zone identical with that formed from an authentic sample of 2-hydroxytetrahydropyran.

Fraction 3 was not definitely identified although it was partly soluble in alkali and must have contained some δ-valerolactone. The properties of fraction 4 indicated that it was a mixture of δ-valerolactone and a product insoluble in 10% alkali. Since this fraction failed to give an aldehyde test, the product insoluble in alkali cannot be 2-hydroxytetrahydropyran which is known[21] to lose readily a molecule of water at high temperatures and to go over to di-2-tetrahydropyran ether. In fact, a carbon and hydrogen analysis of this fraction gave values corresponding to about equal quantities of δ-valerolactone and di-2-tetrahydropyran ether.

1-Hydroxy-1,4-dihydroperoxybutene (V).—To a cold (0°) mixture of sulfuric acid (30 g. of 95.5%) and hydrogen peroxide (70 g. of 48%) was added, dropwise with stirring in the course of one hour, 34 g. (0.5 mole) of furan.[19] The temperature was maintained at 0 ± 5°. Stirring was continued for 1.5 hours longer at 0°, then the mixture was saturated with solid ammonium sulfate and extracted with ethyl ether. The ether extract was shaken once with magnesium carbonate, dried at −9° and the ether removed under reduced pressure. The yellow residual oil was subjected to distillation at 2 mm. and at water-bath temperature of 40°; a small amount (*ca.* 1 g.) of a yellow oil distilled over which gave the following analyses.

Anal. Calcd. for $C_4H_8O_5$ (V): C, 35.30; H, 5.92; (O), 23.6. Found: C, 36.85; H, 4.42; (O), 20.8.

This peroxide decomposes readily to maleic acid which was identified by m.p. and mixed m.p. with an authentic sample. The presence of this acid in the analytical sample would tend to raise the carbon and lower the hydrogen and active oxygen content and therefore account for the results obtained. The yellow oil also gave a positive test with a silver foil for the presence of hydrogen peroxide.

1,4-Dihydroxy-1,4-exocycloperoxene-2 (VII).—When a large sample of the crude peroxide V was repeatedly extracted with a saturated solution of ammonium sulfate another peroxide was formed and isolated as a yellow oil which failed to give a positive test for hydrogen peroxide; $n^{25}\text{D}$ 1.4947.

Anal. Calcd. for $C_4H_6O_4$: C, 40.68; H, 5.12; (O), 13.6. Found: C, 39.00; H, 4.98; (O), 15.7.

On standing at room temperature this peroxide was also converted, in part, into maleic acid and a yellow polymer. When it was reduced in ethanol with hydrogen, using palladium catalyst (2%) deposited on barium sulfate, malealdehyde was isolated and converted into its bis-phenylhydrazone according to a recent method[22]; m.p. 184–186° (lit. 180–184°).

Anal. Calcd. for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.92; H, 6.15; N, 20.93.

2-Methyl-2-hydroperoxy-2,5-dihydrofuran (IX).—Into a cold (0°) mixture of hydrogen peroxide (19.5 g. of 48%) and sulfuric acid (17.3 g. of 95.5%) was added, dropwise with stirring in the course of one hour, 20.5 g. (0.25 mole) of methylfuran.[19] The temperature of the reaction was maintained at 0 ± 5°. A red color developed during the addition of methylfuran and the mixture became thick and sticky and difficult to stir efficiently. It was found essential to add 50 cc. of anhydrous ether to dissolve the sticky material and facilitate stirring. The mixture was stirred for an additional hour, then the non-aqueous layer separated, extracted with saturated ammonium sulfate solution, then shaken with magnesium carbonate and dried. When the ether was removed under reduced pressure a yellowish, peroxidic oil (9 g., 34% of theory) was obtained. This had an active oxygen content of 9.9% as against the theoretical of 13.8%. This preparation was repeated using anhydrous ether as a solvent from the beginning of the reaction. In this case a crude product was obtained in 70% yield with an active oxygen content of 11.2%.

This hydroperoxide cannot be crystallized but can be obtained as a white powder from ethyl ether by the addition of small quantities of petroleum ether. When well dried, it explodes upon heating and decomposes without melting at 80–100°.

