

The infinity volume, V_∞ , for each kinetic run was determined through the ideal gas law formula $V = nRT/p$, where n is the moles of chlorosulfonate, R is the gas constant, T is room temperature and p is the corrected atmospheric pressure. The first-order rate constant was determined through the integrated first-order rate equation, \ln

$(1/1 - x) = kt$, where x is equal to V_t/V_∞ and V_t is equal to the volume of gas evolved at time t .

Acknowledgment.—The helpful discussions with Professor Saul Winstein concerning certain facets of this work are gratefully acknowledged.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

Allylic Rearrangements. II. Displacement Reactions in Trifluoromethylallyl Systems¹

BY J. A. PEGOLOTTI AND W. G. YOUNG

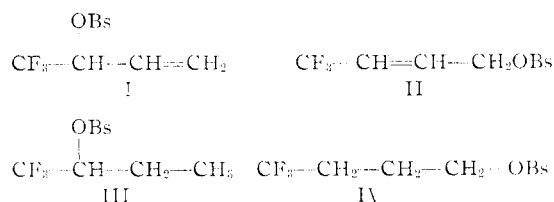
RECEIVED FEBRUARY 2, 1961

Kinetic studies of the reactions of azide ion in 70% acetone–30% water and iodide ion in anhydrous acetone with α - and γ -trifluoromethylallyl *p*-bromobenzenesulfonates and γ -trifluoromethylallyl chloride indicate that a γ -trifluoromethyl group enhances the rate of nucleophilic displacement upon allylic compounds. An S_N2' mechanism for nucleophilic attack upon α -trifluoromethylallyl *p*-bromobenzenesulfonate is discussed.

As part of an investigation to determine the effect of the strong inductive group trifluoromethyl upon reaction mechanisms in the allylic system,² a study of bimolecular reactions was initiated with α - and γ -trifluoromethylallyl compounds. The major amount of previous work investigating displacement reactions upon allylic compounds has concerned the rates of reaction of allylic chlorides with such nucleophiles as iodide ion and ethoxide ion.³ Although γ -trifluoromethylallyl chloride was prepared, the preparation of α -trifluoromethylallyl chloride was unsuccessful.² For this reason, it was necessary to prepare other compounds for the study. The compounds chosen in this respect were the *p*-bromobenzenesulfonate derivatives (brosylates) of α - and γ -trifluoromethylallyl alcohols. Generally, brosylates or tosylates (the *p*-methylbenzenesulfonate derivatives) of allylic alcohols are not stable; however, these brosylates were nicely crystalline stable compounds.

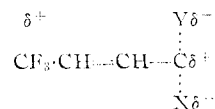
Kinetic studies were undertaken to determine the rate of reaction of α -trifluoromethylallyl brosylate (I), γ -trifluoromethylallyl brosylate (II), 1,1,1-trifluorobutyl brosylate (III), 4,4,4-trifluorobutyl brosylate (IV) and γ -trifluoromethylallyl chloride with potassium iodide in acetone. In addition, the rates of reaction of the allylic brosylates I and II with sodium azide in 70% acetone–30% water were measured. The rates with potassium iodide were followed titrimetrically while those with sodium azide were followed by vapor phase chromatography using an internal standard to measure the amount of product formed at specific intervals. Details of these methods of analysis will be found in the Experimental section. The rate constants derived from these studies are presented in Table I. In Table II, the relative reactivities of allylic chlorides toward potassium iodide in acetone are presented in relation to the reactivity of γ -trifluoromethylallyl chloride, while Table III compares the relative reactivities of the

saturated and unsaturated brosylates toward potassium iodide in acetone.



Discussion of the Results of Displacement Reactions upon γ -Trifluoromethylallyl Compounds.

