The large rate retardation found on the addition of nitrate ion presumably occurs because nitrate ion will compete with the aldehyde in step 3.

Experimental Section

Reagents. All solid inorganic reagents were converted to the anhydrous form before using by heating at 110°. The sodium perchlorate was tested for chloride ion with silver nitrate solution and for chlorate with acidic iodide solution. When either was found, the material was purified by recrystallization from water.

Perchloric acid was reagent grade. Cerium(IV) perchlorate was obtained from the G. F. Smith Chemical Co. as an approximately 0.5 *M* solution in 3 *M* perchloric acid. The ceric ion concentration was determined by titration with sodium thiosulfate solution to a starch–iodine end point. The acid concentration was determined by dissolving samples in acetic acid, adding an excess of acetic anhydride to remove water, and titrating potentiometrically with a standard solution of sodium acetate in glacial acetic acid.

Acetic acid was purified by heating with chromic acid followed by vacuum distillation. The water content was determined spectrometrically using acetic anhydride.[11] Water was purified by distillation from chromic acid.

Benzaldehyde was purified immediately before use by distillation under reduced pressure under a nitrogen atmosphere. A center cut was taken, and was kept under nitrogen. The substituted benzaldehydes were commercial samples. The liquid aldehydes were distilled using the same procedure as for benzaldehyde and the solid aldehydes were recrystallized twice from an ethanol–water mixture and then sublimed at 1 mm at a temperature 10° below their melting point. Benzaldehyde-*d* was prepared as described previously, and was purified in the same fashion as for benzaldehyde. Benzaldehyde-^{14}C was obtained from the New England Nuclear Corp. and was diluted with unlabeled aldehyde to give 3 g of aldehyde having 39.0 μCi/g as determined by liquid scintillation counting.

(11) S. Bruckenstein, Ph.D. thesis, University of Minnesota, 1952.

Solutions. Stock solutions of aqueous acetic acid were prepared gravimetrically in 4-l. quantities taking into account the amount of water present in the acetic acid. Ceric perchlorate solutions in aqueous acetic acid were prepared by weighing samples of the aqueous ceric perchlorate solution, perchloric acid solution, and sodium perchlorate solution into a volumetric flask. Acetic acid was added to compensate for the water in the above solutions, and the flask was filled to the mark with aqueous acetic acid of the correct composition. These solutions were prepared immediately before use because ceric ion slowly oxidizes acetic acid.

Solutions of the aldehydes were prepared by weighing freshly distilled benzaldehyde into a volumetric flask partially filled with solvent. The flask was then filled to the mark with more aqueous acetic acid.

Kinetic Method. Titrimetric runs were made in an apparatus consisting of two flasks joined by a glass U tube. The U tube had a stopcock which could be attached to a vacuum line, and one flask had a semiautomatic pipet. The two solutions were placed in separate flasks and were degassed by a repeated freezing, evacuation, and thawing cycle. After bringing the solutions to the thermostat temperature (25.0°), they were mixed by tilting the assembly. Aliquots were removed *via* the pipet using nitrogen pressure. The solutions were quenched with iodide ion, followed by titration with sodium thiosulfate.

Spectrometric runs were carried out using a two-arm cell which was attached at its center to a rectangular 10-mm reaction cell. The two solutions were placed in separate cells and were degassed. After warming to the thermostat temperature, the cell was inverted and the reaction cell was placed in the light path of a Beckman DU spectrometer. The light path passed through a small water thermostat so that the solution was maintained at 25.0°.

Acknowledgments. We wish to thank Dr. William Richardson for his invaluable assistance in the early phases of this investigation. We also wish to thank Dr. D. W. Kemp and the American Cyanamid Co. for carrying out the determination of the molecular weight of the acrylonitrile polymer *via* gel permeation chromatography.

The Prevalence of *cis*-Addition Products in the Reaction of the Butenyl Grignard Reagent with Sterically Hindered Ketones

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Abstract: The reactions of crotylmagnesium bromide with ethyl isopropyl, diisopropyl, isopropyl *t*-butyl, and di-*t*-butyl ketones have been examined under carefully controlled conditions. The quantity of α-methylallylcarbinol formed in each case was found to decrease and the amount of crotylcarbinol to increase progressively as the steric requirements of the alkyl groups attached to the carbonyl of the ketone increased. This observation probably reflects increasing steric hindrance in the transition state leading to α-methylallyl products. In all cases, the *cis*/*trans* ratio of the crotyl adducts was greater than unity, which can be explained by invoking the hypothesis that the *cis* form of the butenyl Grignard reagent is more thermodynamically stable than the *trans* form. Several mechanistic possibilities have been proposed to account for the results.

A great deal of work has appeared in the last 23 years concerning the structure and mode of reaction of the butenyl Grignard reagent. One of the more interesting reactions of this species is its facile addition to di-*t*-butyl ketone to give crotyldi-*t*-butylcarbinol in 69% yield.[1] To our knowledge, this still remains as the only example of formation of a product which can be considered as derived from the primary form of the

(1) K. W. Wilson, J. D. Roberts, and W. G. Young, *J. Amer. Chem. Soc.*, 72, 218 (1950).

