

bromide is present in the solution. Methylmagnesium bromide does not show an appreciable absorbance in this region. The longer wave length absorption which is present in solutions containing methylmagnesium bromide has been ascribed to a 1:1 complex between the ketone and the Grignard reagent.⁷ The rate of disappearance of both the ketone band and the complex band obeys good first-order kinetics as is illustrated in Table I for the absorbance at 355 m μ

TABLE I
REACTION OF 10^{-4} M I WITH 0.107 M METHYLMAGNESIUM BROMIDE IN DIETHYL ETHER AT 25.0°

Time, sec.	Rel. A, 355 m μ	$10^3 k_t$, sec. ⁻¹ , integrated
0	0.842	...
24	0.763	4.11
42	0.703	4.30
60	0.651	4.29
78	0.594	4.47
102	0.533	4.48
120	0.493	4.46
138	0.453	4.49
162	0.418	4.32
180	0.376	4.48
198	0.353	4.39
220	0.313	4.46
240	0.291	4.43
270	0.255	4.42
300	0.224	4.41
360	0.176	4.35
420	0.133	4.39
480	0.108	4.28
600	0.065	4.27

when 10^{-4} M ketone I and 0.01 to 0.4 M methylmagnesium bromide are employed. The rate constant calculated from data taken at 355 m μ divided by the rate constant obtained at 315 m μ is 1.04 ± 0.03 , indicating that both the ketone and the complex disappear at the same rate.

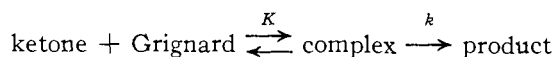
The first-order rate constants, k_t , for the disappearance of either ketone or complex increase with increasing concentration of methylmagnesium bromide (Table II and Fig. 1). Below *ca.* 0.1 M the reaction is approxi-

TABLE II
RATE OF REACTION OF KETONE I WITH METHYLMAGNESIUM BROMIDE IN DIETHYL ETHER AT 25.0°

I_2 titration	Grignard, M		$10^3 k_t$, ^a sec. ⁻¹
	Total base	Total bromide	
0.338	...	0.366	7.8 ± 0.2
0.208	0.219	0.242	6.6 ± 0.6
0.107	0.117	0.121	4.6 ± 0.2
0.0406	0.0452	0.0467	1.98 ± 0.02
0.0161	0.0188	0.0188	0.85 ± 0.01

^a Average of two runs at each concentration.

mately first order in Grignard, while at higher concentrations the apparent order in Grignard is less than one (Fig. 1). These results for ketone I may be quantitatively fitted, for the concentration region investigated, to the scheme⁸



(7) S. G. Smith, *Tetrahedron Letters*, **7**, 409 (1963).

(8) Of course, the data also fit the scheme

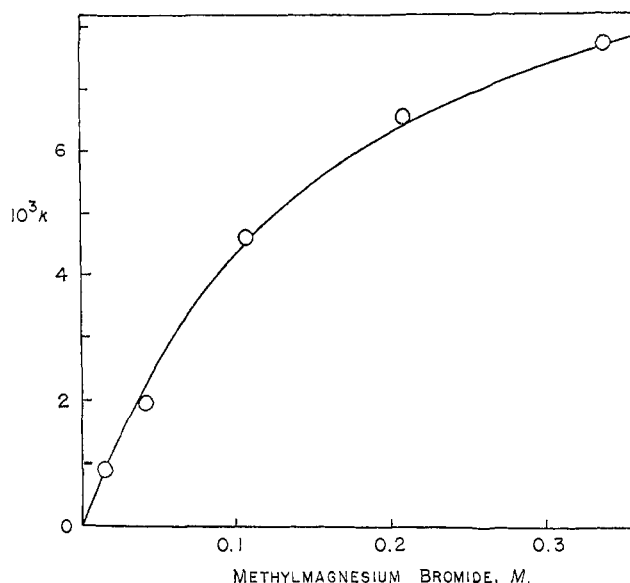
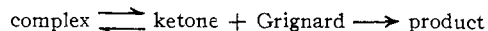


Fig. 1.—Plot of observed first-order rate constant for ketone I in an ether solution of methylmagnesium bromide at 25.0° vs. concentration of methylmagnesium bromide.

