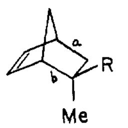
COMMUNICATIONS TO THE EDITOR

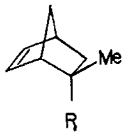
THE MECHANISM OF THE THERMAL ISOMERIZATION OF THE CYCLOPENTADIENE-METHYL METHACRYLATE ADDUCTS[1]

Sir:

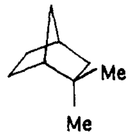
In an examination of the nature of possible intermediates in Diels–Alder processes we have studied the thermal isomerization of the optically active stereoisomeric cyclopentadiene–methyl methacrylate adducts Ia and IIa.



I



II

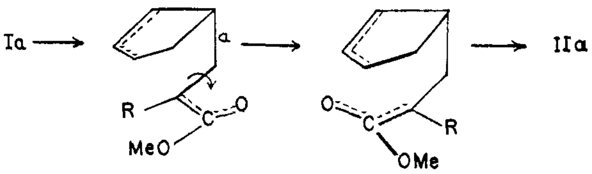


III

a: R = CO_2Me c: R = Me
b: R = CH_2OH d: R = CO_2H

Heating a 0.425 *M* decalin solution of optically active[2] Ia at 170° for 3.5 hours gave some polymethylmethacrylate and a mixture of 94.4 ± 1% of Ia and 5.6 ± 1% of IIa (analysis by gas–liquid partition chromatography). After saponification, Id was recovered 7% racemized and IId was recovered optically inactive, precautions being exercised throughout to prevent optical fractionations. Control experiments showed that racemization of optically active IIa under the reaction conditions was negligibly slow.

Recent results[3,4] suggest that distinct intermediates, in which only one of the two diene–dienophile bonds is formed, may intervene in Diels–Alder additions and retrogressions. This raises the possibility that Ia might be converted to IIa *via* an intermediate of the type IV by rotation about a single bond in the indicated sense and recyclization. (Although such a process would lead to some nonstereospecificity if it occurred, for example, in the addition of an acyclic *cis*-dienophile to a diene, and this generally is not observed, a test as sensitive as the one reported here has not been applied elsewhere.) The indicated mechanism, which predicts the formation of optically active IIa from optically active Ia, clearly does not pertain to the present system, in which completely racemic IIa was formed.



IV

The extent of the Ia → IIa conversion (5.6 ± 1%) corresponded to that anticipated (4.7 ± 0.3%) on the assumption that the addends, cyclopentadiene and methyl methacrylate, are common intermediates for the racemization of Ia and its conversion to IIa. Under such circumstances, the Ia → IIa conversion should have proceeded to an extent equal to the % racemization of Ia times the kinetic ratio (IIa/Ia) for formation of adducts from addends. The latter ratio (0.67) for a temperature of 170° was available by extrapolation of data at other temperatures (see below). (At low conversion, the contribution made by return of racemic IIa to Ia was negligible.) The correspondence implies that conversion and racemization are coupled processes and that IIa is formed from species in which *both* bonds a and b of Ia are broken.

In the above experiment, we could have detected as little as 1% retention of optical purity in IIa. Therefore, if an intermediate such as IV is involved in the retrogression of Ia to addends, the free energy of activation for the indicated rotation about the single bond is at least 4 kcal./mole greater than the free energy of activation for breaking the bond a. The latter barrier cannot vanish if IV is to have meaning as an intermediate and, consequently, the rotational barrier must be substantially more than 4 kcal./mole.

From the effect of temperature on the *kinetically controlled* ratios of stereoisomeric products in each system, we have calculated the activation energy differences ($E_a^{exo} - E_a^{endo}$) for additions to cyclopentadiene in decalin as + 0.35 kcal./mole for methyl acrylate and −0.71 kcal./mole for methyl methacrylate. The latter result is contrary to what would be expected if the attractive forces between non-reacting centers postulated[3,5] to account for the Alder *endo*-addition rule were of overriding importance. It may be that such attraction dominates in cases where the structure of the dienophile is exceptionally favorable but, in the present cases, the attraction must be weak. Whatever contribution it makes to lowering the activation energy for *endo*-addition is sacrificed, without much reluctance, to the demands introduced by a small change in the structure of the dienophile.

The two-stage mechanism[3] as applied to the present system would picture the transition state for *endo*-addition as V, in which dashed lines represent partial bonds and dotted lines represent "secondary attractive forces."[3] The work reported here demonstrates, if one adheres to this mechanism, a marked difference in the strengths of the c and d types of "secondary attractive force." Since the d type is weak in the transition state, the c type must be responsible for the low Arrhenius pre-exponential factor for addition com-

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[1] (a) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. (b) We are indebted to the Office of Ordnance Research (Contract No. DA-04-495-ORD-532) for support of part of this work.

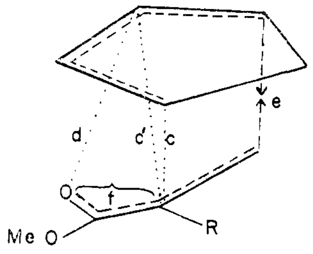
[2] Relative and absolute configurations and maximum optical rotations of Ia-d and IIa-d were determined by methods involving conversion to III and will be reported in our complete paper.

[3] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[4] C. Walling and J. Peisach, THIS JOURNAL, **80**, 5819 (1958).

