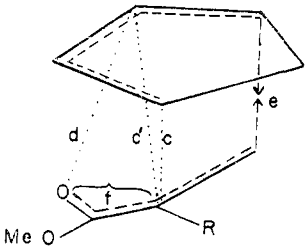
monly observed in Diels–Alder reactions; it must also contribute to the substantial barrier to rotation in the hypothetical *intermediate* IV. To preserve the established distinction between the two ends of the allylic system f, we prefer to call the interaction symbolized by c a partial bond. If both 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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA
JEROME A. BERSON
ALLEN REMANICK
WILLIAM A. MUELLER

RECEIVED JULY 21, 1960

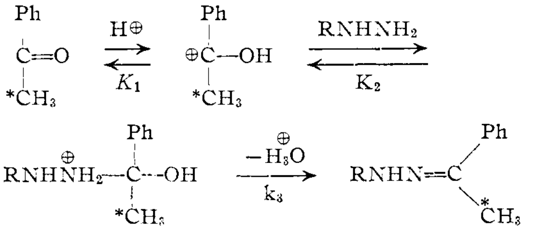
A SECONDARY ISOTOPE EFFECT IN THE FORMATION OF A DERIVATIVE OF ACETOPHENONE-β-C^{14}

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-]



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

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.

puter through a non-linear least-squares code[5] to find the best fit for equation (1); the value of the isotope effect thus was shown to be 1.0085 ± 0.0004.[6] In Fig. 1 are shown the experimental points, together with a plot of equation (1), for a value of $k^*/k = 1.0085$.

TABLE I

RADIOACTIVITY ASSAYS OF ACETOPHENONE-β-C^{14}-2,4-DINITROPHENYLHYDRAZONE FRACTIONS TAKEN DURING SUCCESSIVE STAGES OF REACTION

Fraction taken × 10^2	x^a	f (mid-point)	Molar radioactivity, mc./mole
0 - 2.05	1.0081	0.0103	5.711 ± 0.006
2.05- 63.72	1.0079	.324	5.710 ± .010[b]
63.72- 65.85	0.9958	.6479	5.641 ± .019
65.85- 86.38	...	...	...
86.38- 88.50	.9921	.8744	5.620 ± .000
88.50- 94.62	...	...	...
94.62- 96.66	.9853	.9564	5.582 ± .012
96.66- 98.16	.9795	.9741	5.549 ± .010
98.17- 99.20	.9739	.9868	5.517 ± .036
99.20- 99.82	.9668	.9951	5.477 ± .001
99.82-100.00	.9444	.9991	5.350 ± .019

[a] Obtained by dividing the molar radioactivity of each fraction by 5.665, the molar radioactivity of the acetophenone-β-C^{14}, prior to reaction. This value was obtained by integration of the data of Table I on the IBM-704 computer and compares favorably with the observed value of 5.668 ± 0.018. [b] Largest fraction assayed. Since this point falls on a portion of the curve (equation 1) which is nearly linear, it has been included.

The primary isotope effect in the formation of the 2,4-dinitrophenylhydrazone of carbonyl-labeled acetophenone previously has been determined as 0.908.[7] Both the present and former[7] results are consistent with the scheme outlined in equation (2), in which the dehydration step (k_3) is rate-limiting. In the case of methyl-labeled acetophenone, the stronger carbon-14-carbon-12 bond should facilitate the loss of H_3O^+ by decreasing the electron density at the α-carbon, and thus the labeled molecules should react more rapidly.[8,9]

