The *p*-bromophenacyl ester of VIb had m.p. 89–90°.

Anal. Calcd. for $C_{18}H_{23}O_3Br$: C, 58.85; H, 6.32; Br, 21.76. Found: C, 59.06; H, 6.08; Br, 21.62.

Similarly, the crude diazoketone Vc, formed from 15.0 g. of the hydrazone VIc, produced 2.42 g. (31%) of cyclodecanecarboxylic acid (VIc) as a white, waxy solid of b.p. 95° (0.05 mm.) and m.p. 52° (reported[10] m.p. 53°).

The *p*-bromophenacyl ester of VIc was obtained as white needles, m.p. 82.5–83°.

Anal. Calcd. for $C_{19}H_{25}O_3Br$: C, 59.84; H, 6.62. Found: C, 59.63; H, 6.53.

N,N-Dimethylcyclononanecarboxamide (VIII).—After 24.0 g. of thionyl chloride had been added slowly (1 hr.) to a solution of 12.0 g. of the acid VIb in 100 ml. of benzene, the total mixture was allowed to stand 12 hr. and then refluxed 2 hr., the benzene and thionyl chloride then were removed *in vacuo*. To this mixture there finally was added 25 ml. of benzene and 500 ml. of anhydrous ether, then dimethylamine was gradually passed into the slowly stirred ethereal solution, cooled to 0°. After initial removal of the amine hydrochloride, which separated, and the solvents, there was finally obtained 10.93 g. (79%) of the amide VIII, $n^{24}D$ 1.4939, b.p. 105–106°, and solid at 0°. The amide VIII, purified by five recrystallizations from hexane, liquefied at room temperature.

Anal. Calcd. for $C_{12}H_{23}NO$: C, 73.02; H, 11.77; N, 7.10. Found: C, 73.24; H, 11.84; N, 7.09.

N,N-Dimethylaminomethylcyclononane (IX).—A solution of 6.9 g. of the amide VIII in 50 ml. of anhydrous ether was added slowly (1 hr.) at 0° to a stirred slurry of 1.5 g. of lithium aluminum hydride in 50 ml. of dry ether at 0°. After the entire mixture had been stirred for 24 hr., the excess hydride was decomposed with a solution of saturated ammonium chloride. A standard work-up gave 5.00 g. (78%) of the amine IX, $n^{28}D$ 1.4700, b.p. 90° (2.4 mm.).

Anal. Calcd. for $C_{12}H_{25}N$: C, 78.59; H, 13.77; N, 7.64. Found: C, 78.33; H, 13.58; N, 7.60.

The N-oxide (X) of the amine IX was prepared by essentially the same method previously described.[13] The picrate derivative of X, prepared by a standard method,[14] showed m.p. 119° after three recrystallizations from 95% ethanol and two from absolute methanol.

Anal. Calcd. for $C_{18}H_{26}O_{28}N_4O_8$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.44; H, 6.60; N, 12.97; 13.07.

Methylenecyclononane (XI).—A solution of 3.60 g. of the amine oxide X in 5 ml. of water was placed in a flask filled with glass wool. The products formed upon heating this filled flask at 120–130° (3 mm.) were collected in a trap cooled to −5°. The usual simple work-up of the product gave 1.79 g. (66%) of the olefin XI, $n^{25}D$ 1.4782, b.p. 82° (36 mm.) [reported[15] $n^{19}D$ 1.4808, b.p. 169°].

Cyclononanone (XII).—A solution of 1.15 g. of the exo-olefin XI in 100 ml. of absolute ethanol was treated with dry ozonized air (3% ozone) for 1 hour. Upon isolation of the ozonolysis products 0.81 g. (70%) of the ketone XII was obtained which had $n^{23}D$ 1.4708 and b.p. 45–47° (10 mm.) [reported[7] $n^{20}D$ 1.4768 and b.p. 101–101.5°].

The semicarbazone derivative of the ketone XII, m.p. 180–181°, did not depress the m.p. of an authentic sample of cyclononanone semicarbazone[16] upon admixture.

(13) A. C. Cope, R. A. Pike and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

(14) R. L. Shriner, R. C. Fuson and D. Y. Curtin, ref. 11, p. 229.

(15) F. Sorn and J. Beranek, *Chem. listy*, **47**, 708 (1953).