[5] A. Wasserman, *J. Chem. Soc.*, 828 (1935); 432 (1936).

monly observed in Diels–Alder reactions; it must also contribute to the substantial barrier to rotation in the hypothetical *intermediate* IV. To preserve the established distinction between the two ends of the allylic system f, we prefer to call the interaction symbolized by c a partial bond. If both c and e are partial bonds, the difference between transition state V and that for a one-step four-center reaction becomes a subtle matter of definition. It seems possible that structural changes in the reactants could cause variations in the extent to which bond-making corresponding to e is further advanced in the transition state than that corresponding to c. Those cases in which the fractional bond characters of both potential bonds were identical then would represent one extreme of a graded continuum of mechanisms.



V

The present results also define more precisely the properties that must be exhibited by the proposed[4] diradical mechanism for the Diels–Alder reaction. If this path leads to a triplet diradical intermediate (IV↑↑) the latter is required to suffer a triplet–singlet transition and then cyclize to products. In other diradical intermediates, resulting from additions of what are believed to be triplet species to *cis–trans* olefin pairs,[6] rotation about a single bond apparently is sufficiently fast relative to cyclization to destroy much of the original stereochemical integrity. That such a rotation is unobserved in the Ia→IIa isomerization means that either (i) the triplet-singlet transition-cyclization process is unusually fast; (ii) the rotational barrier is unusually high; or (iii) there is no triplet diradical intermediate.

(6) F. A. L. Anet, R. F. W. Bader and A. M. Van der Auwera, THIS JOURNAL, **82**, 3217 (1960); R. J. Cvetanovic, *Can. J. Chem.*, **36**, 623 (1958); P. S. Skell and J. F. Klebe, Abstracts of Papers, American Chemical Society Meeting, Cleveland, Ohio, April 5–14, 1960, p. 90-O.

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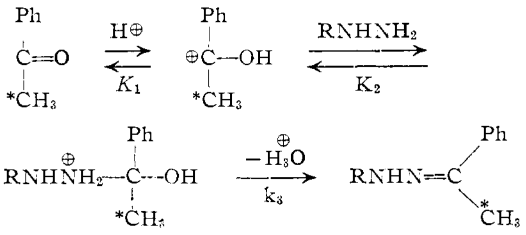
A SECONDARY ISOTOPE EFFECT IN THE FORMATION OF A DERIVATIVE OF ACETOPHENONE-β-C^{14}

Sir:

We wish to report the direct measurement of a secondary isotope effect (k^*/k) of 1.0085 ± 0.0004 in the formation, at 0°, of the 2,4-dinitrophenylhydrazone of acetophenone-β-C^{14}. An expression[1] relating the ratio (x) of the differentials of the fractions of labeled to unlabeled molecules as a function of the isotope effect (k^*/k) and the fraction of reaction (f), equation (1), recently was

$$\ln x = \left(\frac{k^*}{k} - 1\right) \ln (1 - f) + \ln \frac{k^*}{k} \qquad (1)$$

employed[2] to provide plots for several values of k^*/k. Some years ago presumptive evidence was obtained[3] for small, secondary carbon-14 isotope effects during reactions in which the carbon-14 label apparently was not in a position involved in the primary bond-making or bond-breaking process. Since the precision of the radioactivity measurements was very close to the magnitude of the suspected isotope effects, however, it was not possible to state with assurance that these effects were real. From the plots[2] previously mentioned it seemed possible to study such small secondary isotope effects, provided quantitative reactions could be carried out in such a way as to allow removal of small aliquots (1–2%) of reaction at known fractions (f) of completion; the radioactivity assay of each small aliquot divided by the radioactivity assay of the acetophenone should then provide values of x in equation (1). Such a reaction is the formation, at 0°, of β-C^{14}-acetophenone-2,4-dinitrophenylhydrazone [equation 2, R = 2,4-dinitrophenyl-]



$$\mathrm{Ph(^{*}CH_3)C{=}O} \underset{K_1}{\overset{H^{\oplus}}{\rightleftharpoons}} \mathrm{Ph(^{*}CH_3)\overset{\oplus}{C}{-}OH} \underset{K_2}{\overset{RNHNH_2}{\rightleftharpoons}} \mathrm{RNH\overset{\oplus}{N}H_2{-}C(Ph)(^{*}CH_3){-}OH} \xrightarrow[k_3]{-H_3\overset{\oplus}{O}} \mathrm{RNHN{=}C(Ph)(^{*}CH_3)} \qquad (2)$$

The reaction was carried out by the addition of successive aliquots of standardized 2,4-dinitrophenylhydrazine hydrogen sulfate solutions, cooled to 0°, to a cooled alcoholic solution containing a carefully weighed quantity of methyl-labeled acetophenone. After each addition sufficient time was allowed to insure complete precipitation of the derivative. The precipitate was collected on a filter, and to the filtrate was added the next aliquot of reagent solution. The process was repeated until all of the acetophenone had undergone reaction. Each fraction was crystallized 4 to 6 times from tetrahydrofuran–ethanol mixtures, and then dried *in vacuo;* all had melting points of 250°. Given in Table I are the pertinent data, including radioactivity assays,[4] of each sample. The total yield of the fractions collected was 96.0%. The 4.0% deviation from quantitative precipitation was shown to be a consequence of adsorption by the precipitate of unreacted acetophenone. We have assumed no isotope effect during this adsorption, and have normalized the fractions given in Table I to 100%. The reaction was shown to be nonreversible under the conditions employed. The data were next programmed on an IBM 704 com-

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(1) A. M. Downes, *Austr. J. Sci. Res.*, **5A**, 521 (1952).

(2) C. J. Collins and M. H. Lietzke, THIS JOURNAL, **81**, 5379 (1959).

(3) V. F. Raaen, unpublished work.

(4) The method employed was the dry-combustion method of B. M. Tolbert, UCRL Report No. 3595, p. 12.