The line in Fig. 1 corresponds to an equilibrium constant, K , of 6.2 l./mole and a rate constant, k_t , for conversion of complex to product of 1.1×10^{-2} sec.⁻¹ at 25° in diethyl ether. To the extent that phenylmagnesium bromide⁹ and ethylmagnesium bromide¹⁰ may be used as models for the nature of methylmagnesium bromide these reactions would involve a monomeric Grignard reagent at the concentrations employed.

Acknowledgment.—We are indebted to the Dow Chemical Company for supplying the magnesium used in these experiments.

(9) G. D. Stucky and R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 1002 (1963).

(10) A. D. Vreugdenhil and C. Blomberg, *Rec. trav. chim.*, **82**, 453 (1963).

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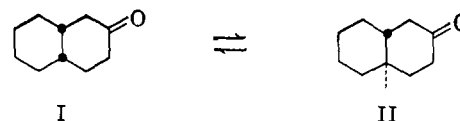
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RECEIVED APRIL 10, 1964

The Thermal Equilibration of *cis*- and *trans*- β -Decalones. An Example of an Unusually Large Entropy of Isomerization

Sir:

In the course of our work on the hydrogenation of unsaturated ketones, it became necessary to determine the relative thermodynamic stabilities of *cis*- (I) and *trans*- (II) β -decalone. It was also felt that such data



would afford more information concerning the 3-alkyl ketone effect first proposed by Klyne¹ and later evaluated by Allinger and Freiberg.²

I and II were equilibrated by heating in sealed ampoules over a Pd catalyst using the procedure described for the equilibration of 3,5-dimethylcyclohexa-

(1) W. Klyne, *Experientia*, **12**, 119 (1956).

(2) N. L. Allinger and L. A. Freiberg, *J. Am. Chem. Soc.*, **84**, 2201 (1962).

none.² Equilibrium was approached from both sides at several temperatures with several equilibrations run at each temperature. The composition of the mixtures was determined by vapor phase chromatography (v.p.c.) through an 8-ft. Ucon column which resulted in the complete separation of the *cis*- and *trans*- β -decalones. A number of side products were also formed during the equilibration. Some of these, presumably alcohols, proved difficult to separate from the ketones by v.p.c. These substances were, however, conveniently removed by treating the sample with concentrated sulfuric acid for a short time, pouring the mixture into water, and extracting with ether.² That this did not affect the equilibrium composition was shown by the fact that a known mixture of I and II was recovered unchanged from the sulfuric acid treatment. The other side products were identified as *cis*- and *trans*-decalin, tetralin, and naphthalene by comparison of their v.p.c. retention times with that of authentic samples. Prolonged heating of the ketone mixture over Pd greatly increased the amount of these side products which were formed but did not change the relative amounts of I and II which were present at equilibrium. The decalone composition for the entire equilibration procedure was reproducible to within $\pm 0.4\%$. The equilibration data are listed in Table I.

TABLE I

Temp., °K.	%I	K	F, kcal./mole
493	24.52 \pm 0.43	3.08 \pm 0.03	-1.10
523	22.71 \pm 0.26	3.40 \pm 0.05	-1.27
573	19.05 \pm 0.23	4.25 \pm 0.07	-1.65
531 ^a		3.52	-1.33 \pm 0.02

^a Temperature used in the calculation of ΔH and ΔS .³ K, at this temperature, was determined graphically.

A plot of $\ln K$ vs. $1/T$ indicated that the enthalpy change for the reaction was not linear with temperature. The thermodynamic data for the *cis* \rightleftharpoons *trans* equilibration, $\Delta H_{531} = +2.25 \pm 0.24$ kcal./mole and $\Delta S_{531} = 6.74 \pm 0.45$ e.u., were evaluated using the method described by Douglas and Crockford.³ *This entropy change is the highest we have found recorded for any cis-trans isomerization.* In fact it is about five to ten times larger than the usual ΔS observed for such reactions. It represents one of the few instances in such equilibrations in which the ΔS is of such a magnitude as to cause a difference in sign between the ΔF and ΔH of the reaction.⁴

