In Eberson's picture of the mechanism,[6] all of the product-forming reactions, both those involving free radicals and those involving ionic intermediates, occur in the solution. The initial step is, again, a one-electron transfer to give a radical, which may then either transfer a second electron or be desorbed from the anode surface. The product distribution will now be determined by this competition between radical desorption and electron transfer. If this view is correct, the carbon electrode favors carbonium-ion products, because the paramagnetic centers impede radical desorption and, therefore, favor electron transfer.

In the reactions now under consideration, it must be assumed that the applied potentials are sufficiently high to permit a second electron transfer from the initially generated radicals, since carbonium-ion products would not be observed on both platinum and carbon if this were not the case. If the radicals all react while adsorbed on the electrode and if the applied potential is supplying sufficient activation energy to permit a second electron transfer, it is difficult to see how radical dimerization can compete successfully with electron transfer, as it does at a platinum anode. The bimolecular, coupling reaction might be expected to have both an unfavorable enthalpy and entropy of activation. Even though the activation energy for radical dimerization in solution is normally low, in this case one must, in addition, overcome the energy by which the two radicals are held on the electrode surface. The entropy of activation might also be expected to be negative, since in addition to being detached from the electrode surface the two radicals will probably require a change in orientation with respect to the electrode before they will be able to attain a configuration suitable for coupling. The radical dimerization reaction is, moreover, a purely chemical process, and the necessary free energy of activation cannot be supplied electrochemically as it is for the electron-transfer reaction.

The Eberson picture of the Kolbe reaction obviates these difficulties. On platinum, the radicals generated are largely desorbed from the electrode, perhaps in a concerted process with elimination of carbon dioxide from an initially generated acyloxy radical. On carbon, the additional binding forces that are available attach the bulk of the radicals generated to the electrode surface, and these undergo a second electron transfer to give a cation. The present results afford some support for this interpretation even if they fall short of proving it.

Registry No.—Phenylacetic acid, 103-822; 1-methylcyclohexaneacetic acid, 14352-58-0.

Slow Rotations in Some Substituted Anilides[1]

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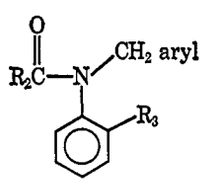
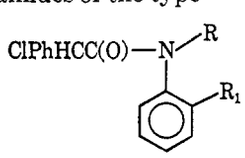
Received December 31, 1968

Barrier heights (kilocalories per mole) for rotation around the nitrogen–benzene bond are reported for 19 anilides of the type

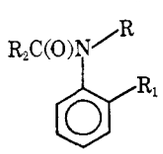


The only amide isomer observed is as shown, with the *ortho*-substituted benzene ring *trans* to oxygen (except for formanilides). However, rotation around the nitrogen–benzene bond is preceded by rotation around the carbonyl–nitrogen bond to give the activated state. Variations in barrier height from compound to compound are rationalized in terms of steric and electronic factors.

We have reported[2] the effects of various substituents, R and R_1, on the rate of rotation around the nitrogen–benzene bond in amides of the type



This paper reports a similar study of amides of the type



where R_2 and R_1 are varied and R is a benzyl (or closely related) group. Data are also included for two thioamides. The rotation rates were determined by signal shape analysis[3] of the nuclear magnetic resonance (nmr) signals (AB quartet) arising from the nonequivalent benzyl methylene protons. These protons are nonequivalent when rotation around the N–C (aromatic) bond is slow on the nmr time scale and give an AB quartet which coalesces into a singlet as rotation becomes rapid.[4–7]

(1) The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

(2) T. H. Siddall, III, and W. E. Stewart, *J. Phys. Chem.*, in press.

(3) J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, **41**, 1033 (1964).

(4) T. H. Siddall, III, and C. A. Prohaska, *J. Amer. Chem. Soc.*, **88**, 1172 (1966).

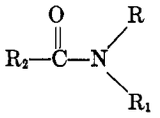
(5) T. H. Siddall, III, *J. Org. Chem.*, **31**, 3719 (1966).

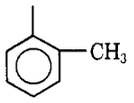
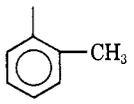
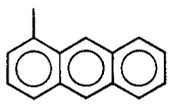
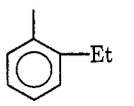
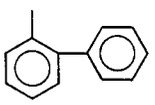
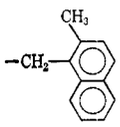
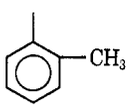
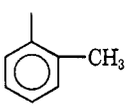
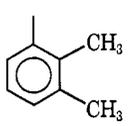
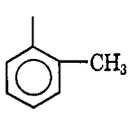
(6) B. J. Price, J. A. Eggleston, and I. O. Sutherland, *J. Chem. Soc., B* 922 (1967).

