Reaction of N-(3-Ethylthio-5,5-dimethylcyclohex-2-en-1-ylidene)-pyrrolidinium Iodide with Pyrrolidine.—To a solution of 0.91 g. (0.0025 mole) of N-(3-ethylthio-5,5-dimethylcyclohex-2-en-1-ylidene)-pyrrolidinium iodide in 1 ml. of methanol was added 0.21 g. (0.0030 mole) of pyrrolidine. A strong odor of ethyl mercaptan was noted. Ethyl acetate (10 ml.) was added, and the solution was evaporated to incipient cloudiness on the steam-bath and allowed to cool. The product was recrystallized from methanol–ethyl acetate, m.p. 201–204° dec., yield 0.89 g. (95%). The iodide salt was discovered (yellow) and was therefore converted to the perchlorate, colorless needles, m.p. 193.5–195.5°, identical with the authentic N-(5,5-dimethyl-3-N′-pyrrolidylcyclohex-3-en-1-ylidene)-pyrrolidinium perchlorate (XIVc).

Reaction of 5,5-Dimethyl-3-N-pyrrolidylcyclohex-2-en-1-one Methiodide with Dilute Hydroiodic Acid.—When a solution of 5,5-dimethyl-3-N-pyrrolidylcyclohex-2-en-1-one methiodide was heated under reflux for 30 minutes with 10% hydriodic acid, an 88% recovery of impure methiodide was realized. In a similar experiment in which the reaction time was increased to 24 hours the crude product, m.p. 110–148° dec., was recrystallized from methanol–ethyl acetate to yield 32% of material, m.p. 195–197° dec., which was shown to be somewhat impure 5,5-dimethyl-3-N-pyrrolidylcyclohex-2-en-1-one hydriodide by recovery of the base in 79% yield and its identity with the 5,5-dimethyl-3-N-pyrrolidylcyclohex-2-en-1-one described earlier.

N-(3-N′-Pyrrolidylcyclohex-2-en-1-ylidene)-pyrrolidinium Iodide (XVIII).—A solution of 6.61 g. (0.040 mole) of 3-N-pyrrolidylcyclohex-2-en-1-one,[6] m.p. 81–82°, in 40 ml. of methyl iodide was heated under reflux for 18 hours. A second liquid phase separated. The excess methyl iodide was removed on the steam-bath. The viscous oil could not be induced to crystallize either alone or from methanol–ethyl acetate solvent. The crude methiodide XVII was dissolved in 15 ml. of methanol, and 2.98 g. (0.042 mole) of pyrrolidine was added. Evolution of heat was observed. The solution was heated, and sufficient ethyl acetate (20 ml.) was added to produce cloudiness. A few milliliters of methanol cleared the solution. The solution was then evaporated on the steam-bath until separation of solid began. The product was separated by cooling and filtration, m.p. 251–252.5° dec., yield 7.54 g. (54%). An additional 1.36 g. (10%) of less pure material could be obtained from the mother liquor. This compound was recrystallized from methanol–ethyl acetate as pale yellow needles, m.p. 251–252° dec., $\nu_{\max}^{\text{Nujol}}$ 1556 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{23}IN_2$: C, 48.56; H, 6.69; N, 8.09. Found: C, 48.69; H, 6.78; N, 7.96.

N-(3-N′-Pyrrolidylcyclohex-2-en-1-ylidene)-pyrrolidinium perchlorate was prepared by adding 0.30 ml. of 70% perchloric acid (containing 0.0035 mole) to a solution of 1.04 g. (0.0030 mole) of the iodide XVIII described in the preceding paragraph in 30 ml. of water. The precipitate was recrystallized from water as colorless needles, m.p. 231.5–233° dec., yield 0.71 g. (74%), $\nu_{\max}^{\text{Nujol}}$ 1556 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{23}ClN_2O_4$: C, 52.74; H, 7.27; N, 8.79. Found: C, 52.93; H, 7.16; N, 8.89.

