detected), but as expected the molar absorptivity is somewhat more than halved.

Experimental Section

Near-Infrared Spectral Procedure.—Near-infrared spectra were measured on an Applied Physics Corp. Cary Model 14 recording spectrophotometer. The instrument was calibrated using didymium glass and polystyrene. Slit width was automatically controlled at 0.1 mm. at 2.000 μ.

Carbon tetrachloride was used as the solvent in all cases. Most of the compounds studied were at a concentration of either 0.500 or 1.000 *M*. These measurements were made using 1-cm. matched silica cells. Molar absorptivities were reproducible when the concentrations were varied by a factor of 10. Wavelength precision in the region 1.600 to 1.700 μ was of the order ±0.0005 μ.

Sources of Compounds.—Compounds **19**, **34**, and **35** were supplied by Dr. Dionis E. Sunko. The other monocyclic cyclopropanes were synthesized, purchased, or obtained from various members of the faculty at The Ohio State University. Compounds **41–58** were synthesized as part of a separate study. The preparation of these compounds will appear in a future publication.

Acknowledgment.—Support of this research by National Science Foundation Grant NSF-G25221 is acknowledged with appreciation. The authors are indebted to many individuals who supplied samples of certain cyclopropanes.

Nuclear Magnetic Resonance Studies of Enolizable Cyclic β-Keto Esters[1]

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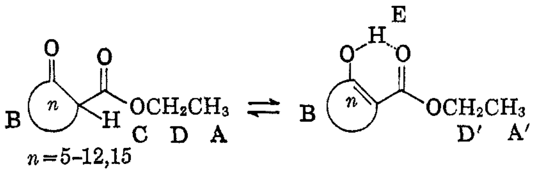
Received August 9, 1965

N.m.r. studies have been made of 2-carbethoxycyclanones of 5–12 and 15 ring members and of two acyclic β-keto esters, ethyl α-ethylacetoacetate and ethyl 2-hexyl-3-ketodecanoate. Within the cyclic series, trends in the chemical shift values and splitting patterns of the enolic hydrogen and of the α-hydrogen of the ketonic species are noted and discussed in terms of the partial geometries and conformations of these molecules. Enol contents are recorded for the tautomeric systems measured as 2.5 *M* solutions in carbon tetrachloride.

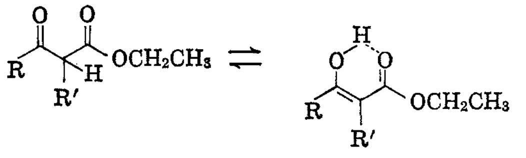
The advantages of the n.m.r. technique in studies of tautomeric phenomena have been amply demonstrated in recent years.[2] In keto–enol equilibria, in which the tautomers are only slowly interconverted at room temperature, the proton signals of the individual isomers are clearly distinguishable. Within a systematically varied series of compounds, analysis of these signals with respect to intensity, position, and splitting pattern might be expected to furnish significant information concerning the influence of a regular structural change on the geometries of the isomers and on the tautomeric equilibria. This paper reports the results of a preliminary study undertaken to test the potentiality of this approach.

In this study, 2-carbethoxycyclanones of 5–12 and 15 ring members, IK ⇄ IE, and two acyclic analogs, ethyl α-ethylacetoacetate (II) and ethyl 2-hexyl-3-ketodecanoate (III), have been examined at 60 Mc. as 2.5 *M* solutions in carbon tetrachloride. The signals of the enolic proton, E, the α-proton of the ketonic species, C, and the methylene, D and D′, and methyl, A and A′, protons of the carbethoxy function are clearly separated in the spectra of these compounds. The methylene hydrogens of the ring, B, including the γ-hydrogens of the keto species ($-CH_2CO-$) and the allylic hydrogens of the enol species ($-CH_2\overset{|}{C}{=}\overset{|}{C}CH_2-$), produce a complex set of overlapping signals at high field (~1–2.5 p.p.m.); no attempt was made to analyze this region in detail. Table I summarizes the chemical shift data for the protons A–E as well as the enol contents for these systems under the conditions studied. Typical spectra, illustrative of the points to be discussed, are displayed in Figure 1.



