

CYCLOADDITION OF TERT-BUTYLCYANOKETENE TO OPTICALLY ACTIVE
2, 3-PENTADIENE

Warren G. Duncan, Walter Weyler Jr., and Harold W. Moore
Department of Chemistry
Irvine, California 92664

(Received in USA 29 August 1973; received in UK for publication 25 September 1973)

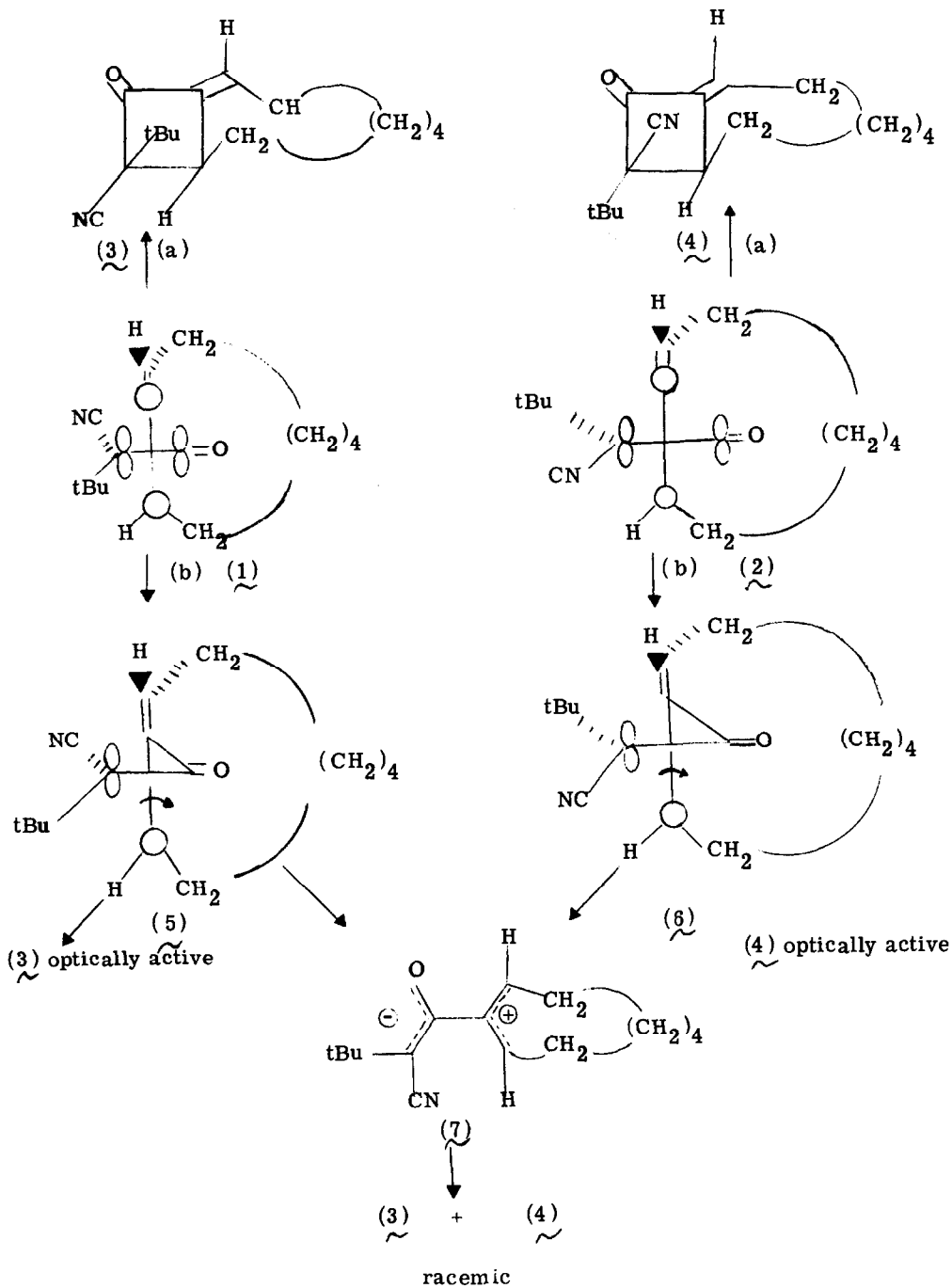
Recently it was shown that tert-butylcyanoketene reacts with optically enriched 1, 2-cyclononadiene to give a mixture of the optically active epimeric cyclobutanones (3) and (4). The lack of knowledge of the optical purity of these products allowed the consideration of two mechanistic consequences which are consistent with these results; the epimers, (3) and (4), could either arise directly from the respective transition states (1) and (2) in formally a $[\pi_s^2 + \pi_a^2]$ cycloaddition (path (a)) or via a two step process (path (b)) in which the intermediates (5) and (6) partition between ring closure to active products or rotation to the allyl stabilized system (7) which can then collapse to racemic products.² With the cyclic allene, the allyl cation (7) can obviously come about only by the rotational mode indicated, and, as a result only those epimers having the observed E-configuration of the exocyclic double bond would be anticipated. Certainly a knowledge of the optical purity of (3) and (4) would distinguish between these two mechanistic extremes since the optical purity of the starting 1, 2-cyclononadiene was known. Unfortunately such data would be most difficult to obtain on the compound in question. However, it was anticipated that resolution of this mechanistic dilemma might be accomplished by investigating the cycloaddition of tert-butylcyanoketene to an optically enriched acyclic allene. In this situation, the above mentioned rotational restrictions on intermediates analogous to (5) and (6) would be relieved and if a nonconcerted pathway is operative, one would anticipate four isomeric products, with only those two having the E-configuration of the exocyclic double bond possibly showing optical activity. On the other hand, a concerted process would, of course, give only optically active cycloaddition products.