N-(4-N′-Pyrrolidyl-3-penten-2-ylidene)-pyrrolidinium Iodide (XX).—To a solution of 6.18 g. (0.020 mole) of 4-N-pyrrolidyl-3-penten-2-one ethiodide (XIX) in 50 ml. of acetone was added 1.70 g. (0.024 mole) of pyrrolidine. Evolution of heat was noted. The solution was warmed on the steam-bath, and 100 ml. of ethyl acetate was added. The product which separated was recrystallized from acetone–ethyl acetate as pale yellow needles, m.p. 144.5–146.0°, yield 4.70 g. (70%), $\nu_{\max}^{\text{Nujol}}$ 1553 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{23}IN_2$: C, 46.71; H, 6.93; N, 8.38. Found: C, 46.91; H, 7.04; N, 8.26.

1,1′-*m*-Phenylenedipyrrolidine.—To a stirred mixture of 55.3 g. (0.40 mole) of anhydrous potassium carbonate and 10.81 g. (0.10 mole) of *m*-phenylenediamine in 200 ml. of absolute ethanol was added over a period of about 10 minutes 43.2 g. (0.20 mole) of 1,4-dibromobutane. The reaction mixture was stirred at the reflux temperature for 12 hours, cooled and filtered, and the salts were washed with ethanol. The filtrate was evaporated to a volume of about 60 ml., cooled and filtered. The crystals which were obtained were washed with ethanol and air-dried to yield 5.82 g. (27%) of colorless prisms of 1,1′-*m*-phenylene-dipyrrolidine, m.p. 92–93°. The salts were extracted repeatedly with boiling alcohol and the extracts were combined with the mother liquor. The alcohol was removed, and the residue (which solidified on cooling) was distilled through a Holzman column. The fraction boiling at 170–178° (1.6–2.0 mm.) constituted most of the distillate. It solidified on cooling and melted at 78–86°, yield 5.15 g. (24% additional). Recrystallization from ethanol gave colorless prisms, m.p. 92–93°. The infrared spectrum exhibited no N–H stretching absorption and was consistent with the structure assigned.

Anal. Calcd. for $C_{14}H_{20}N_2$: C, 77.73; H, 9.32; N, 12.95. Found: C, 77.98; H, 9.10; N, 12.95.

The physical properties observed did not agree with those previously reported by Yuryev *et al.*[42] These authors reported: b.p. 137–139° (8 mm.), $d^{20}{}_4$ 1.071, $n^{20}{}_{\text{D}}$ 1.5910. The only proof of structure was the molar refraction, nitrogen analysis, and method of synthesis. As the latter involved reaction of *m*-phenylenediamine with tetrahydrofuran over alumina at 400°, a procedure which might lead to complications, it was concluded that these authors did not have pure 1,1′-*m*-phenylenedipyrrolidine.

Infrared—$\overset{|}{\underset{|}{\text{N}}}{}^{+}$—H Stretching Frequency for a Tertiary Amine Perchlorate.—Quinolizidine perchlorate (Nujol) was found to exhibit a strong sharp band at 3050 cm.$^{-1}$.

(42) Y. K. Yuryev, L. E. Alexandrov, A. V. Arbatsky, V. M. Karatayev, 1. K. Korobschyna and M. A. Pryanishnikova, *Zhur. Obshcheī Khim.*, **19**, 1730 (1949).

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Rates of Condensation of Sodio Ketones with Esters to Form Sodio β-Diketones in Ether Solution

BY DOUGLAS G. HILL, JOHN BURKUS[1] AND CHARLES R. HAUSER

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Bimolecular rate constants were obtained for a number of acylations of sodio ketones with esters in dilute ether solution at 0 and 30°. The sodio ketones were prepared by means of sodium triphenylmethide. In general the rates of acylation of sodio methyl isobutyl ketone with various esters parallel qualitatively those reported for the alkaline hydrolysis of the esters. Evidence is presented for the intermediate formation of an addition product from the sodio ketone and ester. The formation of this intermediate is considered to involve the nucleophilic attack of the ketone anion on the carbonyl group of the ester within a coördination complex. A lithio ketone underwent acetylation more slowly than the corresponding sodio ketone.

The acylation of a methyl ketone with a methyl or ethyl ester to produce a β-diketone may be effected by means of a strong base such as sodium ethoxide, sodium amide or sodium triphenylmethide.[2] The reaction is called a Claisen condensation. The initial function of the base is to

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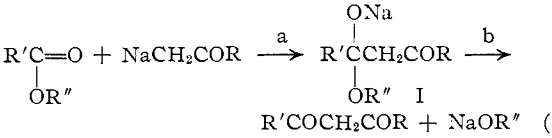
[1] Du Pont Fellow, 1952–1953.