$n = 5\text{–}12, 15$

IK IE



II, $R = CH_3$, $R' = C_2H_5$

III, $R = C_7H_{15}$, $R' = C_6H_{13}$

Attention is first directed to the effect of ring size on the chemical shift parameters of the enolic hydrogen, E, and the α-hydrogen, C, of the keto species. Rather definite and roughly parallel trends are discernible in the two sets of signals.

The strong deshielding effect of internal hydrogen bonding in enolic chelates is well recognized and it is generally accepted that the magnitude of the displacement of the OH signal to lower field is related to the strength of the hydrogen bond.[2f,3,4] In the series at hand, the downfield shift of the signal of proton E increases sharply from the five- to the six-membered ring enol and then changes more slowly through the series to reach a position of maximum deshielding with

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[1] Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964.

[2] (a) See J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 433 ff, for a review of early work in this area. Recent studies include (b) M. T. Rogers and J. Burdett, *Can. J. Chem.*, **43**, 1516 (1965); (c) J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964); (d) E. W. Garbisch, Jr., *ibid.*, **87**, 505 (1965); (e) E. W. Garbisch, Jr., *ibid.*, **85**, 1696 (1963); (f) S. Forsen, F. Merenyi, and M. Nilsson, *Acta Chem. Scand.*, **18**, 1208 (1964); (g) R. W. Hay and P. P. Williams, *J. Chem. Soc.*, 2270 (1964).

[3] Reference 2a, p. 400 ff.

[4] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1959, p. 143.

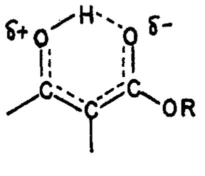
TABLE I

CHEMICAL SHIFT VALUES[a] AND ENOL CONTENTS OF SOME β-KETO ESTERS

	Keto			Enol				
β-Keto ester	Proton A	C	D	A′	D′	E	$W_{1/2}$[b]	% enol[c]
Cyclic								
I, $n = 5$	1.25	3.03	4.13	*d*	4.18	10.42	7	11.5 ± 2
$n = 6$	*d*	3.23	4.13	1.28	4.17	12.12	1.5	85 ± 1
$n = 7$	1.22	3.41	4.11	1.28	4.18	12.68	2	31 ± 2
$n = 8$	1.20	3.45	4.09	1.28	4.19	12.50	3	64 ± 1
$n = 9$	1.22	3.52	4.08	1.29	4.19	12.67	3.5[e]	38 ± 2
$n = 10$	1.22	3.68	4.10	1.30	4.21	12.88	3.5[e]	70 ± 1
$n = 11$	1.22	3.60	4.08	*d*	4.21	13.03	2	13 ± 2
$n = 12$	1.22	3.49	4.11	*d*	4.20	12.85	2	7.5 ± 2
$n = 15$	1.22	3.45	4.13	*d*	4.21	12.82	2.5	7 ± 2
Acyclic								
Ethyl acetoacetate	1.25	3.33	4.13	*d*	*d*	12.07	3	20 ± 2
II	1.25	3.25	4.15	*d*	*d*	12.62	2	5 ± 2
III	1.25	3.35	4.13	*d*	*d*	12.86	2.5	6 ± 2

[a] In parts per million from TMS = 0. [b] Band width of enol signal E at half-height in cycles per second. [c] Based on integrated values of peak intensities of E and C *vs.* (D + D′) or, in cases in which D and D′ were resolved, on D′ *vs.* (D + D′). [d] Signals not detected because of low concentration and/or overlap of peaks. [e] Fine splitting of *ca.* 1.5 c.p.s. observed under high resolution. See text.