The results of the kinetic studies of the reaction of potassium iodide in acetone upon the unsaturated and saturated primary brosylates II and IV and γ -trifluoromethylallyl chloride show that a γ -trifluoromethyl group increases the reactivity of the allylic system to S_N2 displacement. This is illustrated in Table II, where it is noted that α trifluoromethylallyl chloride is 17 times more reactive toward potassium iodide than is allyl chloride itself, a larger increase in reactivity than that supplied by a γ -methyl group. It is also interesting to note that the rate of iodide displacement upon the allylic primary brosylate II is 113 times faster than upon the saturated primary analog IV. These observations are difficult to explain in the manner generally proposed for the increased reactivity of allylic compounds in S_N2 reactions,³ the stabilization of the transition state by the interaction of the π -electrons with the reaction center. If this stabilization did take place, there would necessarily arise a partial positive



charge upon the carbon atom adjacent to the trifluoromethyl group and this partial positive charge cannot be stabilized by the trifluoromethyl group. It is much more desirable that a negative or partial negative charge be placed adjacent to a trifluoromethyl group to satisfy the electron-demanding

(1) This work was supported in part by a grant to W. G. Young from the National Science Foundation.

(2) J. A. Pegolotti and W. G. Young, accompanying paper.

(3) R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

TABLE I

RATE CONSTANTS OF DISPLACEMENT REACTIONS

Reaction of α - and γ -trifluoromethylallyl brosylates and their saturated analogs with potassium iodide in acetone

Compound	1°	25°	10° k , l. mole ⁻¹ sec. ⁻¹	50°	75°
CF ₃ CH=CHCH ₂ OBs	19.2 ± 0.4	366 ± 9			
CF ₃ CH ₂ CH ₂ CH ₂ OBs		2.99 ± 0.07			
CF ₃ CH(OBs)CH=CH		(0.0043) ^a	0.0906 ± 0.0014		1.21 ± 0.03
CF ₃ CH(OBs)CH ₂ CH ₃					0.0011 ^b

Reaction of α - and γ -trifluoromethylallyl brosylates with sodium azide in 70% acetone–30% water

CF ₃ CH=CHCH ₂ OBs	4.4 ± 1.3	
CF ₃ CH(OBs)CH=CH ₂		0.030 ± 0.001
		0.032 ± 0.001

Reaction of γ -trifluoromethylallyl chloride with potassium iodide in acetone

CF ₃ CH=CHCH ₂ Cl	1.38 ± 0.07
	1.31 ± 0.05

^a This rate constant was calculated by extrapolation from higher temperatures. ^b This rate constant should be taken as a maximum only; the rate was too slow to calculate a more precise value.

TABLE II

Compound	10° k , l. mole ⁻¹ sec. ⁻¹	Relative reactivity
CF ₃ CH=CHCH ₂ Cl (<i>trans</i>)	135	17.0
CH ₃ CH=CHCH ₂ Cl ^b (<i>cis</i>)	76 ^a	9.5
CH ₃ CH=CHCH ₂ Cl ^b (<i>trans</i>)	15 ^a	1.8
CH ₂ =CHCH ₂ Cl ^c	8	1.0
CH ₃ CH ₂ CH ₂ CH ₂ Cl ^c	0.061	0.0076

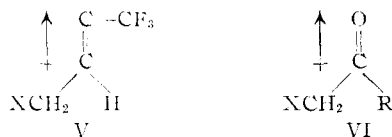
^a Extrapolated from 20°. ^b Ref. 4. ^c Ref. 5.

TABLE III

RELATIVE REACTIVITIES OF α - AND γ -TRIFLUOROMETHYLALLYL BROSYLATES AND THEIR SATURATED ANALOGS WITH POTASSIUM IODIDE IN ACETONE

Compound	Temp., °C.	Relative reactivity
CF ₃ CH=CHCH ₂ OBs	25	113
CF ₃ CH ₂ CH ₂ CH ₂ OBs	25	1
CF ₃ CH(OBs)CH=CH ₂	75	≥ 1100
CF ₃ CH(OBs)CH ₂ CH ₃	75	1
CF ₃ CH=CHCH ₂ OBs	25	78500
CF ₃ CH(OBs)CH=CH ₂	25	1

fluorines. With this thought in mind, a consideration of the similarity between the α -trifluoromethylallyl system V and α -halo ketones VI suggests a reason for the increased reactivity of the allylic system with a α -trifluoromethyl group. α Halo ketones react rapidly in bimolecular displacements. For example, at 50° in acetone, chloroacetone is 30,000 times more reactive toward potassium iodide than *n*-propyl chloride.⁵ Inspection of V and VI suggests a similarity between the re-



activity of these two types of compounds, particularly in view of the orientation of the dipole arising from the polarization of the π -electrons in these compounds. The attraction of the incoming nucleophile for the positive end of the carbon dipole is generally accepted as the basic reason why such a rate enhancement is found in α -halo ketones, or