[2] See C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, Chapter 3.

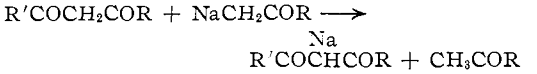
ionize an α-hydrogen of the ketone to form the sodio ketone which is the reactive intermediate. Although the equilibrium of this acid–base reaction with sodium ethoxide is probably on the side of the unchanged ketone, that with the more strongly basic sodium amide or sodium triphenylmethide is far on the side of the sodio ketone.[2] Indeed the acid–base reaction may be carried out as a titration with sodium triphenylmethide, the characteristic red color of which serves as its own indicator (equation 1).

$$HCH_2COR + \underset{\text{(red)}}{NaC(C_6H_5)_3} \xrightarrow{\text{ether}} NaCH_2COR + \underset{\text{(colorless)}}{HC(C_6H_5)_3} \quad (1)$$

In the present investigation several sodio ketones were prepared in this manner, and their rates of condensation with certain esters to form β-diketones were determined in ether solution at 0° and 30°. The condensation has generally been represented by equations 2 and 3, the β-diketones being obtained in the reaction mixtures as their sodium derivatives.[2]



$$R'\underset{OR''}{C}{=}O + NaCH_2COR \xrightarrow{a} R'\overset{ONa}{\underset{OR''}{C}}CH_2COR \;\; \text{I} \xrightarrow{b} R'COCH_2COR + NaOR'' \quad (2)$$



$$R'COCH_2COR + NaCH_2COR \longrightarrow R'CO\overset{Na}{C}HCOR + CH_3COR \quad (3)$$

Evidence is presented below for the intermediate formation of the addition product I from the sodio ketone and the ester (step a, equation 2). The β-diketone might also be an intermediate as indicated in step b of equation 2, or the elimination of ethoxide ion from intermediate I might be accompanied by the simultaneous removal of α-hydrogen to form directly the sodio β-diketone. In either event the kinetics should be the same, since either should be relatively rapid compared to the rate of formation of intermediate I.

Evidence was obtained that, if the β-diketone were an intermediate, it would be converted very rapidly to its sodium derivative by a sodio ketone (equation 3). Thus, this acid–base reaction evidently occurred within a few seconds on adding isovalerylacetone to sodio methyl isobutyl ketone, followed by Dry Ice, since only the β-diketone and ketone were recovered. None of the carbonation product of the ketone was isolated even though a 70% yield of the ketone carboxylic acid was obtained on treating the sodio ketone itself with Dry Ice. The sodio β-diketone was shown not to produce an isolable carbonation product under similar conditions.

The rates of condensation of the sodio ketones with esters were followed by stopping the reaction at appropriate intervals of time with 1 *M* acetic acid, and converting the liberated β-diketone to its copper chelate which was measured colorimetrically.[3] This method was shown to be practically quantitative (96–99%) and reproducible within 2%.

On the assumption that step b in equation 2 is much faster than step a, so that the latter is rate controlling, the bimolecular differential equation would be

$$dx/dt = k(a - 2x)(b - x)$$

where *a* and *b* are the initial concentrations of the sodio-ketone and ester, respectively, and *x* is the concentration of the diketone (actually its sodium salt). This modification of the usual bimolecular equation is required because a second mole of the sodio ketone is used in converting the β-diketone to its sodium derivative (equation 3).[4] The integrated equation which results is

$$k = \frac{2.303}{t(a - 2b)} \log \frac{b(a - 2x)}{a(b - x)}$$

In agreement with this equation, a straight line was obtained from the rates of condensation in dilute solution when the logarithmic term was plotted against time. A typical plot is shown in Fig. 1 for the reaction of sodio methyl isobutyl ketone with ethyl acetate at 30°. This reaction was followed to 72% completion, the initial concentrations being 0.2203 *M* for the ketone and 0.0939 *M* for the ester. The range of concentrations over which this reaction follows the bimolecular equation is indicated in Table I.

