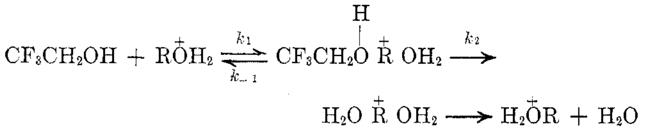
step must generally be the breaking of the C–O bond to give a symetrically solvated carbonium ion.

$$H_2O + ROH_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2O\ \overset{+}{R}\ OH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2\overset{+}{O}R + H_2O$$

The C–O bond cleavage step *itself* must involve racemization. Therefore, the isotope effect refers to the transition state of the heterolytic step (rate constant k_1 in the general scheme) and is smaller than the maximum of ~1.23 characteristic of solvolytic reactions with oxygen leaving groups, found for processes which involve rate-determining formation of a second ion pair from the first product of ionization.[16] The 15% isotope effect is the same as that found for solvolysis of pinacolyl *p*-bromobenzenesulfonate in which formation of the tight ion pair is rate determining because of rapid Wagner–Meerwein rearrangement of the 3,3-dimethyl-2-butyl cation.[24] The *α-d* effect in 97% TFE is larger than in 70% TFE, probably because, in at least a significant proportion of the reaction, the molecule at the rear, after initial heterolysis of the C–O bond, is not a water molecule but trifluoroethanol. Thus, a



$$CF_3CH_2OH + R\overset{+}{O}H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CF_3CH_2\overset{\overset{H}{|}}{O}\ \overset{+}{R}\ OH_2 \xrightarrow{k_2} H_2O\ \overset{+}{R}\ OH_2 \longrightarrow H_2\overset{+}{O}R + H_2O$$

significant fraction of the carbonium ions initially formed would be expected to return to unracemized alcohol *via* k_{-1}; the further dissociation of the unsymmetrically solvated, initially formed carbonium ion would contribute to the rate-determining step and give a larger *α-d* effect, since this transition state involves no partial covalent bond between carbon and oxygen. In this way, it is similar to the rate-determining step in limiting solvolyses which show *α-d* effects in oxygen leaving groups around 1.23.

The 9.4% β-d_3 effect in racemization of the alcohol is small compared to the 22% effect characteristic of the solvolysis of the chloride. However, the latter process involves rate-determining interconversion of ion pairs (see above) in which it is believed that there is no covalent bond between oxygen and carbon. The partial covalent bond in the transition state for the C–O heterolysis step causes both β and α effects to be smaller when this step is rate determining than they are when the step is labeled k_2 is rate determining. The comparison of β-d_3 effects on the solvolysis of isopropyl brosylate in trifluoroacetic acid ($k_H/k_{\beta\text{-}d_3} = 1.46$) and in 70% TFE ($k_H/k_{\beta\text{-}d_3} = 1.24$) gives the best example of the change in a β-d_3 effect on changing rate-determining step from ion-pair interconversion to ion-pair formation. Since for the former case the β-d_3 effect for the 1-phenylethylcarbonium ion is 1.22, the above observed effect on the heterolysis step (1.10) is in line with previous results.

Acknowledgments.—This research was supported in part by Grant AT(11-1)-1008 from the U. S. Atomic Energy Commission (Document COO-1008-22) and in part by Grant GP 32854 from the National Science Foundation. Electronic computations were performed with the facilities of the Indiana University Research Computing Center. We are indebted to Mr. H. E. Ferran for the glc measurements of the yields in the solvolyses of 1-phenylethyl chloride in 97 T.

Registry No.—1-Phenylethyl alcohol, 98-85-1; 1-phenylethyl-*1-d* alcohol, 3101-96-0; 1-phenylethyl-*2,2,2-d*$_3$ alcohol, 17537-32-5; 1-phenylethyl chloride, 672-65-1; 1-phenylethyl-*1-d* chloride, 41203-27-4; 1-phenylethyl-*2,2,2-d*$_3$ chloride, 40662-53-1.

[24] V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *J. Amer. Chem. Soc.*, **91**, 7748 (1969).