(16) R. L. Shriner, R. C. Fuson and D. Y. Curtin, ref. 11, p. 218

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Selective Reductions. I. The Partial Reduction of Tertiary Amides with Lithium Aluminum Hydride. A New Aldehyde Synthesis *via* the 1-Acylaziridines[1,2]

BY HERBERT C. BROWN AND AKIRA TSUKAMOTO[3]

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The partial reduction of tertiary amides by lithium aluminum hydride was explored as a possible synthetic route to aldehydes. Among the amide derivatives which were examined, the 1-acylaziridines exhibited unusually favorable characteristics for this synthesis, producing the corresponding aldehydes in excellent yields. It was demonstrated that the 1-acylaziridine could be synthesized from the acid chloride and ethylenimine, and utilized *in situ* for the aldehyde synthesis. N,N-Diisopropylamides proved to be relatively resistant to reduction by lithium aluminum hydride at 0°, indicating that this group may provide a convenient means of protecting the carboxylic acid grouping from reduction in polyfunctional molecules.

The reduction of tertiary amides by lithium aluminum hydride under ordinary conditions, *i.e.*, with an excess of the reducing agent present, usually produces the corresponding tertiary amines with the same number of carbon atoms.[4] In some cases reductive cleavage to an alcohol and a secondary amine has been observed.[5] The controlled reduction of selected tertiary amides by lithium aluminum hydride, followed by hydrolysis, has been utilized for the synthesis of aldehydes.[6] Thus Wittig and Hornberger obtained a series of unsaturated aldehydes, $C_6H_5(CH{=}CH)_nCHO$(n = 1, 2, 4 and 5) from the partial reduction of the corresponding N-acylcarbazoles with lithium aluminum hydride.[7] Similarly, Weygand and his coworkers demonstrated that the N-methylanilides could be utilized to produce a wide variety of aldehydes in good yields (60–90%).[8] Cyclohexanecarboxaldehyde was obtained in 80% yield by the reduction of N-cyclohexanecarboxylpiperidide.[9] Finally, Ried and Konigstein recently have shown that the partial reduction of the 1-acyl-3,5-dimethylpyrazoles gives a general synthetic route to aldehydes from the carboxylic acids.[10]

(1) Previous studies in this general area have appeared in connection with other series. For a summary of these earlier publications see H. C. Brown, *J. Chem. Educ.*, **38**, 173 (1961). A preliminary communication of some of these results has been published: H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 2016 (1961).

(2) Based upon a thesis submitted by Akira Tsukamoto in June, 1959, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Research assistant on a grant provided by the Eli Lilly and Co., 1957–1959.

(4) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3738 (1948).

(5) V. M. Micović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

(6) E. Mosettig, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 218–257.

(7) G. Wittig and P. Hornberger, *Ann.*, **577**, 11 (1952).

(8) (a) W. Weygand and E. Eberhardt, *Angew. Chem.*, **64**, 458 (1952); (b) W. Weygand, E. Eberhardt, H. Linden, F. Schofer and H. Linden, *ibid.*, **65**, 525 (1953); (c) W. Weygand and H. Linden, *ibid.*, **66**, 174 (1954).

(9) M. Mousseron, R. Jacquier, M. Mousseron-Conet and R. Zagdown, *Bull. soc. chim. France*, **19**, 1042 (1952).

(10) W. Ried and F. J. Konigstein, *Angew. Chem.*, **70**, 165 (1958).

That the structure of the amide groups markedly influences the yields of aldehydes realized in these reductions has been demonstrated by Weygand and his co-workers.[8b] Thus the N,N-diphenylamides or N-methyl-N-cyclohexylamides produce aldehydes only in poor yields, while the N-methylanilides give far more favorable yields of aldehydes.

It was recently demonstrated that the reduction of aromatic acid chlorides by lithium tri-*t*-butoxyaluminohydride produces the corresponding aldehydes in excellent yields (70–90%).[11] In the case of aliphatic acid chlorides, the yields were less favorable, in the range of 40–60%. Accordingly, we decided to examine the reduction of representative aliphatic N-acyl tertiary amides in the hope of increasing our understanding of the factors influencing the selective reduction of this grouping and of developing an improved procedure for the synthesis of aliphatic aldehydes.

Results

A few representative N,N-disubstituted *n*-butyramides were prepared and subjected to partial reduction by the theoretical quantity of lithium aluminum hydride under standard conditions. In these experiments a solution of the hydride (1 mole) in ether was added to a stirred solution of the amide (4 moles) at 0°. After one hour, the reaction mixture was hydrolyzed and the yield of aldehyde determined as the 2,4-dinitrophenylhydrazone. There were observed only minor changes in the aldehyde yield as the groups attached to the amide nitrogen were altered from methyl (25%) to ethyl (22%), or to five- (16%) or six-membered cyclic groups (33%).