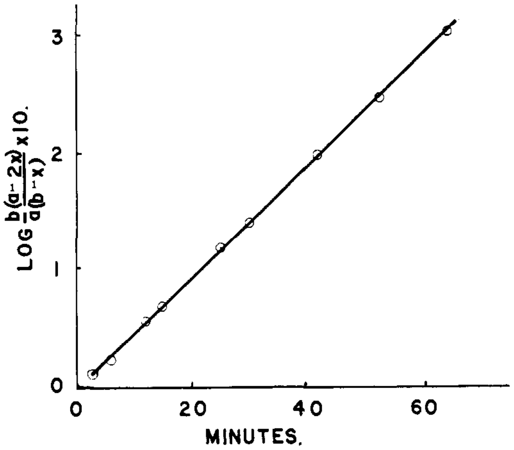


Fig. 1.—Typical plot of experimental data for acylation of sodio methyl isobutyl ketone (0.220 *M*) with ethyl acetate (0.09 *M*) at 30°.

TABLE I

CONDENSATION OF SODIO METHYL ISOBUTYL KETONE WITH ETHYL ACETATE AT 30°

Initial concentrations, molar Sodio ketone	Ester	Completed, %	Time, min.	Constant (from slope)
0.2203	0.0939	86	65	0.315
.1105	.0462	86	120	.312
.1197	.0504	87	120	.316
.2410	.2035	71	10	.306

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[3] This method was developed in this Laboratory by Dr. F. W. Swamer in connection with another study.

[4] It should be pointed out that a second mole of the sodio ketone is required even in the presence of the sodium alkoxide formed as a by-product in equation 2. The latter base might neutralize the β-diketone by a reaction similar to equation 3, but the resulting alcohol would then react with the sodio ketone. To confirm this, an experiment using the reactants of Table I was carried out in the presence of an excess of sodium ethoxide, added at the start. A constant identical to that obtained in its absence was found.

It will be noted that the closely agreeing constants from the first three runs were obtained in dilute solution with an excess of ketone. In such cases, the points do not fall more than 5% off the straight line and show a random scatter. The fourth experiment in more concentrated solution gives a somewhat lower constant, which actually is only an average value obtained from a straight line drawn through points that would more accurately describe a curve. This behavior is generally found in relatively more concentrated solutions, and is shown for a slower and thus more precisely measured case in Fig. 2. Here the logarithmic term from the bimolecular equation is plotted against time for the reaction of sodio methyl isobutyl ketone (0.215 *M*) with ethyl benzoate (0.185 *M*). In general, a second-order reaction, such as step a, responds more rapidly to changes in concentration than does a first-order reaction, as postulated for step b. Therefore, in higher concentrations the hypothesis that step b is much the faster becomes invalid, and the differential equation should be

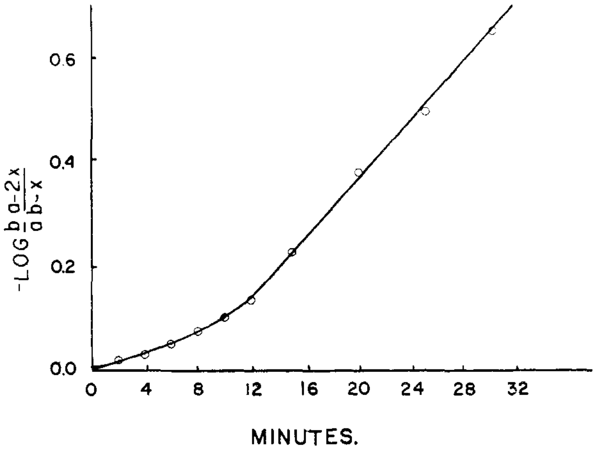

Fig. 2.—Typical plot of experimental data at relatively high concentration; acylation of methyl isobutyl ketone (0.215 *M*) with ethyl benzoate (0.185 *M*) at 30°.

$$\frac{d(c + x)}{dt} = k(a - c - 2x)(b - c - x)$$

where *c* represents the concentration of intermediate. An explicit solution of this equation has not been found, so that we were restricted to dilute solutions where step b is fast.

