150.° The N-methyl peaks and the olefinic doublets started to coalesce between 150 and 160°. At the observed coalescence temperature, 200°, the two N-methyl peaks coalesced into a single, fairly sharp peak. The coalescence of the two olefinic doublets into one doublet was difficult to observe due to the small initial separation of the two doublets. The process was reversible, for as the temperature in the probe was lowered to the ambient probe temperature, the peaks reverted to the previously observed separations. The results were the same in both *p*-anisaldehyde and nitrobenzene solutions.

Cycloheptatriene has been shown,[3,4] on the nmr time scale, to consist of an equilibrium pair of nonplanar conformers at $-140°$.
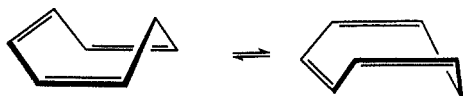
The more rigid 5H-dibenzo[a,d]cycloheptene structure consists of two conformers at even higher temperature[5] (30°). The attachment of the bulky 1-methyl-3-pyrrolidinyl-methylene group to the 5 position of the dibenzocycloheptene system strongly affects the rate of inversion of the cycloheptatriene ring. Below the observed coalescence temperature (200°), the two nonplanar conformers are optical isomers. The 1-methyl-3-pyrrolidinylmethylene group contains an asymmetric carbon atom. These factors made 1 act below the coalescence temperature as though it were a mixture of the *dl* pairs.
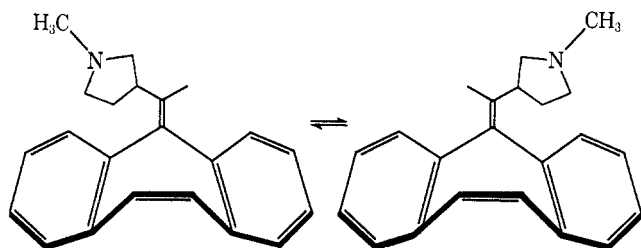
Calculation[6] of the free energy of activation ($\Delta G^{\ddagger}$) and the rate constant (K_1) at the coalescence temperature (T_c) were made with the assumption that the conformers existed in an equimolar ratio and were of equal lifetimes. These assumptions are nearly correct, as the mixture ratio was *ca.* 60:40, and both isomers have small line width signals.

The calculation results are: $T_c = 200°$; $K_1 = 22.2$ sec^{-1}; $\Delta G^{\ddagger} = 25.0$ kcal/mol.

Repeated attempts to separate the two *dl* pairs or to change the isomer ratio were unsuccessful.

Experimental Section

5-Hydroxy-5-(1-methyl-3-pyrrolidinylmethyl)-5H-dibenzo-[a,d]cycloheptene.—The usual Grignard reagent was used for the preparation of 1-methyl-3-pyrrolidinylmethylmagnesium chloride from 10.0 g (0.075 mol) of 1-methyl-3-pyrrolidinylmethyl chloride,[7] 1.82 g of magnesium, and 50 ml of THF.

(3) F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 458 (1964).

(4) F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

(5) W. Tochtermann, U. Walter, and A. Mannschreck, *Tetrahedron Lett.*, 2981 (1964).

(6) J. A. Pople, W. G. Scheider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 218 and 366.

(7) Y. H. Wu and R. F. Feldkamp, *J. Org. Chem.*, **26**, 1519 (1961).

The Grignard reagent was treated with 5H-dibenzo[a,d]cyclohepten-5-one (10.3 g, 0.05 mol) of 50 ml of THF over a period of 30 min. The reaction mixture, after being stirred and refluxed for 18 hr, was decomposed with 35 ml of a saturated NaCl solution. The mixture was filtered and the solid cake was extracted with THF. The combined filtrates and extracts were concentrated to a glass residue (11.6 g, 75.4%). The glass product failed to crystallize. The hydrochloride salt melted at 222–224° (EtOH–ether).

