TABLE I

DECOMPOSITION OF TRICHLOROACETIC ACID IN GLYCEROL. SPECIFIC REACTION VELOCITY CONSTANTS AT 110.1°

Time, sec.	Vol. CO_2 at S.T.P., ml.	Completion of reacn., %	Spec. reacn. velocity
180	11.6	29.0	0.00191
240	14.8	37.0	.00192
300	17.8	44.5	.00196
360	20.4	51.2	.00192
420	23.0	57.6	.00204
480	25.3	63.5	.00208
540	27.2	68.2	.00211
600	28.9	72.3	.00213

One run was made at 109.0° on a 50% by weight mixture of glycerol–water yielding a value of k of 0.00259 sec.$^{-1}$, or nearly twice the value in the case of the 95% glycerol run, a result consistent with the proposed mechanism.

Decomposition of Trichloroacetic Acid Alone.—The average volume of carbon dioxide at S.T.P. evolved per minute from one mole of trichloroacetic acid at 156.4° was 1.51 ml.; at 159.4°, 2.5 ml.; at 163.8°, 5.03 ml.; and at 166.6°, 8.37 ml. These results yield specific reaction velocity constants in sec.$^{-1}$ of 1.12×10^{-6}, 1.865×10^{-6}, 3.71×10^{-6} and 6.17×10^{-6}, respectively. For the temperature range involved E is 60,700 cal.

DEPARTMENT OF CHEMISTRY
PANHANDLE AGRICULTURAL AND MECHANICAL COLLEGE
GOODWELL, OKLAHOMA

Preparation of N-Substituted Hydrazines from Amines and Chloramine

BY L. H. DIAMOND AND L. F. AUDRIETH

RECEIVED FEBRUARY 14, 1955

We have shown in a recent publication[1] that the Raschig hydrazine synthesis may be modified to yield simple monoalkyl hydrazines. The interaction of chloramine with amines has now been shown to constitute a general preparative method as illustrated by the conversion of *n*-hexylamine and cyclohexylamine into the corresponding hydrazines, of allylamine to allylhydrazine, ethanolamine to β-hydroxyethylhydrazine, ethylenediamine to β-aminoethylhydrazine, and morpholine to N-aminomorpholine. Attempts to prepare hydrazinoacetic acid from glycine by this method were unsuccessful.

Experimental

The experimental conditions were similar to those employed previously for the preparation of the simpler monosubstituted aliphatic hydrazines.[1] The cold reaction mixture, consisting of an aqueous chloramine solution prepared from hypochlorite and ammonia containing 0.04 mole of NH_2Cl in 250 ml., 0.25 g. of gelatin and the desired amine (mole ratio NH_2Cl:amine = 1:8), was allowed to warm to room temperature over a period of one hour and then heated on a steam-bath for an additional 10 to 30 minutes to ensure completion of the reaction. An aliquot of the reaction mixture then was analyzed by the iodate procedure to determine the percentage conversion of the amine into the corresponding hydrazine. The N-substituted hydrazines were isolated as salts either by concentration of the reaction mixture for the removal of the excess amine and water, followed by recovery of an aqueous fraction which was converted to the hydrochloride or the sulfate (method A), or by neutralization of the reaction mixture with acetic acid followed by treatment with either benzaldehyde or salicylaldehyde for conversion to the azine, extraction of the latter with ether and treatment of the ether solution with aqueous oxalic acid followed by distillation for the removal of the aldehyde and ether and then subsequent concentration to crystallization, after which the oxalate was purified for analysis (method B).

***n*-Hexylhydrazine Hydrogen Oxalate.**—Method B: from 32.0 g. of *n*-hexylamine; 57% yield. Most of the N-substituted hydrazine was found to separate from solution along with the excess amine as a non-aqueous water-insoluble layer upon cooling. The reaction mixture was neutralized with 200 ml. of glacial acetic acid, filtered, and the filtrate condensed with 8 g. (0.069 mole) of benzaldehyde and extracted with three 75-ml. portions of ether. The ether extracts were added to 7.5 g. of oxalic acid dihydrate dissolved in 100 ml. of water. The suspension was steam distilled to remove benzaldehyde, and *n*-hexylhydrazine hydrogen oxalate was obtained by concentration of the residue. The material was recrystallized from ethanol, m.p. 178°.

Anal. Calcd. for $C_8H_{18}O_4N_2$: C, 46.59; H, 8.80; N, 13.59. Found: C, 46.55; H, 8.91; N, 13.77.

Cyclohexylhydrazine Sulfate.—Method A: from 30.2 g. of cyclohexylamine; 60% yield. The product plus the excess of the amine formed a separate liquid phase. The reaction mixture was fractionated to remove the amine and the aqueous hydrazine fraction treated with an excess of sulfuric acid. Cyclohexylhydrazine hydrogen sulfate was obtained upon evaporation and recrystallized from methanol with the addition of ether, m.p. 117°.