(7) Y. Shvo, E. C. Taylor, K. Mislow, and M. Raban, *J. Amer. Chem. Soc.*, **89**, 4910 (1967).

TABLE IA

FREE ENERGIES OF ACTIVATION FOR ROTATION AROUND AMIDE BOND AND N—C (AROMATIC) BOND IN



Compd	R	R_1	R_2	ΔF^*, kcal/mol (°C) C(O)—N bond	ΔF^*, kcal/mol (°C) N—C (aromatic) bond	Chemical shift $\nu_A - \nu_B$, at 110°, cps (°C)
I	—CH_2Ph		H	20,[a] 19[b] (*endo* → *exo*) 21,[a] 20[b] (*exo* → *endo*)	13 (−25), *endo*[c] 10 (−80), *exo*[d] 18 (−58), *exo*[d]	11 (−25) 33 (−80)
II (thioamide)	—CH_2Ph		H	22 (*endo* → *exo*) 24 (*exo* → *endo*)	18 (100), *endo* 10 (−70), *exo* (d) 10 (−63), *exo* (d)	6 19 (−70)
III	—CH_2Ph		CH_3		22.6 (143) 22.2 (159)	70
IV	—CH_2Ph		*t*-Butyl		19.5 (110) 19.8 (121) 20.0 (134) 19.7 (144)	92
V	—CH_2Ph		*t*-Butyl		17.5 (80) 17.8 (90) 17.9 (110)	109
VI			CH_3		22.9 (159) 22.8 (168)	30
VII	—CH_2Ph		$(C_6H_5)_2(CH_3)C$—		20.6 (101) 20.0 (110) 20.1 (121) 19.8 (128)	74
VIII	—CH_2Ph		CH_3		23.0 (153) 22.7 (161) 22.9 (162) 22.8 (167) 22.7 (173)	43
IX	—CH_2Ph		$(C_2H_5)_3C$—		19.4 (103) 19.4 (110) 19.6 (117) 19.8 (132) 19.5 (142)	88

[a] Signal shape analysis at 100°. [b] Reequilibration at −13°. [c] In $CDCl_3$. [d] In 50:50 $CDCl_3$–"Freon"-11.

Experimental Section

The amides were prepared by the conventional procedures of (1) adding a mixture of the desired amine plus Et_3N (to combine with HCl) to the appropriate acyl chloride or (2) alkylating the unsubstituted anilide *via* its sodio derivative. The formamide was prepared by distilling a large excess of formic acid from an N-benzyltoluidine mixture. The thio compounds were prepared by refluxing the corresponding amide for about 1 hr with an equal weight of P_2S_5 suspended in toluene, then treating the resulting thioamide adduct with dilute Na_2CO_3 solution. All compounds were purified by distillation under high vacuum. Compounds were purified further in most cases by crystallization from various solvents. Samples were made up of 200 mg of amide plus 500 μl of *o*-dichlorobenzene. The *o*-dichlorobenzene had been freshly passed through a column of Linde 5A Molecular Sieve. The *o*-dichlorobenzene was chosen as a solvent because of its relative inertness, freedom from high field nuclear magnetic resonance signals, and its wide-liquid range. It was suggested to us by the work of Sandström.[8] The loaded nmr tubes were bubbled with and then sealed under nitrogen. For low-temperature work, $CDCl_3$ and a 50–50 mixture of $CDCl_3$ and "Freon-11"[9] were used. Nmr tubes containing these solvents were sealed *in vacuo*.

All nmr spectra were obtained with a Varian A-60 spectrometer that was equipped with the variable temperature accessory. Temperatures were measured with the conventional methanol and glycol "thermometers." These were calibrated against thermocouples. Nmr spectra were obtained at different scan rates and spectrometer settings to obtain the best signal-to-noise ratio, always taking care to avoid saturation.

Results and Discussion

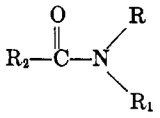
Calculation of Barriers.—The barriers to rotation around the aryl–nitrogen bond in the various com-

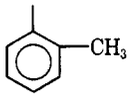
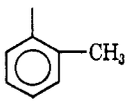
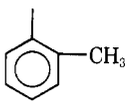
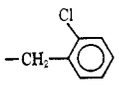
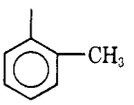
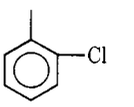
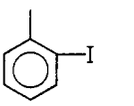
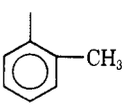
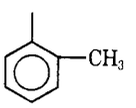
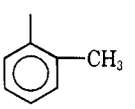
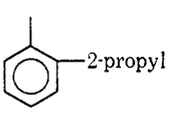
(8) J. Sandström, *J. Phys. Chem.*, **71**, 2318 (1967).