Anal. Calcd. for $C_5H_8O_3$: C, 51.77; H, 6.95; (O), 13.8; (Zerewitinoff H), 1.0. Found: C, 50.66; H, 6.83; (O), 13.2; (Zerewitinoff H), 1.1.

When catalytically hydrogenated in ethanol, using platinum oxide as catalyst, it absorbed 1.1 moles of hydrogen, while in glacial acetic acid, it absorbed 2.2 moles of hydrogen. It also absorbed bromine slowly in ethyl acetate showing definitely that it was unsaturated. An infrared spectrum showed three bands at 2.8–3.1 μ, 9 μ and 11.8–12 μ characteristic, respectively, of the hydroxyl radical of the hydroperoxy group, the ether linkage and the hydroperoxy radical. Molecular weight determinations in dioxane by the cryoscopic method[23] failed to give reproducible results showing that this hydroperoxide may be polymeric or polymerizes in dioxane.

Acknowledgment.—We are indebted to Lucidol Division of Novadel-Agene Corporation and E. I. du Pont de Nemours and Co. for financial support of this investigation. For the combustion analyses and the infrared spectra we wish to thank Dr. Nagy and his associates of this Institute.

CAMBRIDGE, MASS.

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(21) R. Paul, *Bull. soc. chim.*, [5] 1, 971 (1934).

(22) N. Clauson-Kaas, F. Limborg and K. Glens, *Acta Chem. Scand.*, **6**, 531 (1952).

(23) O. L. Mageli, Ph.D. Thesis, M.I.T., April, 1953, p. 16.

[CONTRIBUTION FROM THE DIVISION OF ORGANIC CHEMISTRY OF THE ORTHO RESEARCH FOUNDATION]

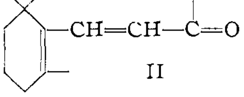
Synthesis of Polyenes. IV. The Reaction of β-Ionone with Grignard Reagents

BY WILLIAM OROSHNIK, GEORGE KARMAS AND ROBERT A. MALLORY

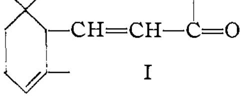
RECEIVED DECEMBER 9, 1953

Contrary to general belief, β-ionone has been found to react normally with Grignard reagents to give the 1,2-adduct as major product and the 1,4-adduct in minor amount. Evidence is presented correlating the predominance of the 1,2-addition with the steric hindrance in β-ionone. The spectral characteristics of the resulting β-ionols are discussed.

For quite some time now, β-ionone (I) has been assumed to react abnormally with ordinary Grignard reagents. This concept stems from the original report on this reaction by Karrer, *et al.*,[1] who could obtain no carbinol from β-ionone with allylmagnesium bromide in spite of the fact that α-ionone (II) gave the expected 1,2-adduct with this



II



I

reagent. To account for these results it was suggested that a 1,4-adduct was formed with β-ionone, but no details of the characteristics of the product were given.[1] Since then similar failures to achieve

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(1) P. Karrer, H. Salomon, R. Morf and O. Walker, *Helv. Chim. Acta*, **15**, 878 (1932).

TABLE I

THE SUBSTITUTED β-IONOLS

R	Yield, %	Boiling point °C.	Boiling point Mm.[a]	n^{20}_D	$\lambda_{max.}$	ϵ	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl	83	68–70	0.002	1.4923	231.5	5300	80.71	80.66	11.61	11.57
Ethyl	71	82–84	.001	1.4958[b]	231.5	5300	81.02	81.08	11.79	11.66
Propyl	75	84–85	.2	1.4930[c]	231.5	5400	81.29	81.16	11.94	12.02
Allyl	71	83–85	.2	1.5019	231.5	5500	81.99	81.71	11.18	11.10
Prenyl	78	82–86	.2	1.5046	231.5	5500	82.38	82.39	11.52	11.64
Phenyl	74	114–117	.2	1.5435	235	6500	84.39	84.58	9.69	9.63
Benzyl	82	124–128	.3	1.5390	231.5[d]	6000	84.45	84.49	9.92	9.93

[a] The recorded pressures are those at the vacuum pump rather than receiver-pressures. [b] The specimen made by hydrogenation of V showed n^{20}_D 1.4971; λ_{max} 231.5 mμ, ϵ 5600. [c] A specimen made from propyllithium according to the procedure of F. B. Kipping and F. Wild[2] showed n^{20}_D 1.4932; λ_{max} 231 mμ, ϵ 5600. [d] Inflection point rather than λ_{max}.

