kohler
Ethyl	Ketone	38.6	75.0	..	0
	Carbinol	41.4	25.0	..	..
	K./C.	0.9	3.0	..	..
t-Butyl	Ketone	54.0	..	0	..
	Carbinol	16.7	..	46	..
	K./C.	3.2	..	..	..

The above results show that with ethylidene acetone, the *t*-butyl reagent again favors 1,4 addition over the ethyl, but the difference here is not nearly so striking as with crotonic aldehyde. Furthermore, the yield of ketone with ethylmagnesium bromide is much nearer to that found by Kohler than to that reported by Gry. While it is of course possible that Gry overlooked the presence of the ketone in his product, it is more likely that, with α,β-unsaturated ketones which are so prone to 1,4 addition, local conditions, such as temperature, concentration of the reagent, etc., as suggested by Kohler, are much more important in determining the mode of addition than with α,β-unsaturated aldehydes.

I am indebted to the Massachusetts Institute of Technology for the facilities of this Laboratory and to the Mallinckrodt Chemical Works for so generously donating the strychnine used in this work. Part of the funds required for this research were privately contributed.

Experimental Part

Tertiary Butylmagnesium Chloride and Crotonic Aldehyde.—A Grignard reagent, prepared from 75 g. of *t*-butyl chloride according to the directions of Whitmore and Badertscher,[15] was cooled to −22 to −28° and treated with 20 g. of freshly distilled crotonic aldehyde. After standing overnight at 25°, the mixture was decomposed with iced sulfuric acid, the products taken up in ether, washed with sodium bicarbonate and water, and the ether distilled *in vacuo*. The residual liquor was then dried over sodium sulfate and distilled, yielding 19.6 g. of a colorless liquid, b. p. 30–100° (40–27 mm.). Aliquot portions (4.9 g.) of this material were treated separately with an excess of semicarbazide, phthalic anhydride and pyridine. The crude semicarbazone weighed 2.7 g., and the crude phthalate 5.9 g. The yield of aldehyde was therefore 20.3%, of carbinol 30.6% and of complex products (14.4 g.) 39.3%. A repetition of this reaction using 260 g. of crotonic aldehyde gave 227 g. of an aldehyde-carbinol mixture, b. p. 70–73° (36 mm.), which was separated by treatment with phthalic anhydride and pyridine. The recovered aldehyde boiled at 70–72° (36 mm.). *t*-Butylmagnesium bromide and 8 g. of crotonic aldehyde under the same conditions gave 2.3 g. of a semicarbazone, a yield of 10.8%. The yield of carbinol as phthalate was only 3%, of complex products 55.4%.

β,γ,γ-Trimethylvaleric Aldehyde $(CH_3)_3CCH(CH_3)CH_2CHO$.—The aldehyde was purified through the semicarbazone, which crystallized as needles from benzene, m. p. 166°.

Anal. Calcd. for $C_9H_{19}ON_3$: N, 22.7. Found: N, 21.7.

The semicarbazone was hydrolyzed by shaking with 6 *N* hydrochloric acid and ether, and the aldehyde then extracted with ether, dried over sodium sulfate and distilled. Considerable amounts of the aldehyde had already polymerized. The pure aldehyde, b. p. 56–57° (19 mm.), possessed a pleasant odor, reduced cold Tollens solution immediately, and gave a red color with Schiff reagent. It absorbed bromine in glacial acetic acid only after an induction period of several minutes and then with the evolution of hydrogen bromide.

Anal. Calcd. for $C_8H_{16}O$: C, 74.9; H, 12.6. Found: C, 74.9; H, 12.5.

Propenyl-*t*-butylcarbinol, $CH_3CH{=}CHCHOHC(CH_3)_3$.—The carbinol was purified through the phthalate and then resolved with strychnine in acetone. The pure carbinol, b. p. 75–76° (36 mm.), $\alpha^{25}\mathrm{D}$ +15° ±, $n^{25}\mathrm{D}$ 1.4369, d^{25}_4 0.8308, MR (calcd.) 40.39, found 40.20, reduced cold aqueous potassium permanganate immediately, and absorbed bromine in glacial acetic acid instantly.