Anal. Calcd for $C_{21}H_{23}NO \cdot HCl$: C, 73.78; H, 7.07; Cl, 10.37. Found: C, 73.94; H, 7.41; Cl, 10.20.

5-(1-Methyl-3-pyrrolidinylmethylene)-5H-dibenzo[a,d]cycloheptene.—A mixture of 5-hydroxy-5-(1-methyl-3-pyrrolidinyl-methyl)-5H-dibenzo[a,d]cycloheptene (13 g, 0.043 mol), glacial acetic acid (200 ml), and concentrated HCl (80 ml) was refluxed for 1 hr. The mixture was concentrated to a syrupy mass, which was treated with 40 ml of water, made basic with 40% NaOH, and extracted with ether. The dried ethereal extract ($MgSO_4$) was concentrated and the oily residue was distilled under reduced pressure, giving an oily product, bp 170–190° (0.2 mm), yield 9.9 g (81%). The fumarate salt melted at 203–205° (absolute EtOH).

Anal. Calcd for $C_{21}H_{21}N \cdot {}^{1}/_{2}C_4H_4O_4$: C, 79.97; H, 6.71; N, 4.06; O, 9.26. Found: C, 79.69; H, 7.01; N, 3.93; O, 9.41.

Nmr Spectra.—Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer using the variable temperature controller. Line positions were measured with respect to tetramethylsilane as an internal reference, with the spectrometer calibration was checked according to the method of Tiers and Hotchkiss.[8]

Registry No.—1, 22158-31-2; hydrochloride of 5-hydroxy-5-(1-methyl-3-pyrrolidinylmethyl)-5H-dibenzo[a,d]cycloheptene, 22158-32-3; 1 (fumarate salt), 22188-55-2.

(8) G. V. D. Tiers and D. R. Hotchkiss, *J. Phys. Chem.*, **66**, 560 (1962).

The *A* Value of the Carbodiimido Group. Conformational Requirements of "sp²-Hybridized" Lone Pairs

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In the course of an investigation of the conformational idiosyncrasies of heterocycles possessing atoms with lone pairs of electrons, we found it necessary to obtain an estimate of the relative steric requirement of sp²-hybridized nitrogen. This report concerns the measurement of the *A* value (eq 1 and 2)[1] of the carbodiimido group (N=C=NR).
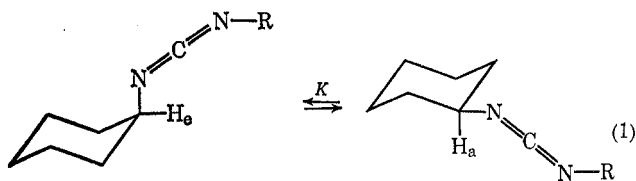
R = cyclohexyl

$$A \text{ value} = -\Delta G^0 = \frac{RT \ln K}{1000} \quad (2)$$

(1) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).

The technique used involves the measurement of the areas under the proton magnetic resonance signals due to the axial methine proton (H$_a$; eq 1) and the equatorial methine proton (H$_e$; eq 1) of dicyclohexylcarbodiimide at low temperature (slow chair–chair exchange on the nmr time scale). The advantages of employing direct peak area measurements in lieu of other nmr methods utilizing "locked" model compounds have been discussed elsewhere.[2]

Examination of the nmr spectrum (60 MHz) of a *freshly prepared sample* of dicyclohexylcarbodiimide[3] in carbon disulfide at −80° revealed two HCN resonances of substantially different intensities at δ 2.91 (large peak) and 3.70 (small peak). The resonance at δ 2.91 is assigned to the axial methine proton (H$_a$; eq 1) and at δ 3.70 to the equatorial methine proton (H$_e$; eq 1) on the basis of coupling constant and chemical shift data in a plenitude of cyclohexane derivatives.[4] Equilibrium constants (K; eq 1) derived from the peak area ratios for 1.0 and 2.0 M solutions of dicyclohexylcarbodiimide in carbon disulfide at −80° and the associated A values are compiled in Table I.