(4) L. F. Hatch and S. S. Nesbitt, *J. Am. Chem. Soc.*, **73**, 358 (1951).(5) J. B. Conant, W. R. Kirner and R. E. Hussey, *ibid.*, **47**, 488 (1925).

other α -substituted ketones.⁶ Winstein has suggested that this initial attraction results in the formation of a triangular transition state (VI) where displacement by the nucleophile is facilitated due to its being held in a position favorable for subsequent displacement.⁷ Similarly, it is seen by analogy how such a transition state is facilitated in displacement reactions in the γ -trifluoromethylallyl system V'. In this transition



state the carbon adjacent to the trifluoromethyl group may attain a partial negative charge, a more energetically favorable situation than the previous transition state discussed which placed a partial positive charge in that position.

Discussion of the Results of Displacement Reactions upon α -Trifluoromethylallyl Brosylate.—From a purely qualitative viewpoint, it is understandable why α -trifluoromethylallyl brosylate (III) reacts 78,500 times faster than α -trifluoromethylallyl brosylate (I) with iodide ion in acetone. Normal nucleophilic attack at a secondary carbon atom is slower than on a primary carbon atom, due primarily to steric hindrance upon the secondary center. For example, α -methylallyl chloride reacts one-fiftieth as fast as *trans*- γ -methylallyl chloride with potassium iodide in acetone at 20°. However, steric hindrance would not be expected to play as large a part in decreasing the rate of normal displacement upon I as does the inductive effect of the trifluoromethyl group adjacent to the reaction site. To illustrate this point, Hine has shown⁸ that the reason why 2,2,2-trifluoroethyl iodide reacts 17,400 times slower than ethyl iodide toward sodium phenoxide in methanol at 20° is the inductive effect of the trifluoromethyl group, not its size. Thus, the rate-retarding effect of this group would favor a very slow rate of displacement

(6) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

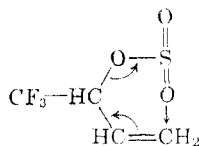
(7) S. Winstein, quoted by P. D. Bartlett in H. Gilman's "Organic Chemistry," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1953.

(8) J. Hine and R. G. Chiriacelli, *J. Org. Chem.*, **23**, 1550 (1958).

upon I as compared to II where neither the inductive effect of the fluorines nor steric hindrance militates against nucleophilic attack.

The kinetic data do not appear to be incompatible with an $\text{S}_{\text{N}}2$ displacement upon the secondary brosylate I by azide ion or iodide ion. However, several facts indicate that an $\text{S}_{\text{N}}2'$ mechanism must be also considered for these reactions. It was found by vapor phase chromatography that the only product formed in the reaction of I with sodium azide in 70% acetone was the primary azide, γ -trifluoromethylallyl azide, the product expected from abnormal ($\text{S}_{\text{N}}2'$) attack upon I. This azide had been previously prepared by the reaction of sodium azide upon α -trifluoromethylallyl chloride. Its infrared spectrum showed the typical strong azide absorption band at 2100 cm^{-1} and the internal double bond band at 1680 cm^{-1} . In addition, the reaction of iodide ion with both I and II produced only one product, as characterized by its retention time in the vapor phase chromatogram. This product was not isolated, but assumed to be the primary iodide, γ -trifluoromethylallyl iodide. It appears, therefore, that with both iodide and azide reactions upon I, the $\text{S}_{\text{N}}2'$ product is formed. Unfortunately, this fact, of itself, is not meaningful since if the secondary allylic products were formed by a normal $\text{S}_{\text{N}}2$ displacement, the resulting secondary allylic azide or iodide might be quite prone to rearrange to the primary isomer, the product observed. Such rearrangements are quite facile with secondary allylic azides and iodides.⁹ These facts indicate that one must be able to rule out such rearrangements occurring in the reaction of azide ion or iodide ion on I before an $\text{S}_{\text{N}}2'$ mechanism can be definitely invoked. However, several arguments may be advanced which indicate that nucleophilic attack upon I may proceed, at least partly, through an $\text{S}_{\text{N}}2'$ mechanism.