Grignard reagent, I. Most of the products of this

$$\underset{\text{I}}{CH_3CH{=}CHCH_2MgBr} \rightleftharpoons \underset{\text{II}}{CH_2{=}CHCH(CH_3)MgBr}$$

reagent can be looked upon as resulting from the secondary form of the Grignard,[2] II, although nmr studies[3] have indicated that the butenyl Grignard reagent in diethyl ether is approximately 99% in form I. These same data are consistent with the equilibrium depicted between I and II provided the equilibration is rapid and lies well on the side of I.

Recently, it was demonstrated that the Grignard reagent derived from 2-bromo-3-pentene reacts with acetone to form the expected α-methylcrotyldimethylcarbinol, III.[4] Significantly, the *cis*/*trans* ratio of the

$$CH_3CH{=}CHCH(CH_3)MgBr \xrightarrow[2.\ H_2O]{1.\ \text{acetone}} \underset{\text{III}}{CH_3CH{=}CHCH(CH_3)COH(CH_3)_2}$$

latter product was found to be about 2. The results were interpreted in terms of an SE2′ mechanism (with respect to the Grignard reagent) in which the allylic moiety possesses substantial carbanion character in the transition state. The latter assumption was used to explain the predominance of the *cis* isomer, since it has been suggested[5] that *cis* allylic carbanions are thermodynamically more stable than the *trans* form.

We are hereby reporting the results of a systematic study of the reaction between the butenyl Grignard reagent and four carefully selected ketones, namely, ethyl isopropyl, diisopropyl, isopropyl *t*-butyl, and di-*t*-butyl ketone. It will be noted that, in such a series, the steric crowding around the carbonyl group is progressively increased by the substitution of a methyl group for a hydrogen atom. Hence, any trends displayed in the reaction products as one proceeds from the least to the most hindered carbonyl compound can reasonably be attributed to steric hindrance in the transition state leading to those products.

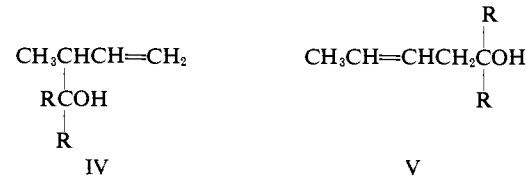
The results of the addition reactions with crotylmagnesium bromide are found in Table I. As can be seen,

Table I. Reactions of Crotylmagnesium Bromide with Various Ketones

Ketone	Carbinol products, % α-Methylallyl[a]	Crotyl[b]	Crotyl product *cis*/*trans* ratio	Total product yield, %
EtC(=O)-*i*-Pr	95	5	4/1	92
i-PrC(=O)-*i*-Pr	66	34	26/8	66
i-PrC(=O)-*t*-Bu	40	60	35/25	75
t-BuC(=O)-*t*-Bu	0	100	61/39	78

[a] Corresponds to structure IV. [b] Corresponds to structure V.

the amount of α-methylallylcarbinol (IV) decreases and the quantity of the crotylcarbinol (V) increases with increasing steric requirements of the R groups on the starting ketone. More striking, however, is the fact



that in all cases the *cis*/*trans* ratio of product V is greater than unity.

The data in Table II demonstrate this even more clearly. In this series, three isomeric butenyl chlorides[6] were utilized to form the Grignard reagent, which, upon reaction with di-*t*-butyl ketone, afforded the *same* amounts of *cis*- and *trans*-crotyldi-*t*-butylcarbinols. Di-*t*-butyl ketone was chosen as the substrate in these cases since the only products formed are the isomeric crotylcarbinols (V).

Table II. Reaction of Crotylmagnesium Chloride with Di-*t*-butyl Ketone

Starting halide	Crotyl product[a] *cis*/*trans* ratio	Product yield, %
trans-$CH_3CH{=}CHCH_2Cl$	70/30	86
cis-$CH_3CH{=}CHCH_2Cl$	68/32	95
$CH_2{=}CHCHClCH_3$	68/32	78

[a] The *only* carbinol obtained in these reactions possessed the crotyl structure V.

The data of Table II can be nicely accommodated by assuming a rapid equilibration between the two Grignard species, I and II, and by the further assumption that the crotyl Grignard species I prefers the *cis* configuration.[5] Stated another way—form II of the Grignard acts as a turntable whereby the *trans*-crotyl Grignard species I can be converted rapidly into its preferred *cis* configuration.[7]

It might be argued that it is not the Grignard reagent which is primarily in the *cis* configuration and is giving rise to the *cis*-crotylcarbinols, but that the starting halide is isomerizing to the *cis* form and then going on to give a stable, nonequilibrating Grignard reagent.

Although confirmatory data are unavailable, it seems likely that *trans*-crotyl chloride (or bromide) should be more thermodynamically stable than the *cis* isomer, especially since it is known that *trans*-2-butene is about 1 kcal/mol more stable than *cis*-2-butene.[8] It seems that the analogous crotyl chlorides would have even a higher propensity to exist in the *trans* configuration, since, in the *cis* form, greater steric interactions between the halomethyl and methyl groups attached to the double bond would occur than exists in *cis*-2-butene.