Cases in which the ester concentration exceeded that of the sodio ketone gave curves in the bimolecular logarithmic plot, so that the simpler equation did not apply. If the explanation offered above is correct, this behavior with excess ester might be expected.

The rate constants obtained at low concentration and with excess ketone for reactions between sodio methyl isobutyl ketone and various esters are given in Table II, while those for reaction between several sodio ketones and ethyl acetate are presented in Table III. The rate constants were generally reproducible to within 4%. Several Arrhenius activation energies and entropies of activation are included in the tables. These values are not very precise, but their changes with changing reactants are of interest.

TABLE II

CONDENSATION OF SODIO METHYL ISOBUTYL KETONE WITH VARIOUS ESTERS IN DILUTE SOLUTION

Ester	Rate constants, liter/mole/min. Temp., °C. 0	30	E_{Att}, kcal./mole	ΔS, kcal./mole/deg.
Ethyl acetate	0.0231	0.315	14.1	−24.4
Isopropyl acetate	.00108	.0467	20.6	− 7.4
t-Butyl acetate	Very slow		..	....
Phenyl acetate	....	13.6[a]	..	....
Ethyl benzoate	.0064	0.156	17.5	−15.2
Phenyl benzoate	4.35	13.4[a]	6.2	−43.4
Ethyl isobutyrate	....	0.0151	..	....
Ethyl isovalerate	....	.0092	..	....

[a] An approximate value. The condensation was too fast for precise measurement.

TABLE III

CONDENSATION OF ETHYL ACETATE WITH VARIOUS SODIO KETONES IN DILUTE SOLUTION

Ketone (sodio salt)	Rate constant, liter/mole/min. Temp., °C. 0	30	E_{Arr}, kcal./mole	ΔS, cal./mole/deg.
Methyl propyl	0.00461	0.0663	14.5	−26.4
Methyl isopropyl	.00561	.0653	13.8	−29.2
Methyl *t*-butyl	.00214	.0242	13.2	−33.1
Methyl isobutyl	.0231	.315	14.1	−24.4
Acetophenone	.00156	.0211	15.6	−25.6
Acetomesitylene	Very slow		..	....

It can be seen from Table II that the relative rates of condensation of sodio methyl isobutyl ketone with various esters are those which might be expected on the basis of equations 2 and 3. In general these rates parallel qualitatively those reported for the alkaline hydrolysis of the esters.[5] Moreover, the fact that the rate with ethyl isovalerate is slower than that with ethyl isobutyrate is in agreement with Newman's rule of six.[6]

It can be seen from Table III that the rates of condensation of ethyl acetate with various sodio ketones varied only two- or three-fold with the exception of the relatively rapid rate with sodio methyl isobutyl ketone and the very slow rate with sodio acetomesitylene. Apparently a steric factor plays a predominant role with the latter sodio ketone.[7]

A comparison of the energies and entropies of activation given in Tables II and III shows that these factors are more responsive to changes in the ester than to changes in the sodio ketone. Moreover, the entropy changes occur generally in the inverse order so that an increase in negative entropy is associated with a decrease in the Arrhenius energy.

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(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 211.

(6) M. S. Newman, THIS JOURNAL, **72**, 4783 (1950).

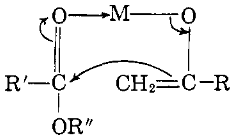
(7) In connection with the present work, an indication was obtained that sodio acetomesitylene and sodio methyl isobutyl ketone are stronger bases than sodio acetophenone. Thus, when acetophenone was added to an equivalent of either of the two former sodio ketones in liquid ammonia and the reaction mixture carbonated after replacing the ammonia by ether, the only ketone carboxylic acid obtained was benzoylacetic acid (50–60% yields). This conclusion is of course valid only on the assumption that the acid-base reaction to form the sodio acetophenone was not due solely to the precipitation of this sodio ketone.

While the deviations from the bimolecular equation indicate that the rate of step b was comparable to that of step a with alkyl esters in relatively concentrated solutions, step b might be expected to be faster than step a with phenyl esters even in the more concentrated solutions, since the phenoxy group should be eliminated from intermediate salt I much more readily than an alkoxy group. In agreement with this, the bimolecular equation was followed and a straight line obtained for the rate of acylation of sodio acetophenone with phenyl isobutyrate in concentrations of 0.207 and 0.152 *M*, respectively. These concentrations are of the order of those that gave the type of curve shown in Fig. 2 for an alkyl ester. The rate constant found in this reaction (at 30°) was 0.79. Essentially the same constant (0.72) was obtained when the concentrations of this sodio ketone and ester were 0.0921 and 0.0337 *M*, respectively.

