1,3-Dichloro-1,1-difluoro-3-methylbutane (111 g.) was placed in a 250-ml. flask equipped as described above. Chlorine (42.6 g.) was added while the flask was irradiated by ultraviolet light. The temperature was maintained at 75–80°. After addition of the chlorine, the product was neutralized with sodium carbonate solution and dried. After recovery of unreacted material, 38 g. of $CH_2ClCCl(CH_3)CH_2CF_2Cl$, b.p. 48.5–52° at 10 mm., $n^{25}_D$ 1.4342, $d^{25}_4$ 1.3906, was obtained.

1,4-Dichloro-1,1-difluoro-3-methylbutane (267.5 g.) was treated with chlorine (107 g.) as described above and 77 g. of $CH_2ClCCl(CH_3)CH_2CF_2Cl$, b.p. 48–50.5° at 10 mm., obtained. Infrared spectra of the products obtained from the isomeric dichloro starting material were identical.

**4-Chloro-4,4-difluoro-2-methylbutene-1.**—Powdered zinc (36 g.), zinc chloride (3 g.) and propanol-1 (75 ml.) were placed in a flask fitted with stirrer, addition funnel and a short column topped with a variable take-off head. The mixture was heated nearly to reflux temperature and a small amount of 1,3,4-trichloro-1,1-difluoro-3-methylbutane added. After reflux had begun, the remainder was added dropwise until a total amount of 45 g. was used. The olefin which resulted was removed at a temperature of 77–78°. This material was then washed, dried and refractionated. The yield of $CH_2{=}C(CH_3)CH_2CF_2Cl$, b.p. 75–75.6°, was 56% (13.5 g.).

**4-Chloro-1,1-difluoro-3-methylbutene-1.**—In the apparatus described above were placed 300 ml. of propanol-1 and potassium hydroxide (56 g.). To this refluxing mixture was added 1,1-difluoro-1,4-dichloro-3-methylbutane (92 g.) dropwise. The resulting olefin was removed at 85–95°. This product was then washed three times with water, dried and fractionated. The yield of $CF_2{=}CHCH(CH_3)CH_2Cl$, b.p. 93.9–94°, was 11% (8.0 g.).

**1-Chloro-1,1-difluoro-3-methylbutene-2.**—In the apparatus described above was placed tri-*n*-butylamine (112 g.). To the hot amine was added dropwise 1,3-dichloro-1,1-difluoro-3-methylbutane. The material refluxing at 90–110° was removed, washed, dried and fractionated yielding a fraction of 1-chloro-1,1-difluoro-3-methylbutene-2, b.p. 77–85°. This material was unstable at room temperature and split out HCl on standing.

**1,1-Difluoro-3-methylbutene-1.**—1,1-Difluoro-1-chloro-3-methylbutane (35 g.) was added dropwise to potassium hydroxide (28 g.) dissolved in propanol-1 (200 cc.) in a 500-cc. flask equipped with stirrer, addition funnel and six-inch column with variable take-off head. Reflux was maintained at 45°. This material was removed, washed, dried and fractionated. The 1,1-difluoro-3-methylbutene-1 (15 g.), b.p. 27.8–28.0°, was obtained in a yield of 59%.

**1,1-Difluoro-3-methylbutadiene-1,3.**—Tri-*n*-butylamine (112 g.) was placed in a three-neck flask equipped with addition funnel, stirrer and six-inch column with variable take-off head. The amine was heated to 180° and small portions of 1,1-difluoro-1,3-dichloro-3-methylbutane were added at intervals. The distillate, which came over at 40–50°, was washed, dried and fractionated. 1,1-Difluoro-3-methylbutadiene, b.p. 34–35.5°, was obtained in a yield of 27%.

The attempted preparation using the 1,1-difluoro-1,4-dichloro-3-methylbutane isomer failed to yield any unsaturated products when refluxed with tri-*n*-butylamine in a similar manner.

**Acknowledgment.**—We wish to acknowledge the interest of Dr. J. C. Montermoso of the Rubber Section of the Office of the Quartermaster General. Funds for this research were supplied under contract DA-44-109-qm-522. We wish to express our thanks to the Naugatuck Chemical Company for providing us a generous quantity of 1,1,1,3-tetrachloro-3-methylbutane.