(2) J. F. Lane, J. D. Roberts, and W. G. Young, *J. Amer. Chem. Soc.*, **66**, 543 (1944); J. D. Roberts and W. G. Young, *ibid.*, **67**, 148 (1945); W. G. Young and J. D. Roberts, *ibid.*, **67**, 319 (1945); W. G. Young and J. D. Roberts, *ibid.*, **68**, 649 (1946).

(3) J. E. Nordlander, W. G. Young, and J. D. Roberts, *ibid.*, **83**, 494 (1961).

(4) H. Felkin, C. Frajerman, and Y. Gault, *Chem. Commun.*, 75 (1966).

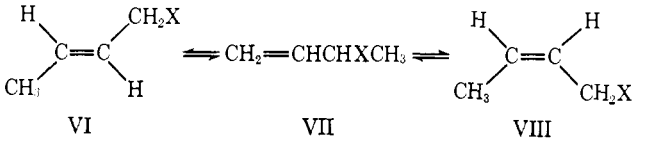
(5) S. Bank, A. Schreisheim, and C. A. Rowe, Jr., *J. Amer. Chem. Soc.*, **87**, 3244 (1965).

(6) These halides were found to be stable to rearrangement when stored for long periods of time in Teflon bottles as ascertained by vpc and infrared data obtained just prior to use.

(7) It will be noted that such a view obviates the problem of whether there can be a *direct* isomerization between the *trans* and *cis* forms of the butenyl Grignard reagent. Since it is commonly accepted that allylic carbonium ions [W. G. Young, S. H. Sharman, and S. Winstein, *J. Amer. Chem. Soc.*, **82**, 1376 (1960)] and allylic radicals [C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961)] retain their stereochemical integrity, it would seem that allylic carbanions should do the same.

(8) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 337.

Therefore, in an equilibrium such as that shown below, form VI would probably predominate over form VIII.



VI VII VIII

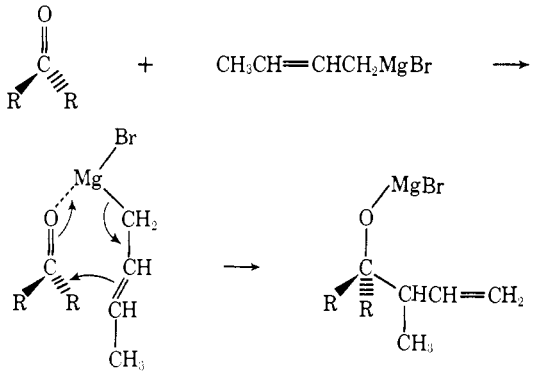
It follows from this argument that, if a Grignard reagent is formed *under nonequilibrating* conditions, then, in all likelihood, the *trans* form of the Grignard should predominate.[9]

It has also been postulated[5] that allylic radicals prefer a *trans* configuration. Hence, one would conclude that the butenyl radical, if it is a discrete entity in the formation of the butenyl Grignard reagent, would probably prefer the *trans* configuration,[10] or, at the very least, would retain its stereochemical integrity.[7]

Another possible explanation for the high *cis*/*trans* ratio in the addition products of type V is that the *cis*-carbinol products are more stable than the *trans* and hence form more rapidly because of a lower activation energy. Molecular models of both *cis*- and *trans*-crotyldi-*t*-butylcarbinols show definite steric interactions between the terminal methyl group on the crotyl moiety and the *t*-butyl group in the *cis* isomer which are absent in the *trans*, so that seemingly this explanation has little merit.

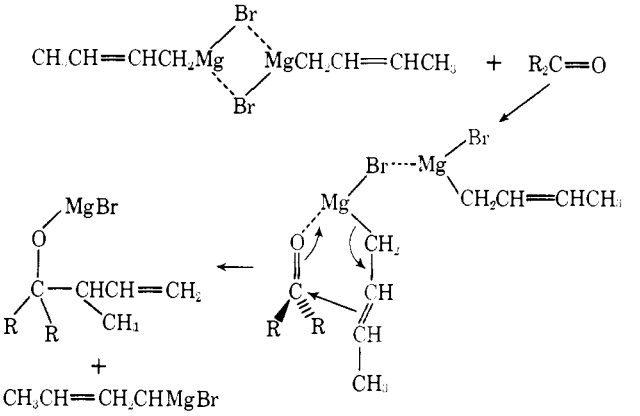
The formation of addition products like IV can probably best be visualized by a six-membered cyclic process proposed in 1946 by Young and Roberts[11] (Scheme I).

Scheme I



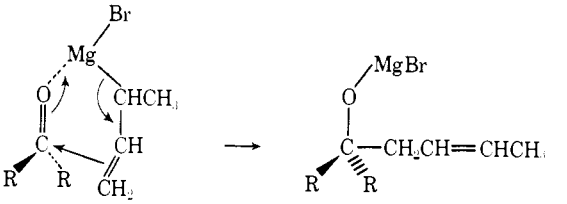
It is not known at this time whether the Grignard reagent which attacks the carbonyl compound is a monomeric or a dimeric species. If the latter is the case, a similar mechanism[12] can be written as shown in Scheme II.