the 10- and 11-membered ring compounds. In general, these changes correspond to the shifts to lower frequencies of the carbonyl and double bond stretching modes in the infrared spectra of these systems as well as to the decrease in acidities of the enols through the series I-5 to I-10 reported recently.[5,6] It appears that the chemical shift of the enolic proton is another manifestation of the extent of electron delocalization in the "quasi-aromatic" system IV which has been interpreted as a function of the changing geometry of the chelate ring imposed by changes in hybridization of the "olefinic" carbons of the carbocyclic system.[5] The variation in breadth (*cf.* $W_{1/2}$ in Table I) and in form of the enolic signals is a point of further interest. With the exception of that of the six-membered ring enol, all of the enolic signals are broader than expected for a true singlet (TMS showed $W_{1/2}$ of 1 c.p.s. in these spectra). It is noteworthy that IE-5, which is the most acidic enol of the series and thus has the least firmly bound enolic proton, displays the broadest signal with $W_{1/2}$ of 7 c.p.s. The enolic hydrogens of the cycles of 8–12 members show relatively sharp, well-defined signals but in each case the signal is somewhat asymmetric. Under ideal conditions of signal strength and resolution, this asymmetry may be partially resolved to reveal fine splitting in the form of a triplet with spacings of *ca.* 1.5 c.p.s. This is illustrated in the spectrum for 2-carbethoxycyclocyclononanone in Figure 1. Although the origin of this splitting in the enolic signal is presently not known, its detection in the medium-ring enols suggests subtle interactions of the tightly bound enolic protons with ring protons which are disposed in a conformationally favorable manner. It may be noted that a similar result was recorded by Freeman, Bhacca, and Reilly[7] for the chelated phenolic proton of methyl salicylate which was demonstrated to be split by a long range interaction with a *meta* hydrogen. Forsen,[2f] also, has commented on his unpublished observation of a "long range coupling between enolic, acetylic and olefinic protons in the enol of ethyl acetoacetate."



IV

The resonance position of the α-hydrogen of the ketonic species, C, also shows a downfield drift with increasing ring size and once more, reaches maximum displacement to low field with the 10- and 11-membered cycles. This same trend has been observed for the α-hydrogens of unsubstituted cyclic ketones of five, six, and seven ring members.[8] Although it is tempting to ascribe this trend, at least in part, to small changes in hybridization of the α-C–H bond induced by ring strain,[9] such speculation seems premature in view of the paucity of n.m.r. data for cyclic systems containing more than six atoms and the absence of any precise information relating to the conformational composition of the keto tautomers in the series.[10] (See below.)

Somewhat unexpected were the differences in the chemical shift values found for the methylene and methyl group protons in the ester function of IE and IK.[14] The methyl triplets, A, of the ketonic species

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(5) S. J. Rhoads, J. C. Gilbert, A. W. Decora, T. R. Garland, R. J. Spangler, and M. J. Urbigkit, *Tetrahedron*, **19**, 1625 (1963).

(6) S. J. Rhoads and A. W. Decora, *ibid.*, **19**, 1645 (1963).

(7) R. Freeman, N. S. Bhacca, and C. A. Reilly, *J. Chem. Phys.*, **38**, 293 (1963).

(8) L. M. Jackman ["Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Ltd., London, 1959, p. 57] reported values of 2.02, 2.25, and 2.42 p.p.m. for the α-methylene protons of cyclopentanone, cyclohexanone, and cycloheptanone.

(9) C. S. Foote, *Tetrahedron Letters*, 579 (1963); K. Mislow, *ibid.*, 1415 (1964).

(10) An alternative explanation which requires no recourse to hybridization and concomitant bond angle change is simply that the chemical shift trend may be a reflection of changes in conformation populations. For example, it is now well established[11,12,13] that in α-halocyclohexanone systems the axial and equatorial protons show chemical shift differences of 0.2–0.5 p.p.m., the axial proton being the more deshielded. If, as seems reasonable, the α-hydrogens of the carbethoxycyclanones show the same behavior, then the trend in δ_C exhibited in the series could be rationalized as a consequence of a population shift to conformations in which the α-H occupies a more "axial-like" position. In this event, however, one would reasonably look for a corresponding increase in the outer line spacings of the C-proton multiplet (*cf.* ref. 13). This is not observed.

(11) K. M. Wellman and F. G. Bordwell, *Tetrahedron Letters*, 1703 (1963).

(12) A. Nickon, M. A. Castle, R. Harada, C. E. Berhoff, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 2185 (1963).

(13) E. W. Garbisch, Jr., *ibid.*, **86**, 1780 (1964).

(14) Inspection of the spectra and data of acyclic β-keto esters recorded by Rogers and Burdett[2b,c] discloses this same phenomenon.