GAINESVILLE, FLORIDA

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

# The Benzidine Rearrangement. V. Kinetics of the Rearrangement of *m*-Hydrazotoluene[1]

BY ROBERT B. CARLIN AND RAYMOND C. ODIOSO

RECEIVED NOVEMBER 21, 1953

Rates of rearrangement of *m*-hydrazotoluene by hydrogen chloride in 95% ethanol have been measured by means of a spectrophotometric analytical method based on an optical density *vs.* composition plot. This analytical scheme was developed because the intrinsically more accurate method used in an earlier study of the rearrangement of *o*-hydrazotoluene could not be applied to the rearrangement of *m*-hydrazotoluene, owing to the similarity of the ultraviolet absorption spectra of *m*-hydrazotoluene and *m*-tolidine. *m*-Tolidine was shown to be the only product formed in detectable amount under the imposed conditions, and its structure was verified by synthesis. The kinetics of the rearrangement of *m*-hydrazotoluene are essentially identical with those of the rearrangement of hydrazobenzene; the reaction is of the first order in *m*-hydrazotoluene concentration and of the second order in hydrogen chloride concentration under the conditions studied. The rate is subject to a positive salt effect of about the same magnitude as those which were observed in investigations of the rates of rearrangement of hydrazobenzene and of *o*-hydrazotoluene. The observed energy and entropy of activation for the process were 19.6 kcal./mole and 3.2 cal./mole-deg., respectively.

Following the completion of studies of the kinetics of the rearrangements of hydrazobenzene[2] and of *o*-hydrazotoluene[3] by hydrogen chloride in 95% ethanol, *m*-hydrazotoluene (3,3′-dimethylhydrazobenzene) was selected as the next member of a series of aromatic hydrazo compounds to be subjected to kinetic investigation in the same medium. Although the rates of transformation of *m*-hydrazotoluene in 90% ethanol have been measured and activation energies, entropies and related quantities computed,[4] the product or products of the transformation were not reported, and the effects on the rate of variations in acid concentration and in ionic strength of the solutions were not determined In the course of the work described in this article, *m*-tolidine (2,2′-dimethyl-4,4′-diaminobiphenyl) was shown to be the only detectable product from *m*-hydrazotoluene under the imposed conditions, the *m*-tolidine structure was proved by synthesis, and the dependency of the rate of rearrangement upon acid concentration and upon ionic strength were measured.

The spectrophotometric analytical method used in the two preceding investigations[2,3] has the advantage over other methods of following the rearrangement rates of aromatic hydrazo com-

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[1] From the D.Sc. Thesis by Raymond C. Odioso.

[2] R. B. Carlin, R. G. Nelb and R. C. Odioso, THIS JOURNAL, **73**, 002 (1951).

[3] R. B. Carlin and R. C. Odioso. *ibid.*, **76**, 100 (1954).

[4] L. J. Croce and J. D. Gettler, *ibid.*, **75**, 874 (1953).

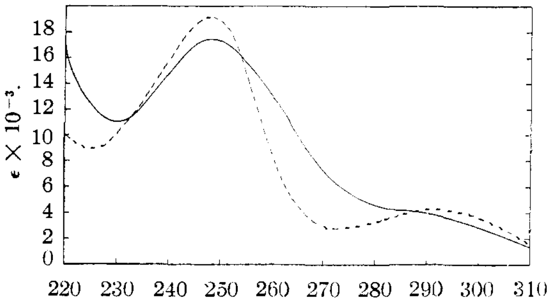
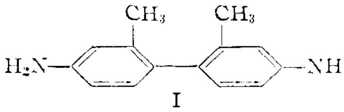


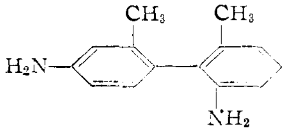
Fig. 1.——, *m*-tolidine; - - - -, *m*-hydrazotoluene.