Anal. Calcd. for $C_6H_{16}O_4N_2S$: C, 33.95; H, 7.60; N, 13.20. Found: C, 34.16; H, 7.80; N, 13.16.

Allylhydrazine dihydrochloride: from 18.9 g. of allylamine; 52% yield by analysis. The product was isolated by method A as the dihydrochloride, m.p. 133–35° (lit. 134–140°[2]).

β-Hydroxyethylhydrazine Hydrogen Oxalate.—From 19 g. of ethanolamine; 58% yield. The hydrogen oxalate, m.p. 106°,[3] was isolated from the reaction mixture using method B.

Anal. Calcd. for $C_4H_{10}O_5N_2$: C, 28.92; H, 6.07; N, 16.86. Found: C, 28.62; H, 6.19; N, 16.60.

β-Aminoethylhydrazine Dioxalate.—From 20 g. of ethylenediamine; 75% yield. The dioxalate, m.p. 206°,[3] was isolated from the reaction mixture by method B.

Anal. Calcd. for $C_6H_{13}O_8N_3$: C, 28.24; H, 5.14; N, 16.47. Found: C, 28.25; H, 5.11; N, 16.70.

N-Aminomorpholine: from 28 g. of morpholine. A yellow oil remained behind with the residual material upon distillation. The product was extracted with ether and then fractionated, that portion boiling at 162–165° being converted to the hydrochloride. N-Aminomorpholine hydrochloride was found to melt at 167° (lit. 164°[4]).

Anal. Calcd. for $C_4H_{11}N_2OCl$: C, 34.65; H, 8.00; N, 20.20. Found: C, 35.08; H, 8.03; N, 19.89.

Acknowledgment.—This investigation was carried out under the sponsorship of the Office of Ordnance Research as one phase of a fundamental study of the synthesis of hydrazine, Contract No. DA-11-022-ORD-828.

---

[1] L. F. Audrieth and L. H. Diamond, THIS JOURNAL, **76**, 4869 (1954).

[2] S. Gabriel, *Ber.*, **47**, 3028 (1914).

[3] G. Gever and K. Hayes, *J. Org. Chem.*, **14**, 813 (1949).

[4] L. Knorr and H. W. Brownsdon, *Ber.*, **35**, 4474 (1902).

NOYES LABORATORY OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

Reductive Cleavage of Esters and Lactones by Grignard Reagents

BY REYNOLD C. FUSON AND DONALD E. BRASURE[1]

RECEIVED JANUARY 29, 1955

Carboxylate ion displacement studies in the dimesitylmethyl ester series with Grignard reagents

---

[1] Socony-Vacuum Fellow, 1952–1953.

having marked reducing power revealed that the displacement was accompanied by reductive cleavage to give dimesitylmethane.[2] The reductive cleavage, which is analogous to that observed earlier in the reaction of dioxolones with *t*-butylmagnesium chloride,[3] has been realized also with triphenylmethyl acetate and with 3,3-diphenylphthalide. Both triphenylmethane and 1,1,1-triphenyl-2,2-dimethylpropane were isolated when triphenylmethyl acetate was treated with *t*-butylmagnesium chloride; and a small amount of *o*-benzohydrylbenzoic acid was obtained when the phthalide was treated with the same reagent. 9-Acetoxyanthracene reacted with the *t*-butyl reagent to give anthracene in a yield of 27%.

A dioxolone was prepared from benzaldehyde and mandelic acid and treated with *t*-butylmagnesium chloride. Reductive cleavage was not observed, however.

Experimental

Triphenylmethyl Acetate.—When triphenylmethyl acetate was treated with the *t*-butyl reagent, triphenylmethane and 1,1,1-triphenyl-2,2-dimethylpropane were obtained in yields of 10 and 20%, respectively. The melting point of the triphenyl derivative corresponded to that given by Gomberg, 185–187°.[4]

Anal. Calcd. for $C_{23}H_{24}$: C, 91.95; H, 8.05. Found: C, 92.02; H, 8.28.

3,3-Diphenylphthalide.—The reaction of *t*-butylmagnesium chloride with 3,3-diphenylphthalide, made by the interaction of phthalyl chloride and diphenylcadmium,[5] was carried out in the usual manner. The reaction mixture, in this case, turned a deep red when the phthalide was added to the Grignard reagent, the color persisting throughout the reaction. *o*-Benzohydrylbenzoic acid was obtained in a 14% yield when the alkaline wash solutions were acidified. The acid, melting at 160–162°, was identical with an authentic sample.[6] From the neutral portion a 60% recovery of phthalide was made.