These results may be interpreted as evidence that intermediate addition product I has a real existence. Bender[8] has presented evidence for the existence of a similar intermediate in the alkaline hydrolysis of esters.

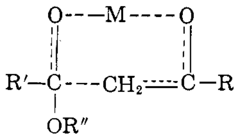
An alternative explanation for the failure of the bimolecular equation in relatively concentrated solutions might be that dimers (or polymers) of the sodio ketones exist in ethereal solution, and that their dissociation should be included in the rate equation. Actually Zook and Rellahan[9] have recently presented evidence that sodio butyrophenone does exist as a dimer in ether solution at concentrations in the range of our experiments. However, since no change in the extent of dimerization with concentration was observed, this explanation seems less attractive.

The mechanism of formation of intermediate I would presumably involve the nucleophilic attack of the ketone anion on the carbonyl group of the ester. However, the ketone anion is evidently not dissociated from the sodium cation since sodio ketones were found in another investigation[10] not to exhibit a detectable electrical conductivity in ether solution. Thus, whereas sodium triphenylmethide (0.25 *M*) shows an appreciable conductivity in this solvent, the addition of an equivalent of acetophenone or methyl isobutyl ketone caused the conductivity to vanish (resistance > 2.5 × 10^6 ohms). Therefore the sodio ketones should probably be regarded as ion-pairs (dipoles) rather than as free ions. In line with this the nucleophilic attack of the ketone anion on the ester may be considered to occur through coördination complex II (M = Na), the transition state for which may be represented by complex III.



II, M = metal

(coördination complex)



III, M = metal

(transition state)

In support of this mechanism the rate was found to be influenced considerably by the metallic cation (*M*). Thus, whereas the rate constant for the acylation of sodio methyl isobutyl ketone with ethyl acetate was 0.315 at 30°, that for the analogous acylation of the corresponding lithio ketone was only 0.0864 at this temperature. The lithio ketone was prepared by means of lithium triphenylmethide.[11]

It should be mentioned that when potassium triphenylmethide was prepared in ether by the method used for the sodium reagent, the resulting red suspension settled very slowly leaving a solution too dilute for accurate rate measurements.

Experimental

Esters and Ketones.—With the exceptions given below, all esters and ketones were obtained from commercial sources and purified. The esters were washed with 5% sodium carbonate solution, followed by a saturated solution of calcium chloride. Ketones were refluxed with a little potassium permanganate. Both were dried over Drierite and distilled. All of the compounds boiled within a 0.2° range or better.

Phenyl isobutyrate was prepared as described previously.[12] This ester boiled at 113–113.5° at 35 mm. (reported 118–119° at 35 mm.).

Acetomesitylene was prepared from acetic anhydride and mesitylene as described by Noller and Adams.[13] It boiled at 119–120° at 17 mm., $n^{28}\text{D}$ 1.5124; reported b.p. 122–122.5° at 19 mm.,[14] $n^{20}\text{D}$ 1.5175.[13]

Sodium Triphenylmethide.—Ethyl ether solutions of sodium triphenylmethide were prepared in two-liter bottles essentially as described previously.[15] The concentration of the solutions, as determined by decomposition with water and titration with standard acid, varied from 0.25 to 0.30 *M*.

The storage and titration apparatus for the triphenylmethide solutions was a modification of an earlier dispenser used in this Laboratory[16] and of one described by Holmes.[17] It consists of an all-glass system in which movement of a mercury column displaces an ether solution of the reagent, the amount dispensed being read on the mercury buret. With this apparatus, solutions of sodium triphenylmethide have been stored and used over a period of five weeks with no measurable change in concentration.