(9) Trademark of Du Pont for its fluorocarbon products.

TABLE IB

FREE ENERGIES OF ACTIVATION FOR ROTATION AROUND AMIDE BOND AND N—C (AROMATIC) BOND IN



Compd	R	R_1	R_2	ΔF^*, kcal/mol (°C) C(O)—N bond	ΔF^*, kcal/mol (°C) N—C (aromatic) bond	Chemical shift, $\nu_A - \nu_B$ at 110°, cps
X	—CH_2Ph		Cl		19.2 (101) 19.5 (110)	27
XI	—CH_2Ph		*t*-Butyl		18.9 (105) 19.1 (105), $CHCl_2CHCl_2$ 18.9 (110) 19.1 (110), $CHCl_2CHCl_2$	81 81, $CHCl_2CHCl_2$
	UO_2Cl_2 adduct of XI in $CHCl_2CHCl_2$				22.1 (123)	98
XII	—CH_2Ph		2-Propyl		20.6 (117) 20.6 (132) 20.7 (142)	52
XIII			CH_3		20.4 (101) 20.0 (110) 20.1 (128)	38
XIV	—CH_2Ph		2-Propyl		19.8 (105) 19.7 (117)	84
XV	—CH_2Ph		CH_3		21.4 (154) 21.5 (161) 21.3 (173)	94
XVI	—CH_2Ph		Cl_3C—		20.0 (105) 20.1 (130) 20.1 (117)	67
XVII (thioamide)	—CH_2Ph		CH_3		>23.5 (170)[a]	60
XVIII	—CH_2Ph		CH_3		20.5 (124) 20.2 (124)[b] 20.0[b] (135)[c] 20.1[d] (142)[e]	44 40
XIX	—CH_2Ph		CH_3		22.6 (172) 22.4 (176)	65

[a] T. H. Siddall, III, and W. E. Stewart, unpublished results. [b] Neat. [c] Reference 7. [d] In nitrobenzene. [e] Reference 6.

pounds were calculated by matching the experimental AB patterns with calculated patterns; the experimental pattern in all cases arose from the nonequivalent methylene protons of the benzyl radical. The calculated spectra were obtained by computer plots of the signal shape equation given by Heidberg, *et al.*[3] The matching of spectra (except in the two cases noted below) was done from plots of signal shape parameters. These parameters were (a) the ratio of signal breadth to chemical shift at 0.2 signal height; (b) the same ratio at 0.6 signal height; (c) the ratio of height of central minimum to signal height maximum (on partly coalesced signals); and (d) the ratio of height of side minima to signal height maxima. At least two parameters were used for each match. Direct visual inspection and matching were also used. A single value of 14.0 cps was used for the AB coupling constant (J), and a single value of $T_2 = 0.11$ was used throughout. All observed J values were within 0.3 cps of 14.0, and T_2 was always within 10% of 0.11, based on observation in the slow exchange region. Since, in all cases (except those noted in Table I), the chemical shift was $\geq$ 20 cps (in most cases $\geq$40 cps), minor variations in T_2 and J do not affect the results significantly.

The chemical shift decreased with temperature in all cases (up to 3 cps/10°). The chemical shifts used in the calculations were obtained by extrapolation of shifts obtained at low temperature in the slow exchange region. The values at 110° are listed in Tables IA and IB.

Measurements were obtained only over the center region of intermediate exchange. In this region, the experimental spectra are most sensitive to the exchange