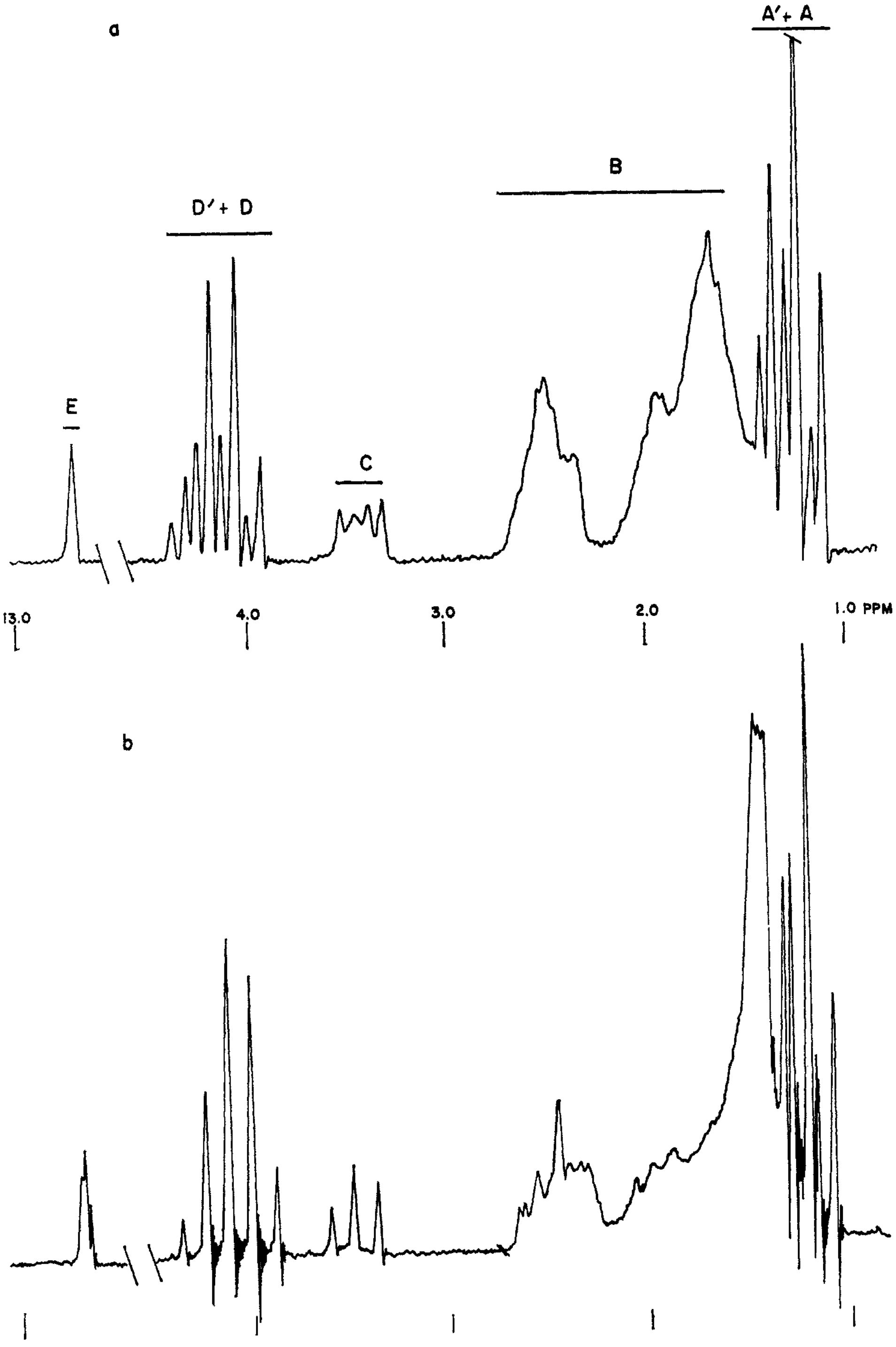

Figure 1.—N.m.r. spectra of (a) 2-carbethoxycycloheptanone, and (b) 2-carbethoxycyclononanone at 60 Mc. in carbon tetrachloride.