TABLE II

THE 1,4-ADDUCTS

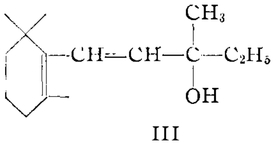
	Semicarbazones								Ketones							
R	M.p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Yield from semicarbazone, %	B.p., °C.	B.p., Mm.	n^{20}_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Methyl	187–188	1	67.87	68.13	10.26	10.29	15.82	15.95								
Ethyl	182–183	15	68.77	68.85	10.46	10.51	15.04	15.08	96	66–67	0.15	1.4841	81.02	80.74	11.79	11.72
Propyl	197–198	14	69.58	69.72	10.65	10.63	14.32	14.46	85	78–79	.2	1.4838	81.29	81.29	11.94	11.72
Allyl		0														
Prenyl		0														
Phenyl	194–196	3[a]	73.35	73.43	8.93	9.00	12.83	12.82	70[a]	115–120	.05	1.5830	84.39	86.90[11]	9.69	9.68
Benzyl	154–155	17	73.85	73.64	9.16	9.09	12.31	12.28	75	108–110	.001	1.5270	84.45	84.49	9.92	9.93

carbinols from β-ionone have been reported with methyl-[2] and phenylmagnesium halides[2] as well as with the magnesium derivative of 1,4-dibromobut-2-ene and of 1,2-dibromoethane.[3]

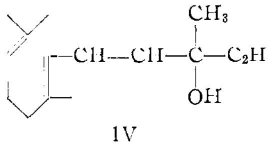
In contrast to these results is the normal behavior of β-ionone with other organometallic reagents. Methyl- and phenyllithium yield the expected carbinols arising from 1,2-addition,[2] as do the numerous acetylenic Grignard reagents[4] and metal acetylides reported during the past decade.[5] Only the 1,2-adduct is obtained in the Reformatsky reaction with ethyl bromoacetate and its vinylogs,[1,6] as well as in the Darzens reaction with ethyl chloroacetate.[7] The recent variation of the Reformatsky reaction employing propargyl bromides instead of bromoesters likewise gives the 1,2-adduct only.[8] Most syntheses of polyenes based on β-ionone employ one or another of these methods, and the possibility of extending the β-ionone side-chain through ordinary Grignard reagents has up to now been universally discounted.

Our attention was recently drawn to this problem when it became increasingly evident that the side-chain double bond in β-ionone is sterically hindered.[9] This arises from interference between one of the ring *gem*-methyl groups and the second hydrogen in the side-chain. The likelihood of any appreciable 1,4-addition of Grignard reagents to such a hindered structure appeared rather remote. This reaction was therefore reinvestigated with a number of Grignard reagents which were so chosen as to include examples derived from alkyl, allyl, aryl and alkaryl halides. The results indeed substantiated the above hypothesis. In every case the expected β-ionols were obtained in good yields. Indeed, with allyl magnesium bromide and prenylmagnesium[10] chloride, these were the sole products. The other Grignard reagents gave, in addition, small quantities of ketonic products which are tentatively designated as the 1,4-adducts.[11] The data are summarized in Tables I and II.

The contention that steric hindrance determined the course of the above reactions is further supported by the fact that ψ-ionone, which is acyclic and therefore has none of the hindrance present in β-ionone, gives mainly ketonic product[11] with ethylmagnesium bromide. Only a minor quantity of ethyl-ψ-ionol (IV) the 1,2-adduct, was obtained in this case.



III



IV

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[2] F. B. Kipping and F. Wild, *J. Chem. Soc.*, 1239 (1940); see also ref. 20.

[3] V. Teterin and A. Ivanov, *Compt. rend. Acad. Sci. U.R.S.S.*, **2**, 259 (1935).