Scheme II



It might be argued in an analogous fashion that crotyl adducts like V are formed by a six-membered cyclic process with the secondary form of the Grignard reagent (II) as the attacking species (Scheme III). It must be noted, however, that the primary adduct which is formed consists mostly of the *cis*-crotylcarbinol.

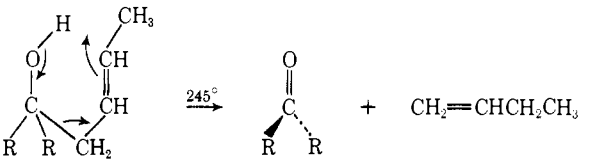
Scheme III



Studies of molecular models show that the transition state leading to the *cis* isomer *via* Scheme III would suffer steric interactions between one of the R groups and the α-methyl group of the secondary Grignard reagent, a situation which would be eased in the transition state leading to the *trans*-crotylcarbinols. Consequently, a cyclic process as pictured in Scheme III for formation of the crotyl adduct would likely lead primarily to *trans* product which is *not* observed.

A recent observation concerning the thermal decomposition of crotyldi-*t*-butylcarbinol tends to support this conclusion.[13] It was found that if a mixture of *cis*- and *trans*-crotyldi-*t*-butylcarbinols is thermally decomposed at 245°, the *trans* adduct decomposes to hexamethylacetone at a more rapid rate than the *cis* isomer. The intramolecular transition state proposed for formation of primary allylic carbinols from secondary Grignard reagent is rather analogous to the transition state proposed[13] for the thermal decomposition reactions (Scheme IV). It was suggested[13] that the reason for the more rapid decomposition rate of the *trans* alcohol might be due to severe steric interactions between one of the methyls of the *t*-butyl group and the terminal methyl of the crotyl group in the *cis* carbinol which is absent in the *trans* isomer. It would seem

Scheme IV



(9) This assumes, of course, that compound VI would form the Grignard reagent either at the same rate, or faster, than VIII.

(10) We must concede that our results do not *exclude* the possibility that isomerization from the *preferred trans*-crotyl chloride and *trans*-crotyl radical *might* be occurring as the radical is undergoing transformation to the Grignard reagent and that the latter is nonequilibrating. We prefer the view that we are dealing with a rapidly equilibrating Grignard reagent—a view which receives strong support from the nmr studies on the butenyl Grignard and related systems. See G. M. Whitesides, J. E. Nordlander, and J. D. Roberts, *Discussions Faraday Soc.*, **34**, 185 (1962), and also ref 3.

(11) W. G. Young and J. D. Roberts, *J. Amer. Chem. Soc.*, **68**, 1472 (1946).

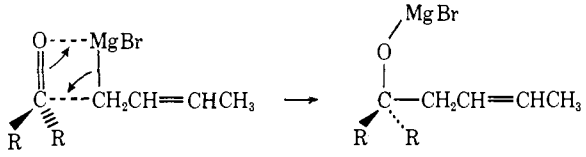
(12) See E. C. Ashby, *Quart. Rev.* (London), **21**, 259 (1967), for a most lucid presentation bearing on the question of the Grignard composition and mechanisms.

(13) R. A. Benkeser and D. A. Jones, Jr., *J. Org. Chem.*, **32**, 1625 (1967).

that formation of a *cis* carbinol by a six-membered cyclic process and its decomposition by a similar mechanism are energetically difficult at best.

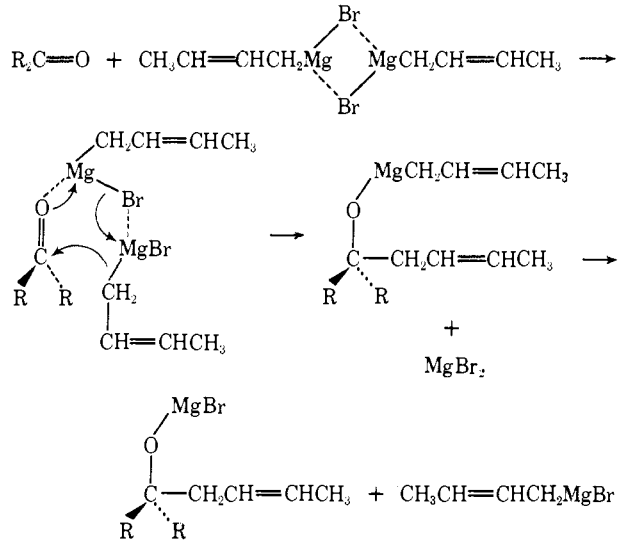
There remain two other possibilities for formation of the crotyl product. One is *via* the classical four-membered transition state for addition of Grignard reagent to a carbonyl group (Scheme V) and the other

Scheme V



is the six-membered cyclic process (Scheme VI) similar

Scheme VI



to that recently proposed[14] for other ketone–Grignard reactions.

Unfortunately it is not possible to distinguish between these two possibilities at this time since the Grignard dimer could also react *via* the four-membered transition state. There is no positive information available regarding the state of aggregation of crotylmagnesium bromide in ether solution, but, it is worthy of note, that many Grignard reagents are extensively associated at the concentration ranges of our experiments.[12]

Experimental Section

Materials. The crotyl bromide (Aldrich) was redistilled and consisted of 83% crotyl bromide and 17% α-methylallyl bromide as determined by refractive index.[15]

The *trans*-crotyl chloride and α-methylallyl chloride (Aldrich) were fractionated prior to use.

cis-Crotyl chloride was synthesized;[16] both this material and the *trans* isomer had the physical properties reported.