Rate Measurements.—The reaction was carried out in Pyrex tubes, 28 mm. × 23 cm., having a $^{19}/_{38}$ $\mathrm{\$}$ female joint at the top and side arm with stopcock. The air originally in the tube was displaced by a stream of nitrogen which had been purified by vanadyl sulfate[18] followed by concentrated sulfuric acid and finally by calcium chloride. A known amount of ketone, sufficient for one reaction, was delivered into the nitrogen-filled tube with a calibrated pipet and, with nitrogen flowing, it was then titrated with the ether solution of sodium triphenylmethide until the first appearance of the characteristic red color of the triphenylmethide ion. The resulting sodio ketone solution, still under nitrogen in the tube, was placed in a thermostated water-bath, and after five minutes a known amount of ester (generally about one-half equivalent) in ether solution of known concentration was added and the stoppered tube thoroughly shaken. The halfway time of ester delivery was considered the starting time of the condensation. The reaction was stopped after the desired time interval by the addition of 0.5 ml. excess of 1.00 *M* acetic acid, the equiva-

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[8] M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

[9] H. D. Zook and W. L. Rellahan, *ibid.*, **79**, 881 (1957).

[10] D. G. Hill, J. Burkus, S. M. Luck and C. R. Hauser, unpublished results.

[11] A 0.05 *M* solution of lithium triphenylmethide in ether was obtained when this reagent was prepared from triphenylchloromethane and lithium amalgam by an adaptation of the method employed for sodium triphenylmethide; see ref. 15.

[12] E. H. Man, F. W. Swamer and C. R. Hauser, THIS JOURNAL, **73**, 801 (1951).

[13] C. R. Noller and R. Adams, *ibid.*, **46**, 1893 (1924).

[14] R. W. Hufferd and W. A. Noyes, *ibid.*, **43**, 925 (1921).

[15] C. R. Hauser and B. Hudson, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, Chapter 9.

[16] E. Baumgarten and C. R. Hauser, THIS JOURNAL, **66**, 1039 (1944).

[17] F. E. Holmes, *Anal. Chem.*, **22**, 512 (1956).

[18] L. Meites and T. Meites, *ibid.*, **20**, 984 (1948).

lent being known from the amount of sodium triphenylmethide used in the titration. Each tube gave one point on the rate curve.

The occasional appearance of a precipitate did not affect the rate. The precipitate dissolved in the acetic acid added to stop the reaction, and was presumably sodium alkoxide.

To the acidified reaction mixture was added an excess of 10% aqueous copper acetate, and the resulting copper chelate of the β-diketone extracted with ethyl ether. The ether was removed by distillation, and the residue taken up in chloroform. The solution was diluted to 100 ml. with more chloroform in a volumetric flask. The optical density of the chloroform solution then was determined in a Cenco photelometer, using a red filter. The concentration of copper chelate, and thus of the diketone, was determined by comparison of the photelometer reading with that of a series of known concentrations of the copper chelates.

The identity over the entire visible spectrum of the absorption of an authentic sample of the copper chelate of *n*-butyrylisovalerylmethane with that obtained from the reaction of methyl isobutyl ketone and ethyl butyrate under the conditions of the rate measurements showed that no interfering colored substances were present. All the copper chelates of β-diketones were found to follow the Lambert–Beer law. Although the presence of a large amount of acid interfered with the determination, presumably by preventing complete extraction of the copper chelate, it was shown experimentally that if the excess did not exceed 0.5 ml. of 1 *M* acetic acid, the colorimetric method was reproducible to within 2%.

The rate constants given in Tables I and II were calculated from the integrated equation, using the colorimetric diketone concentration obtained as just described, and the initial ester and sodio ketone concentrations. They are average constants obtained from three to six different reaction tubes kept in the thermostat for different lengths of time.

Reaction of Sodio Methyl Isobutyl Ketone with Isovalerylacetone.—An ether solution of 1.60 g. (0.016 mole) of methyl isobutyl ketone was converted to its anion with an equivalent of sodium triphenylmethide, and 2.58 g. (0.0182 mole) of isovalerylacetone added. The reaction mixture was thoroughly shaken and immediately poured onto an excess of powdered Dry Ice, the elapsed time being less than five seconds.