TABLE II
PUBLISHED DATA FOR AMIDE BOND ROTATIONAL BARRIERS IN N,N-DIMETHYLAMIDES, $RC(O)NMe_2$

Reference	R	Solution	Method	ΔF^* (T_c, °C)
a	Me	Neat	s.s.	19 (73)
b	Me	Neat	a.s.s.	20.1 (87)
c	Me	Neat	a.s.s.	19 (52)
d	CD_3	Neat	s.s.	18.1 (*75*)
d	CD_3	0.095 mol fraction in $CD_3S(O)CD_3$		18.3 (*75*)
b	Et	Neat	a.s.s.	17.7 (61)
a	Et	Neat	s.s.	18 (54)
e	Et	Neat	a.s.s.	17.6 (62)
e	Et	0.4 mol fraction in CH_2Br_2	a.s.s.	17.7 (60)
		0.1 mol fraction in CH_2Br_2	a.s.s.	18.2 (66)
		0.4 mol fraction in CCl_4	a.s.s.	16.3 (39)
		0.1 mol fraction in CCl_4	a.s.s.	16.6 (44)
a	Pr	Neat	s.s.	18 (57)
f	2-Pr	0.33 mol fraction *o*-$C_6H_4Cl_2$	a.s.s.	16.2 (26)
g	Cl	Neat	s.s.	16.8 (*25*)
b	Cl	Neat	a.s.s.	17.4 (53)
h	Cl	Neat	a.s.s.	16.7 (*25*)
h	Cl	Neat	Spin echo	16.7 (*25*)
e	Cl	Neat	a.s.s.	17.3 (59)
g	Cl	0.1 mol fraction in CCl_4	s.s.	16.3 (*25*)
e	Cl	0.4 mol fraction in CH_2Br_2	a.s.s.	17.4 (59)
e	Cl	0.1 mol fraction in CH_2Br_2	a.s.s.	17.5 (59)
e	Cl	0.4 mol fraction in CCl_4	a.s.s.	15.6 (51)
e	Cl	0.1 mol fraction in CCl_4	a.s.s.	16.8 (51)
b	CCl_3	Neat	a.s.s.	14.7 (14)
a	CCl_3	Neat	s.s.	14 (19)
h	CCl_3	Neat	a.s.s.	15.0 (*25*)
h	CCl_3	Neat	Spin echo	15.0 (*25*)
c	H	Neat	a.s.s.	22 (99)
i	H	0.04 mol fraction in $CHCl_2CHCl_2$	a.s.s.	20.9 (115)
a	H	Neat	s.s.	20 (113)
b	H	Neat	a.s.s.	22.4 (149)
j	H	Neat	a.s.s.	20.8 (*123*)
k	H	In α-chloronaphthalene	a.s.s.	20.6 (128)
l	H	Neat	4 site s.s.	21.0 (118)
m	D	Neat	s.s.	21.8 (126)
n	*t*-Bu	100 λ/500 λ $CDCl_3$	s.s.	11.6 (−36)

[a] C. W. Fryer, F. Conti, and C. Franconi, *Ric. Sci.*, **35**, Series 2, 788 (1965). [b] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962). [c] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956). [d] R. C. Neuman, Jr. and V. Jonas, *J. Amer. Chem. Soc.*, **90**, 1970 (1968). [e] J. C. Woodbrey and M. T. Robers, *ibid.*, **84**, 13 (1962). [f] G. Isaksson and J. Sandström, *Acta Chem. Scand.*, **21**, 1605 (1967). [g] R. C. Neuman, Jr., D. N. Roark, and V. Jonas, *J. Amer. Chem. Soc.*, **89**, 3412 (1967). [h] A. Allerhand and H. S. Gutowsky, *J. Chem. Phys.*, **41**, 2115 (1964). [i] E. S. Gore, D. J. Blears, and S. S. Danyluk, *Can. J. Chem.*, **43**, 2135 (1965). [j] R. C. Neuman, Jr. and L. B. Young, *J. Phys. Chem.*, **69**, 2570 (1965). [k] A. Mannschreck, A. Mattheus, and G. Rissman, *J. Mol. Spectry.*, **23**, 15 (1967). [l] M. Rabinovitz and A. Pines, personal communication; *J. Amer. Chem. Soc.*, **91**, 1585 (1969). [m] F. Conti and W. Von Phillipsborn, *Helv. Chim. Acta*, **50**, 603 (1967). [n] T. H. Siddall, III, and W. E. Stewart, unpulished results.

rate and least sensitive to the other parameters (T_2, J, chemical shift) and to spectrometer performance. Most of the data were obtained where signal parameter (c) is applicable. For chemical shifts of 20 cps or more, this is the most sensitive and reliable matching parameter. The standard deviation in ΔF^* (the free energy of activation) determined in this region is routinely about ±0.2 kcal/mol.

Within this center span of intermediate exchange, ΔF^* is constant within experimental error. On that basis, and because of the extensive overlap of data for different molecules and the small temperature variation in ΔF^* in a similar situation,[2] ΔF^* values provide a valid comparison of the rotational barriers in these compounds. The close agreement of data for XVIII obtained in this laboratory with published data[6,7] is also encouraging.

Because the chemical shifts for the AB pattern of each of the minor isomers of the formanilides (I and II) are small, these two situations required special consideration. Accurate rates could not be determined, and ΔF^* values are considered to be in error by up to 1 kcal/mol. The chief difficulty is that small variations in chemical shift, J, and T_2 significantly affect the signal shape, even in the central region of intermediate exchange. Physically, this is understandable, because spacing between center peaks approaches $1/T_2$ rapidly as the chemical shift falls below about 12 cps. For small chemical shifts, the shape of the small, wing signals is more sensitive to exchange rate than the center peaks. However, as the shift decreases, the intensity of the wing peaks decreases, and signal-to-noise ratios are very poor. The possibility of extracting more information from the wing peaks is under continued study in this laboratory. The data for the minor isomers in Table I were obtained by moving the temperature control back and forth to locate the coalescence temperature and scanning calculated spectra for the exchange rate at which the signals coalesce.