As regards the facility of rearrangement methyl allyl azide and α -trifluoromethylallyl iodide, if these compounds formed, it should be noted that I is stable for 35 days at 50° in 70% acetone with no evident rearrangement, as shown during this investigation. On purely qualitative grounds, it would be expected that compound I should also rearrange if the allylic iodide and azide are so prone. This rearrangement would probably occur



through a non-ionic intermediate,¹⁰ a pathway for which the compound is admirably suited, but

(9) A. Gagneux, S. Winstein and W. G. Young, *J. Am. Chem. Soc.*, **82**, 5956 (1960), have found that the rearrangement of α -methylallyl azide to the thermodynamic mixture of 70% γ -methylallyl azide and 30% α -methylallyl azide is half complete after 2 hours at 25° in 70% acetone, while McDowell [C. A. McDowell, F. P. Lossing, I. H. S. Henderson and J. B. Farmer, *Can. J. Chem.*, **34**, 345 (1956)] in various attempts to prepare α -methylallyl iodide, found that only γ -methylallyl iodide results, apparently due to the ease of rearrangement of the secondary allylic iodide to the primary iodide.

(10) See ref. 2 for a similar reaction in the decomposition of α -trifluoromethylallyl chlorosulfate to γ -trifluoromethylallyl chloride.

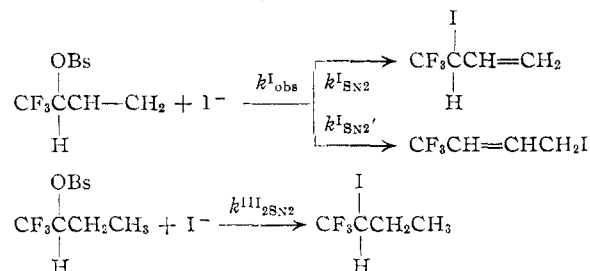
which it does not apparently follow. This may indicate that α -trifluoromethylallyl azide and α -trifluoromethylallyl iodide would be quite stable to rearrangement.

A second indication that an $\text{S}_{\text{N}}2'$ mechanism may be operative in these cases is given by a comparison of relative rates. The unsaturated brosylate I undergoes displacement by iodide ion in acetone at least 1100 faster than its saturated isomer III (see Table III). If we compare the relative reactivities of α -methylallyl chloride and *sec*-butyl chloride toward potassium iodide in acetone at 50° , it is found that α -methylallyl chloride is 100 times faster than *sec*-butyl chloride.¹¹ Assuming that there is normally a difference of about 100 in the rate of a displacement reaction by iodide ion upon a secondary allylic compound and its saturated isomer, a kinetic scheme can be formulated to indicate that percentage of the reaction of iodide ion upon I proceeds by an $\text{S}_{\text{N}}2'$ mechanism. This is Scheme I. The observed rate constant, $k^{\text{I}}_{\text{obs}}$, is a composite of the rate constants for normal and abnormal nucleophilic attack by iodide ion and is formulated in eq. A. The relation in eq. B arises from the aforementioned

$$k^{\text{I}}_{\text{obs}} = k^{\text{I}}_{\text{S}_{\text{N}}2} + k^{\text{I}}_{\text{S}_{\text{N}}2'} \quad (\text{A})$$

$$k^{\text{I}}_{\text{S}_{\text{N}}2} = 100k^{\text{III}}_{\text{S}_{\text{N}}2} \quad (\text{B})$$