The Nature of Solvent Participation in the Restriction of Rotation about Single Bonds. II

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Received June 4, 1973

The activation enthalpy for the racemization of 2,2′-dimethoxy-6,6′-diphenamide decreases by 4.2 kcal/mol when the solvent is changed from acetone to acetic acid. It is shown that this is entirely due to a lowering of the transition state energy. Activation parameters have been determined for the racemization of *N*-benzenesulfonyl-*N*-carboxymethyl-2,4-dimethyl-6-nitroaniline in 26 solvents and heats of solution have been measured in nine of these solvents.

When one considers the fact that reaction rates and equilibrium constants may be altered by several powers of ten through changes in the reaction medium, it becomes obvious that the role of the medium must be understood if one is to arrive at a useful understanding of organic reactions as they take place in solution. A change in the solvent may increase the rate of a reaction either by decreasing the free energy of the transition state or by increasing the free energy of the ground state. It is, therefore, important in the understanding of solvent effects that one be able to tell just how much of the variation in the activation parameters is due to changes in ground-state solvation and how much is due to changes in transition-state solvation. This is conveniently done in the case of the activation enthalpy by measuring the heats of solution of the reactant in the solvent systems under investigation.[1-3] The difference in the heats of solution is the enthalpy difference between the two solvated ground states, $\delta_M\ \Delta\bar{H}^g$. The

[1] E. M. Arnett, P. M. Duggleby, and J. J. Burke, *J. Amer. Chem. Soc.*, **85**, 1350 (1963).

[2] E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

[3] E. M. Arnett and D. R. McKelvey, *Rec. Chem. Progr.*, **26**, 185 (1965).

TABLE I

RACEMIZATION OF 2,2′-DIMETHOXY-6,6′-DIPHENAMIDE

Temp, °K	$k \times 10^3$, hr^{-1} Acetone	$k \times 10^3$, hr^{-1} Acetic acid
363.7[a]	0.3448	1.656
382.1[a]	2.783	7.308
406.7[b]	53.0	127
411.7	77.98	222.8
432.7		904.8

[a] The kinetic data for 363.7 and 382.1°K is from ref 10. [b] The kinetic data for 406.7°K was obtained at 50 and 60 atm pressure by Kay R. Brower, New Mexico Institute of Mining and Technology.

TABLE II

HEATS OF SOLUTION FOR SOME SUBSTITUTED AMIDES IN ACETONE AND ACETIC ACID TOGETHER WITH THE ENTHALPIES OF TRANSFER FROM ACETIC ACID TO ACETONE

Compd	Registry no.	$\Delta\bar{H}_s$, kcal/mol Acetone	$\Delta\bar{H}_s$, kcal/mol Acetic acid	$\delta\Delta\bar{H}_s$, kcal/mol
Benzene	71-43-2	0.11 ± 0.04	0.37 ± 0.04	−0.26
Benzamide	55-21-0	3.97 ± 0.11	2.51 ± 0.06	1.46
o-Methoxybenzamide	2439-77-2	5.18 ± 0.30	3.22 ± 0.14	1.96
m-Methoxybenzamide	5813-86-5	4.59 ± 0.15	3.88 ± 0.11	0.71
p-Methoxybenzamide	3424-93-9	4.70 ± 0.13	2.79 ± 0.20	1.91
2,6-Dimethoxybenzamide	21864-67-5	4.35 ± 0.51	3.04 ± 0.21	1.31
2,4,6-Trimethylbenzamide	4380-68-1	4.28 ± 0.17	2.90 ± 0.13	1.38
2,4,6-Triethylbenzamide	41214-94-2	3.76 ± 0.21	2.14 ± 0.14	1.62

enthalpy difference between the two solvated transition states, $\delta_M\ \Delta\bar{H}^t$, is then obtained by $\delta_M\ \Delta\bar{H}^t = \delta_M\ \Delta\bar{H}^g + \delta_M\ \Delta\bar{H}^\ddagger$, where $\delta_M\ \Delta\bar{H}^\ddagger$ is the difference in the activation enthalpies.[3]

