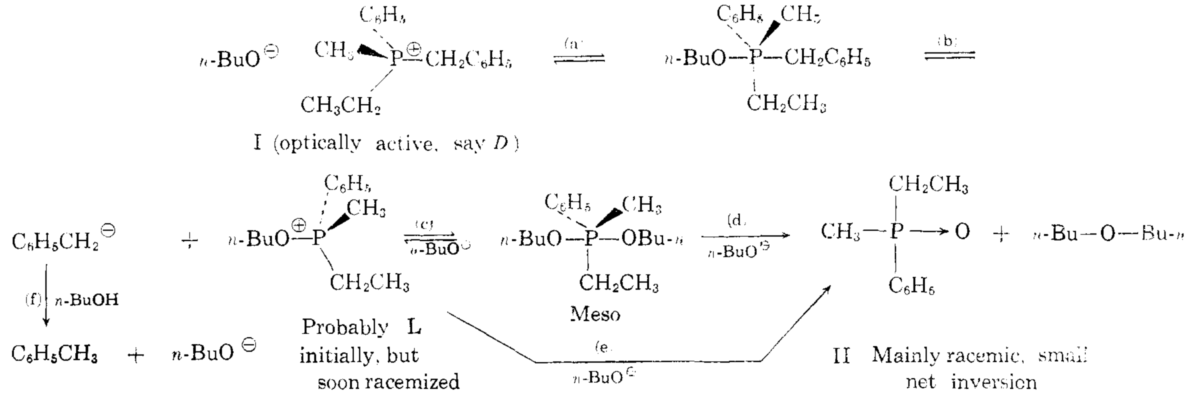
(*c*, 2.155 in methanol), was subjected to the same reaction conditions, the oxide II isolated was very nearly racemic, $[\alpha]^{25}\mathrm{D}$ − 0.7° (*c* 1.940 in methanol).[4] In like manner, the levorotatory phosphonium iodide, $[\alpha]^{25}\mathrm{D}$ − 25.4° (*c*, 2.17 in methanol), gave II having $[\alpha]^{25}\mathrm{D}$ + 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 $[\alpha]^{25}\mathrm{D}$ + 24.5°.

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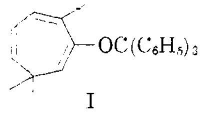
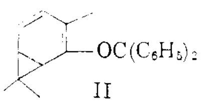
EUCARVONE ENOL TRIPHENYLMETHYL ETHER: A SUBSTITUTED CARADIENE

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.


I


II

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

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(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.

than the other which projects away from the ring. Furthermore, the ratio of hydrogens to be expected for II is 15 (aromatic):2 (vinyl):11(saturated), which closely approximates the observed 14.4: 1.9:11.8. That the absorption due to the cyclopropyl ring hydrogens falls under that for the methyl group hydrogens undoubtedly is due to the allylic character of the cyclopropyl hydrogens.

This evidence points unequivocally to the structure II for eucarvone enol triphenylmethyl ether. Attempts to isolate any substance corresponding to structure I, either from the crude reaction mixtures, from solutions exposed to sunlight for a period of weeks, or from material heated at 200° have met with failure. Attempts to obtain chemical evidence for structure II by hydrogenation (one mole) followed by hydrolysis to carone or carvenone have failed.

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TRIPLET STATES FROM MAGNETO-OPTICAL ROTATORY DISPERSION STUDIES

Sir:

Optical rotatory dispersion studies have been quite useful for investigating the stereochemistry of compounds[1] and polymers.[2] The technique, however, is limited to naturally optically active molecules. By using a magnetic field[3] in conjunction with the optical rotatory dispersion method, it should be possible to extend the scope of the method to all molecules whether they be optically active or inactive. This type of measurement is called magneto-optical rotatory dispersion and has been the subject of a number of studies.[4]

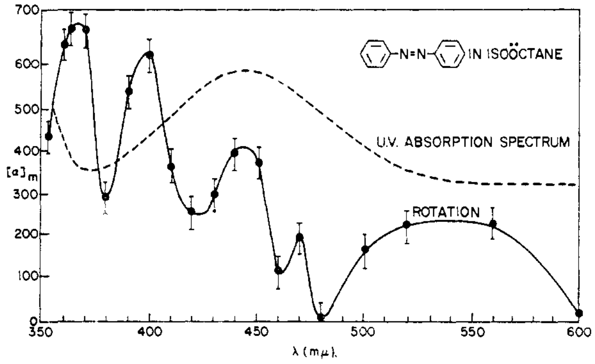

Fig. 1.—A plot of the molar magnetic rotation $[\alpha]_m$ for azobenzene as a function of wave length. The results are calculated from rotations measured in a 1-cm. cell for a 0.1% solution at 30°. $[\alpha]_m = [\theta]_m M/100$ when $[\theta]_m$ and M are the specific magnetic rotation and molecular weight, respectively. The magnitude of experimental error is depicted by the vertical lines at the experimental points.