SCHEME I



difference in rate between α -methylallyl chloride and *sec*-butyl chloride with potassium iodide in acetone. Equation A is transformed into eq. C by the relationship of eq. B. Since $k^{\text{III}}_{\text{S}_{\text{N}}2} = 1$ and $k^{\text{I}}_{\text{obs}} = 1100$ (Table III), these values may be substituted into eq. C. In this manner it is determined that $k^{\text{I}}_{\text{S}_{\text{N}}2'} = 1000$ while $k^{\text{I}}_{\text{S}_{\text{N}}2} = 100$. Therefore,

$$k^{\text{I}}_{\text{obs}} = 100k^{\text{III}}_{\text{S}_{\text{N}}2} + k^{\text{I}}_{\text{S}_{\text{N}}2'} \quad (\text{C})$$

since the rate of abnormal displacement is 10 times that of normal displacement upon I, over 90% of the reaction should proceed by an $\text{S}_{\text{N}}2'$ mechanism *insofar as the initial assumption is correct*. There apparently is a precedent for an $\text{S}_{\text{N}}2'$ reaction in the α -trifluoromethylallyl system since in the reactions of thionyl chloride and α -trifluoromethylallyl alcohol the product α -trifluoromethylallyl chloride arises through an $\text{S}_{\text{N}}2'$ reaction, though intramolecular.²

Until the compounds α -trifluoromethylallyl azide and iodide can be shown not to rearrange under the reaction conditions used, an $\text{S}_{\text{N}}2'$ reaction cannot definitely be invoked here. However, as the previous arguments suggest, an $\text{S}_{\text{N}}2'$ reaction is quite likely for the majority of product found in these

(11) (a) S. Oae and C. A. VanderWerf, *J. Am. Chem. Soc.*, **75**, 2724 (1953); (b) J. B. Conant and R. E. Hussey, *ibid.*, **47**, 476 (1925).

nucleophilic displacements upon α -trifluoromethylallyl brosylate.

Experimental

Preparation and Purification of Reactants. Potassium iodide.—J. T. Baker analyzed reagent grade potassium iodide was recrystallized from water by cooling a solution saturated with the salt at 99° to room temperature. After filtering from the water, it was dried for 10 hours in an Abderhalden drying pistol at 2 mm. over refluxing acetone.

Sodium Azide.—Fisher purified sodium azide was recrystallized from acetone–water and dried in an Abderhalden pistol for several hours at 2 mm.

α -Trifluoromethylallyl *p*-Bromobenzenesulfonate.—The procedure used was similar to that of Winstein and Heck.¹² A solution of 1.0 g. (0.008 mol.) of α -trifluoromethylallyl alcohol² in 10 ml. of anhydrous pyridine was maintained at –20° by means of a Dry Ice–acetone–bath. To this solution was added 3.03 g. (0.012 mol.) of Eastman Kodak Co. white label *p*-bromobenzenesulfonyl chloride in 5 ml. of pyridine, and the resulting mixture set in the refrigerator for 2 days, after which it was added to 100 ml. of water, and extracted with three 15-ml. portions of ether. The combined ether extracts were then washed successively with water, cold dilute hydrochloric acid, water and saturated sodium bicarbonate solution, then dried over calcium sulfate. The ether was removed by an aspirator, and the last traces of solvent removed by a stream of air. The resulting oil crystallized when cooled in Dry Ice. The brosylate was then recrystallized three times from petroleum ether, yielding 1.16 g. (43% yield) of pure brosylate, m.p. 33.0–33.6°.

Anal. Calcd. for $C_{10}H_8F_3BrO_3S$: C, 34.79; H, 2.33. Found: C, 34.86; H, 2.29.

γ -Trifluoromethylallyl chloride was prepared as described previously.²

1,1,1-Trifluoro-2-butanol.—A solution of 3.0 g. (0.024 mol.) of α -trifluoromethylallyl alcohol² in 45 ml. of J. T. Baker analyzed methanol was hydrogenated, with 0.9 g. of 10% palladium-on-charcoal as catalyst, in a low pressure Paar hydrogenation apparatus. Distillation of the hydrogenation solution on a micro-column yielded the desired alcohol, b.p. 90°, n_D^{25} 1.3380.

1,1,1-Trifluoro-2-butyl *p*-bromobenzenesulfonate was prepared by the method previously described for the preparation of α -trifluoromethylallyl *p*-bromobenzenesulfonate. It had m.p. 23° and n_D^{25} 1.4935.