[4] J. Salkind, S. Zonis and N. Blochin, *ibid.*, **2**, 57 (1935); *Chem. Zentr.*, **109, II,** 768 (1938); A. F. Thompson, N. A. Milas and I. Rovno, THIS JOURNAL, **63**, 752 (1941); W. Oroshnik, G. Karmas and A. D. Mebane, *ibid.*, **74**, 3807 (1952); also ref. 12.

[5] W. Oroshnik and A. D. Mebane, *ibid.*, **71**, 2062 (1949).

[6] W. G. Young, L. J. Andrews and S. J. Cristol, *ibid.*, **66**, 520 (1944); D. A. van Dorp and J. F. Arens, *Rec. trav. chim.*, **65**, 338 (1946).

[7] I. M. Heilbron, A. W. Johnson, E. R. H. Jones and A. Spinks, *J. Chem. Soc.*, 727 (1942).

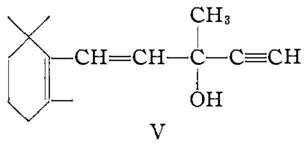
[8] W. Huber and A. Businger, U. S. Patent 2,540,116 (1951); O. Isler, U. S. Patent 2,540,118 (1951).

[9] E. A. Braude, *et al.*, *J. Chem. Soc.*, 1890 (1949); see also ref. 12.

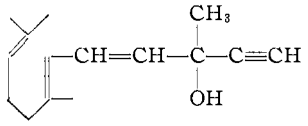
[10] The name prenol has been suggested for γ,γ-dimethylallyl alcohol by E. Späth and J. Bruck to indicate its derivation from isoprene: *Ber.*, **71**, 2709 (1938).

[11] The 1,6-addition, which is also possible, would give β,γ-unsaturated ketones. Such structures would be expected to equilibrate spontaneously with the α,β-unsaturated forms, which show characteristic bands in the ultraviolet. However, all of the ketones obtained were transparent in the ultraviolet. The phenylated ketone was obtained pure only as the semicarbazone which likewise showed no spectral evidence of conjugation. During the acid hydrolysis this ketone apparently rearranges and dehydrates to some extent, as evidenced by the high carbon values and $\lambda_{max.}$ 317 mμ, $E^{1\%}_{1\,cm.}$ 136.

The new β-ionols were readily identified by their characteristic ultraviolet absorption spectra. Those shown by ethyl-β-ionol (III) and ethynyl-β-ionol (V) are typical (Fig. 1). Their pronounced hypsochromic and hypochromic degradation, which arises from the break in coplanarity between the ring and side-chain double bonds,[12] is clearly seen in Fig. 1 where they are compared with their acyclic unhindered analogs, ethyl-ψ-ionol (IV) and ethynyl-ψ-ionol (VI).

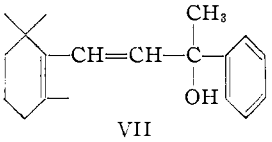


V



VI

It is of interest to note the bathochromic effect of the ethynyl group in V and in VI (Fig. 1) and of the phenyl group in VII (Table I) in spite of the fact that these unsaturated groups are not conjugated with the diene system.



VII

A similar displacement (3.5–4.5 mμ) has been observed in vinyl-β-ionol and in substituted vinyl and ethynyl β-ionols.[12] This effect is undoubtedly due to the hydroxyl group being simultaneously allylic to the unsaturated systems on both sides of it. The hyperconjugative effect of a hydroxyl group on a polyene chromophore to which it is allylic[13] or propargylic[14] already has been demonstrated in a variety of compounds. Since both unsaturated systems in each of the above β-ionols are hyperconjugated with the same hydroxyl group, it stands to reason that there should be some interaction between the two chromophores.[15] Similar spectral effects have been reported by Bohlmann[16] in a series of distyrylcarbinols and their vinylogs, although the role of the mutually hyperconjugated hydroxyl group was not recognized. In that work, a bathochromic effect of 12.5 mμ was observed in going from methylstyrylcarbinol to distyrylcarbinol. The bathochromic effect was still further increased upon vinylogously increasing the size of the interacting groups.