When carbon dioxide ceased to be evolved, water and ether were added and, after shaking, the layers were separated. The aqueous layer was extracted three times with ether and the extracts combined with the ether layer. Careful acidification of the aqueous layer (below 15°) failed to give either an oil or a precipitate, and the acidified solution gave negative tests with ferric chloride and with 2,4-dinitrophenylhydrazine. The combined ether solution was extracted several times with 10% sodium hydroxide until the ether layer failed to give a positive ferric chloride test. The sodium hydroxide solution was then acidified and extracted with ether. After distilling the ether, the residue was dissolved in methanol and the solution added to copper acetate solution. Upon filtering and air drying, a yield of 2.3 g. of copper compound was obtained, corresponding to 73% of the original isovalerylacetone.

The ether remaining after the sodium hydroxide extraction was washed with water, dried and distilled. The residue was transferred to a Büchner funnel and washed with methanol. The methanol washings were treated with 2,4-dinitrophenylhydrazine to give, after recrystallization from ethanol, 4 g. of the bright yellow 2,4-dinitrophenylhydrazone of methyl isobutyl ketone, corresponding to 89% of the original ketone. The compound melted at 93°, reported[19] m.p. 95°.

In a blank experiment, an ether solution of the sodio methyl isobutyl ketone was carbonated with Dry Ice. The mixture was extracted with water and, after extracting with ether to remove any unreacted ketone, the aqueous solution was acidified. The liberated ketone carboxylic acid was taken up in ether and, after drying, the solvent was removed. Decarboxylation was effected on the steam-bath (0.5 hr.), and the residual ketone converted to its 2,4-dinitrohydrazone. There was obtained a 70% yield of this derivative, m.p. 95°.[19]

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(19) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 262.

DURHAM, N. C.

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

The Synthesis and Polymerization of Tetrafluoroallene[1,2]

BY THOMAS L. JACOBS AND RONALD S. BAUER[3,4]

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Tetrafluoroallene was synthesized by dehydrobromination of 3-bromo-1,1,3,3-tetrafluoropropene or 1,3-dibromo-1,1,3,3-tetrafluoropropane and less satisfactorily by zinc debromination of 2,3-dibromo-1,1,3,3-tetrafluoropropene. Small amounts were also obtained by pyrolysis of 3-bromo-1,1,3,3-tetrafluoropropene. Tetrafluoroallene polymerizes at room temperature under autogenous pressure to an insoluble, sharp-melting, highly crystalline powder shown by X-ray and infrared data to be a linear polymeric fluorocarbon with the group $=CF_2$ on alternate carbons along the chain. When this polymerization was inhibited, mild heating converted the monomer to perfluoro-1,2-dimethylenecyclobutane.

Tetrafluoroallene is of special interest as a monomer which might yield useful polymers. When we began attempts to prepare this compound it had not been mentioned in the literature. In 1954, a brief report of its synthesis by the reaction of 2-chloro-3-iodo-1,1,3,3-tetrafluoropropene with zinc in dioxane appeared.[5] However, in a definitive paper published in 1957, Fainberg and Miller reported that this reaction gave an excellent yield of the coupling product, decafluoro-1,5-hexadiene,[6] and no mention was made of tetrafluoroallene or of any other low boiling products.

Dehydrohalogenation has occasionally been used to prepare allenes, but the method is usually unsatisfactory because the isomeric acetylenes accompany the desired products. There is no report in the literature of the preparation of a haloallene by this reaction. However, the hydrogen atoms

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(1) This report is taken from a dissertation submitted by Ronald S. Bauer to the graduate school of the University of California, Los Angeles, in partial fulfillment of the requirements for the Ph.D. degree, June, 1958. The material was presented at the San Francisco Meeting of the American Chemical Society, April, 1958 (Abstracts of that Meeting, p. 51-N). This research was sponsored by the Office of Ordnance Research, U. S. Army.

(2) A preliminary report of this work has appeared, T. L. Jacobs and R. S. Bauer, THIS JOURNAL, **78**, 4815 (1956).

(3) Dow Chemical Co. Fellow, 1957–1958.

(4) We wish to thank Dr. Arnold H. Fainberg for advice during earlier stages of the work.

(5) W. T. Miller, Jr., U. S. Patent 2,668,182, Feb. 2, 1954; *C. A.*, **49**, 2478 (1954).

(6) A. H. Fainberg and W. T. Miller, Jr., THIS JOURNAL, **79**, 4170 (1957).