Oxidation of II by potassium periodate. Due to the sensitivity of II towards acids, the Malaprade reaction was carried out by 0.038*M* potassium periodate solution at *p*H = 6.5. The anhydrofructose (II) was added to the oxidizing system at room temperature, and the amount of the oxidant consumed was estimated by titration of aliquots with arsenic acid and iodine standard solutions. Actually no reaction could be detected, even after 2 days, as was also shown by optical rotation measurements.

2,3-Anhydrofructofuranose ditrityl ether (IV) was prepared by the method used for the tritylation of fructose.[21] To a solution of II 0.5 g. (0.003 mol.) in pyridine (5 ml.) was added trityl chloride (1.7 g., 0.006 mol.). The solution was kept at room temperature for 48 hr., then poured into crushed ice and shaken several times during 4 hr. The solid which separated was filtered, dissolved in a small amount of methanol, and reprecipitated by adding water. Several recrystallizations from ethanol yielded 100 mg. of elongated prismatic rods of IV, melting at 165°.

Anal. Calcd. for $C_{44}H_{38}O_5$: C, 81.88; H, 5.88. Found: C, 81.74; H, 5.74.

The infrared spectrum shows bands (cm.$^{-1}$) at 3420 (free OH), 3030 (C—H), 1590, 1080 (phenyl).

2,3-Anhydrofructofuranose ditosylate (V). A solution of II (1.1 g., 0.007 mol.) in pyridine (8 ml.) was mixed at 0° with a solution containing tosyl chloride (2.6 g., 0.015 mol., m.p. 67°) in pyridine (8 ml.) and allowed to stand at 0° for 3 hr. The temperature was then allowed to rise to 25° and remained so for 20 hr. After the reaction mixture was poured into crushed ice it was allowed to stand overnight, and the brown amorphous precipitate was separated by centrifugation. It was recrystallized first from aqueous methanol and then twice from absolute ethanol, yielding white cubes (500 mg.) of V, melting at 156°.

Anal. Calcd. for $C_{20}H_{22}O_9S_2$: C, 51.48; H, 4.68; S, 12.86. Found: C, 51.52; H, 4.86; S, 12.5. The infrared spectrum shows bands (cm.$^{-1}$) at 3546 (free OH), 1184 (O—SO$_2$).

Recrystallization of V from methanol afforded microcrystals of m.p. 147° containing one mole of methanol of crystallization which could not be removed easily.

Anal. Calcd. for $C_{20}H_{22}O_9S_2.CH_3OH$: C, 50.19; H, 5.17; S, 12.74. Found: C, 50.22; H, 4.86; S, 12.75.

This, upon recrystallization from absolute ethanol, again gave the ditosylate of melting point 156°.

Increasing the molar ratio of II/TsCl from 1:2 to 1:3 had no effect either upon the composition or on the yield of the reaction product. V was invariably produced.

Reaction of V with sodium iodide in acetone. A solution of V (820 mg.) in 10 ml. of dry acetone was mixed with a solution of sodium iodide (1.7 g.) in dry acetone (10 ml.). The resulting homogeneous mixture was placed in a Pyrex ampule, sealed, and then was heated for 48 hr. at 100°. After a few hours, yellowish crystals separated from the reaction system, the amount of which increased while the reaction progressed. At the end, the precipitate of sodium tosylate was filtered, washed several times with acetone, and its weight determined.

Anal. Calcd. for $C_7H_9O_4SNa$: C, 39.60; H, 4.25. Found: C, 39.46; H, 4.14.

From the filtrate, the solvent was removed by evaporation *in vacuo*, and the residue was dissolved in a chloroform-water mixture, washed with sodium thiosulphate and dried over anhydrous sodium sulphate. After removal of solvent under reduced pressure, the residue was crystallized from benzene, yielding an amorphous product, melting at 126–128°. It contained iodine, but could not be further purified by the usual methods.

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[21] B. Helferich, *J. prakt. Chem.*, **147**, 60 (1936).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Mechanism of Carbene Formation from *t*-Butyl Dichloroacetate[1]

WILLIAM E. PARHAM, FREDERIC C. LOEW, AND EDWARD E. SCHWEIZER

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A mechanism is proposed for the formation of dichlorocarbene from the reaction of *t*-butyl dichloroacetate and potassium *t*-butylate, involving a chlorination step with the formation of the intermediate *t*-butyl trichloroacetate.

