nated polymers. In most cases low yields were obtained and in all cases the nitrate ester derivatives obtained decomposed after isolation with the evolution of nitrogen oxides. This instability of the nitrated polymers may be analogous to the reported[5] instability of the structurally related nitrate ester-nitrate salt derivatives of the mono-, di-, and tri-ethanolamines. The acetate derivatives could be prepared in stable form.

The details of the polymer preparation techniques are illustrated in the experimental section together with examples of the derivatives prepared.

EXPERIMENTAL

Materials. The amines employed were either commercial products or were prepared following syntheses given in the literature. Following the method of Siwoloboff,[6] 1,6-dichloro-1,6-dideoxy-D-mannitol was prepared and converted to 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol (I) by the procedure of Wiggins.[3]

Condensation of piperazine with 1,2:5,6-dianhydro-3,4-O-isopropylidene-D-mannitol. Piperazine (0.7 g., 8.1 mmol.) dissolved in 5 ml. of chloroform was added to 5 ml. of chloroform solution containing 1.5 g. (8.1 mmol.) of the diepoxide I. The reaction was allowed to proceed for 24 hr. at room temperature whereupon the solution was poured with stirring into 40 ml. of dry ether. The resulting gummy mass hardened after trituration with additional ether. The white product was soluble in methanol, ethanol, and chloroform; evaporation of such solutions deposited clear, brittle films. No definite melting point was observed but the polymer was liquid at 160°. A solution of the polymer (IV) in chloroform had a reduced viscosity (Nsp/c) of 0.16 deciliter/g. (*c* 0.5, 25°), as measured with an Ostwald viscometer.

Anal. Calcd. for $(C_{13}H_{24}O_4N_2)_n$: C, 57.33; H, 8.88; N, 10.27. Found: C, 56.92; H, 8.68; N, 10.21.

No increase in the viscosity of the polymers obtained resulted when the reaction was carried out at room temperature in pyridine, in methanol containing triethylamine, or in refluxing chloroform. The product obtained by refluxing the polymer in methanol with fresh diepoxide was only partially soluble in chloroform and the viscosity of the soluble fraction had not changed.

The isopropylidene groups were removed by treating the polymer (0.425 g.) with *N* hydrochloric acid (20 ml.) on the steam bath for 18 hr. The polymer dissolved, and after reaction the solution was treated with Amberlite IRA-400[7] exchange resin until the solution was neutral. The resin was removed by filtration and washed with water. The filtrate was lyophilized to yield a nearly white powder; yield 0.28 g. This product was nitrated by suspending it in acetic anhydride (5 ml.) at 0° and slowly adding a cold solution of absolute nitric acid (4 ml.) in acetic anhydride (10 ml.). After standing for 2 hr., the reactants were poured into ice and water to give a low yield of a white powdery product which was recovered by centrifugation. The product decomposed into water- and ethanol-soluble products and could not be isolated in a pure state.

Condensation of 2-amino-2(hydroxymethyl)-1,3-propanediol with 1,2:5,6-dianhydro-3,4-O-isopropylidene-D-mannitol. 2-Amino-2-(hydroxymethyl)-1,3-propanediol (2.8 g., 23.3 mmol.) was dissolved in 20 ml. of refluxing chloroform and 4.9 g. (25.8 mmol.) of 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol dissolved in 10 ml. of chloroform was added in 4 equal parts during 6 hr. After 8 hr. of refluxing, the solvent was distilled and the residual orange gum was dissolved in warm water. Addition of acetone (3 vol.) caused the formation of some precipitate which was discarded. After evaporation of the acetone from the solution, hydrochloric acid was added to the aqueous residue and the polymer was de-acetonated as described above to afford a yellow powder; yield 5.8 g. A sample of the polymer (II) isolated from its aqueous solution by freeze-drying prior to treatment with acid, had a reduced viscosity of 0.06 deciliter/g. (*c* 3, 25°, water).

A portion of the de-acetonated polymer was nitrated as above with similar results. Another portion of the polymer was nitrated with dinitrogen pentoxide in chloroform following the method of Caesar and Goldfrank.[8] At the end of the nitration (14 hr. at 0°), the reaction mixture was concentrated under reduced pressure and the residual solid was washed with ethanol and dried. Although a higher yield was obtained, the nitrate soon decomposed with the evolution of nitrogen oxides.