Perhaps the simplest "reaction" subject to a solvent effect that an organic molecule can undergo is one involving nothing more than rotation about a single bond, *i.e.*, conformational change. That the solvent can indeed influence the height of the energy barriers between conformers was first demonstrated in 1932 by various workers,[4-6] who showed that the rates of racemization for several optically active biphenyls were solvent dependent. In 1959 Leffler and coworkers measured activation parameters for the racemization of several optically active biphenyls in as many as 26 different solvent systems.[7-10] They observed that the racemization of 2,2′-dimethoxy-6,6′-diphenamide (I) was particularly solvent dependent, having an activation enthalpy of 21.49 kcal/mol in acetic acid and 30.59 kcal/mol in acetone. This change of 9 kcal/mol in the activation enthalpy was significantly larger than the usual 2–4 kcal/mol observed by them for the other biphenyls studied. In the process of further investigations concerning this solvent effect it was found necessary to repeat this work. Rate data over a 69° temperature range was gathered from three independent research groups. These data, listed in Table I and shown graphically in Figure 1, give the activation enthalpies as being 33.31 kcal/mol in acetone and 29.08 kcal/mol in acetic acid. The corresponding entropies of activation are +0.48 and −8.22 eu, respectively. Thus the difference in activation enthalpies, $\delta_M\ \Delta\bar{H}^\ddagger$, is 4.23 kcal/mol. The previously reported values for the heats of solution of I in acetone and acetic acid are 2.98 and 1.98 kcal/mol, respectively, giving 1.0 kcal/mol as the enthalpy difference between the two solvated ground states, $\delta_M\ \Delta\bar{H}^g$.[11] Combining this with the $\delta_M\ \Delta\bar{H}^\ddagger$ value of 4.23 kcal/mol gives 5.2 kcal/mol as the enthalpy difference between the two solvated transition states. Clearly then the 4.2 kcal/mol change in the activation enthalpy observed for this solvent change is due entirely to a medium effect on the transition state. In an unsuccessful attempt to characterize the nature of this solvent effect, benzamide and several benzamide derivatives were prepared and their heats of solution were measured in acetone and acetic acid. It was reasoned that if crowding of the amide group in the transition state were responsible for the solvent effect then this should be reflected in the enthalpies of transfer for a series of 2,4,6-trisubstituted benzamides in which the steric requirements of the substituent groups were gradually increased. In this respect the results, shown in Table II, were inconclusive. Attempts at increasing the size of the substituent groups beyond that of the ethyl group were unsuccessful. Attempts to prepare 2,5-di-*tert*-butyl-3,6-dimethoxybenzamide failed when bromination of 2,5-dimethoxy-1,4-di-*tert*-butylbenzene gave 2,5-dimethoxy-1,4-dibromobenzene as the major product. The observation that *o*- and *p*-methoxybenzamide have essentially the same en-

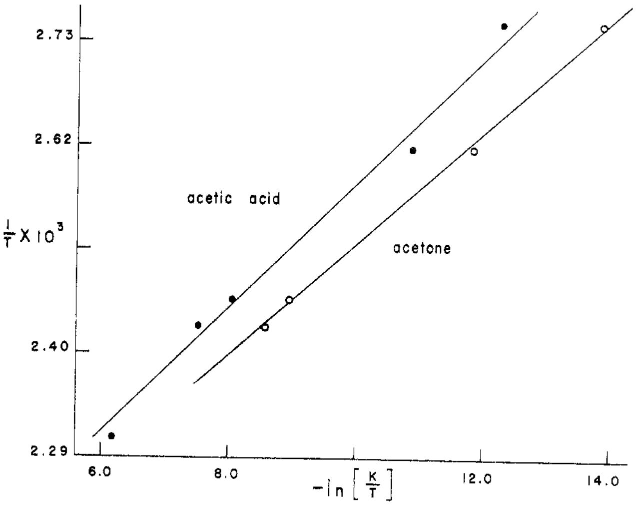

Figure 1.—A plot of $1/T$ *vs.* $-\ln\ (k/T)$ for the racemization of 2,2′-dimethoxy-6,6′-diphenamide in acetone and in acetic acid.

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(4) W. Mills and J. Breckenridge, *J. Chem. Soc.*, 2209 (1932).

(5) R. Adams, *et al.*, *J. Amer. Chem. Soc.*, **54**, 2966, 4426 (1932); **55**, 1649 (1933); **57**, 1565 (1935).

(6) J. Meisenheimer and O. Beisswenger, *Ber.*, **65B**, 32 (1932).

