hydrazone derivative, mp 164–166° (lit.[27] mp 165°), which showed no melting point depression on admixture with an authentic sample.

3-Cyclopentenecarboxaldehyde (9). The two rearrangement products were not readily separable by distillation but were isolated by preparative vapor phase chromatography. The samples used for the following structure determinations showed only single peaks on vpc.

The component subsequently identified as 3-cyclopentenecarboxaldehyde, bp 148–150°, gave an ir spectrum containing pertinent bands at 3020 (m), 2900 (s), 2800 (s), 2700 (m), 1720 (s), 1610 (w), 1440 (m), 1340 (m), 1270 (w), 1170 (m), 1070 (m), 895 (w), 805 (w), and 685 cm^{-1} (s).

The nmr spectrum consisted of bands centered at δ 9.63 (d, 1 H, aldehydic), 5.67 (s, 2 H, olefinic), 3.05 (m, 1 H, methine), and 2.60 (m, 4 H). The spectrum parallels that reported for 3-cyclopentenecarboxylic acid.[28]

Attempted carbon–hydrogen analyses of the compound were unsatisfactory due to sensitivity to oxidation and explosive decomposition in the combustion tube. Consequently, a sample of the compound was converted into its semicarbazone and recrystallized from water to a constant melting point of 174–175°, which is not in accord with the reported[29] value of 213°.

Anal. Calcd for $C_7H_{11}N_3O$: C, 54.80; H, 7.25. Found: C, 54.40; H, 7.40.

Hydrogenation of a small sample of the aldehyde over Pd–C led to absorbtion of 98% of the theoretical amount required to saturate one double bond. The resulting saturated product proved sensitive to air oxidation and a stream of oxygen quantitatively converted it into the corresponding acid. The ir spectrum of the acid was identical with that published for cyclopentanecarboxylic acid.[30] The acid was converted into its amide derivative, mp 178° (lit.[31] mp 178°).

Oxidation of a sample of the cyclopentenecarboxaldehyde with alkaline permanganate gave tricarballylic acid, mp 157–158° (lit.[32] mp 160–161°).

4,5-Hexadienal (8). The component subsequently identified as 4,5-hexadienal, bp 156–169° dec, $n^{25}\text{D}$ 1.4727, gave an ir spectrum containing pertinent bands at 3050 (w), 2900 (m), 2800 (m), 2700 (m), 1950 (m), 1710 (s), 1440 (m), 1410 (m), 1395 (m), 1060 (m), and 850 cm^{-1} (s). The nmr spectrum consisted of a triplet at δ 9.73 (1 H, aldehydic) and complex multiplets at 5.15 (1 H, internal allenic), 4.7 (2 H, terminal allenic), and 2.4 (4 H, aliphatic).

Since the compound was too sensitive to oxidation to afford reproducible carbon–hydrogen analyses, a sample was converted into the 2,4-dinitrophenylhydrazone derivative, mp 91–92°.

Anal. Calcd for $C_{12}H_{12}O_4N_4$: C, 52.17; H, 4.38. Found: C, 51.88; H, 4.67.

Hydrogenation of a small sample of this component led to absorption of 90% of the amount of hydrogen required to saturate two double bonds and gave a product whose vpc retention time and ir spectrum were identical with those of authentic hexanal. The hydrogenated product gave a 2,4-dinitrophenylhydrazone, mp 92–93°, in agreement with the literature value[33] of 93–94° for this derivative of hexanal.

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(27) C. F. H. Allen, *J. Amer. Chem. Soc.*, **52**, 2958 (1930).

(28) G. S. Schmid and A. W. Wolkoff, *J. Org. Chem.*, 32, 254 (1967).

(29) M. Tiffeneau and B. Tchoubar, *C. R. Acad. Sci., Paris*, 212, 581 (1941).

(30) B. Trost, "Problems in Spectroscopy," W. A. Benjamin, Inc., New York, N. Y., 1967, Compound No. 111.

(31) N. Zelinsky, *Chem. Ber.*, **41**, 2627 (1908).