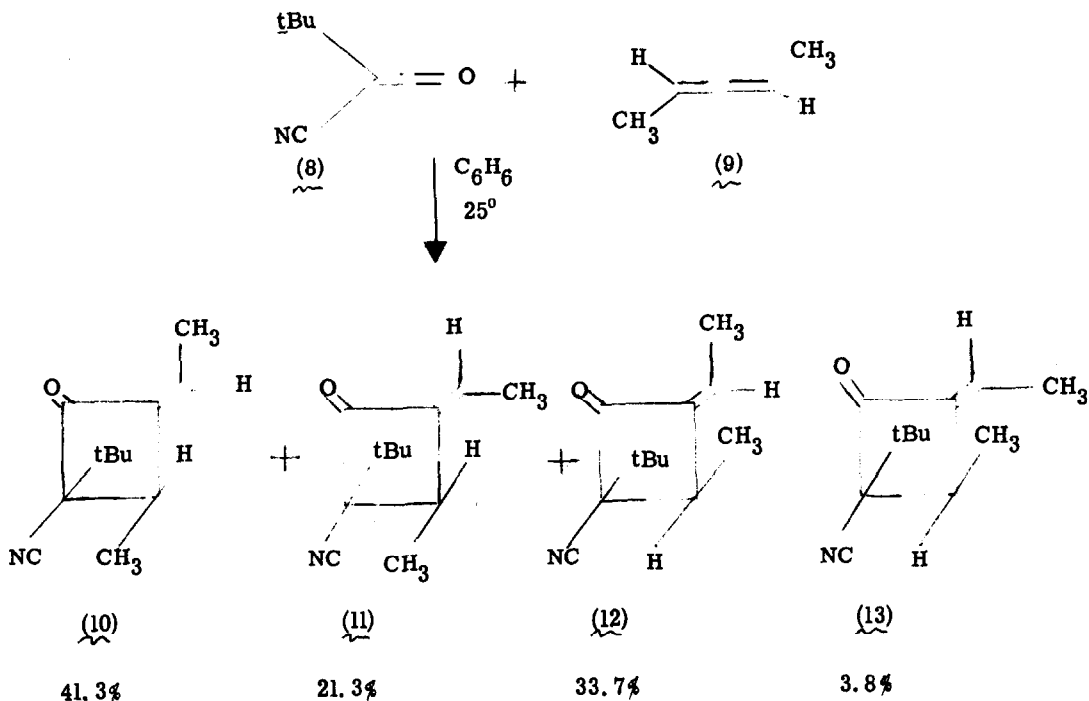
The reaction of tert-butylcyanoketene with enriched S-(+)-2, 3-pentadiene $[\alpha]_D^{25} = 17.0 \pm 0.2$; 11 mmol in CHCl_3]³ was therefore studied and the results are in excellent agreement with the two-step nonconcerted pathway (b). The ketene (3) and the allene (9) in anhydrous benzene at ambient temperature completely reacted after 90 minutes to give a mixture of the four isomeric cyclobutanones (10), (11), (12) and (13) in the respective ratio of 41.3: 21.3: 33.7: 3.8 (glc analysis using 15% DC550 on Crom W⁶⁰/80, 1/8" X 15', 175°). These