(7) J. E. Leffler and W. H. Graham, *J. Phys. Chem.*, **63**, 687 (1959).

(8) W. H. Graham and J. E. Leffler, *J. Phys. Chem.*, **63**, 1457 (1959).

(9) J. E. Leffler and B. M. Graybill, *J. Phys. Chem.*, **63**, 1457 (1959).

(10) B. M. Graybill and J. E. Leffler, *J. Phys. Chem.*, **63**, 1461 (1959).

(11) D. R. McKelvey, J. W. Frederiksen, R. R. Barrick, and G. A. Teas, *J. Amer. Chem. Soc.*, **90**, 6568 (1968).

TABLE III

ACTIVATION PARAMETERS FOR THE RACEMIZATION OF *N*-BENZENESULFONYL-*N*-CARBOXYMETHYL-2,4-DIMETHYL-6-NITROANILINE (II) IN VARIOUS SOLVENTS

Solvent	Registry no.	Temp, °C	$k \times 10^{-3}$, hr^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Methanol	67-56-1	40	31.44 ± 0.56	21.8 ± 0.1	−13.5 ± 0.2
		60	268.9 ± 4.7		
		80	1878 ± 37		
Ethanol (95%)	64-17-5	40	26.80 ± 0.61	20.5 ± 0.7	−17.9 ± 2.2
		50	79.90 ± 1.6		
		57	153.4 ± 3.1		
Absolute ethanol	64-17-5	40	26.84 ± 0.51	22.9 ± 0.3	−10.3 ± 0.8
		57	171.7 ± 4.5		
		60	264.8 ± 4.7		
		80	1948 ± 40		
Isopropyl alcohol	67-63-0	40	27.38 ± 0.52	21.9 ± 0.4	−13.7 ± 1.1
		60	215.3 ± 4.1		
		80	1660 ± 32		
tert-Butyl alcohol	75-65-0	40	23.64 ± 0.71	22.5 ± 0.3	−11.8 ± 1.0
		60	201.0 ± 4.1		
		80	1619 ± 33		
Benzyl alcohol	100-51-6	40	18.86 ± 0.56	24.0 ± 0.2	−7.4 ± 0.6
		60	214.6 ± 3.9		
		80	1681 ± 30		
Acetone	67-64-1	40	37.92 ± 0.67	21.7 ± 0.3	−13.7 ± 0.8
		60	300.0 ± 6.0		
		80	2208 ± 40		
Diethyl ketone	96-22-0	40	31.09 ± 0.55	21.9 ± 0.1	−13.1 ± 0.3
		60	280.0 ± 4.9		
		80	1896 ± 34		
Diisopropyl ketone	565-80-0	40	22.68 ± 0.43	22.9 ± 0.3	−10.8 ± 0.8
		60	205.7 ± 3.8		
		80	1649 ± 29		
Cyclopentanone	120-92-3	40	33.27 ± 0.75	21.9 ± 0.4	−13.0 ± 1.1
		60	327.4 ± 5.6		
		80	2014 ± 39		
Tetrahydrofuran	109-99-9	40	30.14 ± 0.53	22.4 ± 0.4	−11.9 ± 1.3
		60	243.2 ± 4.9		
		80	2003 ± 36		
Dimethylformamide	68-12-2	40	51.58 ± 1.1	19.2 ± 1.0	−20.8 ± 3.2
		50	125.5 ± 2.4		
		57	273.6 ± 5.3		
Dimethyl sulfoxide	67-68-5	40	49.44 ± 0.96	20.3 ± 1.1	−17.2 ± 3.2
		60	552.8 ± 11		
		80	2319 ± 53		
Pyridine	100-86-1	40	48.69 ± 0.92	20.4 ± 0.9	−16.9 ± 2.8
		60	494.3 ± 10		
		80	2238 ± 42		
p-Dioxane	123-91-1	40	27.60 ± 0.59	22.3 ± 0.3	−12.1 ± 0.8
		60	274.8 ± 4.7		
		80	1808 ± 32		
Anisole	100-66-3	40	25.52 ± 0.49	21.9 ± 0.3	−13.5 ± 0.9
		60	246.6 ± 4.0		
		80	1551 ± 29		
Acetonitrile	75-05-8	40	42.72 ± 0.72	22.0 ± 0.1	−12.4 ± 0.2
		60	368.0 ± 7.1		
		80	2632 ± 46		
Benzonitrile	100-47-0	40	31.92 ± 0.71	21.3 ± 0.2	−15.1 ± 0.6
		60	259.2 ± 5.3		
		80	1740 ± 33		
Propionitrile	107-12-0	40	42.53 ± 0.73	21.0 ± 0.1	−15.3 ± 0.2
		60	343.2 ± 6.5		
		80	2210 ± 39		
Nitrobenzene	98-95-3	40	24.14 ± 3.7	21.0 ± 0.4	−16.6 ± 1.2
		60	172.8 ± 3.7		
		80	1258 ± 26		
Acetic acid	64-19-7	40	19.56 ± 0.39	22.4 ± 0.2	−12.4 ± 0.7
		60	193.8 ± 3.5		
		80	1290 ± 26		
1,2-Dichloroethane	107-06-2	40	20.36 ± 0.57	22.8 ± 0.2	−11.2 ± 0.5
		60	205.1 ± 3.6		
		80	1440 ± 27		