The infrared spectra corroborated the structures assigned to the β-ionols. That of ethyl-β-ionol (III) is representative, and its identity with the spectrum of a specimen obtained by hydrogenation of V is shown in Fig. 2. The strong band around 10.3 μ, characteristic of the *trans*-CH=CH— double bond, was exhibited by all of the β-ionols, and by β-ionone as well, showing that the steric configuration of the side-chain double bond is retained through the Grignard reaction.

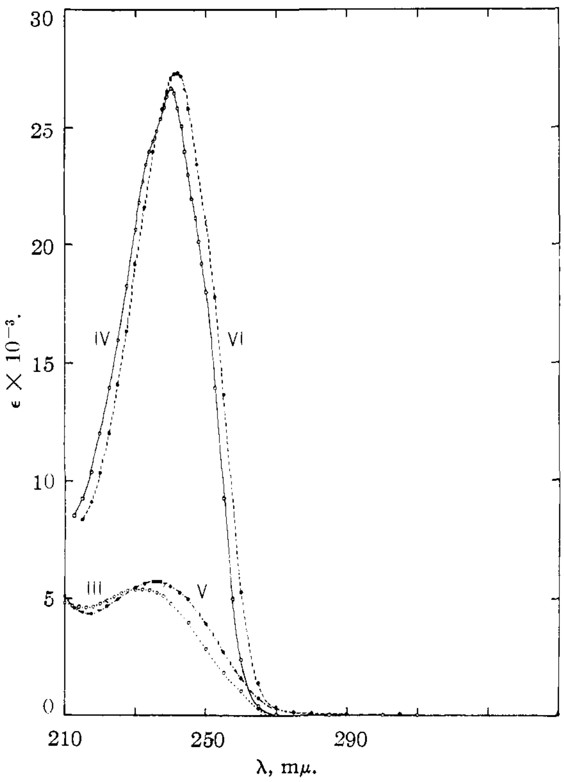
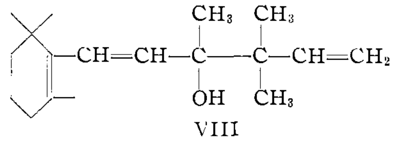
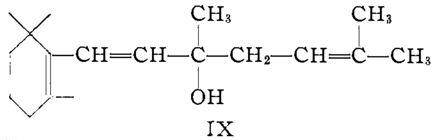


Fig. 1.—The ultraviolet absorption spectra of ethyl-β-ionol (III), ethyl-ψ-ionol, (IV), ethynyl-β-ionol (V),[5] and ethynyl-ψ-ionol (VI).

The spectrum of allyl-β-ionol had, in addition, rather strong bands at 6.1 and 11.0 μ which are characteristic of the terminal vinyl group. Bands at the same location and of comparable strength were observed in the spectrum of the product from prenylmagnesium chloride, indicating that the allylic isomer VIII was formed rather than the primary product IX.[17] The abnormal weakness of the hydrogen-bonding band (2.85 μ) observed in this spectrum has been correlated in other compounds with extensive branching around the hy-



VIII



IX

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[12] W. Oroshnik, G. Karmas and A. D. Mebane, THIS JOURNAL, **74**, 295 (1952).

[13] W. Oroshnik, A. D. Mebane and G. Karmas, *ibid.*, **75**, 1050 (1953).

[14] J. B. Armitage and M. C. Whiting, *J. Chem. Soc.*, 2005 (1952).

[15] In Part I[12] the lower $\lambda_{max.}$ of ethyl-β-ionol with respect to its vinyl and ethynyl analogs was considered anomalous, but it is now apparent from the data acquired in the present work that its spectrum is quite normal. The rather high $\lambda_{max.}$ of carbethoxymethyl-β-ionol, 235 mμ, may perhaps indicate enolization of the carbonyl group.

[16] F. Bohlmann, *Chem. Ber.*, **85**, 1145 (1952).

[17] Such rearrangements frequently have been encountered in reactions of allylic Grignard reagents with carbonyl compounds; *cf.* J. D. Roberts and W. G. Young, THIS JOURNAL, **67**, 148 (1945); K. W. Wilson, J. D. Roberts and W. G. Young, *ibid.*, **72**, 218 (1950).