(32) K. C. Murdock and R. B. Angier, *J. Org. Chem.*, 27, 2397 (1962). All conceivable oxidation products derivable from the other double bond isomers of **9** have considerably lower melting points.

(33) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953).

Steric Hindrance under High Pressure. Reactions of 2,4,6-Tri-*t*-butyl-N-methylaniline with Alkyl Iodides[1]

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Contribution from the Department of Chemical Engineering, New York University, University Heights, New York, New York 10453.

Received May 15, 1968

Abstract: 2,4,6-Tri-*t*-butyl-N-methylaniline (**1**) was treated with methyl iodide under 5000–5500 atm at 100° for 13–15 hr. The reaction gave 2,4-di-*t*-butyl-N,N-dimethylanilinium iodide (**2**) (yield 70%) and isobutylene. Under similar conditions, **1** also was allowed to react with ethyl iodide giving 2,4-di-*t*-butyl-N,N-diethylanilinium iodide (**4**) and isobutylene. Under a shorter reaction period, 2,4-di-*t*-butyl-N-ethyl-N-methylanilinium iodide (**3**) was obtained as the main product. However, **1** did not react with *n*-propyl or isopropyl iodide under 6000 atm at 150–170°. An attempt to treat 2,4-di-*t*-butyl-N,N-dimethylaniline (**6**) with methyl iodide under ~10,000 atm at 150° gave starting compound **6** quantitatively. Radioactive 2,4-di-*t*-butyl-N,N-dimethyl-^{14}C-aniline was synthesized and treated with methyl iodide under the conditions described above. The radioactivity of the recovered **6** was found to be identical with that of the starting material. N-Deuterio-2,4,6-tri-*t*-butyl-N-methylaniline (**1d**) was prepared and was treated with methyl iodide under high pressure. The deuterium content on the *ortho* position of the anilinium salt (**2d**) produced was found to be 10–15% that of **1d**. The mechanism of the de-*t*-butylation reaction from **1** with methyl or ethyl iodide is discussed.

Menshutkin reactions—typical SN2-type reactions of alkyl halides with amines to form quaternary ammonium salts—have been widely investigated for the effects of pressure.[2–4] The rate of the reaction generally increases with increasing pressure of the system. The increase in rate with increasing pressure was attributed to the decrease of the volume at the transition state. The volume decrease is due to the increasing solvation of the ionic charges formed (generally referred to as electrostriction). Thus, the reaction rate of *o*-methyl-N,N-dimethylaniline with methyl iodide in dry methanol or acetone at 50° under 3000 atm was reported higher by a factor of 11 and 7, respectively, than those for the reactions under 1 atm.[5,6] A highly

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(3) S. D. Hamann, "High Pressure Physics and Chemistry," Vol. 2, R. S. Bradley, Ed., Academic Press, New York, N. Y., 1963, p 191.

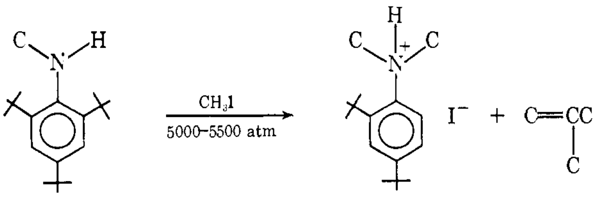
(4) W. J. Le Noble, *J. Chem. Educ.*, **44**, 729 (1967).

hindered amine, 2,4,6-tri-*t*-butyl-N-methylaniline (**1**), however, did not react with methyl iodide under conventional pressure conditions. Wepster and coworkers have attempted to prepare 2,4,6-tri-*t*-butyl-N,N-dimethylaniline from **1** by nine different methylation procedures, *e.g.*, **1** with methyl iodide at 200° in a sealed tube, with dimethyl sulfate at 180°, and with sodium amide–methyl iodide.[7] However, all attempts resulted in no reaction. Therefore, we attempted to treat **1** with methyl iodide by means of high pressure, 5000–5500 atm.

The reaction gave 2,4-di-*t*-butyl-N,N-dimethylanilinium iodide and isobutylene instead of the corresponding anilinium salt, 2,4,6-tri-*t*-butyl N,N-dimethylanilinium iodide.[8] In the present paper, we report further investigations of the effects of pressure of **1** with alkyl iodides and discuss the possible mechanism of the de-*t*-butylation reactions.