9-Acetoxyanthracene.—To a Grignard reagent, prepared from 9.3 g. of *t*-butyl chloride and 2.4 g. of magnesium in 100 ml. of ether, was added a solution of 2.4 g. of 9-acetoxyanthracene in 40 ml. of ether. The reaction mixture was heated under reflux for an hour before being decomposed with an ice–hydrochloric acid mixture. The ether layer was washed with sodium carbonate solution and dried over anhydrous magnesium sulfate. Removal of the ether left 0.48 g. of red-orange crystals melting at 200–215°. Recrystallization of the compound from benzene raised the melting point to 214–217°; the melting point was not depressed when these crystals were mixed with an authentic sample of anthracene.

Preparation of 9-Acetoxyanthracene.—Fifty grams of acetic anhydride was added slowly to a solution of 12 g. of anthrone in 150 ml. of pyridine. After being heated under reflux for 15 minutes, the reaction mixture was cooled and poured into 500 ml. of ice-cold water. Treatment of the crystalline product with Darco and numerous recrystallizations from ethanol gave light yellow needles, m.p. 133–134°, yield 7.2 g. (44%).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.32; H, 4.94.

Preparation of the Dioxolone from Benzaldehyde and Mandelic Acid.—When the procedure for acetone–mandelic acid[2] was applied to mandelic acid and benzaldehyde, the dioxolone was obtained in a yield of 50%, m.p. 104–105°.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 74.98; H, 5.04. Found: C, 74.90; H, 5.21.

The infrared spectrum of this dioxolone contains an absorption band at 1780 cm.$^{-1}$, assignable to a carbonyl group.

THE NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

---

[2] R. C. Fuson, H. L. Jackson, J. A. Fuller, Jr., and D. E. Brasure, THIS JOURNAL, **76**, 499 (1954).

[3] R. C. Fuson and A. I. Rachlin, *ibid.*, **64**, 1567 (1942).

[4] M. Gomberg, *Ber.*, **35**, 1835 (1902).

[5] R. C. Fuson, S. B. Speck and W. B. Hatchard, *J. Org. Chem.*, **10**, 55 (1945).

[6] A. Baeyer, *Ann.*, **202**, 50 (1880); A. Drory, *Ber.*, **24**, 2563 (1891).

The Reaction between Propylene Oxide and the *t*-Butyl Grignard Reagent[1]

BY NORMAN G. GAYLORD AND LAWRENCE D. CAUL

RECEIVED JANUARY 15, 1955

The product of the interaction of the Grignard reagent and an epoxy compound may result from cleavage of the ring in either of the two possible directions or may evolve from an initial isomerization of the epoxide to an aldehyde or ketone, followed by the usual addition of the reagent to the carbonyl group. The actual course of any specific reaction is determined by the structures of the epoxide and the Grignard reagent, and in some cases by the reaction conditions.[2]

The reaction between *t*-butylmagnesium halides and propylene oxide has been the subject of conflicting reports. Stevens and McCoubrey[3] reported that the reaction of *t*-butylmagnesium chloride with the oxide gives 2,2-dimethyl-3-pentanol as well as propylene chlorohydrin. Huston and his co-workers, without referring to the earlier work, reported that the reaction with *t*-butylmagnesium bromide[4] as well as with the chloride[5] yields 4,4-dimethyl-2-pentanol.[6] The present investigation was undertaken to clarify this discrepancy.

Results

The mixture from the reaction of *t*-butylmagnesium chloride and propylene oxide, after decomposition with an aqueous ammonium salt and destruction of propylene chlorohydrin with concentrated alkali, yields an alcoholic component (I) which has proved to be 2,2-dimethyl-3-pentanol (II). This proof is based on the comparison of the physical and chemical properties of I to authentic samples of II and 4,4-dimethyl-2-pentanol (III). In addition, I was oxidized with chromic acid to a ketone (IV) and the physical and chemical properties compared to authentic samples of 2,2-dimethyl-3-pentanone (V) and 4,4-dimethyl-2-pentanone (VI).

The authentic products were prepared by unequivocal methods. II was prepared by the reaction of *t*-butylmagnesium chloride with propionaldehyde and III was prepared by the reduction of VI with lithium aluminum hydride. V was prepared by the reaction of the ethyl Grignard reagent with pivalamide and VI was prepared by the chromic acid oxidation of diisobutylene.

The 3,5-dinitrobenzoates, 1-naphthylurethans and phenylurethans of I, II and III and the 2,4-dinitrophenylhydrazones and semicarbazones of

[1] Abstracted from the M.S. Thesis of L. D. Caul, Canisius College June, 1954.

[2] N. G. Gaylord and E. I. Becker, *Chem. Revs.*, **49**, 413 (1951).

[3] P. G. Stevens and J. A. McCoubrey, THIS JOURNAL, **63**, 2847 (1941).

[4] R. C. Huston and C. O. Bostwick, *J. Org. Chem.*, **13**, 331 (1948).

[5] R. C. Huston and H. E. Tiefenthal, *ibid.*, **16**, 673 (1951).

[6] A summary of the conflicting evidence is given in reference 2, p. 430.