The low yields are not the result of incomplete reaction, since in each case nearly all of the active hydride had been utilized by the end of the reaction period. Only the diisopropylamide was an exception—it appeared to react only very slowly with the reagent, leaving nearly all of the hydride unreacted at the end of the 1-hour reaction period.

In accordance with the results of Weygand, the yield of aldehyde was increased to 58% by the use of the N-methyl-N-phenylamide.

The use of an excess of hydride did not improve matters. Indeed, a decrease in aldehyde yield was observed.

Consideration of these results suggested the desirability of a tertiary amide of low steric requirements which also would resist resonance interactions with the carbonyl group. Accordingly, N-butyrylpyrrole and N-butyrylaziridine were synthesized and tested. The yield was disappointing with the former, only 30%, but the aziridine produced butyraldehyde in a yield of 88%. Indeed, this derivative was quite remarkable in another respect—use of 100% excess of lithium aluminum hydride did not reduce the yield realized.

These results are summarized in Table I.

The conversion of arylamides to the corresponding aldehydes proceeds more readily than the aliphatic derivatives. Thus, under the above conditions, benzaldehyde is obtained from the dimethylamide in a 60% yield, in contrast to the 25% yield realized for *n*-butyraldehyde. Similarly, benzaldehyde has been reported to be formed in a 47% yield from the piperidide[5] in contrast to the 33% yield realized here for *n*-butyraldehyde.

(11) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **80**, 5372 (1958); H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

TABLE I

THE REDUCTION OF *n*-BUTYLAMIDES BY LITHIUM ALUMINUM HYDRIDE AT 0°

Amide	Yield of *n*-butyraldehyde, %	Amide	Yield of *n*-butyraldehyde, %
n-$C_3H_7CONMe_2$	25	n-$C_3H_7CON(CH_2)_5$	33
n-$C_3H_7CONEt_2$	22	n-$C_3H_7CONMePh$	58
n-$C_3H_7CON(i\text{-}Pr)_2$	No reacn.	n-$C_3H_7CON(CH)_4$	30
n-$C_3H_7CON(CH_2)_4$	16	n-$C_3H_7CON(CH_2)_2$	88

The remarkably high aldehyde yield from 1-*n*-butyrylaziridine led us to explore the applicability of this reaction for a general aldehyde synthesis. It was established that the 1-acylaziridine need not be isolated, but could be synthesized in solution by adding the acid chloride to an equimolar mixture of ethylenimine and triethylamine, separating the precipitated triethylammonium chloride, and then adding the lithium aluminum hydride.

This procedure is particularly advantageous in view of the susceptibility of the 1-acylaziridines toward heat which interferes with their ready isolation in pure form.[12] The yields realized with a number of representative aliphatic acid chlorides were quite good. Only in the case of crotonyl chloride is the yield low, evidently because of concurrent attack of the reagent on the double bond.

The results are summarized in Table II.

TABLE II

YIELDS OF ALDEHYDE FROM ACID CHLORIDES *via* THE 1-ACYLAZIRIDINE

Acid chloride	Yield of aldehyde,[a] %	Acid chloride	Yield o aldehyde,[a] %
n-Butyryl	75, 74[b]	Pivaloyl	79, 88[b]
n-Caproyl	81	Crotonyl	40
2-Ethylbutyryl	77	Cyclopropanecarbonyl	67

[a] Determined as the 2,4-dinitrophenylhydrazone. [b] Lithium aluminum hydride was added in 100% excess over the acid chloride used.

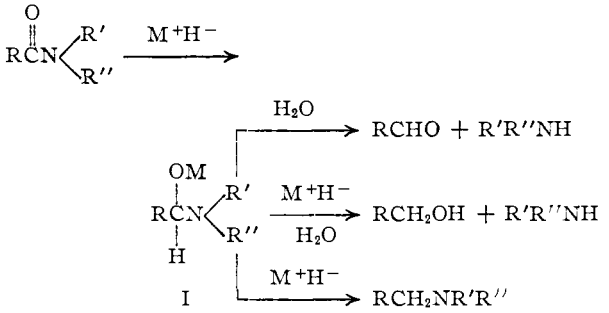
Several aldehydes then were synthesized on a preparative scale, utilizing this procedure. Cyclopropanecarboxaldehyde, pivalaldehyde and α-ethylbutyraldehyde were isolated in yields of 60, 54 and 69%, respectively, from the corresponding acid chlorides.