Results and Discussion

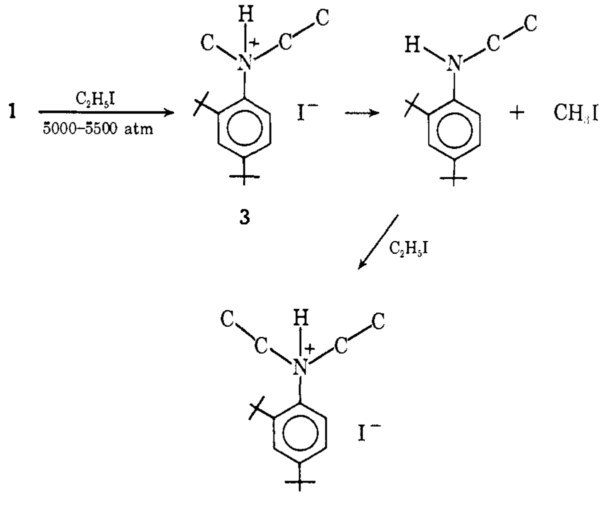
Reaction with Methyl and Ethyl Iodides. **1** was allowed to react with methyl iodide under a hydrostatic pressure of 5000–5500 atm at 100° for 13–15 hr in dioxane solution (or without solvent, using a large excess of methyl iodide) and produced 2,4-di-*t*-butyl-N,N-dimethylanilinium iodide (**2**) (yield 70%) *via* a de-*t*-butylation from the *ortho* position.



1 **2**

Without methyl iodide, **1** did not undergo de-*t*-butylation under these conditions. Furthermore, even when **1** was refluxed with various concentrations of sulfuric acid or phosphoric acid, there was no de-*t*-butylation detected from **1**.[7] Therefore, the de-*t*-butylation observed must be associated with the reaction between **1** and methyl iodide.

1 was also treated with ethyl iodide under the condition described above, using a large excess of ethyl iodide. 2,4-Di-*t*-butyl-N,N-diethylanilinium iodide (**4**) (yield 65–70%) and isobutylene were obtained. Under a short reaction period (8–10 hr), 2,4-di-*t*-butyl-N-ethyl-N-methylanilinium iodide (**3**) instead of **4** was obtained as the main product. When N-methylaniline was treated with a large excess of ethyl iodide at 100° in a sealed tube, N,N-diethylanilinium iodide was produced. Therefore, **3** was probably first produced from **1** with ethyl iodide followed by methyl group exchange with ethyl iodide present in large excess.



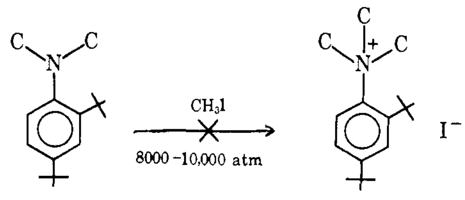
3

4

If the effect of high pressure enabled methyl iodide to react with **1** by overcoming the steric hindrance between *t*-butyl and methyl groups, the presumed intermediate may have a structure close to 2,4,6-tri-*t*-butyl-N,N-dimethylanilinium iodide (**5**). Arnett and coworkers recently determined the strain energy of *o*-di-*t*-butylbenzene as 22.3 ± 0.5 kcal/mol,[9] which is close to Brown's estimate (25 kcal/mol) by the homomorphic analogy.[10] The structure of **5** is a homomorph of 2,4,6-tri-*t*-butylisopropylbenzene, which has as yet not been synthesized. However, the strain energy is expected to be more than that of *o*-di-*t*-butylbenzene.

Thus, in order to obtain the intermediate **5**, the effect of pressure must overcome the strain energy (>22.3 kcal/mol). Without detailed thermodynamic data of the system, it is difficult to estimate the pressure effect, but it is considerably large compared to the data of those in known Menshutkin reactions.[2–4] Therefore, to verify the pressure effect, the reaction of 2,4-di-*t*-butyl-N,N-dimethylaniline (**6**) with methyl iodide was investigated under high pressure. The expected product would be 2,4-di-*t*-butyl-N,N,N-trimethylanilinium iodide (**7**) which is a strained homomorph of *o*-di-*t*-butylbenzene.