Anal. Calcd. for $C_8H_{16}O$: C, 74.9; H, 12.6. Found: C, 74.6; H, 12.5.

β,γ,γ-Trimethylvaleric Acid, $(CH_3)_3CCH(CH_3)CH_2COOH$.—Oxidation of the aldehyde by Tollens solution yielded a very pure acid, b. p. 124.0–124.5° (19 mm.), d^{25}_4 0.9199, $n^{25}\mathrm{D}$ 1.4309, MR (calcd.) 40.68, found 40.54. The acid did not absorb bromine in glacial acetic acid.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.6; H, 11.2. Found: C, 66.6; H, 11.2.

The amide, prepared with thionyl chloride and ammonium hydroxide, was recrystallized from alcohol and water, m. p. 163–164°.

Anal. Calcd. for $C_8H_{17}ON$: N, 9.8. Found: N, 9.5.

Methyl β,γ,γ-Trimethyl-α-bromovalerate, $(CH_3)_3CCH(CH_3)CHBrCOOCH_3$.—The above acid when treated with phosphorus, bromine and methyl alcohol in the usual way gave a very pure bromo ester, b. p. 90.5–91.0° (8 mm.), d^{25}_4 1.2405, $n^{25}\mathrm{D}$ 1.4647, MR (calcd.) 53.18, found 52.80.

Anal. Calcd. for $C_9H_{17}O_2Br$: Br, 33.7. Found: Br, 32.8.

Methyl β-*t*-Butylcrotonate, $(CH_3)_3CC(CH_3){=}CHCOOCH_3$.—The bromo ester was heated with an equal weight of redistilled diethylaniline to 190–200° for five hours.[16] When the temperature reached 200°, a reaction took place

---

[14] Gry, *Bull. soc. chim.*, [4] **3**, 377 (1908).

[15] Whitmore and Badertscher, THIS JOURNAL, **55**, 1559 (1933).

[16] Compare Weinig, *Ann.*, **280**, 252 (1894).

as evidenced by the evolution of a gas. This gas burned with a sooty flame, absorbed bromine in glacial acetic acid and had an odor like isobutylene.[17] The crotonic ester was isolated in the usual way, b. p. 184–186° (765 mm.). It reduced cold aqueous potassium permanganate immediately, but absorbed bromine in glacial acetic acid only slowly: d^{25}_4 0.9109, n^{25}_D 1.4450, MR (calcd.) 44.95, found: 45.61.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.2; H, 10.3. Found: C, 68.9; H, 10.6.

2.3 g. of this ester in glacial acetic acid was treated with ozone. The ozonide was decomposed with zinc according to Helferich[18] and then worked up as usual. The ether–soluble portion yielded upon evaporation and subsequent treatment with semicarbazide, 0.7 g. of a semicarbazone. This was recrystallized from water, m. p. 155°, and was identified as the semicarbazone of pinacolone by a mixed melting point, 155°, with an authentic specimen (m. p. 155°). The aqueous alkaline portion of the reaction mixture reduced Tollens solution, indicating the presence of an aldo-acid or ester.

Tertiary Amylmagnesium Chloride and Crotonic Aldehyde.—A Grignard reagent prepared from 86 g. of the chloride was treated with 28 g. of crotonic aldehyde exactly as described for *t*-butylmagnesium chloride; 26 g. of a colorless liquid, b. p. 35–100° (5 mm.), was obtained. The yield of aldehyde as semicarbazone was 22.6%, of carbinol as phthalate 16.3%, and of complex products, 45.7%. The semicarbazone, undoubtedly that of β,γ,γ-trimethylcaproic aldehyde, crystallized from benzene as needles, m. p. 172°.

Anal. Calcd. for $C_{10}H_{21}ON_3$: N, 21.1. Found: N, 20.1.

The semicarbazone was decomposed with a hot oxalic acid solution, and the resulting aldehyde steam distilled. It possessed a pleasant though somewhat penetrating odor, gave a red color with Schiff reagent immediately, but reduced Tollens solution only slowly.