A detailed study of the conditions necessary for optimum yields was not made. Consequently, the above yields are not necessarily the best realizable through this procedure. However, they are quite satisfactory and clearly establish the utility of the 1-acylaziridines for the synthesis of aldehydes. The simplicity of the method should make this procedure a useful synthetic route to the aldehyde from the corresponding carboxylic acid.

(12) S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895).

Discussion

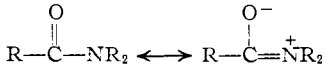
It has been suggested that the reduction of tertiary amides proceeds to its various products through a common intermediate.[5,8b] In this mechanism the first step is postulated to be the nucleophilic attack of the metal hydride, M^+H^-, on the carbonyl group to form the intermediate complex I. Treatment with water transforms this complex to the aldehyde and secondary amine. Alternatively, it can be reduced further to the tertiary amine or to a secondary amine and alcohol by nucleophilic displacement of the oxygen atom or the nitrogen atom by a hydride anion.



According to this mechanism, the achieving of a successful aldehyde synthesis involves a rapid addition of the hydride reagent to the carbonyl group, with a rate much more rapid than the undesirable nucleophilic displacements.

It is evident that amide groups with large steric requirements should be undesirable, since they would hinder the initial addition of the metal hydride to the carbonyl group. Presumably, the slow reaction of lithium aluminum hydride with *n*-butyryl-N,N-diisopropylamide is due to this factor. Moreover, there is some evidence that the presence of large steric effects may influence the direction of the undesired second reduction stage. The presence of bulky substituents appears to favor the formation of alcohols rather than of tertiary amines, possibly the result of the relief of steric strain arising from the displacement of the amide group by the hydride reagent.[13]

In addition to increasing the ease of attack of the reagent at the carbonyl group by reducing the steric requirements of the amide grouping, it is evident that an increase in the reactivity of the carbonyl group brought about by electronic effects also should be favorable. Resonance interactions between the amide nitrogen and the carbonyl group can only stabilize that group and decrease its reactivity. Presumably, the effectiveness of



the N-methyl-N-phenylamides is due to the effect of the phenyl substituent in reducing this resonance contribution to the carbonyl group.

On the basis of these arguments the N-acylpyrroles and the N-acylaziridines appeared to offer the most favorable combination of low steric requirements and low resonance interactions with the carbonyl group.

The carbonyl stretching frequencies observed for these amides offer support for low resonance interactions involving these amides. Thus, most tertiary amides exhibit a carbonyl stretching frequency at 1631–1667 cm.$^{-1}$. However, this frequency for 1-*n*-butyrylpyrrole is at 1755 cm.$^{-1}$, and that of 1-*n*-butyrylaziridine is at 1730 cm.$^{-1}$.

In view of these arguments, the low yield realized with *n*-butyrylpyrrole was disappointing. However, this may be due to a complicating side reaction of lithium aluminum hydride with the pyrrole ring, since we realized very poor material balances in this reaction. On the other hand, it was gratifying to achieve an 88% yield of *n*-butyraldehyde from 1-*n*-butyrylaziridine.

The evident high reactivity of the carbonyl group of the 1-acylaziridines should find other applications in synthetic chemistry.[14] Finally, the resistance exhibited by N,N-diisopropylamides to attack by lithium aluminum hydride at 0° suggests that this group may provide a convenient means of protecting the carboxylic acid grouping from reduction in polyfunctional molecules.

Experimental Part

Materials.—All commercially available chemicals were carefully purified by standard methods. Solutions of lithium aluminum hydride in ether were prepared by mixing commercial absolute ether and commercial lithium aluminum hydride (Metal Hydrides Inc., purity 95%) and the solution was used after the insoluble material precipitated. The concentration of the solution was established by analysis for hydride by hydrolysis. All apparatus used was flamed in a dry nitrogen atmosphere and allowed to cool in this atmosphere prior to use.