TABLE I

THE A VALUE OF THE CARBODIIMIDO
GROUP IN CARBON DISULFIDE

Dicyclohexyl-carbodiimide concn, mol/l.	K^a	A value, kcal/mol
1.0	11.9 ± 0.9	0.96 ± 0.08
2.0	13.3 ± 0.6	1.00 ± 0.08

^{a} According to eq 1 and measured at −80 ± 0.5°.

The reported deviation in the A value at a given concentration (Table I) arises from the usual sources of error[4] and from the definite possibility of differential saturation effects in these samples.[4] In order to obtain reasonable reproducibility in the area under the small equatorial HCN resonance (δ 3.70), a moderately high radiofrequency power level was necessary.

The deviation of the A value of the carbodiimido group with concentration is small and within experimental error. It may indicate some association in the more concentrated solutions.

The nmr spectrum of dicyclohexylcarbodiimide in carbon disulfide was examined under conditions of intermediate and very fast exchange on the nmr time scale, *i.e.*, −80° to room temperature, to ascertain that the peaks observed at low temperature were indeed due to slow ring inversion.

There have been few reports concerning the A value of the various forms of nitrogen attached to the cyclohexane ring, although data are available for nitro (NO$_2$)[4,5] isonitrile (N≡C),[4] isocyanate (N=C=O),[4] and isothiocyanate (N=C=S).[4] The pertinent data

(2) (a) F. R. Jensen and B. H. Beck, *J. Amer. Chem. Soc.*, **90**, 3251 (1968); (b) E. L. Eliel and R. J. L. Martin, *ibid.*, **90**, 682, 689 (1968).

(3) Upon prolonged standing (*ca.* 30 days) in carbon disulfide, there was evidence of reaction and/or decomposition of the dicyclohexylcarbodiimide.

(4) F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Amer. Chem. Soc.*, **91**, 344 (1969).

(5) (a) R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **31**, 587 (1966); (b) W. C. Niekam and B. P. Dailey, *J. Chem. Phys.*, **38**, 445 (1963); (c) N. C. Franklin and H. Feltkamp, *Angew. Chem. Intern. Ed. Engl.*, **4**, 774 (1965); (d) W. Hofman, L. Stefaniak, J. Urbanski, and W. W. Tanowski, *J. Amer. Chem. Soc.*, **86**, 554 (1964); (e) A. C. Corfield and A. Crawshaw, *Chem. Commun.*, 1055 (1967); (f) H. Feltkamp and N. C. Franklin, *J. Amer. Chem. Soc.*, **87**, 1616 (1965).

are summarized in Table II with other relevant A values.

TABLE II

PERTINENT A VALUES

| Group	A value, kcal/mol
N=C=NC$_6$H$_{11}$	1.00^a
N=C=O	0.51^b
N=C=S	0.28^b
N≡C	0.21^b
NO$_2$	1.05^b
CH=CH$_2$	1.35^c
C≡CH	0.41^b

^{a} This work (See Table I). ^{b} Ca. 2.0 M in 90% carbon disulfide–10% tetramethylsilane by volume at −80° except for nitro at −90°. ^{c} R. J. Ouellette, K. Liptak, and G. E. Booth [*J. Org. Chem.*, **31**, 546 (1966)] used carbon tetrachloride as solvent at 38°.

From a consideration of Table II, it would appear that the carbodiimido group (N=C=NR) exerts a significant preference for the equatorial position, being comparable in "size" to the nitro (NO$_2$) substituent. If the preferred conformation of the axial carbodiimido group is that with the lone pair directed into the center of the cyclohexane ring (1), it is apparent that the

1   2
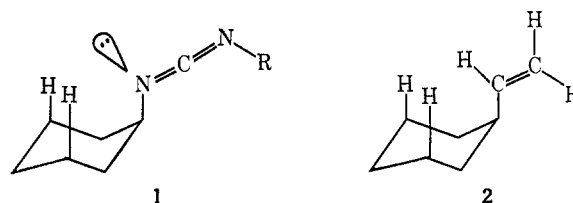
lone pair experiences a significant nonbonded compression with the *syn*-axial hydrogens. However, the nonbonded compressions are apparently not as severe as those experienced by the vinyl substituent (2). The dramatic effect of group cylindrical symmetry is illustrated by a comparison of the A value of the carbodiimido group and those of the isonitrile and ethynyl groups (Table II).