products were isolated in pure form by preparative gas chromatography and only (11) and (13) showed CD curves, respectively, $\Delta\epsilon_{245} = -3.75$ (methanol) and $\Delta\epsilon_{240} = -9.44$ (methanol). Table I lists spectral properties of these cyclobutanones which are in accord with their formulations. A clear assignment of the configuration of the propylidene moieties at position-2 was made on the basis of the chemical shifts of their vinyl protons; those two showing the greatest deshielding are the E-isomers, ie, (11) and (13). This assignment is based upon the fact that the adjacent carbonyl group is ideally located such that these olefinic protons fall in the deshielding zone of its anisotropy cone.^{4,5} The remaining stereo structure of these adducts is less firmly established, and is based primarily upon the fact that the methine protons in (12) and (13) are strongly deshielded relative to those in (10) and (11). The respective chemical shifts for these protons are 3.43, 3.62, 3.00 and 3.10. Such deshielding is expected for those isomers have the 3,4-E configuration, ie, (12) and (13), since the proton appears (models) to be in the deshielding region of the cyano group.

Table I
Spectral Properties of α -Alkylidenecyclobutanones

compound	ir (film, cm^{-1})	nmr (CCl_4)	uv (CCl_4 , nm)
(10)	2230, 1753, 1665	1.07 s(9), 1.40 d(3) J=7Hz, 2.05 m(3), 3.00 m(1), 5.77m(1)	353 (2.20) 248(4.01)
(11)	2225, 1750, 1663	1.07 s(9), 1.47 d J=7Hz, 1.80 m(3), 3.10 m(1), 6.43 m(1)	347 2.06) 245 (4.09)
(12)	2220, 1743, 1660	1.17 s(9), 1.52 d(3) J=7.5Hz, 2.05m (3), 3.43 m(1), 5.75 m(1)	353 (2.02) 250 (3.89)
(13)	2222, 1750, 1662	1.17 s(9), 1.61 d(3) J=7.5Hz, 1.84 m(3), 3.62 m(1), 6.42 m(1)	247 (3.99)





References

1. W. Weyler, Jr., L. R. Byrd, M. C. Caserio and H. W. Moore, J. Amer. Chem. Soc., **94**, 1027 (1972).
2. A two step process in which the initial approach of the reagents is nonorthogonal is certainly also possible.
3. W. L. Waters, W. S. Linn and M. C. Caserio, J. Amer. Chem. Soc., **90**, 6741 (1968).
4. M. R. Silverstein and G. C. Bassler, Spectroscopic Identification of Organic Compounds, J. Wiley and Sons, New York, N. Y., 1967, p. 117.
5. Also in agreement with this assignment is the fact that the propylidene methyl groups in (10) and (12) are deshielded by approximately 13 Hz relative to those in the E-isomers, (11) and (13).
6. C, H, N-Analysis for these isomers were in complete agreement with their formulations.