Ethyl-, Propyl-, Isopropyl- and Phenylmagnesium Bromides and Crotonic Aldehyde.—These reactions were all carried out as described above for *t*-butylmagnesium chloride. In every case a large excess of the Grignard reagent was used. The product from ethylmagnesium bromide and 162 g. of crotonic aldehyde, after treating with phthalic anhydride and pyridine, yielded a small amount of material which in turn gave only 0.33 g. of a semicarbazone. This crystallized from benzene as plates, m. p. 128–129°, and was identified as the semicarbazone of β-methylvaleric aldehyde by a mixed melting point, 128–129°, with an authentic specimen (m. p. 128–129°). The product from propylmagnesium bromide, however, yielded only a trace of aldehyde, and no semicarbazone was obtained. The product from isopropylmagnesium bromide and 165 g. of crotonic aldehyde yielded 0.9 g. of a semicarbazone which crystallized from benzene and petroleum ether as leaves, m. p. 136–137°. It is undoubtedly the semicarbazone of β,γ-dimethylvaleric aldehyde.

Anal. Calcd. for $C_8H_{17}ON_3$: N, 24.5. Found: N, 23.9.

The crude product, 46 g. (90% ±), from phenylmagnesium bromide and 23 g. of crotonic aldehyde gave no semicarbazone, but when shaken with Tollens solution yielded 0.045 g. of an acid with a butyric odor, which partially crystallized. Lack of material prevented positive identification as β-phenylbutyric acid. The carbinol, contaminated with diphenyl,[19] was purified by distillation, b. p. 91–92° (0.5 mm.), d^{25}_4 1.005, n^{25}_D 1.5603.

It absorbed bromine in glacial acetic acid immediately. After some time it slowly solidified to a crystalline mass, m. p. 33–35°.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.0; H, 8.2. Found: C, 80.9; H, 8.2.

Allylmagnesium Bromide and Crotonic Aldehyde.—The Grignard reagent was prepared from 90 g. of allyl bromide according to the directions of Gilman and McGlumphy.[20] The yield, however, was only about 25% (by titration). The reaction with 12 g. of crotonic aldehyde was carried out exactly as described above. Due however to the large excess of magnesium, some difficulty was encountered in the decomposition with iced sulfuric acid, whereby considerable material was lost. As, however, the expected carbinol and aldehyde have approximately the same boiling point, the product obtained, b. p. 69–71° (25 mm.), 10.5 g., was a fair sample for analysis. It reduced Tollens solution immediately but not to any great extent. It slowly gave a red color with Schiff reagent. The material was therefore the unsaturated carbinol, containing only a trace of the aldehyde. The carbinol had a typical allylic odor, $n^{14.8}_D$ 1.4558,[21] n^{25}_D 1.4510. When treated with semicarbazide, no semicarbazone could be detected.

β-Methylvaleric Aldehyde, $CH_3CH_2CH(CH_3)CH_2$-CHO.—This aldehyde was prepared by the action of ozone on 3-methylhexene-1, which was formed from *s*-butylmagnesium bromide and allyl bromide, b. p. 86–87° (763 mm.)[22] uncorrected. Ozonolysis was carried out in glacial acetic acid, and the ozonide decomposed with zinc according to Helferich. After removal of the ether, the crude aldehyde was converted directly into the semicarbazone, which formed plates from benzene and petroleum ether, m. p. 128–129°.

Anal. Calcd. for $C_7H_{15}ON_3$: N, 26.7. Found: N, 26.1.

The aldehyde, regenerated from the semicarbazone by aqueous oxalic acid, possessed a sharp, later choking odor. Lack of material prevented further purification, and hence it was immediately oxidized by cold Tollens solution to β-methylvaleric acid, then identified by conversion into the amide m. p. 123–124°. A mixed melting point with an authentic specimen (m. p. 123–124°) was 123–124°.