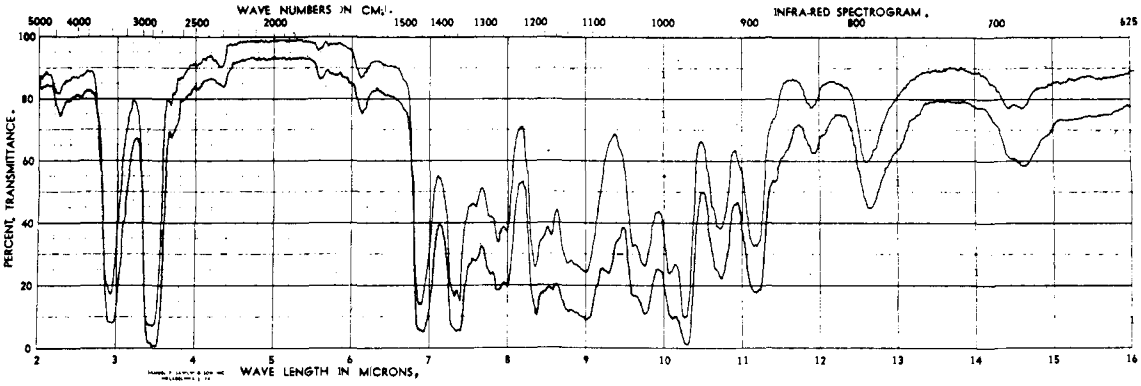

Fig. 2.—The infrared spectrum of ethyl-β-ionol: top curve, specimen obtained by hydrogenation of V; bottom curve, specimen obtained by the Grignard reaction.

droxyl group,[18] and hence is likewise more consistent with formula VIII than with IX. This structure was confirmed by ozonolysis, which gave a 59% yield of formaldehyde.

It is of interest to note that the acetylenic band in the infrared spectrum of ethynyl-β-ionol (V) was almost completely extinguished. This is unusual for a compound with a terminal acetylenic group. Extraordinary weakening of the acetylenic band has been observed previously only when the triple bond is more centrally located in the molecule.[19]

Another point of interest was the region around 12.6 μ. Allyl, benzyl and the saturated alkyl β-ionols all showed a moderately strong band at this location. In phenyl-β-ionol (VII) and ethynyl-β-ionol (V) this band was quite weak, and in VIII it was almost completely absent. The only structural correlation that is immediately apparent is the prominence of this band in the presence of a $>C(OH)-CH_2-$ group in these compounds.

To account for the failure of previous workers to obtain β-ionols by this method, one can only surmise that their Grignard reaction mixtures were hydrolyzed with dilute acids rather than neutral reagents. β-Ionols are extremely sensitive to acids and will allylically rearrange and dehydrate to *retro*ionylidene compounds in their presence.

Giacalone[20] has reported the evolution of methane on adding methylmagnesium iodide to β-ionone. This contention that β-ionone reacts to some degree in its enolic form was confirmed in the present study. A Zerewitinoff determination on pure β-ionone showed 12% active hydrogen. In addition, it was observed that a considerable portion of the original ionone always was found in Grignard reaction mixtures when the excess of reagent used was less than 15%. With a 20% excess of Grignard reagent, the β-ionone was completely consumed, the enolic salt apparently being capable of further reaction with the Grignard reagent. Possibly this secondary reaction is the source of the 1,4-adducts encountered in this study.

Experimental

Absorption Spectra.—All the ultraviolet absorption spectra were determined in 95% ethanol with a Beckman DU spectrophotometer. The infrared spectra were determined on neat samples of the same specimens with a Baird double-beam spectrophotometer by Samuel P. Sadtler and Son, Inc., Philadelphia, Penna.