The enthalpy change for *cis* \rightleftharpoons *trans* decalin equilibration is -2.72 ± 0.20 kcal./mole.⁵ Subtracting the ΔH for the decalone equilibration from this value results in an energy assignment for the 3-alkyl ketone effect of 4.97 kcal./mole, a value which is clearly inconsistent with the empirical correlations initially proposed. By use of a similar comparison of the enthalpy changes for the *trans* \rightleftharpoons *cis* isomerizations of 1,3-dimethylcyclohexane and 3,5-dimethylcyclohexanone, Allinger and Freiberg have reported the magnitude of the 3-alkyl ketone effect to be no larger than 0.6 kcal./mole,² a value more in agreement with theoretical con-

siderations. However, the ΔH for the 3,5-dimethylcyclohexanone isomerization was calculated from a ΔF determined from equilibration data obtained at only one temperature and an entropy change (-1.4 e.u.) based on an entropy of mixing term which bears no relationship to the equilibration. This assumption, that the entropy of mixing approximates the entropy of isomerization, invalidates the entire argument.

This fact, in conjunction with the data presented for the decalone isomerization, raises doubts not only about the validity of the assignment made for the magnitude of the 3-alkyl ketone effect but also about the soundness of the experimental method used to obtain this information.

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Secondary α -Deuterium Isotope Effects in Acetolyses of *endo*- and *exo*-Norbornyl and 2-(Δ^3 -Cyclopentenyl)ethyl Arenesulfonates

Sir:

Recently, Brown and co-workers¹ reported some kinetic data which suggest doubts on certain mechanistic interpretations of solvolysis based on the nonclassical norbornyl cation. Some of the conclusions based on relative rates were necessarily indirect, these authors themselves pointed out that results from tertiary cations cannot be extrapolated to the norbornyl system, and comparisons between bicyclic and cyclopentyl systems may be complicated by solvent participation. We wish to report the secondary α -deuterium kinetic isotope effects observed in the acetolyses of *endo*- and *exo*-norbornyl-2-*d* *p*-bromobenzenesulfonates (I-*d* and II-*d*, respectively) and 2-(Δ^3 -cyclopentenyl)-ethyl-1,1-*d*₂ *p*-nitrobenzenesulfonate² (III-*d*₂). The relative magnitudes of these isotope effects may shed further light on the mechanisms of these solvolyses.

endo-Norboreneol-2-*d* was obtained from reduction of norcamphor with lithium aluminum deuteride. After conversion to I-*d*, the presence of any minor amount of *exo* isomer, II-*d*, was removed by selective solvolysis in aqueous acetone.³ Treatment of I-*d* with dry tetramethylammonium acetate in acetone⁴ gave *exo*-norbornyl-2-*d* acetate which was reduced with lithium aluminum hydride and then converted to II-*d*.⁵ From 4-bromocyclopentene,⁶ using the malonic ester synthe-

(1) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1246, 1247, 1248 (1964).

(2) R. G. Lawton, *ibid.*, **83**, 2399 (1961); P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); P. D. Bartlett, *Ann.*, **653**, 45 (1962).

(3) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954).

(4) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958).

(5) The correctness of this assignment is confirmed by n.m.r. II-*d* prepared in this way gave no detectable absorption for any C-2 proton. On the other hand, the *endo* isomer I showed n.m.r. absorption of an *exo*-proton at C-2 and after its conversion to II by this method the spectrum showed the presence of only an *endo*-proton at C-2, corresponding to pure *exo* isomer II. (For some of the spectra, see E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).)

(6) M. R. Rice, Ph.D. Thesis, Harvard University, 1957; P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

(3) T. B. Douglas and H. D. Crockford, *J. Am. Chem. Soc.*, **57**, 97 (1935).

(4) See, for instance, the various isomerization data reported by Allinger, as well as R. M. Gascoigne, *J. Chem. Soc.*, 876 (1958). A sign inversion between the ΔF and ΔH for the isomerization of *cis*- and *trans*-cyclohexene is reported by A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **81**, 3153 (1959).

(5) N. L. Allinger and J. L. Coke, *ibid.*, **81**, 4080 (1959).