Tertiary Butylmagnesium Chloride and Crotonic Aldehyde. The Complex Products.—The high boiling material constituting about 40% of the reaction product was dis-

---

[17] A formation of isobutylene here is in complete harmony with the formation of isobutylene from the dehydration of di-*t*-butylcarbinol [Whitmore and Stahly, THIS JOURNAL, **55**, 4153 (1933)]. The molecular fragment, $(CH_3)_3CCH(CH_3)CH^{\oplus}$—$COOCH_3$ formed by a removal of bromine from the bromo ester, is very similar to that assumed by Whitmore and Stahly to be the dehydration intermediate from di-*t*-butylcarbinol.

[18] Helferich, *Ber.*, **52**, 1123 (1919).

[19] Diphenyl, b. p. 82° (0.5 mm.).

[20] Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

[21] Enklaar, *loc. cit.*, found b. p. 68–69° (24 mm.), $n^{14.8}_D$ 1.45527.

[22] Soday and Boord reported 87.2–87.5° (760 mm.), THIS JOURNAL, **55**, 3293 (1933).

tilled at 1 mm., yielding a yellowish oil which after very careful fractionation boiled at 96.3–97.9°, d^{25}_4 0.8747, n^{25}_D 1.4698.

Anal. Calcd. for $C_{16}H_{30}O$: C, 80.6; H, 12.7. Found: C, 80.2; H, 12.6.

On standing the substance became very viscous. When shaken with Tollens solution and then redistilled, the compound remained mobile and no longer reduced Tollens solution. It reduced cold aqueous potassium permanganate and absorbed bromine in glacial acetic acid instantly.

The residue from the above first distillation partially crystallized, yielding a white solid, insoluble in petroleum ether. When recrystallized from ether, it melted at 128–129°. It absorbed bromine and reduced potassium permanganate in glacial acetic acid immediately. Attempts to prepare a semicarbazone failed. The molecular weight in camphor was 266. A Zerewitinoff determination[23] showed two active hydrogen atoms with a consumption of two equivalents of the Grignard reagent.

Anal. Calcd. for $C_{16}H_{32}O_2$: C, 74.9; H, 12.6. Found: C, 75.2; H, 12.2.

The remaining material was very viscous and soluble in petroleum ether. It was not further investigated. None of the complex products from isopropylmagnesium bromide or *t*-amylmagnesium chloride crystallized. From the former were isolated two liquids b. p. 84–89° (3 mm.) and b. p. 120–121° (2 mm.). This second liquid, which corresponded to the crystalline solid mentioned above (m. p. 128–129°), was, however, soluble in petroleum ether.

Tertiary Butylmagnesium Chloride and Ethylidene Acetone.—16.5 g. of ethylidene acetone, b. p. 120.5–121.5° (prepared from hydroacetylacetone by dehydration with iodine) was added to a cooled (−9 to −12°) Grignard reagent prepared from 55.5 g. of the chloride. The reaction mixture was kept at the same temperature for two hours after the addition was complete, and then allowed to stand overnight at 25°. After decomposition with iced sulfuric acid, the reaction product was washed with aqueous sodium carbonate and water, and the ether carefully evaporated *in vacuo* through an efficient column. The residual liquor was then distilled, yielding 19.6 g. of a light yellow liquid, b. p. 70–73° (20 mm.) and a residue of much higher boiling material, 4.6 g.; 4.0 g. of the carbinol-ketone fraction gave 4.3 g. of a semicarbazone. The net yields of ketone and unsaturated carbinol were therefore 54.0 and 16.7%, respectively. The filtrate from the semicarbazone precipitation gave, after extraction with ether, a small amount of a liquid which reduced aqueous potassium permanganate immediately, and added bromine in glacial acetic acid instantly. It possessed a more ethereal odor than the ketone.

β,γ,γ-Trimethylhexanone-2, $(CH_3)_3CCH(CH_3)CH_2COCH_3$.—The ketone was purified through the semicarbazone, which after recrystallization from benzene melted at 200–201° with decomposition. The pure ketone, b. p. 72° (20 mm.), d^{25}_4 0.8294, n^{25}_D 1.4238; MR (calcd.) 43.77; found 43.70, had a fine, slightly aromatic odor.