Brown and Nelson reported that reaction between **6** and methyl iodide did not occur even after refluxing for 12 days.[11] An attempt to treat **6** with methyl iodide under 8000–10,000 atm at 150° was made for 22 hr. However, the starting compound **6** was quantitatively recovered from the reaction mixture. The failure to detect the reaction product, however, may be due to an unfavorable equilibrium. The reaction product may only exist under high pressure and, upon decreasing the pressure, the equilibrium is rapidly shifted to the left (to release the strain energy). To test this possibility, the radioactive 2,4-di-*t*-butyl-N,N-dimethyl-^{14}C-aniline was synthesized and allowed to react with methyl iodide under the above-mentioned conditions.



6 **7**

The radioactivity of **6** recovered was found to be identical with that of the starting material.

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(5) K. E. Weale, *J. Chem. Soc.*, 2959 (1954).

(6) K. E. Weale, *Discussions Faraday Soc.*, 22, 122 (1956).

(7) J. Furgers, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M. Wepster, *Rec. Trav. Chim.*, 77, 491 (1958).

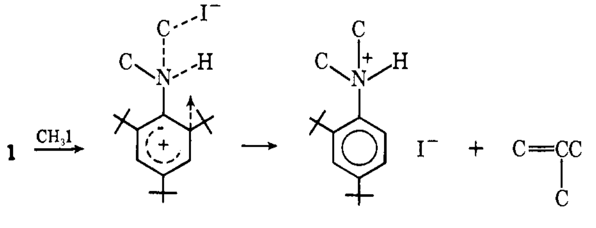
(8) See Okamoto and Shimizu, ref 1.

(9) E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Am. Chem. Soc.*, **89**, 5389 (1967).

(10) H. C. Brown, G. K. Barbaras, H. L. Berneis, W. H. Bonner, R. B. Johannesen, M. Grayson, and K. L. Nelson, *ibid.*, **75**, 1 (1953).

(11) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 24 (1953).

These results suggest that the effect of pressure (~10,000 atm) does not overcome the strain energy introduced (~22 kcal/mol) and that the mechanism of the de-*t*-butylation from **1** with methyl or ethyl iodide under high pressure is a concerted process rather than *via* the intermediate **5**. That is, as methyl or ethyl iodide approaches the nitrogen for bond formation, the proton on the nitrogen simultaneously migrates to the *ortho* position, followed by the de-*t*-butylation.



Thus, N-deuterio-2,4,6-tri-*t*-butyl-N-methylaniline (>90% deuterium content) (**1d**) was prepared and allowed to react with methyl iodide under high pressure. The anilinium iodide (**2d**) produced was treated with with aqueous Na_2CO_3 to yield the corresponding base. The deuterium content at the *ortho* position of the compound was found to be 10–15% that of **1d**.

The small amount of deuterium content at the *ortho* position could be attributed as follows. If the de-*t*-butylation steps are much faster than that of the previous reaction step, the proton eliminated from the *t*-butyl cation may exchange rapidly with the labile deuterium in **1d**.[12]

Reaction with Propyl and Isopropyl Iodides. An attempt was made to treat **1** with *n*-propyl and isopropyl iodides under somewhat severe conditions, *e.g.*, under 6000 atm at 150–160° for 15–20 hr. However, no reactions were observed, and the starting compound (**1**) was recovered quantitatively.

We are pursuing further aspects of the effects of high pressure in sterically hindered systems.

Experimental Section

Solvents and Reagents. Dioxane of reagent grade was purified by distillation and stored over sodium wire. Methyl, ethyl, *n*-propyl, and isopropyl iodides (Eastman Kodak Co.) were dried over phosphorus pentoxide and purified by distillation.