Another portion (1.0 g.) of the de-acetonated polymer was dissolved in a mixture of pyridine and acetic anhydride (20 ml. each). After 24 hr. at room temperature, the mixture was poured into water. The precipitate was washed with water, ethanol, and petroleum ether to afford 1.29 g. of white powder after drying.

Anal. Calcd. for $(C_{24}H_{36}O_{14}N)_n$: C, 51.34; H, 6.24; N, 2.50. Found: C, 51.19; H, 6.36; N, 2.44.

Condensation of other amines with 1,2:5,6-dianhydro-3,4-O-isopropylidene-D-mannitol. The diepoxide also condensed with hydrazine, ethylenediamine, and ammonia to give yellow to brown colored brittle materials which were insoluble in solvents and whose isopropylidene groups were, in general, difficult to remove. The polymers obtained by condensation of the diepoxide with methylamine, 2-aminoethanol, or *N,N'*-dimethylethylenediamine III were yellow or orange in color but did dissolve in chloroform.

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(5) J. Barbière, *Bull. soc. chim. France*, [5], **11**, 470 (1944); Aubry, *Mem. poudres*, **25**, 189 (1932).

(6) A. Siwoloboff, *Ann.*, **233**, 368 (1886).

(7) A product of the Rohm & Haas Co., Philadelphia, Pa.

(8) G. V. Caesar and M. Goldfrank, *J. Am. Chem. Soc.*, **63**, 372 (1946).

Reaction of *t*-Butylmagnesium Chloride with a Number of Alkyl Aryl Ketones

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This paper reports a further extension of the investigation of the reactions of 17 alkyl aryl ketones with various reagents.[4] Each of the ketones reacted with *t*-butylmagnesium chloride under conditions as nearly like those previously reported as possible.[4b] The reactions were designed to measure

(1) Oak Ridge National Laboratory.

(2) Taken in part from (a) the M.S. thesis of R. W. Kennedy, Emory University, 1954, and (b) the Ph.D. Dissertation of B. F. Landrum, Emory University, 1950.

(3) To whom inquiries should be directed.

(4) (a) M. J. Craft, B. F. Landrum, E. C. Suratt, and C. T. Lester, *J. Am. Chem. Soc.*, **73**, 4462 (1951). (b) B. F. Landrum and C. T. Lester, *J. Am. Chem. Soc.*, **74**, 4954, (1952); *J. Am. Chem. Soc.*, **76**, 5797 (1954).

TABLE I

t-BUTYLMAGNESIUM CHLORIDE AND ALKYL 4-ALKYLPHENYL KETONES

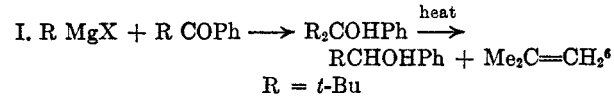
			Analysis of Alcohols[a]							
			Secondary				Tertiary			
			% Carbon		% Hydrogen		% Carbon		% Hydrogen	
4-R	R[b]	A[c]	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
					4-R—C_6H_4—$COCH_3$					
H	30	65	78.6	78.8	8.20	8.48	80.9	80.6	10.1	9.97
Me	45	49	79.4	79.7	8.82	8.52	81.3	81.5	10.4	10.1
Et	48	49	80.0	80.2	9.33	9.46	81.6	81.5	10.7	10.5
i-Prop	50	43	80.5	80.8	9.76	9.88	81.8	81.7	10.9	10.6
t-Bu	48	47	80.9	81.2	10.1	10.3	82.1	82.0	11.1	11.2
					4-R—C_6H_4—$CO_2C_2H_5$					
H	33	61	79.4	79.7	8.82	8.63	81.3	81.0	10.4	10.2
Me	46	48	80.0	80.1	9.33	9.34	81.6	81.3	10.7	10.5
Et	44	50	80.5	80.2	9.76	10.0	81.8	81.6	10.9	10.6
i-Prop	45	51	80.9	81.2	10.1	10.4	82.1	81.8	11.1	10.0
t-Bu	42	52	81.3	81.4	10.4	10.7	82.3	82.3	11.3	11.0
					4-R—C_6H_4—$COCH(CH_3)_2$					
H	25	70	80.0	80.3	9.33	9.72	81.6	81.4	10.7	10.8
Me	33	60	80.5	80.8	9.76	10.0	81.8	81.6	10.9	10.6
Et	30	62	80.9	80.8	10.1	10.4	82.1	81.8	11.1	10.9
i-Prop	34	63	81.3	81.0	10.4	10.7	82.3	82.4	11.3	11.3
t-Bu	33	62	81.6	81.3	10.7	10.4	82.4	82.1	11.5	11.1
					4-R—C_6H_4—$COC(CH_3)_3$					
H	100	0	80.5	80.2	9.76	9.82	..	..	..	..
Me	100	0	80.9	80.7	10.1	10.1	..	..	..	..