pounds that the concentrations of the hydrazo compound and of its products can be followed simultaneously. The nature of the reaction or reactions whose rates are being measured is thereby demonstrated and is subject to continuous surveillance. Unfortunately the adaptation of the method used previously could not be applied to the measurement of the rate of conversion of *m*-hydrazotoluene to *m*-tolidine because of the close similarity of the ultraviolet extinction curves of these two compounds. It is apparent from Fig. 1 that no two "ideal" analytical wave lengths exist for solutions containing both *m*-hydrazotoluene and *m*-tolidine, for in order that there be two such wave lengths, the extinction curve for each component must show a maximum in a region where the curve for the other component is at or near a minimum. Only some combination of two of the wave lengths 220, 265 and 270 mμ appeared to offer any hope of yielding satisfactory analytical data. Accordingly, specific extinction coefficients for both components were determined at each of the three wave lengths from plots of optical density *vs.* concentration, but analyses based on these coefficients gave incorrect results with known mixtures. It was therefore necessary to resort to the intrinsically less accurate method involving the use of an optical density *vs.* composition curve. This curve was constructed from optical density data read at 220 mμ, where the extinction coefficients of *m*-hydrazotoluene and *m*-tolidine differ more than at any other wave length investigated. The procedure employed in constructing and using the optical density *vs.* composition plot is described in the Experimental section. To check the accuracy of the method, ten solutions containing known concentrations of *m*-hydrazotoluene and *m*-tolidine were analyzed. The sum of the concentrations of the two solutes in each solution was identical with that used in determining the optical density *vs.* composition plot and with that in solutions from the rate runs, and the composition of the solute mixture varied throughout the series of solutions between the limits 20 and 80% in one component. The average deviation from the known value for the ten determinations was 1.8%. The method is therefore less than half as accurate as the more rigorous spectrophotometric method used to analyze *o*-hydroazotoluene-*o*-tolidine mixtures[3], but it is about as accurate as the latter method was when it was applied to the three-component mixtures encountered in the work on hydrazobenzene.[2]

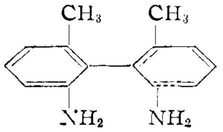
The ultraviolet extinction curve for *m*-tolidine is strikingly different from those for benzidine[2] and *o*-tolidine[3] in the same solvent; in fact, the curve for *m*-tolidine resembles that for diphenyline[2] (2,4′-diaminobiphenyl) or for aniline[5] more closely than it does that for benzidine. Its ultraviolet absorption spectrum therefore could not be considered evidence supporting the structure which has been assigned to *m*-tolidine, and a literature survey disclosed that no satisfactory structure proof has been reported. Jacobson and Fabian[6] isolated only one rearrangement product from *m*-hydrazotoluene and showed that this product was a diamino derivative of 2,2′-dimethylbiphenyl, but the amino groups were not located. Therefore, no available information could distinguish among the three structures I–III for the product



I

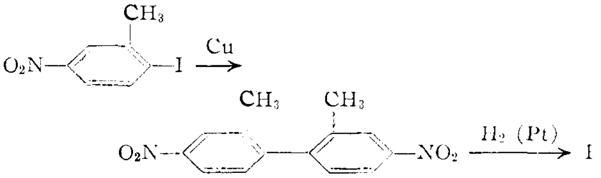


II



III

although experience points to I as the most likely and III the least.[7] A synthesis of I has now been carried out in accordance with the formulated



scheme, and its crystalline diacetyl derivative has been shown to be identical with the diacetyl derivative of the rearrangement product. Thus *m*-tolidine, the rearrangement product of *m*-hydrazotoluene, is indeed represented by structure I, and the deviation of its ultraviolet absorption spectrum from those of benzidine and *o*-tolidine undoubtedly can be attributed to steric interference on the part of the methyl groups with the coplanar configuration of the two aromatic rings. O'Shaughnessy and Rodebush,[8] for example, observed that the intense absorption band with a maximum at 250–260 mμ, which is characteristic of the spectra of biphenyl and 3,3′- and 4,4′-dimethylbiphenyl, is absent from the spectrum of 2,2′-dimethylbiphenyl, and they attributed the absence of this band to the steric properties of the *o*-methyl groups, which tend to prevent the 2,2′-dimethylbiphenyl molecule from adopting a coplanar configuration.

After a sample of *m*-hydrazotoluene was exposed to the action of hydrogen chloride in 95% ethanol under the conditions imposed during the rate runs,

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(5) R. B. Carlin and W. O. Forshey, Jr., This Journal **72**, 793 (1950).