Instrumental Analyses. Nuclear magnetic resonance spectra were obtained on a Varian Associates Model A-60 spectrometer with tetramethylsilane as an internal reference. A Perkin-Elmer Model 154 gas chromatograph with a tributyl phosphate column was used for the analysis of olefin products. Infrared spectra were recorded with a Perkin-Elmer Infracord. A liquid scintillation spectrometer (Nuclear Chicago Corp., Model 701) was used for the ^{14}C radioactivity measurement. Mass spectra were obtained on a Hitachi-Perkin-Elmer Model RMU-60 operating at 13 and 75 V with a heated inlet system at 150°.

2,4,6-Tri-*t*-butyl-N-methylaniline. 2,4,6-Tri-*t*-butyl-N-methylaniline was synthesized according to the procedure of Wepster and his coworkers,[7] mp 147–148° (lit.[7] mp 147–148°); nmr in CCl_4, δ 1.28 (singlet, 9 *p*-*t*-butyl protons), 1.44 (singlet, 18 *o*-di-*t*-butyl protons), 7.06 (singlet, 2 aromatic protons), and 2.60 (3 N-methyl protons).

2,4-Di-*t*-butyl-N,N-dimethylaniline. 2,4-Di-*t*-butyl-N,N-dimethylaniline was prepared by the method of Fedtke and Gernhardt.[13] The compound was recrystallized from 90% aqueous ethanol, mp 77–78° (lit.[13] 77–78°); nmr in CCl_4, δ 1.28 (singlet, 9 *p*-*t*-butyl protons), 2.56 (singlet, 6 N-dimethyl protons), 1.40 (singlet, 9 *o*-*t*-butyl protons), and 7.12–7.24 (3 aromatic protons).

2,4-Di-*t*-butyl-N,N-dimethyl-^{14}C-aniline. The radioactive aniline derivative was synthesized by the reaction between 2,4-di-*t*-butyl-N-methylaniline, prepared from 2,4-di-*t*-butylformanilide,[7] with CH_3I (^{14}C) (New England Nuclear Corp.), mp 78°. The radioactivity was determined in toluene solution by a liquid scintillation spectrometer and found to be 13.0 × 10^3 cpm/mg (using Liquifluor, Nuclear-Chicago Inc.).

Reactions under High Pressure. The reactions of aniline compounds with alkyl iodides under high pressure were carried out either in dioxane or without solvent. The following is a typical procedure for the reaction. 2,4,6-Tri-*t*-butyl-N-methylaniline, 2.2 g (8 mmol), and 7 g (50 mmol) of methyl iodide were mixed in a drybox. The capsule was filled with the solution under dry nitrogen atmosphere in such a way that all gas bubbles were completely eliminated from the capsule.

The cylindrical capsule was made of Teflon (0.7 cm i.d., 1–1.5 cm long) with a snug-fitting lid. The capsule was placed in a 1.0 cm diameter hole in a special tungsten carbide die, and two carbide pistons were impinged upon the capsule by a hydraulic press. The die was 15 cm o.d., 10 cm high, and equipped for heating by an external band heater. The temperature of the reaction was determined by a fine thermocouple inserted near the sample through a hole. A larger capsule (1.8 cm i.d., 2 cm long) with a larger die was also used for the reactions.

These designs were able to pressurize liquids such as the reaction systems described in this paper up to 10,000 atm at 200°.

Reactions between 2,4,6-Tri-*t*-butyl-N-methylaniline and Alkyl Iodides. A solution of 2,4,6-tri-*t*-butyl-N-methylaniline, 2.2 g (8 mmol), and 7 g (50 mmol) of methyl iodide was prepared in a drybox. The solution was placed in a Teflon capsule (1.8 cm i.d., 2 cm long), and the capsule was pressed by a hydraulic press under 5000 atm at 100° for 13 hr. 2,5-Di-*t*-butyl-N,N-dimethylanilinium iodide (70% yield) was obtained. After treatment of the salt with Na_2CO_3, the aniline compound was identified as 2,4-di-*t*-butyl-N,N-dimethylaniline by infrared and nmr measurements. The melting point was 77–78°, no depression on mixing with pure compound. The isobutylene produced was identified qualitatively by direct injection of the vapor or solution on a gas chromatograph.

