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 × 10²	x^a	f (midpoint)	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]

(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.

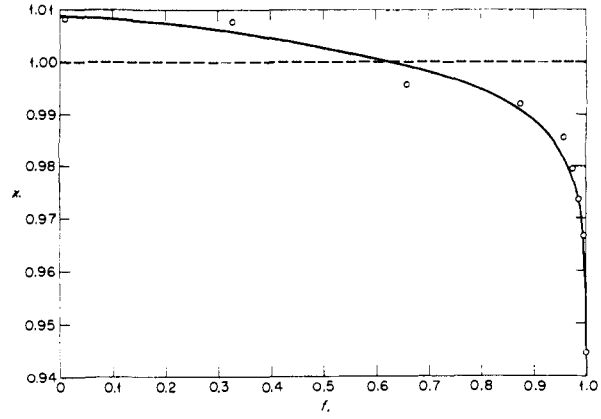


Fig. 1.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE
VERNON F. RAAEN
ATHANASSIOS K. TSIOMIS[10]
CLAIR J. COLLINS

RECEIVED AUGUST 5, 1960

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, $[\alpha]^{25}D + 25.0°$

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

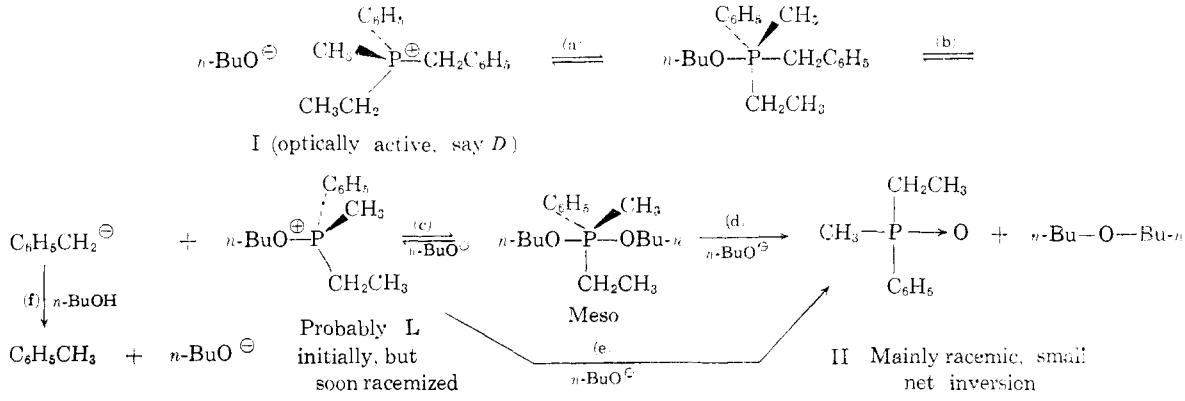
(2) A. Bladé-Font, C. A. VanderWerf and W. E. McEwen, *ibid.*, **82**, 2396 (1960).

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

(c, 2.155 in methanol), was subjected to the same reaction conditions, the oxide II isolated was very nearly racemic, $[\alpha]^{25}D$ — 0.7° (c 1.940 in methanol).[4] In like manner, the levorotatory phosphonium iodide, $[\alpha]^{25}D$ — 25.4° (c, 2.17 in methanol), gave II having $[\alpha]^{25}D$ + 0.9° (c 5.65 in methanol). Toluene and n-butyl ether were obtained in high yields in these experiments also.

A very significant result was obtained when the decomposition of racemic I was allowed to proceed at room temperature, aliquots being removed for analysis at regular intervals. It was found that toluene was produced at a much faster rate than n-butyl ether. After 48 hr., toluene had been formed in 98% yield while the ether had been produced in but 8% yield.

These results are accommodated readily by this mechanism of reaction, steps (d) and/or (e) being the slowest of all of the reactions shown and step (c) relatively fast



Acknowledgment.—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.

(4) For optically pure II $[\alpha]^{25}D$ + 24.5°.

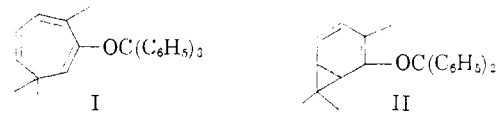
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF KANSAS
LAWRENCE, KANSAS
CHARLES B. PARISEK
WILLIAM E. MCEWEN
CALVIN A. VANDERWERF

RECEIVED SEPTEMBER 2, 1960

EUCARVONE ENOL TRIPHENYLMETHYL ETHER: A SUBSTITUTED CARADIENE

Sir:

There are ample illustrations of the tendency of cycloheptatriene ring systems to react as if they existed in the bicyclo[4.1.0]hepta-2,4-diene (caradiene) form in a variety of chemical reactions.[1,2,3] On the other hand, all known cycloheptatrienes, including eucarvone enol esters, exist in the seven-membered ring form as evidenced by u.v. and/or n.m.r. spectroscopy.[3,4,5] This striking dichotomy has led to speculation[5] about the possible existence of a valence tautomerization (I ⇆ II), even though no evidence has yet been adduced to indicate the independent existence of the caradiene tautomer. I now wish to report the isolation and characterization of such a compound which exists in the norcaradiene valence tautomer.



Some work on the effect of electrophiles on alkyltropilidenes and related compounds in progress in this laboratory[6] led to the investigation of the action of trityl perchlorate on eucarvone. One major product (38%) gave correct analyses for eucarvone enol triphenylmethyl ether (Found: C, 88.97; H, 7.41), m.p. 196–200° after repeated crystallization from absolute ethanol. The same substance was prepared from sodio-eucarvone[1] and triphenylmethyl chloride in 71% yield. The constitution of the substance was further secured by hydrolysis by dilution of a concentrated sulfuric acid solution to triphenylcarbinol (73%) and eucarvone, isolated as the dinitrophenylhydrazone (37%).

Analogy with the eucarvone enol esters would suggest that this substance should exhibit a maximum in the ultraviolet near 270 mμ and should exhibit absorption in the vinyl hydrogen region in the n.m.r. spectrum from four hydrogens and two singlets in the saturated C–H region from the lone (3 H's) and geminal (6 H's) methyl groups, corresponding to the valence tautomer I.[4] In fact, the enol ether has λ max at 230 mμ (log ε 4.26) and the n.m.r. spectrum shows absorption as follows: (τ values, average areas in parentheses) 2.76(14.4) (aromatic), 3.54(0.9) (vinyl), 5.66(1.0) (vinyl), 8.36(3.8) (lone methyl) and 8.76, 8.87(8.0) (geminal methyls and cyclopropyl). The most noteworthy feature of the spectrum is that the absorption due to the geminal methyl groups is a doublet. This splitting can only be accommodated on the basis of the valence tautomer II, in which one of the two methyl groups projects back over the π-electrons of the diene system and is thus differently shielded

(1) E. J. Corey and H. J. Burke, THIS JOURNAL, **78**, 174 (1956).

(2) K. Alder, K. Kaiser and M. Schumacher, *Ann.*, **602**, 80, 94 (1957), and earlier papers.

(3) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, THIS JOURNAL, **78**, 5448 (1956).

(4) E. J. Corey, H. J. Burke and W. A. Remers, *ibid.*, **77**, 4941 (1955).

(5) E. J. Corey, H. J. Burke and W. A. Remers, *ibid.*, **78**, 180 (1956).

(6) K. Conrow, *ibid.*, **81**, 5461 (1959); Abstracts 138th ACS meeting, N. Y., 1960, p. 6-P.