Most of the *n*-butyryl N,N-disubstituted amides were prepared by treating *n*-butyryl chloride with the corresponding amines in ether. 1-*n*-Butyrylpyrrole was prepared from the potassium salt of pyrrole and *n*-butyryl chloride following the method of Pictet.[15]

1-*n*-Butyrylaziridine.—A mixture of 43 g. (1.0 mole) of ethylenimine and 111 g. (1.1 moles) of triethylamine in 400 ml. of benzene was placed in a 1-liter 3-necked flask equipped with a mechanical stirrer, a condenser and a dropping funnel and cooled by an ice-bath. To the stirred solution was added over a period of 1 hour 106.5 g. (1.0 mole) of *n*-butyryl chloride. The reaction was allowed to proceed to completion by stirring for further 30 minutes at 0°. The precipitated triethylamine hydrochloride was filtered off and washed several times with a total of 200 ml. of benzene. The benzene was removed at room temperature *in vacuo* from the combined fractions and 1-*n*-butyrylaziridine (characterized by its infrared spectrum) was collected at 48–50° at 8 mm., n^{20}D 1.4422, while the bath temperature was kept below 65°. The yield was 56 g., 50% of the theoretical. The purity, based upon its infrared spectrum and by low temperature gas chromatography analysis, was estimated to be 95%.

In another experiment an attempt was made to obtain the product in the same manner as above, except for distillation at a higher temperature. The main product, b.p. 54–55° at 25 mm., n^{25}D 1.4750, was obtained, together with a large amount of tar. This particular product was not reduced by lithium aluminum hydride and infrared examination characterized it to be 2-*n*-propyloxazoline, presumably formed by the thermal isomerization of 1-butyrylaziridine.[12]

Table III summarizes the physical constants of the *n*-butyramides.

Reduction of Tertiary Amides.—The typical procedure utilized for the reduction follows: In a 100-ml. 3-necked

(13) The electronegativity of the amine component also influences the direction taken by the second stage: A. W. Burgstahler, *J. Am. Chem. Soc.*, **73**, 3021 (1951).

(14) In this connection, the unusually rapid methanolysis of 1-*p*-nitrobenzoylaziridine, catalyzed by iodide ion, is noteworthy: H. W. Heine, M. E. Fetter and E. M. Nicholson, *ibid.*, **81**, 2202 (1959).

(15) A. Pictet, *Ber.*, **37**, 2796 (1904).

TABLE III

PHYSICAL CONSTANTS OF *n*-BUTYRAMIDES

NR'R'' in *n*-$C_3H_7CONR'R''$	B.p. °C.	B.p. Mm.	$n^{20}D$	Ref.
Dimethylamine	86.0	10	1.4418	*a*
Diethylamine	73–74	5	1.4421	*b*
Diisopropylamine	80–81	8	1.4438	*c*
N-Methylaniline	141–141.5	17	1.5215	*d*
Piperidine	65–66	1	1.4777	*e*
Pyrrolidine	95–96	5	1.4727	*f*
Ethylenimine	48–50	8	1.4422	*g*
Pyrrole	83.8–84.0	10	1.4978	*h*
N,N-Dimethylbenzamide	M.p. 42–43			*i*

[a] J. R. Ruhoff and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 401 (1934): $n^{25}D$ 1.4391. [b] J. Brown and A. Heymons, *Ber.*, **62**, 411 (1928): $n^{25}D$ 1.4403. [c] S. I. Gertler and A. Yerington, *C. A.*, **50**, 17297 (1956): $n^{25}D$ 1.4344. [d] Ref. *c*: $n^{25}D$ 1.5183. [e] J. D. Ianni and H. Adkins, *J. Am. Chem. Soc.*, **60**, 1675 (1938): $n^{25}D$ 1.4750. [f] *Anal.* Calcd. for $C_8H_{16}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 68.02; H, 10.28; N, 9.83. [g] See Experimental Part. [h] *Anal.* Calcd. for $C_8H_{11}NO$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.23; H, 8.35; N, 10.26. [i] H. Staudinger and N. Kon, *Ann.*, **384**, 114 (1911): m.p. 43°.

flask was placed 0.040 mole of N,N-dimethylbutyramide in 40 ml. of ether cooled by an ice-bath. To the stirred solution was added 10 ml. of a 1 *M* solution of lithium aluminum hydride over a period of 30 minutes. The reaction mixture was stirred for an additional 1 hour at 0° and then decomposed with a saturated aqueous solution of potassium sodium tartarate. The aqueous layer was washed with 20 ml. of ether. An aliquot of the ethereal solution was analyzed for the aldehyde with 2,4-dinitrophenylhydrazine. Hydrogen evolved on decomposition was measured to determine the hydride consumption. The yield of the aldehyde was established by weighing the 2,4-dinitrophenylhydrazone after drying to constant weight. The hydrazone thus obtained was essentially pure, giving the same melting point as authentic pure specimen, m.p. 121–122° (lit.[16] 122°).