(6) P. Jacobson and O. Fabian, *Ber.*, **28**, 2553 (1895).

(7) *Cf.* P. Jacobson, *Ann.*, **428**, 76 (1922).

(8) M. T. O'Shaughnessy and W. H. Rodebush, This Journal, **62**, 2906 (1940).

the spectrum of the product solution was almost but not quite identical with that of a solution of pure *m*-tolidine. The differences between the two spectra were too small to make an appreciable contribution to the uncertainty inherent in the analytical method, but they were of sufficient magnitude to indicate the presence in the product solution of a small amount of some compound or compounds other than *m*-tolidine. Efforts to isolate other products than *m*-tolidine were unsuccessful; consequently the nature of the by-products remains unknown.

## Experimental[9]

***m*-Hydrazotoluene** was prepared in 28% yield by the action of zinc dust and sodium hydroxide on *m*-nitrotoluene in aqueous ethanol. After recrystallization from petroleum ether (b.p. 20–40°), it formed faintly yellow prisms, m.p. 37.5–38°.[10] Additional recrystallizations did not affect the m.p. or the spectrum. To minimize air oxidation, *m*-hydrazotoluene was stored at 0° under petroleum ether (b.p. 20–40°). Samples which were removed from storage and washed with ice-cold petroleum ether (b.p. 20–40°) and air dried before weighing showed only traces of surface oxidation and were stable in air at room temperature for 8–12 hours.

***m*-Tolidine.**—A solution of 10 g. of *m*-hydrazotoluene in 200 ml. of 95% ethanol was treated with 20 ml. of concentrated hydrochloric acid. After boiling for one hour, the mixture, which contained crystals of *m*-tolidine hydrochloride, was concentrated by distillation, and the crystals (9.15 g., 68%) were collected by filtration. A solution of these crystals in a minimum volume of water was cooled in an ice-bath, stirred and slowly neutralized with aqueous ammonia. The white, gummy precipitate was dissolved in petroleum ether (b.p. 20–40°); after a day at 0° the solution deposited a colorless oil which crystallized when scratched with a glass rod to a white, microcrystalline solid, m.p. 101–102°. Recrystallization from water gave white crystals, m.p. 103–104°, and neither the m.p. nor the spectrum was changed by additional recrystallizations. The m.p. 106–107° has been reported.[6]

The **N,N′-diacetyl** and the **N,N′-bis-salicylal derivatives** formed small white needles, m.p. 284–285°, and yellow needles, m.p. 200–201°, respectively. The respective m.p.'s 281° and 198–199° have been reported.[6]

**2-Iodo-5-nitrotoluene.**—A solution of 15 g. of 2-amino-5-nitrotoluene (Eastman Kodak Co.) in 45 ml. each of glacial acetic acid and concentrated hydrochloric acid was cooled to 0° and treated with a solution of 9 g. of sodium nitrite in 100 ml. of water. The diazonium solution was filtered and treated with an aqueous solution of 17 g. of potassium iodide, and the mixture was heated for 10 minutes on the steam-bath. The brown crystalline solid (19.5 g., 75%), m.p. 92–95°, was collected by filtration and washed with three portions of aqueous sodium thiosulfate. Purification of the washed solid by sublimation and recrystallization from ethanol yielded white needles, m.p. 102–104°.[11]

**2,2′-Dimethyl-4,4′-dinitrobiphenyl.**—A thoroughly blended mixture of 8 g. of 2-iodo-5-nitrotoluene, 11 g. of copper bronze (O. B. Hommel Co.) and 8 g. of white sand was covered in a test-tube with about a 1-inch layer of copper bronze and heated at 205–210° for 12 hours. The cooled reaction mixture was powdered and then extracted with benzene in a Soxhlet apparatus. Removal of the benzene from the extract solution left a solid residue which yielded orange crystals, m.p. 155–162°, from ethanol. Additional recrystallization from ethanol gave 0.420 g. (10%) of pale yellow crystals, m.p. 166.5–169°.[12]

**2,2′-Dimethyl-4,4′-diacetamidobiphenyl.**—A solution of 0.295 g. of 2,2′-dimethyl-4,4′-dinitrobiphenyl in 100 ml. of thiophene-free benzene was treated with hydrogen at 36 lb./sq. in. for three hours, in the presence of 0.177 g. of Adams catalyst. After being filtered free of catalyst, the benzene solution was concentrated to 75 ml. and treated with 5 ml. of acetic anhydride. The solid (0.240 g., 75%), m.p. 280–284°, which deposited on cooling yielded white needles, m.p. 283–285°, from ethanol. Mixtures of this substance with N,N′-diacetyl-*m*-tolidine from the rearrangement of *m*-hydrazotoluene showed no m.p. depression.