Valeryl chloride (Eastman) and ethyl isopropyl ketone (Columbia) were used as purchased. The diisopropyl ketone (Aldrich) was redistilled before use.

Di-*t*-butyl ketone and isopropyl *t*-butyl ketone were prepared in about 56% yield each.[17]

3-Pentenoic acid was prepared in 22% yield[18] and 2-methyl-3-butenoic acid was synthesized (84% yield) by carbonation of the butenyl Grignard reagent.[19]

The isopropyl- and *t*-butyllithium (Alfa Inorganics) were used as received.

Grignard Reagents and Addition Reactions. A standard procedure was followed for the preparation of all Grignard reagents and for their reaction with individual ketones. A sample preparation is given below for butenylmagnesium bromide, although the same quantities were not always employed. Grignard reagents obtained from the various chlorides were formed in an analogous manner.

To a flamed-out, 1-l., three-necked flask equipped with a mechanical stirrer, dropping funnel, and an efficient condenser and swept with a slow stream of dry, prepurified nitrogen, was added 25.5 g (1.05 g-atoms) of dry magnesium turnings and 50 ml of anhydrous diethyl ether. With vigorous stirring, a solution of 47.3 (0.350 mol) of crotyl bromide in 500 ml of ether was then added over a 5–7-hr period. After the addition was completed, the Grignard reagent was stirred for an additional 0.5 hr and then an aliquot removed for titration. The yield ranged from 68–85%.

To the Grignard reagent was added 10% less than an equimolar quantity of ketone in 75 ml of ether at such a rate as to maintain gentle reflux. After the addition was completed, the mixture was stirred overnight at room temperature and then hydrolyzed with ammonium chloride solution.

The organic and aqueous layers were separated and the latter extracted with several portions of ether. The combined ether layers were washed with water and then dried ($MgSO_4$). Removal of the solvent after filtration left an oil which was distilled under reduced pressure.

Reactions of Butenylmagnesium Bromide with Various Ketones (Table I). A. Ethyl Isopropyl Ketone. A 91% yield of isomeric alcohols was realized boiling at 53–57° (3 mm).

The product was analyzed by gas chromatography utilizing a 150 ft × 0.01 in., UCON Polar capillary column programmed from 60 to 125° at 5°/min after initially remaining at 60° for 8 min. The maximum temperature was held for 10 min. Four components were found, having retention times and compositions as follows: 19.7 min (47%), 20.3 min (48%), 21.0 min (1%), and 21.7 min (4%).

The first, second, and fourth peaks were collected from a 19 ft × 0.25 in., 20% XF 1150 on Chromosorb P column at 115°. It was not possible to collect the 21.0-min peak due to its extremely low concentration and its extensive overlap with the 20.3-min peak. Other columns tried gave no better success, however, its identical retention time with authentic *trans*-crotylethylisopropylcarbinol suggested it was likely this product.

The 19.7- and the 20.3-min peaks were identified as diastereomeric α-methylallylethylisopropylcarbinols by nmr (Table III) and infrared spectroscopy. Infrared bands were at 2.85 (OH), 6.10 (C=C), 9.95 and 10.93 (–CH=CH_2), and 10.55 μ.

Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found (19.7-min peak): C, 77.07; H, 13.13. Found (20.3-min peak): C, 76.56; H, 12.89.

The 21.7-min peak was shown to be *cis*-crotylethylisopropylcarbinol by its nmr and infrared spectra; infrared bands at 2.90 (OH), 6.10 (C=C), 10.53, and 13.50 μ (*cis* internal C=C).

Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 77.05; H, 13.05.

B. Diisopropyl Ketone. The yield of pure alcohols boiling at 50–51° (0.5 mm) varied from 56 to 77%. The retention times and product distributions (150 ft × 0.01-in. UCON Polar capillary column at 120°, 20 psi) were: 9.6 min (66%), 10.5 min (8%), and 11.75 min (26%).

The peak at 9.6 min was collected (20 ft × 0.25 in., 25% Carbowax 1540 on Firebrick column at 150°) and its structure established as α-methylallyldiisopropylcarbinol by its nmr and infrared spectra. Pertinent infrared bands were found at 2.84 (OH), 6.09 (C=C), 10.15 and 10.99 (–CH=CH_2), and 10.50 μ.

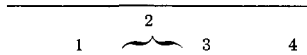
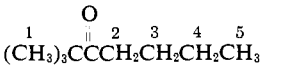
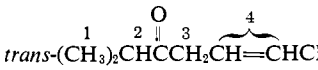
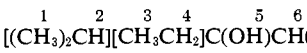
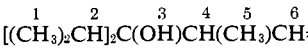
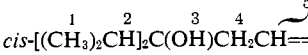
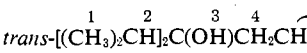
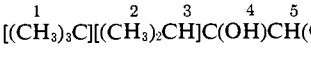
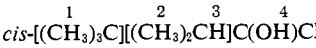
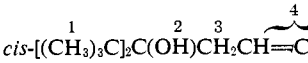
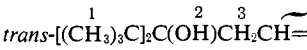
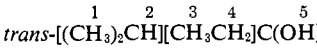
Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.78; H, 13.01.