4,4,4-Trifluorobutyl Alcohol.—Ethyl 4,4,4-trifluorocrotonate (3.53 g., 0.021 mol.) in 25 ml. of anhydrous ether was hydrogenated in a low pressure Paar shaker apparatus with 0.2 g. of platinum oxide as catalyst. The calculated amount of hydrogen was taken up in 1 hour. After filtering from the catalyst, the ether solution was added over a 10-minute period with magnetic stirring to 0.95 g. (0.025 mol.) of lithium aluminum hydride in 50 ml. of anhydrous ether, and the solution was refluxed for 8 hours. The flask was then cooled in an ice–water–bath while water was added cautiously until the hydrolysis solids stopped the magnetic stirring bar. Distillation on a micro-column gave the desired alcohol, 1.62 g. (60% yield), b.p. 68° (70 mm.), n_D^{25} 1.3420. Attempted preparation of this alcohol by hydrogenation of γ -trifluoromethylallyl alcohol was unsatisfactory due to the formation of several by-products which were not identified.

4,4,4-Trifluorobutyl *p*-bromobenzenesulfonate was prepared in the same manner as γ -trifluoromethylallyl *p*-bromobenzenesulfonate described below. It had m.p. 62.5–63.0°, and gave a negative Baeyer test for unsaturation.

Anal. Calcd. for $C_{10}H_{10}F_3BrO_3S$: C, 34.65; H, 2.90. Found: C, 34.67; H, 2.82.

γ -Trifluoromethylallyl *p*-Bromobenzenesulfonate.—A solution of 2.0 g. (0.0158 mol.) of γ -trifluoromethyl allyl alcohol² in 20 ml. of ether was added to 0.40 g. (0.018 mol.) of sodium hydride in 100 ml. of ether over 15 minutes. The resulting mixture was refluxed overnight. A solution of 4.04 g. (0.0158 mol.) of Eastman Kodak Co. white label *p*-bromobenzenesulfonyl chloride in 50 ml. of ether was then added to the alkoxide in ether, cooled in an ice–water–bath, and the reaction mixture stirred 1 hour longer, after which the solution was extracted with water three times and the ether portion resulting dried over calcium sulfate. A crys-

talline solid remained after removing the ether through an aspirator. The brosylate was recrystallized four times from petroleum ether–diethyl ether mixed solvent. The amount of pure brosylate was 1.49 g. (28% yield), m.p. 63–63.5°.

Anal. Calcd. for $C_{10}H_8F_3BrO_3S$: C, 34.79; H, 2.33. Found: C, 34.74; H, 2.22.

γ -Trifluoromethylallyl Azide.—To 70 ml. of 70% acetone–30% water was added 2.0 g. of γ -trifluoromethylallyl chloride and 5.65 g. of sodium azide. The resulting solution was refluxed for 20 hours, after which 100 ml. of water was added, and the mixture extracted with 50 ml. of petroleum ether. The petroleum ether extract was then washed with three 10-ml. portions of water to remove acetone, after which the petroleum ether extract was dried over calcium sulfate. Distillation resulted in 0.72 g. (35% yield) of γ -trifluoromethylallyl azide, b.p. 53° (65 mm.), n_D^{25} 1.3864. A vapor phase chromatogram showed the azide to be 99.5% pure. Its infrared spectrum showed the characteristic strong azide absorption at 2100 cm^{-1} , and the strong internal double bond band at 1680 cm^{-1} .

Anal. Calcd. for $C_4H_4F_3N_3$: C, 31.79; H, 2.67. Found: C, 31.88; H, 2.80.