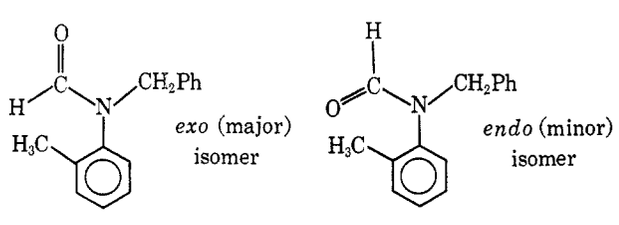
The data (Table II) for rotation around the carbonyl–nitrogen (amide) bond for I and II were obtained by direct, visual matching of computer plots (of Naka-

gawa's[10] formulation of the Gutowsky–Holm equation) with experimental spectra. Since the isomer population ratio, (minor isomer)/(major isomer), was as low as 0.07, these data were also obtained in unfavorable circumstances, causing errors of up to 1 kcal/mol. The signal from the major isomer, below coalescence, and the coalesced signal are both insensitive to the exchange rate. Only the shape of the minor isomer signal is responsive to exchange rate. This leads to unfavorable signal-to-noise ratios in the only part of the spectrum useful for exchange studies. It will also lead to a difficult statistical weighting problem in any computer program designed to match observed and calculated spectra. Both the computational and experimental problems are receiving further study in this laboratory. The barrier for I was also obtained by observing the growth of the methylene signal of the *endo* isomer at $-13°$ when crystalline *exo* isomer was dissolved.[2,11] This rate measurement also suffers from the adverse isomer ratio, but probably is more reliable than the value from signal shape analysis.

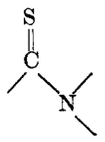
Results for rotation around the aryl–nitrogen bond are tabulated as ΔF^* (the free energy of activation) in Table I. Data for rotation around the carbonyl–nitrogen (amide) bond are given in Table II.

The Formamide (I) and Thioformamide (II).—The data for the formamide (I) and thioformamide (II) appear to be comparatively straightforward and will be discussed first. In both formamides, the minor amide isomer is assigned as the isomer with the benzene ring *cis* to the oxygen (or sulfur) atom (*endo* isomer). The benzene ring is held out of plane with respect to the amide framework. The proximity of the formyl proton to, and in a plane perpendicular to, the benzene ring in the major isomer (*exo* isomer, ring *trans* to the carbonyl oxygen) causes the relative upfield shift of the signal from the formyl proton in this isomer. This reasoning is justified in quantitative detail by Rae.[12]

This assignment is consistent with the observed rotational barriers. For I, the barrier is about 4 kcal/mol larger in the *endo* isomer. This is expected on simple steric grounds. The oxygen atom is "larger" than the formyl proton. The analogy with biphenyls[13] is seen when the activated states are shown. The trigonal amide framework replaces the second ring in a biphenyl. The effect is even more pronounced (8 kcal/



mol) in the thioformamide. The increased barrier in the thioamide *endo* isomer, compared with the amide *endo* isomer, can probably also be rationalized on the steric grounds—the larger sulfur atom inhibits the rotation. However, in part, the increase may be due to the stiffer amide bond (see Table I) of the thio compound. The thioamide framework is less capable of



distortion to relieve strain in the activated state. The effect of sulfur vanishes in the case of *exo* isomers. Here the sulfur cannot have a direct steric effect, though it is surprising that it does not have at least small indirect steric effect through buttressing.[14] The increased barrier to rotation around the amide bond in the thio compound is expected from the literature.[15] For both I and II, the barrier to rotation around the C(O)–N (amide) bond is high compared with rotation around the aryl–nitrogen bond in both isomers.

The Route to Rotation in the Other Amides.—It is not so clear that the amide bond barrier is higher than the aryl–nitrogen bond barrier in the other amides, and this leads to doubt that rotation takes place directly around the aryl–nitrogen bond in the *exo* isomer. The chief experimental difficulty is that, for acetanilides and anilides with still larger carbonyl substituents (R_2), the *endo* isomer is generally not abundant enough to be observed. As a consequence, there is no way of directly observing the aryl–nitrogen barrier in the *endo* isomer or of observing the amide barrier. On steric grounds it is to be supposed that the aryl–nitrogen barrier would be smaller in the *endo* isomer. The R_2 groups will generally be much larger than the carbonyl oxygen atom. If this is true and the aryl–nitrogen barrier is greater than the amide bond barrier, the observations in Table I might apply to either (a) rotation around the amide bond or (b) rotation around the aryl–nitrogen bond in the *endo* isomer, depending on which of these, a or b, were larger. The barrier for the aryl–nitrogen bond in the *exo* isomer would not be observable. This situation has already been recognized for certain N-unsubstituted anilides.[16] In that case, rotation around the amide bond is larger, a is larger than b, and rotation around the aryl–nitrogen bond in the *exo* isomer is probably not observed.