Similarly, the material with a retention time of 11.75 min was identified as *cis*-crotyldiisopropylcarbinol. Infrared absorptions were at 2.87 (OH), 6.04 (C=C), 10.52, and 13.77 μ (*cis* internal C=C).

Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.65; H, 13.30.

(14) E. C. Ashby and M. B. Smith, *J. Amer. Chem. Soc.*, **86**, 4363 (1964).
(15) S. Winstein and W. G. Young, *ibid.*, **58**, 104 (1936).
(16) L. F. Hatch and S. S. Nesbitt, *ibid.*, **72**, 727 (1950).
(17) N. C. Cook and W. C. Percival, *ibid.*, 4141 (1949).
(18) R. P. Linstead, E. G. Noble, and E. J. Boorman, *J. Chem. Soc.*, 557 (1933).
(19) J. F. Lane, J. D. Roberts, and W. G. Young, *J. Amer. Chem. Soc.*, **66**, 543 (1944).

Table III. Nmr Spectral Data[a-d]

Compound	Spectrum no.	τ values
	1	4.53 (H^2 multiplet), 6.45 (H^4 singlet), 7.18 (H^3 multiplet), 8.37 (H^1 multiplet)
	2	7.57 (H^2 triplet), 8.58 (H^3, H^4 multiplet), 8.98 (H^1, H^5 singlet superimposed on triplet)
	3	4.50 (H^4 multiplet), 6.95 (H^3 multiplet), 7.42 (H^2 septet), 8.30 (H^5 multiplet), 8.95 (H^1 doublet).
	4	4.13 (H^8 multiplet), 5.00 (H^9 multiplet), 7.55 (H^6 quintet), 8.28 (H^2, H^4 multiplet), 9.05 (H^1, H^3, H^5, H^7 multiplet)
	5	4.50 (H^7 multiplet), 7.83 (H^6 complex doublet), 8.41 (H^2, H^4, H^8 multiplet), 9.08 (H^1, H^3, H^5 multiplet)
	6	3.93 (H^6 multiplet), 5.00 (H^7 multiplet), 7.37 (H^4 quintet), 8.02 (H^2, six-lone multiplet), 8.97 (H^1, H^3, H^5 multiplet)
	7	4.53 (H^5 multiplet), 7.50–8.80 (H^2, H^4, H^6 complex pattern), 8.80–9.18 (H^1, H^3 two doublets)
	8	4.53 (H^5 multiplet), 7.70–8.50 (H^2, H^4, H^8 complex pattern), 9.00–9.20 (H^1, H^3 two doublets)
	9	4.05 (H^7 multiplet), 5.00 (H^8 multiplet), 6.98–8.20 (H^3, H^5 complex pattern), 8.58 (H^4 singlet), 8.92 (H^1, H^2, H^6 multiplet)
	10	4.40 (H^6 multiplet), 7.65 (H^5 doublet), 7.90 (H^3 multiplet), 8.38 (H^4, H^7 multiplet), 9.00 (H^1, H^2 multiplet)
	11	4.50 (H^6 multiplet), 7.88 (H^3, H^5 multiplet), 8.33 (H^7 complex doublet), 8.72 (H^4 singlet), 9.03 (H^1, H^2 multiplet)
	12	4.45 (H^4 multiplet), 7.59 (H^3 doublet), 8.37 (H^5 doublet), 8.48 (H^2 singlet), 8.94 (H^1 singlet)
	13	4.50 (H^4 multiplet), 7.63 (H^3 complex doublet), 8.20–8.38 (H^2, H^5 complex pattern), 8.97 (H^1 singlet)
	14	4.55 (H^7 multiplet), 7.90 (H^6 doublet), 8.10–8.87 (H^2, H^4, H^8 complex pattern), 8.95–9.44 (H^1, H^3, H^5 multiplet).

[a] Nmr spectra run on a Varian A-60 nmr spectrometer. [b] TMS used as an internal standard. [c] The spectrum of **1** was run neat, spectra of **11**, **13**, and **14** in $CDCl_3$, and the remainder in CCl_4. [d] In each case, the peak areas are quite consistent with the proton assignments made

The retention time (vpc) of the 10.5-min peak was identical with that of an authentic sample of *trans*-crotyldiisopropylcarbinol.

C. Isopropyl *t*-Butyl Ketone. The products were obtained in 65–85% yield and boiled from 40 to 49° (0.2 mm). The retention times and product distributions (UCON Polar capillary column previously described, programmed at 5°/min from 60 to 130°) were: 21.4 min (40%), 21.9 min (25%), and 23.3 min (35%).

The last peak was collected (20 ft × 0.25 in., 15% UCON Polar 50B 2000 on Chromosorb W column, 140°) and identified by its nmr and infrared spectra as *cis*-crotylisopropyl-*t*-butylcarbinol. Infrared bands were located at 2.83 (OH), 6.09 (C=C), and 13.30 μ (*cis* internal C=C).

Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.12. Found: C, 78.02; H, 13.15.

The 21.4- and 21.9-min peaks could not be separated, but were provisionally identified as α-methylallylisopropyl-*t*-butylcarbinol and *trans*-crotylisopropyl-*t*-butylcarbinol, respectively, by comparing their retention times with authentic samples (vide infra). An elemental analysis of the mixture indicated they were structural isomers.

Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.12. Found: C, 78.02; H, 13.09.

D. Di-*t*-butyl Ketone. The yield of pure alcohols, bp 69° (2.4 mm) was 78%. Analysis by vpc (Carbowax 1540 column, conditions as above) showed two components—*trans*-crotyldi-*t*-butylcarbinol (retention time, 41.4 min; 39%), identified by its nmr and infrared spectra (also identical retention time and matching infrared spectrum as authentic sample)[20] and *cis*-crotyldi-*t*-butylcarbinol (retention time, 51.5 min; 61%). The latter was identified by its nmr and infrared spectra with salient infrared bands at 2.80 (OH), 6.05 (C=C), 10.65, and 13.65 μ (*cis* internal C=C).

Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found (*trans*): C, 78.49; H, 13.29. Found (*cis*): C, 78.45; H, 13.39.

Hydrogenation of a mixture of these isomeric alcohols (ethyl acetate, PtO_2 catalyst) gave a single product (82%) identified as *n*-butyldi-*t*-butylcarbinol by matching its retention time (vpc) infrared and nmr spectra with an authentic sample.

Anal. Calcd for $C_{13}H_{28}O$: C, 77.92; H, 14.08. Found: C, 78.23; H, 14.40.

Reaction of Butenylmagnesium Chlorides with Di-*t*-butyl Ketone. The carbinols obtained from the reactions of di-*t*-butyl ketone and Grignard reagents derived from the various isomeric butenyl chlo-

(20) This material was prepared in low yield by treatment of *trans*-methyl 3-pentenoate and *t*-butyllithium in pentane. It had infrared bands at 2.80 (OH), 6.04 (C=C), 10.27 (*trans* internal C=C), and 10.65 μ.

rides were treated in the same manner as described above. Yields and isomer distributions are summarized in Table II.

trans-**Crotyldiisopropylcarbinol.** All samples of authentic carbinols were synthesized by modifications of the method of Petrov and coworkers.[21]

To 0.25 mol (125 ml of a 2.0 *M* solution) of isopropyllithium in pentane, cooled to −35 to −40° in a 500-ml, three-necked flask equipped with a dropping funnel, mechanical stirrer, and condenser and swept with a slow stream of dry, prepurified nitrogen was added 7.28 g (0.0638 mol) of *trans*-methyl 3-pentenoate[22] in 50 ml of dry, olefin-free pentane over a 1-hr period. After the addition was completed, the mixture was stirred for an additional 1.5 hr at the low temperature, then allowed to warm to room temperature over a 1.5-hr period where it was stirred for 5 hr.

Hydrolysis of the orange mixture was effected with 100 ml of a 5 *M* ammonium chloride solution followed by the usual work-up. The product consisted of 27% *trans*-crotyldiisopropylcarbinol, 20% the starting ester, and 54% *trans*-crotyl isopropyl ketone. Identification was accomplished by their infrared and nmr spectra. *trans*-Crotyldiisopropylcarbinol showed infrared bands at 2.87 (OH), 10.34 (*trans* internal C=C), and 10.54 μ, and *trans*-crotyl isopropyl ketone had bands at 5.84 (C=O) and 10.29 μ (*trans* internal C=C).

Anal. Calcd for $C_{11}H_{22}O$ (*trans*-crotyldiisopropylcarbinol): C, 77.58; H, 13.02. Found: C, 77.52; H, 13.26.

α-**Methylallylisopropyl-***t*-**butylcarbinol.** Methyl 2-methyl-3-butenoate[23] (11.4 g; 0.1 mol) in 45 ml of dry pentane was treated with 0.1 mol (68 ml of a 1.47 *M* solution) of *t*-butyllithium in pentane at −50°. The product (α-methylallyl *t*-butyl ketone in low yield) was isolated on a preparative vpc column (15 ft × 3/8 in., 20% Carbowax 20M on Chromosorb P at 140°). It exhibited infrared bands at 5.89 (C=O), 6.14 (C=C), 10.04, and 10.93 μ (−CH=CH_2).

To a solution (0.45 g; 0.0032 mol) of α-methylallyl *t*-butyl ketone thus obtained in 20 ml of dry pentane cooled to −55° was added over a 0.25-hr period, 0.0064 mol of isopropyllithium in pentane. After stirring for an additional 2 hr at −55°, hydrolysis was performed with a saturated ammonium chloride solution. The usual work-up afforded 0.45 g of product. Analysis by vpc (20 ft × 0.25 in., 25% Carbowax 1540 on Firebrick column; 130°) disclosed three components: 59.2 min (76%), 69 min (20%), and 77 min (4%).