Anal. Calcd. for $C_9H_{18}O$: C, 76.0; H, 12.7. Found: C, 76.3; H, 12.9.

Ethylmagnesium Bromide and Ethylidene Acetone.—A Grignard reagent prepared from 56 g. of the bromide was treated with 11.4 g. of ethylidene acetone, b. p. 120–122°, exactly as described above. The product was carefully fractionated at 60 mm.; forerun 0.5 g. ±, main fraction 12.3 g., b. p. 50–80° (mostly 72–74°), residue (black) 0.8 g. 4.0 g. of the main fraction, $n^{12.5}_D$ 1.4272,[24] n^{25}_D 0.4212, gave 2.9 g. of a semicarbazone. The net yield of ketone and unsaturated carbinol was therefore 38.6 and 41.4%, respectively. The semicarbazone was recrystallized from aqueous alcohol, m. p. 128–128.5°.[25]

Tertiary Butylmagnesium Chloride and Mesityl Oxide.—A Grignard reagent prepared from 280 g. of the chloride was treated with 95 g. of mesityl oxide, b. p. 127–128.3°. The addition took place at −10 to −20°. The colored complex products initially formed did not disappear completely, however, until the temperature had risen to about 0°. The reaction mixture was allowed to stand overnight at 25° and then worked up as usual. The ether was evaporated on the steam-bath, and the remaining material was distilled *in vacuo*, yielding after two distillations the following fractions: A, b. p. 38–50° (30 mm.—strong odor of mesityl oxide)[26] 11.0 g.; **B**, b. p. 50–89° (23 mm.) 70.5 g., yield 46%; C, residue from the first distillation, a very high boiling and highly colored material, 30 g.; D, residue from the second distillation, 4 g. Fractions A, B and D were shaken separately for six and one-half hours with a saturated solution of sodium bisulfite. Each aqueous solution was then extracted with ether twice, freed from ether *in vacuo*, neutralized (B and D now combined) with sodium carbonate and distilled. No organic material passed over into the distillate. There was, therefore, no saturated ketone formed by 1,4 addition.

β,δ,ε,ε-Tetramethylhexene-2-ol-4, $(CH_3)_2C{=}CHCOH(CH_3)C(CH_3)_3$.—The ethereal extract from B above was distilled, yielding the unsaturated carbinol, b. p. 66.5–68.0° (11 mm.), d^{25}_4 0.8499, n^{25}_D 1.4484, MR (calcd.) 49.44, found 49.22.

Anal. Calcd. for $C_{10}H_{20}O$: C, 77.5; H, 12.8. Found: C, 77.1; H, 12.8.

Unlike the tertiary carbinols prepared by Jacquemain[27] from mesityl oxide and various alkyl Grignard reagents, this carbinol did not dehydrate when distilled at the ordinary pressure, b. p. 178–180°. It did dehydrate, however, very readily with iodine, yielding a liquid, b. p. 146–153°, presumably a substituted hexadiene.

Summary

1. Crotonic aldehyde forms both 1,2- and 1,4-addition products with organomagnesium halides.
2. The amount of 1,4 addition with phenyl-, ethyl-, propyl-, allyl-, and isopropylmagnesium bromides is extremely small.

---

[23] I am indebted to Professor E. P. Kohler for this determination.

[24] Gry, *loc. cit.*, who obtained no ketonic product, found $n^{12.5}_D$ 1.4268 for the unsaturated carbinol.

[25] Chavanne, *Bull. soc. chim. Belg.*, **36**, 206 (1927), reported 129°. Davies, Dixon and Jones, *J. Chem. Soc.*, 468 (1930), found 120–121° (typographical error?).

[26] A and C are probably the results of enolization and condensation; see Conant and Blatt, THIS JOURNAL, **51**, 1227 (1929).

[27] Jacquemain, *Compt. rend.*, **198**, 482 (1934).

3. The amount of 1,4 addition with *t*-butylmagnesium chloride, on the contrary, is large, and with *t*-amylmagnesium chloride, exceeds that of 1,2 addition.