Similarly, **1** was allowed to react with ethyl iodide for 8 hr under 5000 atm at 100° and 2,4-di-*t*-butyl-N-ethyl-N-ethylanilinium iodide (60% yield) was obtained. The HCl salt decomposed at 152°; nmr of the aniline compound in CCl_4: δ 1.10 (multiplets, 3 methyl protons for N-C_2H_5), 2.72 (quartets, 2 methylenes for N-C_2H_5), 2.50 (singlet, 3 protons for N-CH_3), 1.30 (singlet, 9 protons for *p*-*t*-butyl), 1.43 (singlet, 9 protons for *o*-*t*-butyl), and 7.07–7.22 (3 aromatic protons).

1 was allowed to react with ethyl iodide for 13–15 hr under 5000 atm at 100° and 2,4-di-*t*-butyl-N,N-diethylanilinium iodide (65–70% yield) was obtained. The anilinium iodide was also isolated from the reaction of 2,4,6-tri-*t*-butyl-N-ethylaniline, mp 79–80° (lit.[7] 77–79°), with ethyl iodide under conditions similar to those described above. of 2,4-Di-*t*-butyl-N,N-diethylanilinium chloride was melted at 141–142°; nmr of the aniline compound in CCl_4, δ 1.06 (triplet, 6 methyl protons for N-C_2H_5), 2.89 (quartet, 4 methylene protons for N-C_2H_5), 1.30 (singlet, 9 protons for *p*-*t*-butyl), 1.44 (singlet, 9 protons for *o*-*t*-butyl), and 7.07–7.33 (3 aromatic protons).

1 was allowed to react with *n*-propyl and isopropyl iodides under 6000 atm at 150–160° for 15–20 hr. No reactions were observed in these systems.

Reactions between 2,4-Di-*t*-butyl-N-methylaniline or 2,4-Di-*t*-N-methyl-^{14}C-aniline and Methyl Iodide. A solution of 2,4-di-*t*-butyl-N-methylaniline, 2.3 g (10 mmol), and 7 g (50 mmol) of methyl iodide was placed into a Teflon capsule (1.8 cm i.d., 2 cm long). The mixture was pressurized up to 10,000 atm at 150° for 22 hr. After removing the methyl iodide from the reaction mixture, the residue was recrystallized from aqueous ethanol. 2,4-Di-*t*-butyl-N-methylaniline, mp 77–78°, was recovered in 70–80% yield.

A solution of 2,4-di-*t*-butyl-N-methyl-^{14}C-aniline, average radioactivity 13,000 cpm/mg and methyl iodide was pressurized under the conditions described above. The recovered 2,4-di-*t*-butyl-N-methylaniline had a radioactivity of 12,300 cpm/mg.

Reaction between 2,4,6-Tri-*t*-butyl-N-deuterio-N-methylaniline and Methyl Iodide. The deuterium compound was synthesized from 2,4,6-tri-*t*-butyl-N-methylaniline by treatment with a large

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[12] In order to account for the deuterium content of the *ortho* position, the isotope effect in the rearrangement step should be 2–3. The value is considerably higher for the usual proton transfer process, However, under such high pressure, the isotope effect for the proton transfer is not known and would be expected to be higher than that at an ordinary pressure.

[13] M. Fedtke and M. Gernhardt, *J. Prakt. Chem.*, 29, 259 (1965).

excess of D_2O in dried dioxane solution. The infrared spectrum in carbon tetrachloride showed an N–D band at 2470 cm^{-1} and an N–H band at 3410 cm^{-1} which was absent in this compound. The compound was allowed to react with methyl iodide under high pressure as described above. The anilinium iodide produced was treated with aqueous Na_2CO_3 to yield the corresponding base. From the mass and nmr spectra, the compound was calculated to be 10–15% deuterated in the *ortho* position of 2,4-di-*t*-butyl-N,N-dimethylaniline. The peaks at mass 233 [$(t\text{-}C_4H_9)_2C_6H_3N(CH_3)_2$] and 218 (demethylated ion) were used for the analysis.