**Determination of the Optical Density *vs.* Composition Plot.**—A solution of *m*-hydrazotoluene and one of *m*-tolidine were prepared by dissolving 0.0100 g. of the appropriate compound in 95% ethanol in a 1-liter volumetric flask and diluting to the mark with ethanol. From these stock solutions aliquots were transferred to each of a series of 100-ml. volumetric flasks, so that each flask contained a solution of total concentration 0.0100 g./l. in both components. The solute composition varied through the series of solutions from 10–90% in each component. The optical density (log $I_0/I$) at 220 mμ of each solution was then read. This procedure was carried out four times, and the four optical density readings corresponding to each solute composition were averaged. The average values, when plotted against solute composition, gave a linear relationship for the optical density *vs.* composition (Fig. 2). Unknown solutions from the rate runs were diluted to the same total solute concentration used in determining the optical density *vs.* composition plot, and their optical densities were read. The solute composition was then immediately available from the plot.

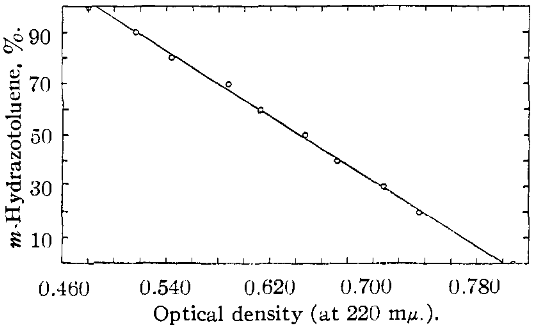

Fig. 2.

**Procedure.**—The initial weight of *m*-hydrazotoluene used in all rate runs was 0.0400 g. All apparatus and procedures were identical with those employed in preceding studies,[2,3] except that 5 ml., rather than 1 ml., aliquots were withdrawn and pipetted into 100-ml. volumetric flasks which contained enough ethanolic sodium hydroxide to neutralize the acid. The solutions were diluted to the mark with ethanol, and the optical density at 220 mμ of each solution was read within a half-hour after withdrawal of the aliquot. The larger aliquots were used in this case in an effort to minimize the errors inherent in the use of the optical density *vs.* composition plot.

Reagents, solvents and solutions used in the rate studies were identical with those employed previously.[2,3]

Pseudo first-order rate constants ($k_1$) were calculated from the slopes of the best straight line plots of log (100/% unchanged *m*-hydrazotoluene) *vs.* time in minutes. Figure 3

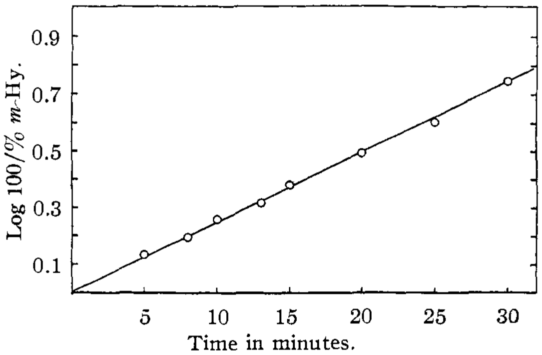

Fig. 3.

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[9] Melting points are corrected.

[10] M. Gonze, *Bull. Sci. acad. roy. Belg.*, **20**, 789 (1934), reported the m.p. 38°.

[11] F. Reverdin and K. Kacer, *Ber.*, **30**, 2999 (1897), reported the m.p. 103–104°.

[12] F. Ullmann and L. Frentzel, *ibid.*, **38**, 725 (1905), reported the m.p. 170°.

shows a plot of the data from a typical run (no. 2). Each straight line was determined by 8–11 experimental points.