[a] The b.p. and refractive index or the m.p. of the individual alcohol checked well with values reported in cases where the alcohol has been previously prepared. [b] Reduction per cent based on weight of secondary alcohol from distillation. [c] Addition per cent based on weight of tertiary alcohol from distillation. Intermediate fractions were assumed to consist of equal parts of secondary and tertiary alcohol. This introduces no serious error because the intermediate fractions were always quite small. Although the sum of the per cent reduction and per cent addition does not equal 100%, we were unable to find any evidence of enolization, since all the gas evolved was unsaturated.

the extent of enolization, reduction, and addition. The difficulty of separating butenes from ether[5] led us to check the per cent reduction in each case, indicated by the volume of isobutylene gas evolved, against the per cent yield of secondary alcohol. Similarly we computed the per cent addition by the weight of tertiary alcohol isolated from each reaction. The results are recorded in Table I.

In the reactions involving the acetophenones, propiophenones, and isobutyrophenones from two thirds to one fourth of the isobutylene gas was evolved during the addition of the ketone and the subsequent 30-min. reflux period.[4b] In the case of the pivalophenones, however, only one tenth of the isobutylene gas was evolved during the addition and reflux period. Furthermore, when the reaction mixture of pivalophenone was processed and the solvent ether removed through a distilling column, the remaining nine tenths of the isobutylene was collected in a Dry Ice trap.

These observations led us to consider the possibility of some unusual series of reactions such as:



I. $R\,MgX + R\,COPh \longrightarrow R_2COHPh \xrightarrow{heat} RCHOHPh + Me_2C{=}CH_2$[6]

R = *t*-Bu

If C^{-14} were incorporated into *t*-butylmagnesium chloride and if a series of reactions such as indicated in I were occurring, some of the C^{-14} would appear in the secondary alcohol. This line of investigation was pursued and the resulting radiochemical assays are shown in Table II.

These results eliminate as a possibility any series of reactions such as I and indicate that reduction of the pivalophenones proceeded in the usual fashion.[7] The cause of the unusually small per cent of isobutylene evolved in the reactions of the pivalophenones was not investigated.[8] The reactions of

(5) K. W. Wilson, J. D. Roberts, and W. G. Young, *J. Am. Chem. Soc.*, 72, 215 (1950).

(6) The possibility of some unusual reaction between *t*-butylmagnesium chloride and pivalophenone appeared more plausible when it was discovered that the addition of phenylmagnesium bromide to di-*t*-butyl ketone yielded diphenyl-*t*-butylcarbinol (Ph_2COH *t*-Bu)—a reaction to be described later.

(7) H. S. Mosher and E. LaCombe, *J. Am. Chem. Soc.* **73**, 3994 (1950).

(8) If the isobutylene evolved is expressed as a per cent of total reduction the values for the different series are: acetophenones, 66%; propiophenones and isobutyrophenones, 20–25%; pivalophenones, 10%.

TABLE II

CARBON-14 ASSAYS

Compound	Activity in C./M. Mole
t-Butyl *p*-nitrobenzoate (from *t*-butyl alcohol)	0.283; 0.280
Pivalanilide (from *t*-butyl-magnesium chloride)	0.266; 0.263
2,4-Dinitrophenylsulfenyl chloride adduct of isobutylene	0.277[a]; 0.277[a]; 0.271[b]
Phenyl-*t*-butylcarbinol[c]	0.000; 0.000

[a] Isobutylene collected during addition of *t*-butylmagnesium chloride to pivalophenone. [b] Isobutylene collected in Dry Ice trap after Grignard complex was destroyed with water. [c] This compound is a solid, m.p. 44–45°.

pivalophenone and *t*-butylmagnesium chloride was repeated many times without significant variation on the amount of isobutylene evolved. Even when the reaction was run in butyl ether, only 10% of the isobutylene was evolved during the addition and reflux period.