Preparation of Aldehydes *via* 1-Acylaziridine. Cyclopropanecarboxaldehyde.—Cyclopropanecarbonyl chloride (42.2 g., 0.40 mole) was added over a period of 1 hour to a stirred solution of ethylenimine (17.5 g., 0.40 mole) and triethylamine (40.0 g , 0.40 mole) in 200 ml. of ethyl ether cooled by an ice–salt mixture. The reaction mixture was stirred for an additional 0.5 hour and precipitated triethylamine hydrochloride was filtered off and washed with 100 ml. of ether. The combined ether solution was cooled to 0° and 80 ml. of 1.25 *M* lithium aluminum hydride in ether was added to the stirred solution over 0.5 hour. After an additional hour, cold 5 *N* sulfuric acid was added, the ether layer was separated, and the aqueous layer extracted. The combined ether extracts were washed with water, sodium bicarbonate, water again, and dried over sodium sulfate. Analysis of an aliquot with 2,4-dinitrophenylhydrazine indicated a yield of 67%. Distillation yielded 16.8 g. of cyclopropanecarboxaldehyde, b.p. 97–100° at 740 mm., $n^{20}D$ 1.4302, a yield of 60%.

Similarly, α-ethylbutyraldehyde, b.p. 116–119° at 740 mm., $n^{20}D$ 1.4020 (lit.[17] b.p. 117–118°, $n^{15}D$ 1.40398), was obtained in 69% yield, and pivalaldehyde, b.p. 73–75° at 740 mm., $n^{20}D$ 1.3790 (lit.,[18] b.p. 71–74° at 730 mm., $n^{20}D$ 1.3791), was obtained in 54% yield from the corresponding acid chlorides.

(16) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 229–230.

(17) A. Behal and M. Sommelet, *Bull. soc. chim. France*, **31** 300 (1904).

(18) K. N. Campbell, *J. Am. Chem. Soc.*, **59**, 1982 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF DELAWARE, DOVER, DEL.]

Studies on the Effect of Remote Substituents on Reactivity: The Rates of Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Cyclohexenes and Norbornenes (I)[1a]

BY HAROLD KWART[1b] AND LEROY J. MILLER

RECEIVED MAY 8, 1961

The second-order rate constants for the addition of 2,4-dinitrobenzenesulfenyl chloride to a number of transannularly substituted cyclohexenes and norbornenes have been determined in glacial acetic acid at 30.1°. The rates for the 4-substituted cyclohexenes could be correlated by means of Taft's equation, $\log k/k_0 = \sigma_I\rho_I$, thereby indicating that the substituents effects were almost entirely electronic in character. The *cis*-4,5-disubstituted cyclohexenes fit the correlation in only an approximate manner, presumably because of the inequivalence of the axial and the equatorial positions into which the substituents are forced in the modified chair conformation. The substituent effects appear to be similar for the transannularly substituted norbornenes, although *endo* and *exo* substituents affect the rate to a different degree. These results permit some discussion of the nature of transmission of inductive effects on the rates of reactions. The ρ_I value measured for the monocyclic series is significantly greater than the ρ_H value reported for the Hammett series of *p*-substituted styrenes. These and other data are interpreted in the context of the discussion of how inductive effects are transmitted.

Introduction

Electronic effects of polar groups have often been assumed to be transmitted *via* a chain of connecting atoms; for such cases Roberts and Moreland,[2] in 1953, reserved the term "inductive effect." The term "field effect" was applied by these authors to those electronic influences which are transmitted across intraannular space. These authors as well as Grob and his co-workers[3] have extensively explored the interactions between nonadjacent atoms and functional groups in cyclic and bicyclic structures that regulated the positions of acid–base equilibria.

Transannular interactions involving the formation of a partial bond or a field effect influencing cyclic structures have been ascertained by Leonard and co-workers.[4] Transannular reactions implying the formation of a full bond or the shift of a bond across intraannular space have been shown by several groups of workers to be capable of con-

(1) (a) Taken in part from the dissertation of Leroy J. Miller, submitted in partial fulfillment of the requirements of the Ph.D. degree at the University of Delaware, June, 1959. (b) Support of this work by the National Science Foundation under Grant NSF-G6037 is gratefully acknowledged.

(2) J. D. Roberts and W. T. Moreland, *J. Am. Chem. Soc.*, **75**, 2167 (1953).

(3) (a) C. A. Grob, E. Renk and A. Kaiser, *Chem. & Ind. (London)*, 1222 (1955); (b) 598 (1957).

(4) See N. J. Leonard, *Record Chem. Progr.*, **17**, 243 (1956), for discussion and references pertaining to this work.