Table III (*Continued*)

Solvent	Registry no.	Temp, °C	$k \times 10^{-3}$, hr^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Methyl acetate	79-20-9	40	29.60 ± 0.69	20.9 ± 0.6	−16.5 ± 1.8
		50	90.16 ± 1.9		
		57	175.0 ± 3.7		
Ethylene glycol	107-21-1	40	20.16 ± 0.49	23.0 ± 0.6	−10.7 ± 1.7
		60	166.4 ± 3.8		
		80	1508 ± 33		
Butyrolactone	96-48-0	40	34.74 ± 0.64	22.4 ± 0.3	−11.3 ± 1.0
		60	343.2 ± 7.2		
		80	2317 ± 43		
Ethyl malonate	105-53-3	40	26.42 ± 0.55	22.8 ± 0.2	−10.7 ± 0.5
		60	263.9 ± 4.5		
		80	1888 ± 35		

thalpy of transfer while that of the meta isomer is significantly different makes it seem likely that there is no steric inhibition of solvation in the ortho isomer despite the close proximity of the substituent groups, and that the differences in solvation between the ortho–para isomers and the meta isomer are due to differences in the electronic distributions caused by mesomeric effects.

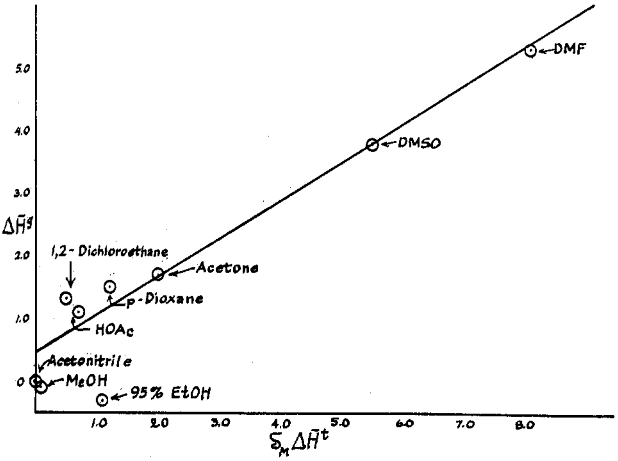

Figure 2.—A plot of δ_M $\Delta\bar{H}^g$ *vs.* δ_M $\Delta\bar{H}^t$ for the racemization of *N*-benzenesulfonyl-*N*-carboxymethyl-2,4-dimethyl-6-nitroaniline in various solvents.