A somewhat more interesting comparison can be made in the sequence isothiocyanate (N=C=S), isocyanate (N=C=O), carbodiimide (N=C=NR). It would seem that the contribution of the dipolar canonical structure (4) decreases relative to 3 as one proceeds

3   4

X=S, O, N—R
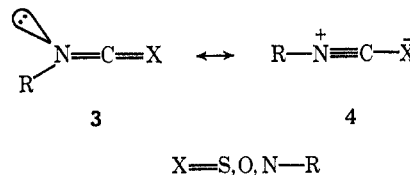
from sulfur to oxygen to nitrogen. The resultant increase in the directional character of the lone pair on nitrogen (bound to cyclohexane ring) apparently increases the conformational preference for the equatorial position.

Experimental Section

Nmr spectra were obtained using a Varian Associates HR-60A spectrometer equipped with a special variable-temperature probe. Spectral calibrations were performed using the audio-modulation technique.

Temperature measurements were performed using a calibrated copper–constantan thermocouple placed below the sample.

Measurement of the temperature at the sample is accurate to $\pm 0.1°$.

Dicyclohexylcarbodiimide was purchased from Matheson Coleman and Bell, further purified by fractional distillation, and collected at bp 150° (11 mm) [lit. bp 148–152° (11 mm)].[6]

Registry No.—Dicyclohexylcarbodiimide, 538-75-0.

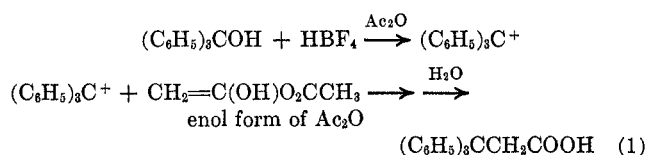(6) A. Amiard and R. Heymes, *Bull. Soc. Chim. Fr.*, 1360 (1956).

The Alkylation of Acetic Anhydride by Triphenylmethyl Cation

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A common method for preparing triphenylcarbonium ion salts is to add triphenylmethanol to acetic anhydride containing a strong acid such as HBF_4.[1] It was noticed that when such systems were allowed to stand, alkylation of acetic anhydride occurred, undoubtedly *via* traces of the enol form of acetic anhydride. The product was 3,3,3-triphenylpropionic acid (I), as shown in eq 1.

$$(C_6H_5)_3COH + HBF_4 \xrightarrow{Ac_2O} (C_6H_5)_3C^+$$

$$(C_6H_5)_3C^+ + CH_2{=}C(OH)O_2CCH_3 \xrightarrow{H_2O} \underset{\text{enol form of Ac}_2O}{\longrightarrow}$$

$$(C_6H_5)_3CCH_2COOH \quad (1)$$

The reaction was briefly explored to determine its scope and limitations. The optimum yield was 50%, as shown in Table I. Higher yields are prevented by subsequent cyclization of I to 3,3-diphenylindanone (II, eq 2) and acylation of this to a compound that is probably 2-acetyl-3,3-diphenylindanone (III, eq 3).

$$(2)$$

$$(3)$$

III (?)
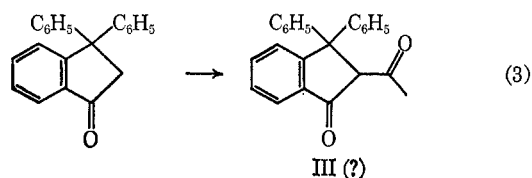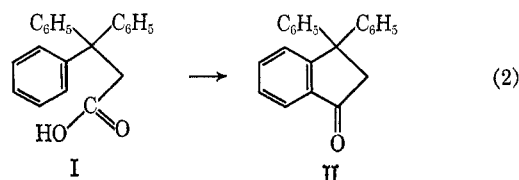
The yields of I, II, and III as a function of time (Table I) indicate the sequence I → II → III.

