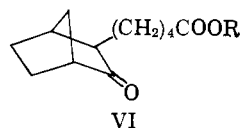


acid to the corresponding keto acid VI (R = H), infrared absorption (CCl₄) at 3.6–4.3 and 5.84 μ due to carboxyl and 5.73 μ due to the bridged ring



carbonyl.⁸ Esterification of the keto acid with diazomethane produced the ester VI, R = CH₃,⁴ infrared absorption (liquid film) at 5.73 μ due to ester and ketone carbonyls.⁸ The keto acid and keto ester obtained by these reactions were identical with authentic samples of VI obtained by an unambiguous route: alkylation of bicyclo[2.2.1]heptanone-2 with 5-bromopentene-1, hydroboration, and chromic acid oxidation.

The tricyclic ketone III was also obtained when 2-cycloheptenone in glassy methylcyclohexane at -195° was irradiated with ultraviolet light for 6 hr. (>300 mμ), maintained in the dark at -195° for 5 min., and then treated with a cold (-78°) solution of excess cyclopentadiene in pentane. The resulting solid mixture was allowed to warm slowly with vigorous agitation during the process of melting. The formation of the adduct III under the conditions of this experiment shows that this product results not from an electronically excited state of 2-cycloheptenone but from a transformation product of 2-cycloheptenone which is in the ground electronic state; the stereochemistry of III indicates that the reactive intermediate is *trans*-2-cycloheptenone.⁹

The irradiation of 2-cycloheptenone and excess furan in pentane leads to the formation of two stereoisomeric Diels–Alder adducts. As might be expected, however, the reactive *trans*-enone is not trapped as efficiently by furan as by cyclopentadiene.

The photochemical isomerization of *cis*-2-cycloheptenone is of interest not only as a route to the highly strained *trans*-cycloheptene series, but also as a method for effecting Diels–Alder additions which cannot be carried out thermally from the stable *cis* isomer.

We have also obtained direct spectroscopic evidence for the photochemical generation of *trans*-2-cycloheptenone.¹⁰

A 0.4% solution of *cis*-2-cycloheptenone in methylcyclohexane–isopentane (95:5) was cooled in an infrared cell with sodium chloride windows to -190° to produce a clear rigid glass. The sample cell was itself enclosed in a Pyrex vessel which could be evacuated and which had sodium chloride windows on opposite sides to allow the passage of infrared light through the sample. The infrared absorption due to the carbonyl group of *cis*-2-cycloheptenone in the solid hydrocarbon matrix was found to be a maximum at 6.01 μ.¹¹ Irradiation of the frozen mixture with ultraviolet light through Pyrex filters (to remove light of wave length below 300 mμ) resulted in a steady de-

(8) The position of the ketonic carbonyl band is inconsistent with that expected for the cyclobutanone derivative (5.60–5.63 μ) which would be derived from the photoproduct with fused five-, four-, and seven-membered rings.

(9) The photoadduct was obtained in 9.8 and 12.6% yield (based on 2-cycloheptenone) in two runs. Unchanged 2-cycloheptenone and its dimers and some polymer account for the remaining material.

(10) These results, first received on March 29, 1965, were added to the earlier results received on March 16, 1965.

(11) The same mixture exhibited absorption in the liquid state at 25° at 5.94 μ with a shoulder at 5.98 μ.

crease in the absorption at 5.94–6.07 μ with a concomitant increase in a new absorption band at 5.84 μ. After about 45 min. a steady-state condition was reached in which the new absorption band was much more intense than the original; the latter though attenuated by ca. 90% at this time did not disappear completely. The new absorption band persisted for 1 hr. at 190° after cessation of irradiation without loss of intensity. When the frozen, irradiated mixture was allowed to warm slowly the original carbonyl band of *cis*-2-cycloheptenone reappeared and the absorption at 5.84 μ had greatly diminished. After thawing, the absorption at 5.84 μ still remained but was less than that characteristic of *cis*-2-cycloheptenone. Vapor phase chromatographic analysis revealed that 45% of the original *cis*-2-cycloheptenone remained at the end of the experiment. The balance of the material was mainly a mixture of dimers of 2-cycloheptenone, clearly formed during the thawing of the irradiated material.