General Procedure.—A solution of 19.2 g. (0.1 mole) of β-ionone in 50 ml. of dry ether was added at reflux temperature to an ethereal solution of 0.12 mole of the appropriate Grignard reagent.[21] The concentration of the latter was usually about 0.5 *M*, and, except for prenylmagnesium chloride, was determined exactly in each experiment by titration. Prenylmagnesium chloride is only partially soluble in ether, making titration infeasible. In this case, an adequate excess of Grignard reagent was assured by starting with 0.15 mole of prenyl chloride.[22]

After refluxing for 30 min. the mixture was cooled to −10° and hydrolyzed with 30% ammonium acetate solution. The ether layer was separated, filtered through anhydrous potassium carbonate and concentrated under vacuum. To the concentrate was added a methanolic solution of semicarbazide acetate which was prepared by stirring a mixture of 35.0 g. of semicarbazide hydrochloride and 26.0 g. of anhydrous sodium acetate in 400 ml. of methanol for one hour, and filtering off the precipitated sodium chloride. After standing at room temperature for 24 hr., most of the methanol was removed under vacuum and the residue treated with 250 ml. of water and 500 ml. of petroleum ether. In some cases part of the semicarbazone precipitated at this stage and was filtered off. The petroleum ether solution was then filtered through anhydrous potassium carbonate and stored at −5° overnight. Any additional precipitated semicarbazone was filtered off and combined with the first crop. The filtrate was then concentrated under vacuum and the β-ionol distilled through a modified Claisen flask. The products obtained at this point were analytically pure. Redistillation produced no change in properties. Considerable caution is indicated in not overheating the distillation residue, which may contain more semicarbazone. The latter was removed therefrom by precipitation with a little petroleum ether.

The combined crops of semicarbazone were recrystallized from ethanol. The yields in Table II are those of the recrystallized products.

The semicarbazones were hydrolyzed by stirring a refluxing mixture of 10.0 g. of the compound, 200 ml. of 3 *N* sulfuric acid and 100 ml. of ligroin (b.p. 80–90°) for 10–16 hr. The ligroin was separated and the aqueous layer extracted twice with petroleum ether. The combined extracts were dried with anhydrous potassium carbonate and distilled.

Ethyl-ψ-ionol.—A 19.2-g. sample of ψ-ionone was condensed with ethylmagnesium bromide as described above for β-ionone. The absorption spectrum of the crude product showed no unreacted ψ-ionone.

Removal of the 1,4-adduct as the semicarbazone proved infeasible here because of the failure of this derivative to

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[18] F. A. Smith and E. C. Creitz, *J. Research Natl. Bur. Standards*, **46**, 145 (1951).

[19] J. H. Wotiz and F. A. Miller, THIS JOURNAL, **71**, 3441 (1949).

[20] A. Giacalone, *Gazz. chim. ital.*, **67**, 464 (1937).

[21] The bromides were used in all cases except for the benzyl and prenyl reagents which were chlorides.

[22] The prenyl chloride was prepared by saturating isoprene with dry hydrogen chloride according to the procedure of W. J. Jones and H. W. T. Chorley, *J. Chem. Soc.*, 832 (1946).

crystallize properly as well as its tendency to decompose during attempts to distil the ethyl-ψ-ionol from it. Oximation of the ketone and separation of the oxime by alumina chromatography was found the most convenient method for obtaining the ethyl-ψ-ionol in pure form.

The concentrate from the Grignard reaction was accordingly added to a solution of hydroxylamine, prepared from 35.0 g. of hydroxylamine hydrochloride and 20.0 g. of sodium hydroxide (95% pellets) in 100 ml. of water. Enough methanol was added to effect complete solution of the oil (about 300 ml.) and the precipitated sodium chloride filtered off. The filtrate was warmed to 50° and allowed to stand at room temperature for 24 hr. It was then worked up with water and petroleum ether. After drying with anhydrous potassium carbonate and concentrating to about 100 ml., the petroleum ether solution was poured onto a 4 × 60 cm. column of Alcoa F-20 alumina and the chromatogram developed with additional petroleum ether. The bands were not visible and elution (20% ether in petroleum ether) was followed spectroscopically. The ethyl-ψ-ionol, λ_{max} 240 mμ, came off first. Elution was continued with this solvent until the concentration of 240-mμ material substantially decreased. On changing then to 30% ether in petroleum ether, the 240-mμ band rather abruptly disappeared, giving way to only end-absorption. This proved to be the oxime, which was completely removed by this solvent. No other fractions were obtained.

The ethyl-ψ-ionol fraction was distilled, yielding 5.0 g. of product at 94.5–96° (0.75 mm.), $n^{20}\mathrm{D}$ 1.5028; λ_{max} 240, ϵ 26,700.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.92; H, 11.85.