There are certain exceptions to the rule that the *endo* isomer is not abundant enough in N-substituted anilides to be observable by nmr.[5] These are, first, the formanilides; and second, other anilides that have electronegative substituents on the α-carbon atom in the R group (carbonyl substituent). It was for that reason that compounds I, II, and XVI specifically were investigated. The significant amide-bond barrier is the barrier in passing from the major (*exo*) to the minor (*endo*) isomer, and not the reverse. For the formanilide, this barrier is 21 ± 1 kcal/mol (see Table I) or 20 ± 1 kcal if the reequilibration result is used. As discussed in the section on barrier calculations, the error here is large because of the disproportionate isomer ratio (*endo*/*exo* = 0.14 at 41°).

One way to estimate the barrier for anilides with other R groups is to extrapolate from the formamide. The barriers in a series of amides with varying R groups serve as the obvious (though not necessarily 100% reliable) means of making such an extrapolation.

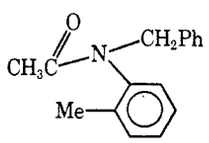
(10) T. Nakagawa, *Bull. Chem. Soc. Jap.*, **39**, 1006 (1966).
(11) H. S. Gutowsky, J. Jonas, and T. H. Siddall, III, *J. Amer. Chem. Soc.*, **89**, 4300 (1967).
(12) I. D. Rae, *Can. J. Chem.*, **44**, 1334 (1966).
(13) R. Adams, *Rec. Chem. Progr.*, **10**, 91 (1949).
(14) For a discussion of buttressing, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Co., Inc., New York, N. Y., 1962.
(15) G. Schwenker and H. Rosswag, *Tetrahedron Lett.*, 4237 (1967), and references therein.
(16) H. Kessler, *Tetrahedron*, **24**, 1857 (1968).

Published data for N,N-dimethylamides are collected in Table II. The values of ΔF^* were either taken directly from the original articles or calculated from data given in these articles.

Unfortunately, published values sometimes show rather wide variations. The six determinations for dimethylformamide (DMF) average to $\Delta F^* = 21.3 \pm 0.8$ (mean deviation) kcal/mol. For comparison below the barrier, ΔF^* is taken as 21 kcal/mol. For the closely related N-benzyl-N-methylformamide, ΔF^* (*exo* → *endo*) is 21.6 kcal/mol at 0° by the equilibration technique and ΔF^* is 21 kcal/mol at 100° by signal shape analysis.[11] The amide barrier in these *o*-substituted anilides is not more than it is in N,N-dimethylamides.

When R = Me (dimethylacetamide), the barrier is 2 kcal/mol lower than the barrier for DMF. The average value of the barrier (neat) is 19 kcal/mol. If the value from ref *d* is accepted, the increment is 3 kcal. The value from ref *d* has the best credentials because it was done for $CD_3C(O)NMe_2$ with deuterium decoupling and very careful signal shape analysis.

From these data and the reasoning above, it is probable that the barrier to rotation around the nitrogen–benzene bond was observed in the *endo* isomer in

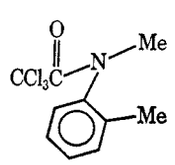


XVIII (and also XIII)

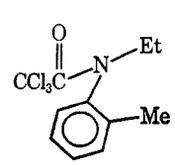
The indirect determination (19 kcal/mol) for rotation around the amide bond may be in error by 1.2 to 1.5 kcal/mol. In that case, the observed barrier would be the amide barrier.

In all other cases, the probable amide barrier is so low compared with our measurements that it seems certain that the barrier to rotation around the nitrogen–benzene bond in the *endo* isomer is being observed. For example, the calculated amide barrier where R = 2-propyl is 16 kcal/mol. For XII and for XIV the observed barriers are 4–5 kcal larger, and when R = *t*-butyl the observed barriers are about 7 kcal larger than the amide barrier.

With XVI (R = CCl_3), it was possible to verify the probable value of the amide barrier. In the closely related compound



two amide isomers are observable, in about equal abundance. In $CDCl_3$, the amide barrier is 15.3 kcal/mol (unpublished results, this laboratory). For $CCl_3C(O)NMe_2$, the average published value is 14.7 kcal/mol. In another related compound



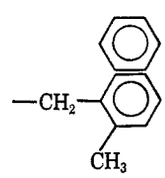
isomers were observed qualitatively, with coalescence of separate isomer signal sets occurring at about 10°. The 16-line pattern of the nonequivalent methylene protons of the ethyl group coalesces above 100°.