resonate at 1.20–1.25 p.p.m., while the signals of the corresponding protons of the enolic species (A') are found slightly downfield from these at 1.28–1.30 p.p.m. A similar shift is observed in the methylene quartets, δ_D = 4.08–4.13 p.p.m. and $\delta_{D'}$ = 4.17–4.21 p.p.m. An interesting point in this connection is that in the keto series (IK), the δ_D value reaches a minimum with the medium rings (a shielding effect), whereas in the enolic series (IE) the trend is to higher values of $\delta_{D'}$ with increasing ring size. The combination of these effects often serves to separate the resonance signals of the keto and enol methylene groups completely and to provide an independent measure of the equilibrium composition. This may be seen in the spectrum of 2-carbethoxycycloheptanone (Figure 1) in which the two quartets of the methylene protons and the two triplets of the methyl protons are cleanly resolved.

Table I also tabulates the percentages of enolic forms in the equilibrium mixtures as revealed by intensity measurements of various signals. In general, the variations in enol content in the series agree with those reported by other workers for the same or similar compounds[2b,c,15] and with values found by titration in our own work.[16] Inasmuch as the percentages given in Table I refer to solutions in carbon tetrachloride, a solvent which favors the enol tautomer, no direct com-

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(15) G. Schwarzenbach, M. Zimmerman, and V. Prelog, *Helv. Chim. Acta*, **34**, 1954 (1951).

(16) S. J. Rhoads and C. Pryde, *J. Org. Chem.*, **30**, 3212 (1965).

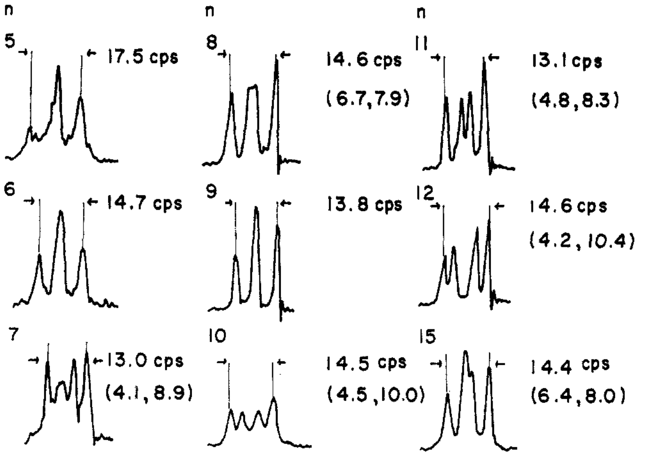

Figure 2.—Splitting patterns of proton C of the keto tautomers, IK-*n*, where *n* is the number of ring members. The outer line separations are shown in cycles per second; the values in parentheses give the spacings in the multiplets.

parison with measurements made in other solvents is possible.

A final point of interest in the spectra of the β-keto esters is the splitting pattern shown by the α-hydrogen, C. In the cyclic systems involved, it would be expected that the α-hydrogen would couple with the two nonequivalent hydrogens of the adjacent methylene group at C-3 to yield an ABX spectrum in which the α-hydrogen constitutes the X component of the three-spin system. Unfortunately, the AB portion of the pattern is obscured in these spectra so that a complete analysis is not possible without more sophisticated techniques. The splitting patterns of the C proton are noteworthy, however, and are shown in Figure 2.

Inspection of the splitting patterns of the X-multiplets reveals provocative changes both in the apparent multiplicities and in the magnitudes of the X-spacings, changes which are related to the conformations about the C-2–C-3 bond in these molecules. In the absence of any knowledge of the other parameters which determine the form of ABX spectra, the most that safely can be inferred is that the outer line separation of the X-multiplet represents the sum of the coupling constants J_{AX}[17] and J_{BX}.[17,18,19] Two features of the outer line separation parameter deserve comment. First is the "even–odd alternation" of the magnitude of the separation through the series of cyclic compounds from IK-6 to IK-12, a pattern often observed in the behavior of cyclic systems.[20] Secondly, despite the variation in the splitting pattern in the series, it is striking that the outer line separation of the X-multiplet is fairly constant from the six-membered cycle upward ($\sim$13–14.7 c.p.s.) and, moreover, is fairly large.[21] In view of the usual range of values for vicinal coupling constants and their dependence on dihedral angles, this value suggests either that one of the coupling constants is large ($\sim$10–14 c.p.s.) or that both of them are sizeable ($\sim$6–8 c.p.s.) and would seem to exclude, for any of the β-keto esters in the series, a dominant contribution from a conformation in which the two dihedral angles made by the X-proton with the A and B protons are close to 60° as in the ideal chair model with an equatorially disposed α-hydrogen.[22] Although the observed values of ($J_{\mathrm{AX}} + J_{\mathrm{BX}}$) are consistent with the general picture of a major conformation (or conformations[23]) in which the relationships between the α-hydrogen and the two hydrogens at C-3 are synclinal and antiparallel as deduced from infrared studies for the majority of these compounds,[5] they do not uniquely require such a relationship. More intensive investigations of these systems are planned.