In a previous communication[2] the reaction of *t*-butyl dichloroacetate(I) and potassium *t*-butylate in the presence of isobutylene was described and reaction (a) was suggested as a possible route for the formation of dichlorocarbene. The final product, 1,1-dichloro-2,2-dimethylcyclopropane(V), was isolated in 13% yield. Further experiments have furnished data which required that the simple mechanism (a) be replaced by the mechanism illustrated by steps (b) to (f), inclusive.

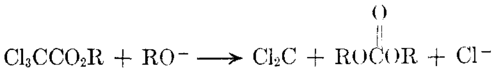
$$\underset{\text{I}}{Cl_2CHCO_2R} + RO^- \rightleftarrows Cl_2\bar{C}CO_2R \longrightarrow Cl_2C + CO + RO^- \quad \text{(a)}$$

$$Cl_2CHCO_2R + RO^- \rightleftarrows Cl\bar{C}H{-}CO_2R + ROCl \quad \text{(b)}$$

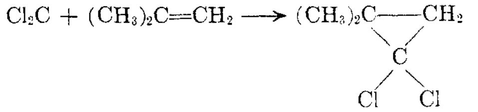
$$Cl\bar{C}HCO_2R + ROH \rightleftarrows \underset{\text{II}}{ClCH_2CO_2R} + RO^- \quad \text{(c)}$$

$$Cl_2CHCO_2R + RO^- \rightleftarrows Cl_2\bar{C}CO_2R + ROH \quad \text{(d)}$$

$$Cl_2\bar{C}CO_2R + ROCl \longrightarrow \underset{\text{III}}{Cl_3CCO_2R} + RO^- \quad \text{(e)}$$



$$Cl_3CCO_2R + RO^- \longrightarrow Cl_2C + \underset{\text{IV}}{RO\overset{\overset{\displaystyle O}{\|}}{C}OR} + Cl^- \quad \text{(f)}$$



V

(g)

It is proposed that *t*-butyl dichloroacetate is converted, in the presence of *t*-butylate, into a mixture of *t*-butyl monochloroacetate(II) and *t*-butyl tri-

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[1] This work was supported by a grant (G-7382) from the National Science Foundation.

[2] W. E. Parham and F. C. Loew, *J. Org. Chem.*, **23**, 1705 (1958).

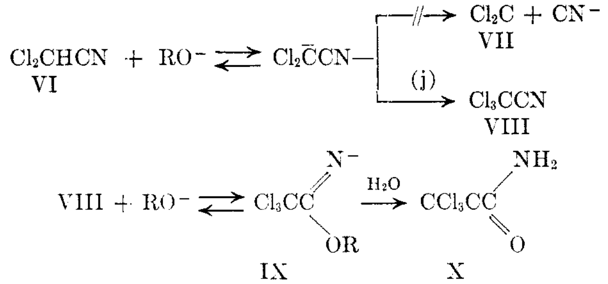
chloroacetate(III). The authors[2] have previously shown that compound II is converted into higher molecular weight condensation products in the presence of potassium *t*-butylate, whereas compound III is converted into dichlorocarbene and di*tert*-butyl carbonate(IV). Thus, if such a shift of chlorine occurs, the maximum yield of 1,1-dichloro-2,2-dimethylcyclopropane(V), obtained from compound I, would be less than one half of that obtained from pure compound III under the same conditions.

The reaction of equimolar ratios of pure *t*-butyl dichloroacetate(I), potassium *t*-butylate and *t*-butyl hypochlorite in the presence of isobutylene and pentane yielded 1,1-dichloro-2,2-dimethylcyclopropane (V, 45%) and di-*t*-butyl carbonate (IV, 55%), analyzed by gas chromatography. *t*-Butyl trichloroacetate(III) was also isolated in 5% yield. The yield of compound V was thus comparable to that obtained previously[2] from the reaction of *t*-butylate with *t*-butyl trichloroacetate(III) (see step f and g, i.e. 55% of compound V), establishing that chlorination of the initial *t*-butyl dichloroacetate(I) may be accomplished by positive halogen, and lending support for step e. Step b has not been substantiated because of the authors' inability to isolate any *t*-butyl hypochlorite; however, the intermediate formation of *t*-butyl hypochlorite as the chlorinating agent seems more feasible than chlorination of the *t*-butyl dichloroacetate carbanion by *t*-butyl dichloroacetate (h). Chlorination of carbanions by

$$\mathrm{Cl_2\bar{C}CO_2R + Cl_2CHCO_2R \longrightarrow Cl_3CCO_2R + Cl^{-}CHCO_2R} \quad \text{(h)}$$

t-butyl hypochlorite is well established.[3]

More compelling evidence for reactions of the type shown in equations b–e was obtained by a study of the reaction of dichloroacetonitrile(VI) and potassium *t*-butylate in the presence of isobutylene.