Table IV

Enthalpies of Transfer from Various Solvents to Acetonitrile for the Ground State and the Transition State of *N*-Benzenesulfonyl-*N*-carboxymethyl-1-amino-2,4-dimethyl-6-nitrobenzene

Solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta\bar{H}_s$, kcal/mol	δ_M $\Delta\bar{H}^t$	δ_M $\Delta\bar{H}^g$
DMF	19.2 ± 1.0	−0.17 ± 0.20	8.1	5.3
DMSO	20.3 ± 1.1	1.28 ± 0.12	5.5	3.8
Ethanol (95%)	20.5 ± 0.7	5.37 ± 0.29	1.2	−0.3
Acetone	21.7 ± 0.3	3.36 ± 0.12	2.0	1.7
Methanol	21.8 ± 0.1	5.20 ± 0.20	0.1	−0.1
Acetonitrile	22.0 ± 0.1	5.10 ± 0.24	0.0	0.0
p-Dioxane	22.3 ± 0.3	3.60 ± 0.12	1.2	1.5
Acetic Acid	22.4 ± 0.2	3.98 ± 0.12	0.7	1.1
1,2-Dichloroethane	22.8 ± 0.2	3.76 ± 0.37	0.5	1.3

N-Benzenesulfonyl-*N*-carboxymethyl-2,4-dimethyl-6-nitroaniline (II) was prepared and resolved. The activation parameters for the racemization of II in 26 different solvents were determined. These data are shown in Table III. Heats of solution were also measured in nine of these solvents. The heats of solution were then coupled with the activation enthalpies to give enthalpies of transfer for the transition state δ_M $\Delta\bar{H}^t$. These enthalpies of transfer are from each of the nine solvents studied to acetonitrile. These data are shown in Table IV and a plot of δ_M $\Delta\bar{H}^g$ *vs.* δ_M $\Delta\bar{H}^t$ is shown in Figure 2. The most notable feature of Figure 2 is that all four of the dipolar aprotic solvents studied (acetonitrile, acetone, dimethyl sulfoxide, and dimethylformamide) are fairly well spread out and lie along a straight line while the other five solvents are bunched and randomly located about the line determined by the dipolar aprotic solvents. However, only ethanol is separated from this line by more than 0.5 kcal. The observation, for the dipolar aprotic solvents, that changes in solvent involvement in the transition state can be predicted from changes in solvent involvement in the ground state indicates that no solvent properties which are unimportant in the ground state are becoming important in the transition state. Solvation of the transition state can differ from that of the ground state because of two changes which take place during the transformation of ground state into transition state. Firstly, steric crowding in the transition state could lead to steric inhibition of solvation. Thus solvation of the interfering groups could be decreased in the transition state. Secondly, previous experiments have shown that the mesomeric effect of electron-withdrawing groups para to the nitrogen atom causes an increase in the rate of racemization by stabilization of the planar intermediate.[12] The same phenomenon should occur in the racemization of II and the resulting changes in polarization should be accompanied by changes in solvation. It is difficult to say which of these two solvent effects might be of more importance in this situation. It might be argued that steric inhibition of solvation in the transition state is unimportant, since this would bring into importance in the transition state a solvent property relatively unimportant in the ground state, that of solvent size. However this argument fails to the extent that the nine solvents studied resemble each other in steric requirements.

Experimental Section

2,2′-Dimethoxy-6,6′-diphenamide (I) was prepared by the method of Leffler and Graybill[9] with the modifications described in ref 11.

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[12] R. Adams and K. V. Y. Sundstrom, *J. Amer. Chem. Soc.*, **76**, 5474 (1954).

N-Benzenesulfonyl-N-carboxymethyl-2,4-dimethyl-6-nitroaniline (II) was prepared by the method of Adams and Gordon[13] as modified by Adams and Brower.[14]

Calorimetry.—The calorimeter used was similar to that already described by Arnett.[2] The errors reported with the heats of solution are 95% confidence limits. The relatively large errors are due to the extremely small temperature change resulting from the solution of 100 mg of sample in 175 ml of solvent. It was not practical to work with a larger sample size because of the slow rates of solution. In some solvents it was not possible to measure heats of solution because of the slow rates of solution.

Kinetics.—Resolved compound (0.1 g) was dissolved in 25 ml of solvent. Aliquots (2 ml) were placed in 12 13 × 100 mm Pyrex test tubes which were then flushed with nitrogen, sealed off, and placed in a constant-temperature bath. Temperature values known to within 0.1° were obtained with an N. B. S. calibrated thermometer. The 12 ampoules were removed in pairs over the course of the reaction and quenched by immersion in ice-water. After quenching the tubes were opened and the contents were placed in a polarimeter tube. A Rudolph photoelectric polarimeter (Model 520-M) equipped with a sodium vapor lamp was used to measure the optical rotation. Rates were measured at three different temperatures, usually 40, 60, and 80°. A least-squares program written by A. Ault of Cornell College was used to calculate the best values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from the kinetic data. The errors listed are 95% confidence limits.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—I, 23306-01-6; II, 41391-02-0.