## Results and Discussion

The results of twelve rate runs appear in Table I. Two rate runs were carried out under each set of experimental conditions required for the computation of the activation energy and for the estimation of the salt effect on the rate.

TABLE I

REARRANGEMENT OF *m*-HYDRAZOTOLUENE ($9.4 \times 10^{-4}$ *M*) BY HYDROGEN CHLORIDE IN 95% ETHANOL

| Run no. | Temp., °C. | [HCl], mole/l. | Total ionic strength[a] | $k_1 \times 10^2$, min.$^{-1}$ |
|---|---|---|---|---|
| 1 | 25.00 | 0.0510 | 0.0510 | 5.72 |
| 2 | 25.00 | .0510 | .0510 | 5.44 |
| 3 | 34.82 | .0510 | .0510 | 15.3 |
| 4 | 34.82 | .0510 | .0510 | 15.0 |
| 5 | 14.99 | .0510 | .0510 | 1.73 |
| 6 | 14.99 | .0510 | .0510 | 1.68 |
| 7 | 14.99 | .0510 | .1020 | 2.53 |
| 8 | 14.99 | .1020 | .1020 | 15.0 |
| 9 | 14.99 | .0510 | .1020 | 2.88 |
| 10 | 14.99 | .0600 | .1020 | 5.41 |
| 11 | 14.99 | .0800 | .1020 | 7.60 |
| 12 | 14.99 | .0700 | .1020 | 5.71 |

[a] Lithium chloride was used in those solutions whose total ionic strength exceeds that owing to hydrogen chloride.

The effect on the rate of varying acid concentration at constant ionic strength and temperature is shown graphically in Fig. 4, in which log $k_1$ *vs.* log [HCl] data from runs 7–12 are plotted. A straight line of slope 2.0 has been drawn among the points, and though there is some scattering of points about the line, it is apparent that the line does fit the points within the limits of error of the method used to determine the rate constants and that no line of appreciably different slope will fit the points as well. Under the imposed conditions and within the limits of experimental error, therefore, $k_1$ is proportional to the square of the concentration of hydrogen chloride ($k_1 = k_3[\text{HCl}]^2$). In this respect *m*-hydrazotoluene during its rearrangement behaves like hydrazobenzene[2,4,13] but unlike *o*-hydrazotoluene,[3] whose rate of rearrangement under like conditions shows a 1.6-order dependency on hydrogen chloride concentration.

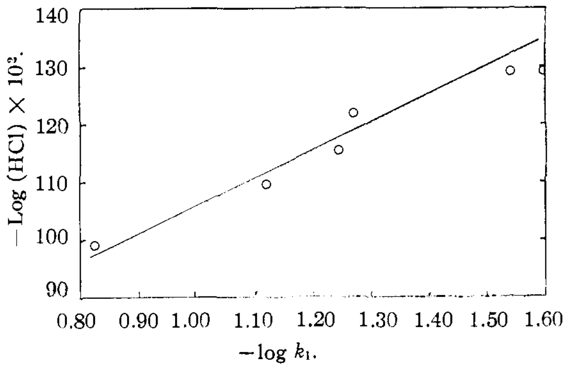

Fig. 4.

The results of runs 5, 6, 7 and 9 show a positive salt effect on the rate; this effect is of about the same magnitude as those observed on the rates of rearrangement of hydrazobenzene[2] and *o*-hydrazotoluene[3] under similar conditions.

The observed activation energy ($E^a$) for the rearrangement of *m*-hydrazotoluene was computed from the least-squares slope of the good straight line plot of log $k_1$ *vs.* $1/T$ data for runs 1–6 (Fig. 5).

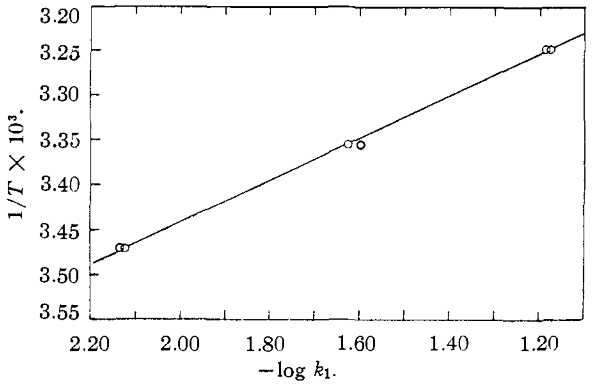

Fig. 5.