A considerable amount of tarry material resulted; no cyanide ion was formed, and trichloroacetamide (X, 10% yield) was isolated from the reaction mixture upon subsequent hydrolysis. The starting material was pure (vaporphase chromatography), thus the isolation of trichloroacetamide establishes a chlorination step in the above reaction analogous to that postulated earlier for the reaction with *t*-butyl dichloroacetate(I).

While the evidence at hand strongly supports the chlorination mechanism discussed (b–e), the results do not, of course, rule out Equation (a) as a possible source for the formation of dichlorocarbene from *t*-butyl dichloroacetate(I). However, attention was called earlier[2] to the fact that dichlorocarbene and *t*-butyl alcohol do react to form carbon monoxide; consequently, there are no data currently available supporting equation (a).

EXPERIMENTAL

Vapor-phase chromatography was carried out as previously described.[4]

The Reaction of t-Butyl Dichloroacetate (I) *with Potassium t-Butylate and t-Butyl Hypochlorite in the Presence of Isobutylene*. A mixture of *t*-butyl dichloroacetate[5] (46.25 g., 0.25 mole) and *t*-butyl hypochlorite[6] (27.14 g., 0.25 mole) was added over a 1.5-hr. period to a cold (−15°) mixture of powdered potassium *t*-butoxide[7] (0.25 mole), isobutylene (75 ml. at −80°, ca. 1 mole), and olefin-free pentane (125 ml.). The resulting mixture was stirred for an additional 1.5-hr. period at −10°. The Dry Ice condenser and cooling bath were removed, and the isobutylene was allowed to evaporate overnight. Water (150 ml.) was added, the organic layer was separated and the water phase was extracted with three 75-ml. portions of pentane. The organic layer and the pentane extracts were combined and dried ($MgSO_4$). The mixture was filtered and the filtrate was concentrated. The residue was distilled and two fractions were collected: (1) 65.34 g., boiling below 82° (55 mm.); (2) 4.7 g., b.p. 82° (55 mm.) to 59° (7 mm.). Analyses of fraction (1) by vapor-phase chromatography showed that it consisted mainly of 1,1-dichloro-2,2-dimethylcyclopropane (15.8 g., 45%) and di-*t*-butyl carbonate (24.0 g., 55%). Distillation of fraction (2) yielded 2.81 g. (5%) of *t*-butyl trichloroacetate, b.p. 54–55° (7 mm.), n_D^{25} 1.4392 (reported[8] b.p. 37° (1 mm.), n_D^{25} 1.4398). The material had an infrared spectrum essentially identical with that of an authentic sample.

Dichloroacetonitrile (VI) used was obtained from L. Light and Co., Ltd., England. This material (95–99% pure) was redistilled, b.p. 112–114° (735 mm.) (reported[9] b.p. 112–113°). The vapor-phase chromatogram of the distilled material showed only one symmetrical peak—there was no evidence of impurity.

The Reaction of Dichloroacetonitrile with Potassium t-Butylate in the Presence of Isobutylene. Dichloroacetonitrile (55 g., 0.50 mole) was added over a 1-hr. period to a cold (−15°) mixture of powdered potassium *t*-butylate (0.60 mole), isobutylene (150 ml. at −80°, ca. 2 mole), and olefin-free pentane (100 ml.). The resulting black mixture was stirred for an additional two hours at −15°; the Dry Ice condenser and cooling bath were removed, and the isobutylene was allowed to evaporate overnight. Water (200 ml.) and pentane (300 ml.) were added to the mixture, and

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(3) (a) M. Anbar, I. Dostrovsky, D. Samuel, and A. P. Yoffee, *J. Chem. Soc.*, 3603 (1954); (b) M. Mousseron and P. Froger, *Bull. soc. chim. France*, **12**, 69 (1945); (c) The referee suggests that reaction *h* is more probable than reaction *b*, in view of the greater bond energy of the carbon-chlorine bond compared to the oxygen-chlorine bond. *Cf.* K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 2140 (1948).

(4) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

(5) W. E. Parham and R. R. Twelves, *J. Org. Chem.*, **22**, 730 (1957).

(6) *Org. Syntheses*, **32**, 20 (1952).

(7) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(8) W. E. Scovill, R. E. Burk, and H. P. Lankelma, *J. Am. Chem. Soc.*, **66**, 1039 (1944).

(9) L. Bisschopinck, *Ber.*, **6**, 732 (1873).

the organic layer was separated. The water layer was washed once with pentane. The organic layers were combined and dried ($MgSO_4$). A significant amount (20 g., dried) of black amorphous material remained, which was insoluble in both water and pentane. The composition of this amorphous material was not determined.