The initial experiments were conducted on a number of optically inactive compounds and polymers using a Rudolph polarimeter instrument[5] suitably modified to allow the application of the magnetic field of 1200 gauss parallel to the light beam. Figure 1 shows the type of magnetic rotation spectrum obtained for a solution of azobenzene in isoöctane. The results in the region of the long-wave-length absorption band (singlet→singlet transition) of the compound clearly resemble the spectra obtained for optically active compounds by the optical rotatory dispersion technique. Both the magnitude (approximately 700°) and detailed features of the molar magnetic rotation results indicate that such spectra may provide useful stereochemical information about molecules in an analogous manner to the optical rotating dispersion technique. Moreover, the presence of a magnetic rotation peak at 540 mμ outside the region of the singlet →singlet transition shows that factors other than the Cotton effect[6] are involved.

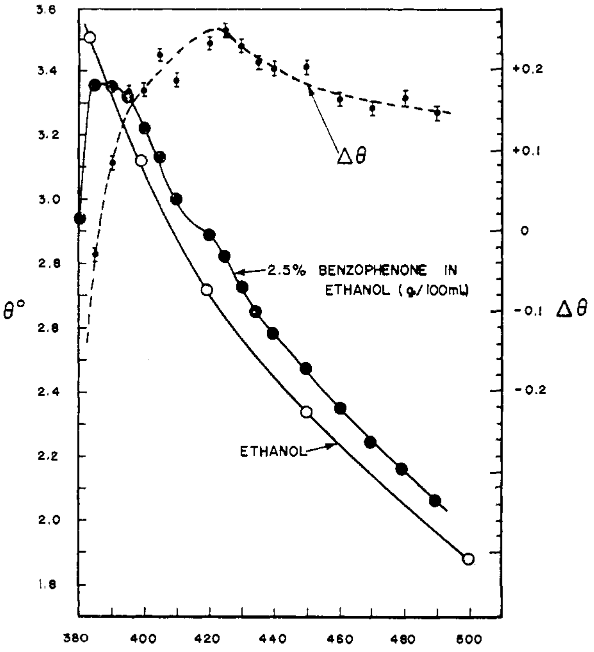

Fig. 2.—A plot of the observed magnetic rotations θ *versus* wave length (λ): the rotations were measured in a 5-cm. cell at 30°: $\Delta\theta = \theta - 0.975\theta_0$ where θ_0 is the rotation for the solvent ethanol.

Figure 2 depicts the observed magnetic rotations (θ) for a solution of benzophenone in ethanol at wave lengths longer than the 265 mμ singlet → singlet absorption band of the compound. A plot of $\Delta\theta$ *vs.* λ gives a magnetic rotation maximum at 425 mμ, quite close to the previously observed singlet → triplet transition for benzophenone at 410 mμ.[7] In phenazine a series of magnetic rotation peaks was obtained at 680, 625, 578, 538, 510 and 490 mμ. These occur at much longer wave lengths

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(1) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., New York, N. Y., 1960.

(2) P. Doty and J. T. Yang, THIS JOURNAL, **78**, 498 (1956).

(3) This in effect is a combination of the Faraday effect with the Cotton effect.[6]

(4) A. Cotton and M. Scherer, *Compt. rend.*, **195**, 1342 (1932); F. H. Garner, C. W. Nutt and A. Labbauf, *J. Inst. Petrol.*, **41**, No. 383, 329 (1955).

(5) Rudolph spectropolarimeter (Model 200AS/80Q/650), Rudolph & Sons, Caldwell, New Jersey. This instrument has a sensitivity of 0.003°. The experimental error in measurement was 0.01°.

(6) A. Cotton, *Compt. Rend.*, **120**, 989 (1895).

(7) G. N. Lewis and M. Kasha, THIS JOURNAL, **66**, 2100 (1944).