For reasons that are not clear to us, XVI itself gives no direct evidence for amide isomerism. The high field half of the AB pattern does become very broad at about 25°, while it is sharp below about 0° and above about 60°. However, two separate signal sets never emerge. The lack of two *o*-methyl signals may be due to degeneracy rather than to lack of amide isomerism. Only one *o*-methyl signal is observable in I even at low temperature, when two formyl signals and two methylene quartets are clearly observable.

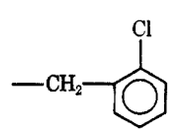
Effects of Various Substituents on the Barrier to Rotation around the Benzene–Nitrogen Bond.—Since rotation around the nitrogen–benzene bond is observed only for the *endo* isomer (except for I and II), the R_2 group (carbonyl substituent) cannot have a direct effect. However, there are some fairly large indirect effects. For example, the order of barrier heights is (for different R_2) Me = 2-propyl > *t*-butyl < CEt_3. The decrease with *t*-butyl may be due to the low amide barrier. The amide bond can be distorted easily, in a cooperative manner, to allow rotation around the benzene–nitrogen bond. However, another effect operates in the opposite direction—the buttressing effect.[13] For that reason, when $R_2 = Et_3C$, the barrier around the benzene–nitrogen bond increases again. In similar manner, the two effects operate in opposite directions to make Me = 2-Pr. The effect of the group $(C_6H_5)_2CH_3C$ (VII) to increase the barrier over that in XI and IX has no ready explanation at our hands. We can only assume that this group achieves some small interlocking effect.

The size and nature of the R_1 (aryl) group appear to have straightforward effects, in close analogy to rotation in biphenyls. Increased size or rigidity for the *ortho* substituent increases the barrier significantly. Compare IV with XI; XV with XIV; and XIV, XIX, and III with XVIII. It is not obvious, however, that the benzene ring should be "smaller" than the methyl group —compare V with XI. The data for VIII provides a clear case of buttressing.[12,13]

A size effect is noted when the other nitrogen substituent (R) is



rather than simple $PhCH_2$–. However, the modest increase of size of the group



has no observable effect.

The oxygen atom can be "made larger." A 3-kcal increase in barrier is observed when the uranyl ion is attached to the oxygen atom of XI. There is probably

also some electronic contribution to the increase in barrier. The exact nature of bonding of such molecules as amides to the uranyl group is subject to discussion.[14] However, whatever the exact nature of the bond, there must be a shift in electron density toward the oxygen atom. This requires an increased double-bond character and greater stiffness in the amide bond. To a much smaller extent, the oxygen atom is "made larger," presumably by hydrogen bonding to $CHCl_2CHCl_2$. The small increase in barrier (0.2 kcal) with this solvent compared with *o*-dichlorobenzene is at least qualitatively real. Very careful experiments were performed in which samples of XI in the two solvents were alternated in the spectrometer at 110°. In the latter solvent, the signals were definitely more nearly coalesced.

Registry No.—I, 17372-54-2; II, 20678-83-5; III, 13936-76-0; IV, 13936-78-2; V, 13936-77-1; VI, 20643-10-1; VII, 20643-11-2; VIII, 20643-12-3; IX, 13936-74-8; X, 20643-14-5; XI, 17372-56-4; XII, 17372-55-3; XIII, 13936-79-3; XIV, 20643-18-9; XV, 20633-57-2; XVI, 20633-58-3; XVII, 20633-59-4; XVIII, 6840-46-6; XIX, 20633-61-8.

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A Study of the Photoaddition Reactions of Norbornadiene with 2-Cyclohexenones[1]

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To gain mechanistic information on photoaddition reactions of 2-cyclohexenones, the additions of 2- and 3-methyl-2-cyclohexenone and 2-cyclohexenone to bicyclo[2.2.1]heptadiene have been studied. The products are of the following types: (i) cyclobutane derivatives (*cis*- and *trans*-fused structures are formed); (ii) α- and β-nortricyclyl-2-cyclohexenones; and (iii) α- and β-(7-*anti*-norbornenyl)-2-cyclohexenones. The nortricyclyl compounds were prepared by independent routes, and one of the norbornene derivatives was degraded to 7-norbornanecarboxylic acid. Other structure assignments rest on infrared and nmr spectra. In the reaction of 3-methyl-2-cyclohexenone and norbornadiene a 16% yield of 9-methyl pentacyclo[7.4.0.0^{2,7}.0^{3,5}.0^{4,8}]tridecan-13-one (9) is obtained. It is proposed that this and the cyclohexenone derivatives are formed *via* biradical intermediates. Hydrogen shifts are involved in the formation of the latter products, and a deuterium-labeling experiment showed that one such shift is intramolecular and stereospecific. Naphthalene quenching experiments imply that the cyclohexenone derivatives are formed by a triplet-state reaction.