The first component (with the same retention time as the 21.4-min peak obtained in the reaction of crotylmagnesium bromide with isopropyl *t*-butyl ketone) was shown to be α-methylallylisopropyl-*t*-butylcarbinol by its nmr and infrared spectra. Important infrared bands were found at 2.82 (OH), 6.14 (C=C), 10.12, and 10.85 μ (−CH=CH_2).

Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.12. Found: C, 78.24; H, 13.18.

trans-**Crotylethylisopropylcarbinol.** *trans*-Crotyl isopropyl ketone was synthesized in essentially the same manner as α-methylallyl *t*-butyl ketone using 12.0 g (0.0936 mol) of *trans*-methyl 3-pentenoate in 75 ml of pentane and 0.117 mol (58.5 ml of a 2 *M* solution) of isopropyllithium in pentane. A total of 12.0 g of crude products was obtained after solvent removal. Analysis of this liquid on the 150 ft × 0.01 in. UCON Polar capillary column, under the conditions described earlier, indicated that three components were present: 6.5 min (22%), 11.9 min (41%), and 26.0 min (37%).

The first component was identified by its retention time as unreacted ester. The 11.9-min peak was collected from a 15 ft × 3/8 in., 20% Zonyl E-7 on Chromosorb P preparatory vpc column at 140° and identified by its infrared spectrum as the desired ketone. In addition, this compound had an infrared spectrum identical with the material isolated in 54% yield during the preparation of *trans*-crotyldiisopropylcarbinol (*vide supra*).

Enough ketone was collected from the Zonyl E-7 column to carry out the subsequent reaction, and no attempt was made to isolate it by distillation. The third component was not identified.

To 0.050 mol (50 ml of a 1 *M* solution) of ethyllithium in pentane was added, at room temperature with stirring over a 20-min period, 0.380 g (0.00318 mol) of *trans*-crotyl isopropyl ketone in 30 ml of anhydrous ether. The reaction mixture was then stirred for an additional 1 hr and then hydrolyzed with saturated ammonium chloride solution.

After work-up in the usual fashion, vpc analysis (20 ft × 0.25 in., stainless steel, 25% Carbowax 1540 on Firebrick column, 130°) indicated an 81% yield of the desired alcohol (retention time, 30.6 min) which was collected and identified by nmr and infrared spectroscopy. The important infrared absorptions occurred at 2.87 (OH), 10.24 (*trans* internal C=C), 10.42, and 10.83 μ.

Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.54; H, 13.16.

This compound had a vpc retention time (150-ft capillary column, same conditions as above) identical with the 21.0-min peak obtained from the reaction of crotylmagnesium bromide with ethyl isopropyl ketone.

The remainder of the product was found to be starting ketone (14%; retention time 13.4 min) and *cis*-crotylethylisopropylcarbinol (5%; retention time 33.5 min).

trans-**Crotylisopropyl-***t*-**butylcarbinol.** This compound was prepared from 0.387 g (0.00300 mol) of *trans*-crotyl isopropyl ketone in 20 ml of pentane and 0.00690 mol (4.75 ml of a 1.47 *M* solution) of *t*-butyllithium in pentane.

Gas chromatographic analysis of the reaction mixture on the previously described Carbowax 1540 column indicated about a 50% yield of the desired alcohol, identified by nmr and infrared spectroscopy; 2.81 (OH), 10.27 μ (*trans* internal C=C).

Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.12. Found: C, 78.31; H, 13.00.

This material had a vpc retention time identical with that of the 21.9-min peak obtained in the reaction of the butenyl Grignard reagent with isopropyl *t*-butyl ketone.

n-**Butyldi-***t*-**butylcarbinol.** Methyl valerate (7.27 g; 0.0620 mol) in 100 ml of pentane was added dropwise over a 2-hr period to 0.125 mol (166 ml of a 1.5 *M* solution) of *t*-butyllithium in pentane, cooled to −12° by an ice–salt bath. The mixture was stirred at −12° for an additional 1.5 hr, then warmed to room temperature (2 hr) and held therefore 0.5 hr. After hydrolysis and the usual work-up, 6.24 g (50%) of product was obtained, bp 110–112° (14 mm); $n^{20}D$ 1.4558 (lit.[21] bp 121.5–123° (24 mm); $n^{20}D$ 1.4540).

Anal. Calcd for $C_{13}H_{28}O$: C, 77.92; H, 14.08. Found: C, 78.23; H, 14.10.

This compound was identical (infrared and nmr spectra) with the hydrogenated product of the butenyl Grignard with di-*t*-butyl ketone.

A by-product of this reaction (3.03 g) was identified by its nmr and infrared spectra as *n*-butyl *t*-butyl ketone.

Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 76.28; H, 12.97.

Acknowledgment. This research was supported by the U. S. Army Research Office (Durham) and the National Science Foundation to whom the authors are deeply indebted.

(21) A. D. Petrov, E. B. Sokolova, and K. Ching-lang, *Zh. Obshch. Khim.*, 30, 1107 (1960).

(22) Prepared by treating *trans*-3-pentenoic acid with thionyl chloride followed by anhydrous methanol in conventional fashion. *Anal.* Calcd for $C_6H_{10}O$: C, 63.13; H, 8.83. Found: C, 63.08; H, 8.91.

(23) Prepared in 89% yield by treatment of the acid with diazomethane in conventional fashion.