The oxime fraction yielded 10.5 g. at 98° (0.001 mm.), $n^{20}\mathrm{D}$ 1.4861.

Anal. Calcd. for $C_{15}H_{27}NO$: C, 75.89; H, 11.47. Found: C, 76.03; H, 11.51.

Ethynyl-ψ-ionol.—A specimen of this compound was prepared from lithium acetylide and ψ-ionone by the method of Oroshnik and Mebane.[5] The absorption spectral constants, which were not previously reported, are λ_{max} 242 mμ, ϵ 27,400.

Ozonolysis.—The apparatus and procedure was that described in Part I.[12]

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[CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE LABORATORY]

Catalytic Esterification by Metal Halides[1]

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2,2,2-Trichloro-, tribromo- and trifluoroethanol and 2,4,6-trichlorophenol can be esterified under mild conditions in the presence of catalytic quantities of aluminum chloride or bromide. The halides of iron, titanium, antimony, tin and zinc and boron trifluoride are also effective in varying degree. The optimum concentration of catalyst is usually 10 to 30 mole per cent. of the reactants. The reaction proceeds by the formation of an acyl halide-metal halide complex and subsequent reaction with the alcohol.

Alcohols substituted in the beta position by halogens are difficult to esterify because of their acidic nature caused by the inductive effect of the halogens. Such alcohols as 2,2,2-trichloroethanol are not easily esterified directly by an acid. With an acid halide, esterification has previously been accomplished by heating the alcohol and halide at temperatures up to 130° for periods up to several hours without a solvent medium.[2] Only a few esters of 2,2,2-tribromoethanol and 2,2,2-trifluoroethanol have been reported in the literature. Recently, some experiments were reported in which trichloroethanol and tribromoethanol were easily esterified with acyl halides under mild conditions using catalytic amounts of aluminum chloride or aluminum bromide.[3] This paper reports some results of subsequent investigation on the nature of the reaction and its applicability in regard to the use of various metal halides and of acyl halides. Trifluoroethanol and 2,4,6-trichlorophenol have been esterified easily. Additional esters of trichloroethanol and tribromoethanol have been prepared from unreactive and sterically hindered acid chlorides.

Results

The esterifications of trichloroethanol, trifluoroethanol and trichlorophenol were accomplished simply by adding 10 to 30 mole % of anhydrous aluminum chloride to a carbon tetrachloride solution of equimolar quantities of the reactants. In reactions with tribromoethanol the use of aluminum bromide improved the yield. Reaction was vigorous at temperatures from 25 to 50° in most cases, with only a short period at reflux temperature necessary to complete reaction. If no solvent was used, the reaction was extremely vigorous. The product was isolated by the usual Friedel–Crafts procedures. The results of the preparations of esters of representative acid chlorides, some of which are unreactive, are summarized in Table I which lists the melting point, % yield of recrystallized materials and the elemental analysis of new compounds.

The extent of the catalytic effect of aluminum chloride under preparative conditions was indicated by a series of experiments in which uncatalyzed reactions were run as controls at the same time as catalyzed reactions. Thus benzoyl chloride heated with trichloroethanol without solvent or catalyst at 100° for seven hours gave a 72% yield of ester. With 10 mole % of aluminum chloride, a 93% yield of ester was obtained in 25 minutes at 50°. With carbon tetrachloride as a solvent no esterification of benzoyl chloride occurred in five hours at 65°

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[1] Presented in part before the Organic Division at the 124th National Meeting, Chicago, September, 1953.

[2] (a) J. W. Cusic and A. L. Raymond, U. S. Patent 2,584,846 (1952); (b) H. M. Woodburn and C. E. Sroog, THIS JOURNAL, **71**, 1709 (1949); (c) J. R. Geigy, Swiss Patent 250,801 (1947); *C. A.*, **44**, 1530e (1950); (d) R. Nakai, *Biochem. Z.*, **152**, 272 (1924); (e) K. Garzarolli-Thurnlackh, *Ann.*, **210**, 63 (1881).

[3] M. E. Hill, THIS JOURNAL, **75**, 3020 (1953).