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[13] R. Adams and J. R. Gordon, *J. Amer. Chem. Soc.*, **72**, 2458 (1950).

[14] R. Adams and K. R. Brower, *J. Amer. Chem. Soc.*, **78**, 663 (1956).

Notes

Synthesis of Trineopentylamine

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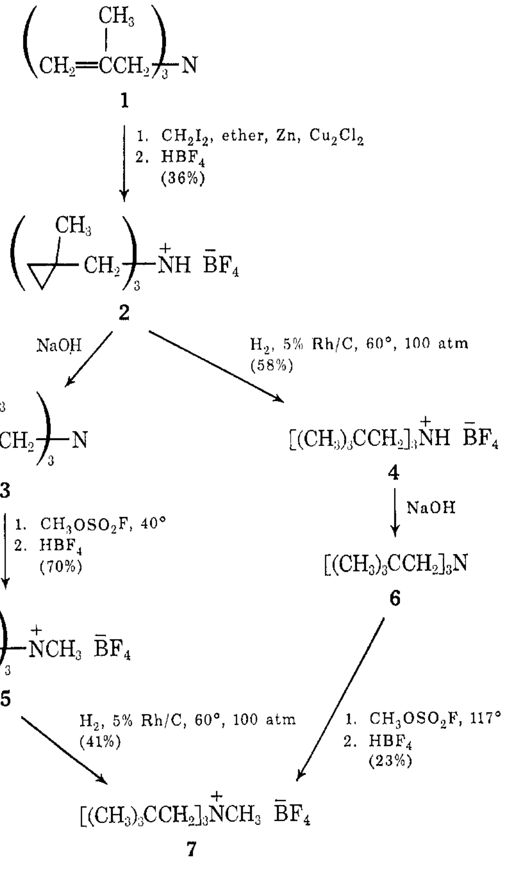
Received May 15, 1973

In attempts to prepare base-resistant quaternary ammonium ions, with tetraneopentylammonium ion as a fanciful goal, I have synthesized two new highly crowded tertiary amines, tris(1-methylcyclopropylmethyl)amine (**3**) and trineopentylamine (**6**), directly from tris(2-methylallyl)amine (**1**). The synthetic methods and results are summarized in Scheme I. Little effort has been made to optimize the yields.

SCHEME I



Several features of the synthesis may be of general interest. (1) A modified Simmons–Smith reaction,[1] the triple cyclopropanation of **1**, proceeds readily in the presence of a tertiary amine in 36% yield. (2) Hydrogenations of hindered cyclopropanes **2** and **5** proceed under milder conditions with rhodium than with the previously used[2] palladium catalyst. With 5% palladium on carbon, hydrogenations of **2** and **5** at 100 atm required temperatures of 130–150° and gave poorer yields of less pure **4** and **7**. As with other 1,1-dialkylcyclopropanes, catalytic hydrogenation of **2** and **5** occurs exclusively at the unsubstituted cyclopropane bond.[3] (3) Tertiary amines and tetraalkylammonium ions were handled whenever possible as their tetrafluoroborate salts, which are in general more stable and easier to crystallize than the free amines or the halide salts.[4] Trifluoromethanesulfonates may serve as well as tetrafluoroborates for this purpose.[5]

The highly crowded nature of amines **3** and **6** is demonstrated by their resistance to alkylation. Only methyl fluorosulfonate, at 40 and 117° respectively, gave reasonable yields of their corresponding methyl-

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[1] R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, **35**, 2057 (1970).

[2] A. L. Schultz, *J. Org. Chem.*, **36**, 383 (1971).

[3] C. W. Woodworth, V. Buss, and P. v. R. Schleyer, *Chem. Commun.*, 569 (1968).

[4] H. O. House, E. Feng, and N. P. Peet, *J. Org. Chem.*, **36**, 2371 (1971).

[5] K. Rousseau, G. C. Farrington, and D. Dolphin, *J. Org. Chem.*, **37**, 3968 (1972).