Experimental Section

The compounds used in this study were prepared by methods described earlier.[5] The solutions of the β-keto esters in carbon tetrachloride containing a small amount of TMS as an internal standard were allowed to equilibrate at least 2 weeks at room temperature before the spectra were recorded with a Varian A-60 instrument at instrument temperature. The sweep of the instrument was calibrated with chloroform prior to each day's runs. Peak positions were read directly from the spectra and are estimated to be accurate to 0.02 p.p.m.

Acknowledgments.—This work was supported by Grant No. GP-1571 of the National Science Foundation. A portion of the study was carried out at the California Institute of Technology while the author was on sabbatical leave in 1963. The hospitality of Professor J. D. Roberts of that institution is gratefully acknowledged. Special thanks are extended to Mr. Glenn Cook and Mr. Francis MacDonald of the Laramie Petroleum Research Center, U. S. Bureau of Mines, for their help in obtaining the n.m.r. data.

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[17] To the extent that these ketonic species are rapidly equilibrating among two or more conformations, these are time-averaged coupling constants.

[18] J. D. Roberts, "An Introduction to the Analysis of Spin–Spin Splitting in Nuclear Magnetic Resonance," W. A. Benjamin, Inc., New York, N. Y., 1961, Chapter 3.

[19] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, Chapter 6.

[20] See J. Sicher, *Progr. Stereochem.*, **3**, 202 (1962), for a review.

[21] The five-membered ring β-keto ester is omitted from this comparison since, regardless of its *conformational preference, it might* be expected to show fairly large and comparable values for J_{AX} and J_{BX}. *cis* and *trans* vicinal coupling constants in cyclic carbonates show values of $\sim$7–9 c.p.s. [F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 747 (1962)], and, in cyclopentanone, itself, rather large coupling constants occur [F. A. L. Anet, *Can. J. Chem.*, **39**, 2316 (1961)].

[22] The best models for judging the magnitudes of the coupling constants to be expected in these cases appear to be the α-bromocyclohexanones studied recently by Garbisch.[13] Conformationally homogeneous isomers gave values of ($J_{\mathrm{ea}} + J_{\mathrm{aa}}$) of 18.3 c.p.s. and ($J_{\mathrm{ea}} + J_{\mathrm{ee}}$) of 5.7 c.p.s.

[23] Conformational possibilities increase rapidly with increasing ring size; though there may be one strongly preferred conformation for the carbon skeleton, there may be several reasonable ways of distributing the carbonyl and ester functions. For example, if it is assumed that the cyclodecane carbon skeleton exclusively adopts the "diamond lattice" conformation (Figure 3) which permits complete staggering of the hydrogens on adjacent carbons, there are two conformationally nonequivalent positions in the ring where the carbonyl function may reasonably be placed, *i.e.*, at carbons with the *partial conformation of type I or III.*[24] If the carbonyl group is located on a carbon with a type I conformation the α-carbon bearing the ester function would possess a partial conformation of type II, whereas location of the carbonyl at a carbon of type-III conformation provides two conformational possibilities (II and III) for the monosubstituted α-carbon. For further discussion, see ref. 24.

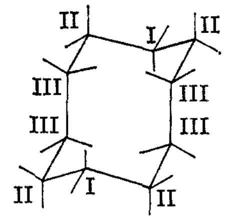

Figure 3

[24] J. D. Dunitz and V. Prelog, *Angew. Chem.*, **72**, 896 (1960).