The $E^a$ value 19.6 kcal./mole may be compared with 18.7 kcal./mole for the rearrangement of *o*-hydrazotoluene, for the measurements were carried out under identical conditions of ionic strength and acid concentration. Because the $E^a$ value 20.6 kcal./mole for the rearrangement of hydrazobenzene was derived from measurements made in more concentrated acid solutions, it is not rigorously comparable with the 19.6 and 18.7 values. However, $E^a$ measurements for the rearrangement of *o*-hydrazotoluene derived from rate determinations at both acid concentrations (18.7 and 19.1 kcal./mole) show that the change in acid concentration has little effect on $E^a$, and the decreasing order of $E^a$ values for the three rearrangements is hydrazobenzene > *m*-hydrazotoluene > *o*-hydrazotoluene. The total spread over the three values, however, is but about 2 kcal./mole.

An entropy of activation ($\Delta S^{\ddagger}$) for the rearrangement of *m*-hydrazotoluene was computed from $k_3$ ($= k_1/[\text{HCl}]^2$) and the equation $k_3 = (ekT/h)e^{-E^a/RT}e^{\Delta S^{\ddagger}/R}$.[14] The $\Delta S^{\ddagger}$ value calculated from $k_3$ measurements at 25° was 3.2 cal./mole-deg. For the rearrangements of hydrazobenzene and *o*-hydrazotoluene, the respective $\Delta S^{\ddagger}$ values 2.9[2] and −0.62[3] cal./mole-deg. were calculated in a similar way.

The fallacies inherent in efforts to draw conclusions concerning the rearrangement mechanism from $E^a$ and $\Delta S^{\ddagger}$ values, or from comparisons of them, have been considered previously.[2,3]

The measure of precision in the observations of the rates of rearrangement of *m*-hydrazotoluene was again[2,3] considered to be the reproducibility of the individual rate constants. For four rate constants, each of which was determined in two separate runs, the average deviation from the mean was 2.8% and the range of deviations was

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[13] G. S. Hammond and H. J. Shine, THIS JOURNAL, **72**, 220 (1950).

[14] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 197.

from 1–6%. Thus the precision in these measurements was essentially identical with that of the determinations of the rates of rearrangement of hydrazobenzene but of appreciably lower order than the precision of the rate measurements in the *o*-hydrazotoluene investigation. The precision of the rate measurements in the three investigations therefore reflects exactly the accuracy of the analytical methods used to follow the rates.

The close similarity of the rate expressions, rates, $E^a$ and $\Delta S^{\ddagger}$ for the rearrangements of hydrazobenzene and of *o*- and *m*-hydrazotoluenes suggests that all proceed by the same mechanism. Even the observation that the rate expression for the rearrangement of *o*-hydrazotoluene contains acid concentration to the power 1.6, whereas the other two rates are proportional to the square of acid concentration, has been reconciled with the reaction sequence proposed by Hammond and his collaborators,[13,15] which seems compatible with the evidence now available.

Hammond has proposed that the rate determining step in the rearrangement sequence is not the molecular rearrangement step itself, but rather the interaction of acid with the first conjugate acid of the aromatic hydrazo compound.[13,15] A comparison of the $\Delta S^{\ddagger}$ values for the rearrangements of hydrazobenzene and of *m*-hydrazotoluene, which are identical kinetically, may afford evidence in support of Hammond's proposal. The ultraviolet absorption spectra of *m*-tolidine and of benzidine suggest steric interference by the methyl groups with ring coplanarity in *m*-tolidine which, of course, does not exist in benzidine. A similarly derived steric factor might well be expected to intervene in the transition state of the rearrangement, and if this be true, then $\Delta S^{\ddagger}$ for the rearrangement *step* by which *m*-tolidine is formed might be expected to be less than that for the rearrangement *step* which leads to benzidine. The fact that the observed $\Delta S^{\ddagger}$ for the *m*-tolidine rearrangement is not significantly less than that for the benzidine rearrangement might then be considered an argument against the postulate that the rearrangement step is rate controlling. The $\Delta S^{\ddagger}$ value for the *o*-tolidine rearrangement probably is not comparable in this sense with the $\Delta S^{\ddagger}$ values for the other two rearrangements for reasons which have been considered previously.[3] The foregoing argument must be advanced with caution because of uncertainty in the meaning of the observed $\Delta S^{\ddagger}$ values.