The chemistry of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) is rich in reactions, in which both double bonds of the diene are involved. Such reactions include ionic[3] and free-radical[4] additions, photoisomerization,[5] and the 2,6 cycloaddition known as the homo Diels–Alder reaction.[6] Nortricyclene derivatives and 7-substituted norbornenes are oft-encountered products of these reactions.

In this paper we describe some photoadditions of norbornadiene with simple[7] 2-cyclohexenones, which are of particular interest for the following reasons. First, although photoadditions of alicyclic enones and unsaturated esters have long been known[8,9a] and have been extensively studied,[9,10] attention has been focussed on dimerizations of the carbonyl compounds or cross additions with uncomplicated alkenes. No work prior to our communication[1] had been reported in which a homoconjugated diene was employed as the substrate in a cross addition. It was, therefore, of interest to see to what extent the spatial relationship of the double bonds in norbornadiene modified the course of enone photoadditions to this diene. Such modification might result, for example, if biradical species were discrete intermediates in the addition reaction.[9a]

A further interesting aspect of photoadditions with this diene was the question of whether the symmetry-forbidden 2,6 cycloaddition[6] would occur. This is symmetry allowed,[11] and well known,[6] in ground-state chemistry.

To determine whether homoconjugated dienes do differ from alkenes in their photoaddition behavior, a study of the photoreactions of 2-cyclohexenone,

(1) For preliminary reports, see J. J. McCullough and J. M. Kelly, *J. Amer. Chem. Soc.*, **88**, 5935 (1966); J. J. McCullough and P. W. W. Rasnussen, *Chem. Commun.*, 387 (1969).

(2) Author to whom requests for reprints should be addressed.

(3) See J. A. Berson, "Molecular Rearrangements," Part I, Interscience, New York, N. Y., 1963, p 198.

(4) (a) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Amer. Chem. Soc.*, **80**, 635 (1958); (b) D. J. Trecker and P. Henry, *ibid.*, **85**, 3204 (1963); (c) N. O. Brace, *J. Org. Chem.*, **27**, 3027 (1962); (d) S. J. Cristol and D. J. Davies, *ibid.*, **29**, 1282 (1964); (e) T. V. Van Auken and E. A. Rick, *Tetrahedron Lett.*, 2709 (1968).

(5) (a) S. J. Cristol and R. L. Snell, *J. Amer. Chem. Soc.*, **76**, 5600 (1954); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron Lett.*, **15**, 197 (1961); (c) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Amer. Chem. Soc.*, **83**, 4674 (1961).

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(7) "Simple" is taken here to mean derivatives whose π system is similar to 2-cyclohexenone—*i.e.*, alkyl derivatives.

(8) Early examples are W. Treibs, *Chem. Ber.*, **63**, 2738 (1930); *J. Prakt. Chem.*, **138**, 299 (1933). A. Butenandt, L. K. Poschmann, G. Failer, U. Siebert, and E. Biekert, *Ann.*, **575**, 123 (1952).

(9) (a) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964); a summary of early examples is given here. (b) Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966). (c) M. Brown, *ibid.*, 340 (1965). (d) R. A. Schneider and J. Meinwald. *J. Amer. Chem. Soc.*, **89**, 2023 (1967). (e) P. Yates, S. N. Eğe, G. Büchi, and D. Knutsen, *Can. J. Chem.*, **45**, 2927 (1967). (f) S. N. Eğe and P. Yates, *ibid.*, **45**, 2933 (1967). (g) R. L. Cargill, M. E. Beckham, A. E. Sibert, and J. Dorn, *J. Org. Chem.*, **30**, 3647 (1965).

(10) (a) O. L. Chapman, "Photocycloaddition Processes," Abstracts of the 20th National Organic Symposium, Burlington, Vt., June 1967, p 127; (b) P. E. Eaton, *Accounts Chem. Research*, **1**, 50 (1968); (c) A. Cox, P. de Mayo, and R. W. Yip, *J. Amer. Chem. Soc.*, **88**, 1043 (1966); (d) H. D. Scharf and F. Korte, *Ber.*, **99**, 1299 (1966); (e) R. L. Cargill and M. R. Willcott, III, *J. Org. Chem.*, **31**, 3938 (1966).

(11) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).