Acid-Promoted Rearrangements Involving Transannular Ether Oxygen Participation[1]

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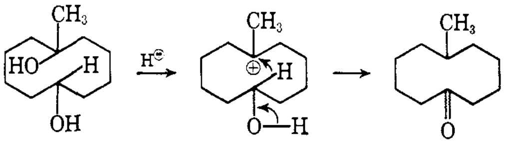
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 24, 1968*

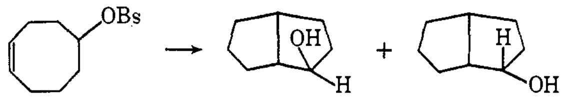
Abstract: When 7,8-dihydro-2H-oxocin-3(4H)-one (**14**) was heated with hydrochloric acid for several minutes, transannular rearrangement involving participation of ether oxygen was encountered and 5-(3-chloropropyl)dihydro-3(2H)-furanone (**13a**) was isolated in good yield. Exposure of **14** to hydrobromic acid gave rise to the corresponding bromide (**13b**). Under similar conditions, 7,8-dihydro-5-phenyl-2H-oxocin-3(4H)-one (**22**) and 5-phenyl-3,6,7,8-tetrahydro-2H-oxocin (**26**) were likewise converted to a dihydrofuranone and tetrahydrofuran, respectively. On the other hand, 5,6,7,8-tetrahydro-2H-oxocin-3(4H)-one (**15**) and 7,8-dihydro-4,4-dimethyl-2H-oxocin-3-one (**24**) were not acid labile and could be recovered unchanged from such treatment. The rearrangements are therefore the result of the generation of carbonium ion character at C-5, transannular oxygen participation, and solvolytic ring opening of the resulting oxonium ion. The various facets of this mechanism are discussed.

The phenomenon of transannular reaction is perhaps the most remarkable of a number of unique features exhibited by medium-sized rings. The origin of this characteristic is found in the existence of certain conformations wherein opposite sides of the ring are brought into close proximity. The pioneering work in this area, due to Prelog[2] and to Cope,[3] has centered predominantly upon transannular hydride shifts. These studies have shown that when substantial carbonium ion character develops in reaction intermediates involving mesocycles, transannular rearrangements are very likely to be of great importance. For example, the action of phosphoric acid on **1** results in the formation of 6-methylcyclodecanone (**2**) by a 1,6-hydride shift.[4]



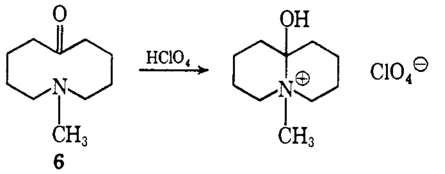
1 **2**

A further distinguishing feature of medium-sized rings is their tendency to go bicyclic to relieve existing nonbonded interactions. To illustrate, solvolysis of 4-cycloocten-1-yl brosylate (**3**) in acetic acid yields acetates of **4** and **5** in addition to 4-cyclooctenyl 1-acetate.[5]



3 **4** **5**

Leonard, in a broadening of such concepts to heterocyclic molecules, was able to detect transannular N–C_{CO} and S–C_{CO} interactions as revealed by the spectra of ketones such as **6** and **7**.[6,7] In addition, such ketones could be converted to their respective bicyclic salts when treated with strong acids. This effective electron-donating ability was found, however, to be restricted only to those molecules in which the interacting groups are diametrically opposed. Thus, treatment of **8** with acid does not lead to the formation of a



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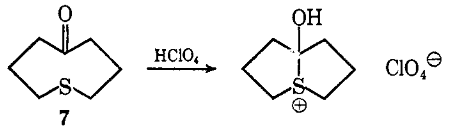

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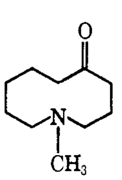

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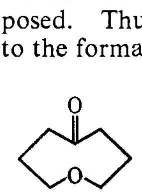

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[1] Unsaturated Heterocyclic Systems. XLV. For the previous paper, see L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, **90**, 3898 (1968).

[2] V. Prelog and J. G. Traynham in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 593.

[3] A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), 20, 119 (1966).

[4] V. Prelog and W. Küng, *Helv. Chim. Acta*, **39**, 1394 (1956).

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