Kinetic Studies.—The methods used in attaining the rate data assembled in Table I will be described here. In the rate measurements made in acetone, the acetone used was J. T. Baker reagent grade which had been dried for 12 hours over calcium sulfate, distilled and stored in a glass stoppered reagent bottle. For the kinetic measurements of potassium iodide with brosylates in acetone, an accurately weighed amount of potassium iodide was transferred to a 50-ml. volumetric flask and dissolved in acetone at 25°. An equimolar amount of brosylate was transferred to the flask and acetone added to the 50-ml. mark. For the rate measured at 1°, the potassium iodide solution was equilibrated to that temperature in the ice–water–bath before addition of the brosylate. In each of the kinetic runs, the reactants were approximately 0.02 molar. For rate measurements at 50° and 75° aliquots were pipetted into ampoules which were then sealed and placed in the appropriate constant temperature bath. At specific intervals, rate tubes were withdrawn from the bath, quenched in an ice–bath and then immersed in a water–bath at room temperature for 10 minutes. A 5-ml. aliquot was transferred by means of a calibrated automatic pipet from the rate tube into a separatory funnel containing 10 ml. of water and 25 ml. of J. T. Baker petroleum ether. For rate measurements at 25°, a 5-ml. aliquot was transferred directly from the flask into the separatory funnel. The contents of the funnel were shaken 40 times, the water layer separated, then an additional 10 ml. of water added and the procedure repeated. To the combined water portions was added 2 ml. of 6 *N* acetic acid and 10 drops of a 1% solution of the sodium salt of eosin in water. Titration for unreacted iodide ion was performed by adding standard silver nitrate solution from a microburet until the sharp pink end-point was achieved.

In the rate measurements with potassium iodide and γ -trifluoromethylallyl chloride, the 50 ml. of acetone rate solution was 0.10 *M* in γ -trifluoromethylallyl chloride and 0.02 *M* in potassium iodide. The procedure used for the measurement of unreacted iodide ion was that of Conant and Kirner.¹³

The kinetic studies with sodium azide were carried out in a solution 70% by volume of acetone and 30% by volume of water. Rate measurements at 50° were conducted by the sealed tube method, while that at 1° by the method described above for the potassium iodide rate at that temperature. An excess of sodium azide was used, and a weighed amount of ethyl *n*-butyl ether was added to the solution as an internal standard for vapor phase calculations, since the rate was calculated from the amount of product observed at specific intervals.² For this purpose, an aliquot was transferred to a 10-ml. flask containing 1 g. of sodium chloride. Vigorous shaking "salted out" the acetone layer, which was analyzed for product by vapor phase chromatography. An ether extraction of the water layer from several of these aliquots did not contain any of the organic product as indicated by vapor phase chromatography.

(12) S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **78**, 4801 (1956).

(13) J. B. Conant and W. R. Kirner, *ibid.*, **46**, 232 (1924).

All rate constants were corrected for volume change of the solvent from 25° to the temperature at which the rate study was made. The density measurements of Schwes on acetone and acetone-water mixtures at various temperatures were used for these corrections.¹⁴

Acknowledgment.—The helpful discussions with Professor Saul Winstein concerning certain facets of this work are gratefully acknowledged.

(14) F. Schwes, *J. chim. phys.*, **9**, 15 (1911).

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PLANT NEMATOLOGY, UNIVERSITY OF CALIFORNIA, RIVERSIDE CALIF.]

The Role of Halide in the Reduction of Carbonium Ions by Chromium(II)

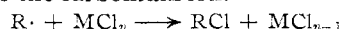
BY C. E. CASTRO

RECEIVED OCTOBER 25, 1960

Chromous salts alter the course of reactions that proceed by way of the 1,1-diphenylethyl cation such that dimers of this fragment are obtained rapidly and in high yield. Halide ions are essential for these transformations. This fact has been interpreted to indicate that polyarylmethyl cations are not reduced by Cr^{++} but rather that a direct reduction of the intermediate organic halide occurs. In accord with this contention, benzhydryl bromide is coupled by chromous sulfate and by titanous chloride. Allyl chloride is reduced to propylene.

Introduction

The reducing power of organic free radicals¹ has been found to be of significance to synthetic² and polymer³ chemistry. Recent findings indicate that the oxidation of alkyl radicals to alkyl halides by cupric and ferric chloride⁴ most likely results from a direct radical displacement rather than prior oxidation to the carbonium ion.



The large number of reactions that proceed by way of intermediate cations suggested that a study of the converse process, that is, the reduction of carbonium ions, could be of value. In particular, the possibility of diverting these ionic reactions with metal salts such that free radical products might be obtained was attractive.