The new carbonyl absorption band produced by irradiation of *cis*-2-cycloheptenone in the solid hydrocarbon matrix at -190° can be reasonably assigned only to the *trans* isomer of this ketone which is expected to exhibit a carbonyl band in the region 5.84–5.86 μ since the carbonyl and α,β-carbon π-systems are essentially orthogonal in the *trans*-2-cycloheptenone structure. Other isomeric structures which do not have a carbonyl group such as I can be ruled out. The circumstance that the reactive inter-



mediate (VII) reverts to *cis*-2-cycloheptenone, dimerizes, and forms Diels–Alder adducts of *trans*-2-cycloheptenone allows no other ketonic structure than that of *trans*-2-cycloheptenone.

Similar experiments performed with *cis*-2-cyclooctenone showed clearly that it is converted to the *trans* isomer by ultraviolet irradiation in rigid hydrocarbon matrix at -190°.² In contrast, however, the irradiation of *cis*-2-cyclohexenone under the same conditions for 45 min. causes neither disappearance nor shift of the carbonyl absorption band.¹²

Acknowledgment. We thank the National Science Foundation for generous support of this work.

(12) After submission of this work for publication we learned that Professor P. E. Eaton and co-workers had also carried out studies on 2-cycloheptenone. The results of the two investigations are being published simultaneously by mutual agreement.

E. J. Corey, Masaru Tada
Ronald LaMahieu, Lawrence Libit
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138
Received March 16, 1965

trans-2-Cycloheptenone¹

Sir:

In a previous communication we described the preparation and properties of *trans*-2-cyclooctenone.² We

(1) By mutual agreement, this work and that of E. J. Corey, M. Tada, R. A. LeMahieu, and L. Libit on the same subject have been submitted for simultaneous publication.

wish now to report on *trans*-2-cycloheptenone, an extraordinarily strained system many thousand times more reactive than the higher homolog.

A thin film of pure *cis*-2-cycloheptenone held between two sodium chloride plates was mounted in a low-temperature infrared cell specially constructed for this work.³ The cell was cooled to -160° , and the infrared spectrum of the starting material was recorded. The film at this low temperature was then exposed through the salt windows of the cell for 1 hr. to a filtered beam of ultraviolet light ($\lambda \geq 300 \text{ m}\mu$).⁴ After the ultraviolet light source was removed, the infrared spectrum of the irradiated film was taken. The spectrum of the *cis* isomer was replaced almost completely by a new set of absorptions (Figure 1). If the sample were kept in the dark at -160° , the new spectrum remained unchanged for at least 1 hr. If, however, the cell were warmed to -120° and then immediately recooled to -160° , the absorptions at 6.42, 9.12, 9.90, and 13.33 μ disappeared entirely, and the spectrum of *cis*-2-cycloheptenone reappeared at a reduced intensity superimposed on the ill-defined absorptions of the dimers of cycloheptenone.⁵ The carbonyl group absorption at 5.83 μ diminished in intensity, broadened, and shifted to the slightly higher wave length characteristic of the cycloheptenone dimers. The experiment could be repeated on the lesser amount of the *cis* material now in the film with exactly the same results.

The major infrared absorption bands of a low-temperature film of *trans*-2-cycloheptenone as determined in a similar experiment appear at 5.83, 6.18, 8.55, 9.92, 12.06, 12.44, and 13.61 μ . A comparison of this information with that given in Figure 1 for the unstable irradiation product of *cis*-2-cycloheptenone provides fine evidence for the existence of *trans*-2-cycloheptenone. Particular attention is drawn to the equivalence of the carbonyl group absorption at 5.83 μ and to the marked similarity of the very characteristic *trans* olefin out-of-plane deformation near 10 μ in both homologs. The geometric requirements in each system preclude conjugation between the double bond and the carbonyl chromophores. The notable shift to lower energy of the double bond stretching vibration in the lower homolog is probably due to a significant torsional distortion at the double bond and the consequent reduction in p-orbital overlap.