**Acknowledgment.**—The authors are grateful to the Research Corporation for a Frederick Gardner Cottrell grant in support of this work.

PITTSBURGH 13, PENNSYLVANIA

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(15) M. D. Cohen and G. S. Hammond, THIS JOURNAL, **75**, 880 (1953).

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

# 1,3,5-Tri-*t*-butylbenzene and Some Derivatives[1]

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The reaction of *t*-butyl chloride and aluminum chloride with *p*-di-*t*-butylbenzene yields *m*-di-*t*-butylbenzene and hydrocarbons melting at 72.5–73° and 209–210°. The product of m.p. 72.5–73° is 1,3,5-tri-*t*-butylbenzene. It has been converted to 2,4,6-tri-*t*-butylaniline and 2,4,6-tri-*t*-butylphenol. Bromination in the presence of iron displaces one *t*-butyl group yielding 1-bromo-3,5-di-*t*-butylbenzene. The tri-*t*-butylbenzene has been obtained also from the condensation of pinacolone by means of metallic sodium. Potentiometric titration in 90% methanol reveals that 2,4,6-tri-*t*-butylaniline is not detectably basic under the conditions used, *i.e.*, the $pK_A$ of the anilinium ion is substantially less than 2.

In connection with interest in this Laboratory in the properties of highly branched molecules we sought to prepare derivatives of 1,3,5-tri-*t*-butylbenzene (III) other than the well-known 2,4,6-tri-*t*-butylphenol[4,5] (VII) which is readily available by the *t*-butylation of phenol and which is so highly hindered as not to be appreciably acidic. Attempts to dehydroxylate this phenol with zinc dust were unsuccessful and although phosphorus pentachloride and thionyl chloride both reacted with it we did not succeed in this way in obtaining the desired chloro compound. 2,4,6-Tri-*t*-butylphenyl chlorosulfinate was isolated as a solid melting at 100.5–101.5°.

**Preparation and Properties of 1,3,5-Tri-*t*-butylbenzene.**—By means of aluminum chloride and *t*-butyl chloride at temperatures below 5° *p*-di-*t*-butylbenzene (I) was about half converted into a mixture consisting of similar amounts of *m*-di-*t*-butylbenzene (II) and two solid hydrocarbons melting at 72.5–73° and 209–210°. Both these solids gave analytical figures close to those calculated for tri-*t*-butylbenzene. However, the higher melting hydrocarbon also was sufficiently higher boiling to indicate that it was not isomeric with the lower melting. Its structure was not established. The compound melting at 72.5–73.0° and boiling under 12 mm. pressure at 121–122° was shown to be 1,3,5-tri-*t*-butylbenzene (III) by two independent procedures. It was shown to be identical with a hydrocarbon found among the products of reaction between pinacolone and sodium react

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(1) Most of the material of this paper formed a part of the Ph.D. thesis of Max Roha at Harvard University in 1949. The preparation from pinacolone and the conversion of 1,3,5-tri-*t*-butylbenzene into 2,4,6-tri-*t*-butylphenol are from the Ph.D. thesis of R. Martin Stiles, 1954. In the interpretation of our results we were aided by exchange of information with the research group at the Standard Oil Co. (Indiana), headed by Dr. A. P. Lien,[2] and with Dr. B. M. Wepster of Delft.[10]

(2) D. A. McCaulay, A. P. Lien and Philip J. Launer, THIS JOURNAL, **76**, 2354 (1954).

(3) National Science Foundation Predoctoral Fellow, 1952–1953.

(4) G. H. Stillson, D. W. Sawyer and C. K. Hunt, THIS JOURNAL, **67**, 303 (1945).

(5) D. R. Stevens and W. A. Gruse, U. S. Patent 2,248,828 (1941); *C. A.*, **35**, $7176^6$ (1941).