4. Ethylidene acetone forms more 1,4 addition product with *t*-butylmagnesium chloride than with ethylmagnesium bromide.

5. Mesityl oxide forms no 1,4 addition product with *t*-butylmagnesium chloride.

CAMBRIDGE, MASS. RECEIVED APRIL 18, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

The Decomposition of Triphenylmethyl Hyponitrite

BY M. A. SPIELMAN[1]

Alkoxyl radicals have been postulated as fugitive intermediates in certain organic reactions,[2] but the study of their behavior is complicated by the fact that the temperatures at which they are formed are too high to permit distinction between primary reactions and secondary pyrolytic effects. The decomposition of alkyl hyponitrites offers an attractive method of forming such radicals at moderate temperatures, and this paper presents a preliminary investigation of the problem.

The few esters of hyponitrous acid in the literature, prepared from silver hyponitrite and alkyl halides, are said to decompose below 100° to give nitrogen, an aldehyde and an alcohol.[3] This may be viewed as a prefatory decomposition to nitrogen and two alkoxyl radicals, followed by disproportionation of the latter.

$$RCH_2{-}O{-}N{=}N{-}O{-}CH_2R \xrightarrow{-N_2} 2RCH_2{-}O{-} \longrightarrow RCHO + RCH_2OH$$

In the present study, the triphenylmethoxyl radical was selected for investigation because simple disproportionation is impossible, and because a previous preparation by an independent method allows a comparison of results to be made.

Triphenylchloromethane in benzene reacted readily with silver hyponitrite, but evolution of nitrogen began at once, and the triphenylmethyl hyponitrite proved to be too unstable for isolation. Its transitory existence was clearly shown, however, by measuring a significant escape of nitrogen after the reaction mixture had been filtered from inorganic matter. The products of the reaction were, in order of amounts isolated, benzopinacol diphenyl ether, benzophenone, triphenylmethyl peroxide, phenol, triphenylmethyl, triphenylcarbinol and *p*-hydroxytetraphenylmethane. Large amounts of nondescript oily and resinous material were also encountered. This series of products is seen to parallel that which Wieland[4] found to result from the dissociation of triphenylmethyl peroxide in boiling xylene. He isolated benzopinacol diphenyl ether, benzophenone, phenol and triphenylcarbinol.

The first step in the decomposition of the ester (I) undoubtedly incurs the formation of the triphenylmethoxyl radical (II), and the combination of two of these yields the triphenylmethyl peroxide (III) present in the end-products. Rearrangement antecedent to combination, as suggested by Wieland, explains the origin of the benzopinacol diphenyl ether (V). The source of benzophenone is obscure. An effort was made to show that it came directly from the triphenylmethoxyl radical with concomitant elimination of a phenyl radical, much as the ethoxyl radical may throw off a methyl radical to give formaldehyde.[5] No trace of the phenyl radical could be found, either by careful search for diphenyl or by carrying out the reaction in the presence of quinone and making examination for quinhydrone.[6] A possible precursor of benzophenone is the mixed benzophenone acetal (VI), some of which must certainly result from the combination of the triphenylmethoxyl radical with its rearrangement product (IV). Presupposing inherent instability in such a molecule, there is no difficulty in explaining the series of substances actually found. Thus, fission at a, followed by

---

[1] National Research Council Fellow.

[2] Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935, pp. 115, 139.

[3] Zorn, *Ber.*, **11**, 1630 (1878); Hantzsch and Kaufmann, *Ann.*, **292**, 329 (1896); Partington and Shah, *J. Chem. Soc.*, 2593 (1932).

[4] Wieland, *Ber.*, **44**, 2551 (1911).

[5] Rice and Rodowskas, THIS JOURNAL, **57**, 350 (1935). In this connection compare also the decomposition of *t*-butyl hypochlorite to acetone and methyl chloride, Chattaway and Backeburg, *J. Chem. Soc.*, **123**, 2999 (1923).

[6] Wieland, *Ann.*, **514**, 145 (1934), has shown that the free phenyl radical combines instantly with benzene to form diphenyl with the liberation of atomic hydrogen which may be captured by quinone.