Unlike equivalent experiments with 2-cyclopentenone^{6a,b} and 2-cyclohexenone,^{6c} irradiation of *cis*-2-cycloheptenone in simple olefins or acetylenes does not lead to significant amounts of crossed condensation products; instead, the dimers of cycloheptenone are formed preferentially. If, however, the irradiation is carried out in the presence of the diene furan, two

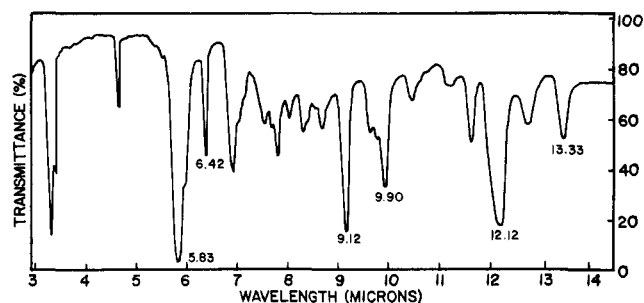
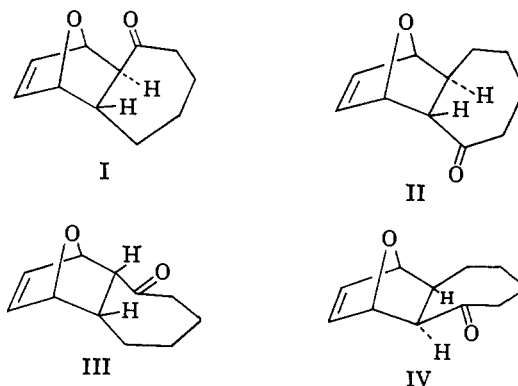


Figure 1. The low-temperature infrared spectrum of a *trans*-2-cycloheptenone film produced by ultraviolet irradiation of *cis*-2-cycloheptenone. This spectrum is a tracing of one recorded on a Perkin-Elmer 137B spectrophotometer. The wave lengths given were taken from a spectrum run on a Beckman IR-7. The band at 4.74 μ is due to a secondary photochemical product, probably a ketene, and does not disappear on warming the film to -120° . The shoulder on the carbonyl band is due to unchanged *cis* isomer.

crystalline adducts can be obtained in excellent yield⁷: I, m.p. 68–69 $^{\circ}$, and II, m.p. 87–88.5 $^{\circ}$. From straightforward spectral evidence⁸ both compounds are Diels–Alder adducts, derivatives of 7-oxanorbornene; accordingly,⁹ each can be converted readily to benzo-suberone.

On treatment with 1% sodium methoxide in methanol at room temperature I and II are epimerized, respectively, to III, m.p. 36.5–38 $^{\circ}$, and IV, m.p. 60–61.5 $^{\circ}$. Thus both the original adducts I and II possess the less stable *trans* ring junction appropriate to the products of the reaction of a diene with a *trans* olefin.²

In the n.m.r. spectrum of II and of III the absorption of the proton α to the carbonyl group and on the ring junction appears 0.4–0.5 p.p.m. below the main group of high-field absorptions. In compounds I and IV this absorption is not separated from the high-field group. As *exo* protons in both norbornene and 7-oxanorbornene derivatives are known to absorb at significantly lower fields than those of *endo* stereochemistry¹⁰ the proton α to the carbonyl group and on the ring junction in adducts II and III is assigned *exo* stereochemistry. This information taken in conjunction with the epimerization data is sufficient to establish the indicated structures of each of the furan adducts I through IV.



(7) The reaction with furan is remarkably facile. Neither cyclopentenone nor cyclohexenone on irradiation add as readily.

(8) E.g., adduct II, m/e 178, λ 5.84 μ , τ 3.6 (2 H, broad singlet), 5.1 (1 H, doublet $J \sim 4$ c.p.s.), 5.5 (1 H, broad singlet), 7.0 (1 H, doublet of doublets, $J \sim 4$ and $J' \sim 6$ c.p.s.), and 7.4–8.9 (9 H, unresolved multiplet) p.p.m.

(9) J. A. Norton, *Chem. Rev.*, **31**, 469 (1942).