In reviewing the reactions of these ketones with various Grignard reagents[4b] certain generalizations are evident: (1) isopropylmagnesium bromide has the greatest tendency to promote enolization; (2) ethylmagnesium bromide gives the greatest amount of addition; (3) *t*-butylmagnesium chloride gives the largest amount of reduction. These results are consistent with previous reports on the reaction of ketones with Grignard reagents.[9]

EXPERIMENTAL[10]

Reaction of t-butylmagnesium chloride and ketones. The same molar quantities and same procedure as previously reported[4b] were used in studying the reaction of each ketone with *t*-butylmagnesium chloride. Each reaction product was fractionally distilled and the fractions corresponding to secondary and tertiary alcohols were isolated and analyzed as shown in Table I. When *t*-butylmagnesium chloride was added to pivalophenone and to *p*-methylpivalophenone, only a small amount of gas was evolved. However, when after heating, refluxing, and carefully decomposing the magnesium complexes with water,[4b] the ether was removed prior to fractional distillation, almost the entire theoretical amount of isobutylene was collected.

Experiments using C-14. 1-C-14 acetone (activity 0.285μ c./m. mole) was converted in 83% yield into C-14-*t*-butyl alcohol. The *p*-nitrobenzoate ester, m.p. 114–114.5°, reported,[11] showed an activity of 0.282μ c./m. mole. C-14-*t*-Butyl alcohol was converted in 85% yield into C-14-*t*-butyl chloride.[12] A small sample of the Grignard reagent made from this chloride was treated with phenylisocyanate[13] to produce C-14 pivalanilide, m.p. 129–129.5°,[14] with an activity of 0.2666μ c./m. mole. Pivalophenone was added to the bulk of the C-14-*t*-butylmagnesium chloride as previously described.[4b] The isobutylene gas evolved during the addition of the ketone was collected in a Dry Ice trap and a portion converted to the solid 2,4-dinitrosulfenyl chloride adduct m.p. 86–87°.[15] This showed an activity of 0.277μ c./m. mole. A 2,4 dinitrosulfenyl chloride adduct of the isobutylene gas collected after decomposition of the magnesium complex showed an activity of 0.271μ c./m. mole. The secondary alcohol, phenyl-*t*-butylcarbinol was subsequently isolated by distillation of the reaction products. There was no forerun or residue in the distillation. The first and each subsequent fraction collected crystallized on standing. The m.p. of each fraction was 44–45°. The secondary alcohol showed no C-14 activity.

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(9) M. S. Kharasch and Otto Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, Inc., New York, N. Y., 1954, pp. 138–76.

(10) All boiling points and melting points are uncorrected. The C-14 used in this work was obtained as 1-C-14-acetone from the Oak Ridge National Laboratory as part of Subcontract 647 under W-7405 eng-26.

(11) S. M. McElvain, *The Characterization of Organic Compounds*, The Macmillan Co., New York, N. Y., 1953, p. 201.

(12) Robertson, G. R., *Laboratory Practice of Organic Chemistry*, 3rd ed. The Macmillan Co., New York, N. Y., 1954, p. 194.

(13) Ref. 10, p. 243.

(14) I. M. Heilbron, *Dictionary of Organic Compounds*, Vol. IV, Oxford University Press, New York, N. Y., 1953, p. 224.

(15) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949).

Methyl Hydrogen Fumarate

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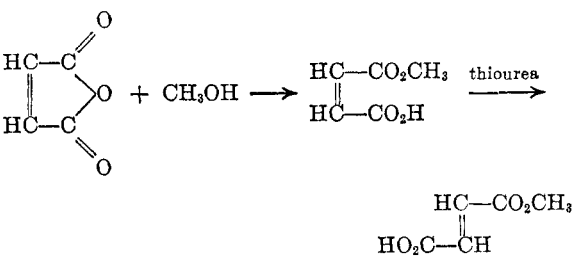
The preparation of a half-ester from a dibasic anhydride, such as maleic or phthalic is, as a rule, effected very simply by the controlled, mild heating of a stoichiometric mixture of the anhydride and the alcohol. On the other hand, the half-esterification of a dibasic acid (as fumaric, adipic, terephthalic) is, in theory and practice, complicated by the formation of an equilibrium consisting of the free acid, the half-ester, and the diester.

In connection with other studies requiring a convenient source of alkyl hydrogen fumarates, it was found that the *cis-trans* inversion effect of thiourea[1] and substituted thioureas,[1] converting maleic to fumaric acid, could be applied to methyl hydrogen maleate. Thus, an aqueous solution of the latter was isomerized by thiourea at room temperature to yield the relatively insoluble methyl hydrogen fumarate in quantity.



(1) S. M. Spatz (to Allied Chemical & Dye Corp.), U. S. Patent 2,548,687, (April 10, 1951).