The reaction is of interest as the first case of alkylation of acetic anhydride by a carbonium ion. It is also

(1) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

Table I

PRODUCTS FROM THE REACTION OF
$(C_6H_5)_3C^+BF_4^-$ WITH ACETIC ANHYDRIDE

Temp, °C	Time, hr	Yield, % I	II	III	Recovered $(C_6H_5)_3COH$, %
25	336	35			
50	1.0	31	0	0	69
	4.0	50	19	0	31
80	1.0	16	42	32	12
	4.0	2	18	76	3
100	0.5			55	
	1.0	1	30	69[a]	0
	5.0			70	

[a] Three identical runs gave yields of 62, 68, and 70%. Addition of 10% of 50% aqueous HBF_4 gave a yield of 60%, so that added HBF_4 does not seem to have much effect.

of interest as a side reaction to be avoided in the preparation of carbonium salts. Unfortunately, the scope seems quite limited and there are better ways of producing I.

In regard to scope, a variety of conditions with propionic and succinic anhydrides failed to produce an acidic carboxylic acid product. Thus, at the moment, the reaction is limited to acetic anhydride as the anhydride component. As for the carbonium ion component, presumably a variety of stable carbonium ions would have been successful in varying degrees, though this was not examined. In regard to the preparation of I, the alkylation of malonic acid with triphenylmethanol would be preferred.[2,3] We have also found that introduction of ketene[4] into a solution of $(C_6H_5)_3C^+BF_4^-$ in acetic anhydride followed by hydrolysis precipitates a >90% yield of I.

An attempt was made to alkylate acetone with $(C_6H_5)_3C^+BF_4^-$. Even after 500 hr at 25° or 75 hr at 55°, no trace of 4,4,4-triphenyl-2-butanone was observed. The nmr would have detected a 2% yield. Mesityl oxide appeared from self-condensation of acetone. Triphenylmethanol was recovered and the recovery was in 96% yield from the 25° run.

4,4,4-Triphenyl-2-butanone was prepared in 90% yield by adding a solution of $(C_6H_5)_3C^+BF_4^-$ in CH_2Cl_2 to isopropenyl acetate, letting the mixture stand for 10 hour, and hydrolyzing (eq 4). Curiously, addition of triphenylchloromethane to isopropenyl acetate failed to give any 4,4,4-triphenyl-2-butanone even after refluxing for 42 hr. Triphenylmethanol was recovered in 95% yield after hydrolysis.

$$(C_6H_5)_3C^+ + CH_2{=}C(CH_3)O_2CCH_3 \xrightarrow{H_2O} \longrightarrow$$
$$(C_6H_5)_3CCH_2COCH_3 \quad (4)$$
$$>90\%$$
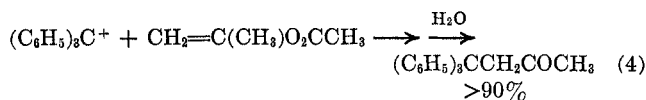
The alkylation of acetic anhydride by $(C_6H_5)_3C^+$ (eq 1) is closely related to the alkylation of malonic acid[2,3] and a variety of malonic acid derivatives[3] by $(C_6H_5)_3C^+$.

Experimental Section

All nmr spectra were recorded on solutions in CH_2Cl_2 or CCl_4 and are expressed in δ ppm.

The acetic anhydride solutions of triphenylmethyl tetrafluoroborate were held under N_2 as a precautionary measure.

(2) L. Hellerman, *J. Amer. Chem. Soc.*, **49**, 1737 (1927).

(3) S. Patai and S. Dayagi, *J. Chem. Soc.*, 716 (1962).

(4) Prepared by decomposition of acetone in a ketene lamp; J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).