(10) (a) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964); (b) F. A. L. Anet, *Tetrahedron Letters*, **25**, 1219 (1962).

(2) P. E. Eaton and K. Lin, *J. Am. Chem. Soc.*, **86**, 2087 (1964).

(3) The cell is similar in design to that of E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950). The temperatures given are those of the cell itself and approximate the actual temperature of the film.

(4) The ultraviolet source was an Osram 500-watt high-pressure mercury arc. The light was focused to a parallel beam by a quartz lens and then filtered through Pyrex glass. The apparatus was constructed by Mr. William Hurt.

(5) We have completed proofs of structure for these dimers. The details will be published in a subsequent paper. The products obtained are consistent with expectation for the thermal dimerization of *trans*-2-cycloheptenone.

(6) (a) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962); (b) P. E. Eaton, *Tetrahedron Letters*, **48**, 3695 (1964); (c) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

Full verification of these assignments of structure can be obtained by examining those proton-proton couplings extractable from the various n.m.r. spectra. In the spectrum of I and of II only one of the bridgehead protons is split into an observable doublet ($J \sim 4$ c.p.s.). In adduct IV neither bridgehead proton is coupled significantly to the hydrogens at the ring junction. On the other hand, in compound III both are coupled to those at the junction ($J \sim 4$ c.p.s.). Anet has demonstrated that significant coupling occurs between the bridgehead protons and those at the ring junction in 7-oxanorbornene derivatives only when the latter protons are in the *exo* position.^{10b} Thus, once more, we can conclude that the stereochemistry of the hydrogens at the ring junction is in I, *endo,exo*, in II, *exo,endo*, in III, *exo,exo*, and in IV, *endo,endo*. One final confirming point, in accord with the literature^{10a} the coupling constant (6 c.p.s.) between the protons on the ring junction in II (*exo,endo*) is smaller than that in the *exo,exo* isomer III (11 c.p.s.).

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(11) Alfred P. Sloan Foundation Research Fellow.

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The Chemiluminescence of Tetrakis(dimethylamino)ethylene¹

Sir:

The phenomenon of chemiluminescence has recently become the subject of increased study.² Among those

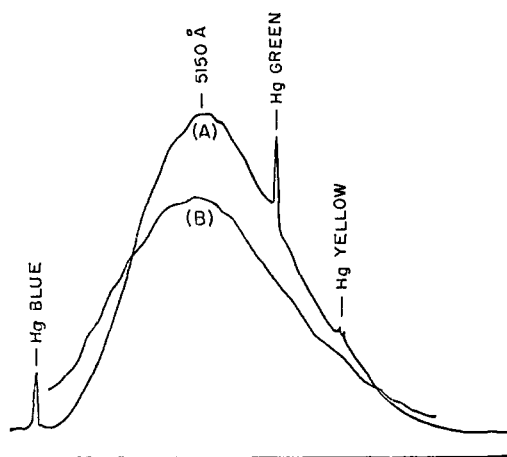


Figure 1. Fluorescent (A) and oxyluminescent (B) spectra of TDE.

systems which chemiluminesce, tetrakis(dimethylamino)ethylene (TDE) is of special interest because of the bright, prolonged, blue-green oxyluminescence

(1) This study by E. I. du Pont de Nemours and Co. was carried out in part under a U. S. Naval Ordnance Test Station Contract supported by A.R.P.A.

(2) E.g., (a) "A Symposium on Light and Life," W. D. McElroy and B. Glass, Ed., The Johns Hopkins Press, Baltimore, Md., 1961,

induced simply by exposing the compound to air.³ The chemistry of TDE including its intermediate oxidation states and possible dissociation to a carbene has been discussed in recent publications.⁴ In this communication we report on the centrosymmetric structure of TDE and on its chemiluminescent reaction, including identification of TDE as the light-emitting species, the quantum efficiency, and the need for protonic activation.