Concentration of the dried organic solution yielded a dark, solid residue which was sublimed under vacuum (150°, 0.1 mm.). The sublimate (6.5 g.) was crystallized from benzene, affording 6.0 g. (10%) of trichloroacetamide, m.p. 142–143° (m.p., mixture m.p. and infrared spectra identical with an authentic sample).

Acidification (dil. HNO_3) of the remaining aqueous layer and subsequent precipitation with silver nitrate solution yielded silver chloride. An infrared spectrum of the dried precipitate showed no absorption in the 2000–2300 cm.$^{-1}$ region (silver cyanide absorbs[10] strongly at 2178 cm.$^{-1}$), thus it was concluded that no cyanide ion was formed in the reaction.

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(10) W. D. Stallcup and D. Williams, *J. Chem. Phys.*, **18**, 199 (1942).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Migration of Aryl Groups in the Deamination of Amines

J. C. MARTIN AND W. G. BENTRUDE

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The evidence on aryl group migration in the nitrous acid deamination of amines has been examined insofar as it bears on the problem of the mechanism by which nitrogen is lost in the reaction. It has proved possible to reconcile the results of Curtin[8,18] on the migration aptitudes of aryl groups in the 1,1-diaryl-2-amino-1-propanols with the scheme proposed by Collins[5] to explain results using C^{14} labeling experiments in the same system. The relative rates of aryl migration and interconversion of rotational isomers of the open carbonium ion intermediates have been calculated.

The concept of the phenonium ion[1] has become quite firmly established in organic chemistry in recent years. The study of limiting solvolysis reactions of systems yielding carbonium ions which could be expected to gain energetically by the bridging of a neighboring phenyl[2] has yielded much good evidence for this bridged ion as an intermediate. Phenyl participation to give a phenonium ion has come to be expected in such cases, although modification of the molecule in a manner calculated to stabilize the open (nonbridged) carbonium ion may decrease the importance of such bridging.[3]

It is of interest, in this context, that recent studies[4,5,6] of the nitrous acid deaminations of amines with neighboring aryl groups has produced evidence that open carbonium ions are important intermediates in such reactions, even in systems which give only bridged ions in ordinary solvolysis reactions.

The deamination reaction is closely related to other solvolysis reactions with the principal difference being that the leaving group, a nitrogen molecule, is unusually stable, compared to the usual leaving groups in solvolysis reactions.

Because of the driving force for the deamination reaction, which originates in this great stability of one of the products, the diazonium ion is a very unstable intermediate which may lose a nitrogen molecule as an integral part of the mechanism of any one of several exothermic reactions. The exothermic nature of these reactions would be expected to cause all of the reactions of the diazonium ion (rearrangement, solvolysis, elimination) to have activation energies not only smaller but more closely similar than those of related reactions of the alkyl halides or sulfonate esters.[7]

Such reasoning was used by Curtin and Crew[8] to explain the small size of the increase in migration aptitude of a neighboring phenyl when it is substituted by a *p*-methoxy group in the semipinacolic deaminations of the 2-amino-1,1-diarylethanols. If the loss of nitrogen is exothermic, the transition state resembles starting material[7] and the small substituent effect results from the limited amount of bonding in the transition state between the migrating aryl group and the developing carbonium ion center.

Streitwieser[9a,b] and Huisgen[10] have explained the products observed in a variety of deamination reactions on the basis of a similar argument, the high energy diazonium ion reacting rather indiscriminately in the various possible modes.

If, indeed, activation enthalpy terms are monotonously constant and small in reactions involv-

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(1) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863, 3875, 3883 (1949).

(2) S. Winstein and K. S. Schreiber, *J. Am. Chem. Soc.*, **74**, 2165 (1952).

(3) D. J. Cram and J. Allinger, *J. Am. Chem. Soc.*, **79**, 2858 (1957).

(4) D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2866 (1957).

(5) B. M. Benjamin, H. S. Schaeffer, and C. J. Collins, *J. Am. Chem. Soc.*, **79**, 6160 (1957).

(6) C. J. Collins, W. A. Bonner, and C. T. Lester, *J. Am. Chem. Soc.*, **81**, 466 (1959).

(7) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(8) D. Y. Curtin and M. C. Crew, *J. Am. Chem. Soc.*, **76**, 3718 (1954). See also D. Y. Curtin and M. von Wilhelm, *Helv. Chim. Acta*, **40**, 2129 (1957).

(9) (a) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957). (b) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

(10) R. Huisgen and C. Ruchardt, *Ann.*, **601**, 1 (1956).