As a part of the comprehensive studies of Conant⁵ and colleagues concerning the homogeneous reduction of organic compounds, the reduction of a carbonium ion to a free radical was proposed to explain the coupling of polyarylcabinols by acidic vanadous and chromous chloride.⁶ Similar mechanisms have been suggested to accommodate the production of ditrityl peroxide from the reaction of ferrocene with trityl chloride in nitromethane⁷ and the coupling of benzyl chloride upon exposure to a boiling water suspension of iron powder.⁸ This process now has been examined by exposing the 1,1-diphenylethyl cation to Cr^{II} and Ti^{III} under a variety of conditions. The acid-catalyzed dimerization of 1,1-diphenylethylene⁹ and the acid-catalyzed dehydration of diphenylmethylcarbinol¹⁰ were employed as model systems for this study.

(1) R. M. Haines and W. A. Waters, *J. Chem. Soc.*, 4256 (1955).

(2) J. K. Kochi, *J. Am. Chem. Soc.*, **79**, 4815 (1957).

(3) C. H. Bamford, A. D. Jenkins and R. Johnston, *Proc. Roy. Soc. (London)*, **A239**, 214 (1957).

(4) J. Kumamoto, H. E. De La Mare and F. F. Rust, *J. Am. Chem. Soc.*, **82**, 1935 (1960).

(5) For a survey with key references see J. B. Conant and H. B. Cutter, *ibid.*, **48**, 1016 (1926).

(6) J. B. Conant, L. F. Small and B. S. Taylor, *ibid.*, **47**, 1959 (1925).

(7) M. F. Hawthorne, *J. Org. Chem.*, **21**, 363 (1956).

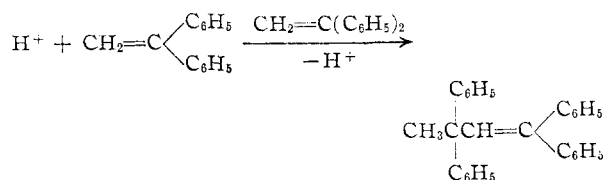
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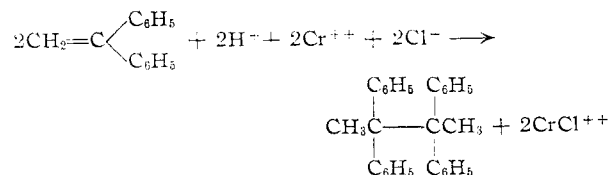
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Results and Discussion

The Perchloric Acid Dimerization of 1,1-Diphenylethylene.—In the absence of metal ions a stirred mixture of the olefin and 70% perchloric acid yielded 1,1,3,3-tetraphenylbutene-1 in 95% yield. Added solutions of TiCl_3 or CrSO_4 reagent¹¹ to this heterogeneous system had no effect. The metals were not oxidized.



A homogeneous solution composed of dioxane, 70% perchloric acid, an excess of the CrSO_4 reagent and 1,1-diphenylethylene after five days under nitrogen at room temperature provided only starting olefin (87%), a small yield of tetraphenylbutene (9%) and a trace of telomer.¹² That is, the typical carbonium ion products were obtained. Chromium was not oxidized.¹³ Under identical conditions except that concentrated hydrochloric acid was substituted for one-fourth of the perchloric acid employed, the solution immediately changed to an apple-green (CrCl^{++}), and 2,2,3,3-tetraphenylbutane gradually crystallized from the solution in 70% yield. Semi-quantitative analysis indicated that one mole of Cr^{II} per mole of olefin had been consumed. Thus, the addition of chloride ion to the chromous sulfate solution has altered the normal course of the acid dimerization.



(11) From the zinc powder reduction of $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$.

(12) E. Hepp, *Ber.*, **7**, 1409 (1874); G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2355 (1929).

(13) At the end of this period the solution had darkened somewhat. This may have been due to a slow leak or a slow reaction with dioxane, $\text{SO}_4^{=}$ or ClO_4^- . A blank not containing olefin also darkened slowly.