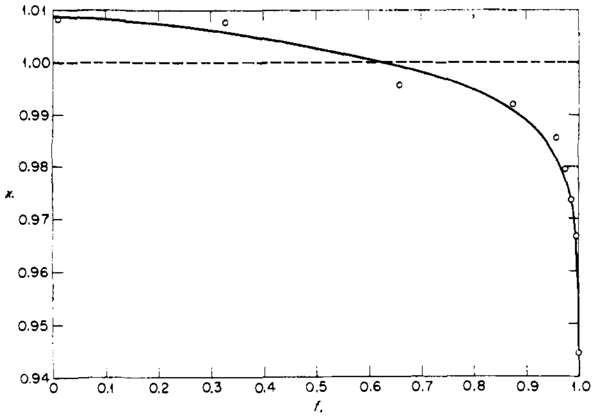

Fig. 1.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

VERNON F. RAAEN
ATHANASSIOS K. TSIOMIS[10]
CLAIR J. COLLINS

RECEIVED AUGUST 5, 1960

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(5) We are indebted to Dr. M. H. Lietzke for performing the calculations on the IBM 704 computer.

(6) The uncertainty in this value is expressed as standard deviation.

(7) G. A. Ropp and V. F. Raaen, *J. Chem. Phys.*, **22**, 1227 (1954).

(8) This is equivalent to the suggestion of Dr. J. Bigeleisen of Brookhaven National Laboratory that the faster reaction of the methyl-labeled molecules may be due to their increased ability to contribute, in the transition state, to the double-bond character of the carbon-carbon side chain. See also W. P. Jencks, THIS JOURNAL, **81**, 475 (1959), and references contained therein. A referee has suggested that: "Hyperconjugation in the transition state of the dehydration step would cause an increase in C–CH_3 bond strength. As a result, the zero point energy difference for the two isotopic transition state species would be greater than the difference for the initial state species and reaction of the labeled molecule would be favoured." Our studies of secondary carbon-14 isotope effects are continuing: we prefer not to commit ourselves at the present time concerning the possible role of hyperconjugation.

(9) This paper is based upon work performed at Oak Ridge National Laboratory which is operated by Union Carbide Corporation for the Atomic Energy Commission.

(10) Participant of the International Coöperation Administration from Salonika, Greece.

DECOMPOSITION OF OPTICALLY ACTIVE METHYLETHYLPHENYLBENZYLPHOSPHONIUM *n*-BUTOXIDE

Sir:

The recent report[1] that phosphonium alkoxides of the type $[R_3PCH_2C_6H_5]^+OR^-$ undergo decomposition to produce toluene, the phosphine oxide, $R_3P{\rightarrow}O$, and the ether, ROR, led us to investigate the stereochemistry of this reaction as applied to both enantiomorphs of methylethylphenylbenzylphosphonium *n*-butoxide (I), in which the phosphorus atom is the sole center of asymmetry. In marked contrast with the decomposition of the corresponding phosphonium hydroxides, which gave methylethylphenylphosphine oxide(II) with 100% inversion of configuration of the asymmetric phosphorus atom,[2,3] the alkoxide decomposition produced the phosphine oxide II with over 90% racemization (a slight net inversion in each case).

To 58.5 g. of absolute 1-butanol was added 0.23 g. (0.01 mole) of sodium. When the sodium had dissolved 3.7 g. (0.01 mole) of racemic methylethylphenylbenzylphosphonium iodide was added and the solution refluxed for 18 hr. The solution was cooled and an aliquot withdrawn for analysis by means of vapor phase chromatography. The only volatile products were toluene and *n*-butyl ether, obtained in 96 and 83% yields, respectively. The reaction mixture was distilled to dryness *in vacuo*, and vapor phase chromatographic analysis of the distillate gave results identical with those cited above. The solid residue was treated with sodium hydroxide solution and extracted with benzene. After removal of the benzene, methylethylphenylphosphine oxide (II) was obtained in 77% yield by vacuum distillation. When dextrorotatory methylethylphenylbenzylphosphonium iodide, $[\alpha]^{25}D + 25.0°$

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(1) M. Grayson and P. T. Keough, THIS JOURNAL, **82**, 3919 (1960).

(2) A. Bladé-Font, C. A. VanderWerf and W. E. McEwen, *ibid.*, **82**, 2396 (1960).

(3) K. F. Kumli, W. E. McEwen and C. A. VanderWerf, *ibid.*, **81**, 3805 (1959).