The Raman and infrared spectra⁵ provide strong evidence for a centrosymmetric ground-state structure for TDE. The C=C stretching frequency at 1630 cm^{-1} is absent from the infrared spectrum but appears as a strong, highly polarized Raman line. That TDE in the ground state exists as the simple centrosymmetric structure without tendency to dissociate into the corresponding carbene is further confirmed by its proton magnetic resonance.⁶ This consists of a single sharp resonance at -2.55 p.p.m. (tetramethylsilane internal reference), showing all protons to be equivalent.

The fluorescence and oxyluminescence spectra⁷ of TDE at ambient temperatures are essentially equivalent. The spectra (Figure 1) are continuous without fine-line structure and with the maxima at 5150 Å. The known oxidation products^{3b} of TDE do not fluoresce under these conditions. It thus appears that an electronically activated TDE molecule (TDE*) is the emitting species.⁸ This conclusion is confirmed by further observations that at low temperatures both the fluorescence and oxyluminescence spectra of TDE change from blue-green to blue.⁹ TDE* could originate during the

part III, p. 173; (b) E. H. White, O. Zafiriou, H. H. Kägi, and J. H. M. Hill, *J. Am. Chem. Soc.*, **86**, 940 (1964); (c) E. H. White and M. M. Bursey, *ibid.*, **86**, 941 (1964); (d) E. H. White and M. J. C. Harding, *ibid.*, **86**, 5687 (1964); (e) J. Sonnenberg and D. M. White, *ibid.*, **86**, 5685 (1964); (f) E. A. Chandross, *Tetrahedron Letters*, 761 (1963); (g) E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964); (h) D. M. Hercules, *Science*, **145**, 808 (1964); (i) A. U. Khan and M. Kasha, *J. Chem. Phys.*, **39**, 2105 (1963); **40**, 605 (1964); (j) R. F. Vassilèv and A. A. Vichutinskii, *Nature*, **194**, 1276 (1962); (k) R. F. Vassilèv, *ibid.*, **196**, 668 (1962); (l) J. Stauff, H. Schmidkunz, and G. Hartmann, *ibid.*, **198**, 281 (1963).

(3) (a) R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *J. Am. Chem. Soc.*, **72**, 3646 (1950); (b) N. Wiberg and J. W. Buchler, *Z. Naturforsch.*, **19b**, 5 (1964).

(4) (a) N. Wiberg and J. W. Buchler, *Angew. Chem.*, **74**, 490 (1962); (b) N. Wiberg and J. W. Buchler, *J. Am. Chem. Soc.*, **85**, 243 (1963); (c) ref. 3b; (d) N. Wiberg and J. W. Buchler, *Z. Naturforsch.*, **19b**, 9 (1964); (e) N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3000 (1963); (f) N. Wiberg and J. W. Buchler, *ibid.*, **96**, 3223 (1963); (g) N. Wiberg and J. W. Buchler, *ibid.*, **97**, 618 (1964); (h) K. Kuwata and D. H. Geske, *J. Am. Chem. Soc.*, **86**, 2101 (1964); (i) work of D. M. Lemal, R. A. Lovald, and K. I. Kawano, *ibid.*, **86**, 2518 (1964), indicates the absence of a dissociation equilibrium in other peraminoethylenes.

(5) Reference 3b. This article reports inability to obtain either the ultraviolet or the Raman spectrum (green Hg line) of TDE because of its instability to ultraviolet radiation. TDE was reported to become turbid on storage in a sealed tube in the dark. We have not observed these effects while determining the spectra of pure TDE or on storage of the compound for several years in glass.

(6) References 4a and 3b give the chemical shift as -2.32 p.p.m. (tetramethylsilane external).

(7) The fluorescence spectrum was determined using 3660 Å activation. The oxyluminescence spectrum was obtained from the air-induced light emission of TDE floating on water.

(8) The configuration of TDE* has not been determined because of lack of resolution of vibrational and rotational fine structure in the absorption and emission spectra. The ultraviolet spectrum of TDE vapor possesses a maximum at 2650 Å and a shoulder at 3500 Å. The solution spectrum has two bands near 2400 and 2700 Å. The large Stokes shift from the absorption bands to the center of the fluorescence or chemiluminescence spectrum at 5150 Å (approximately 9000 cm^{-1} from 3500 Å, or approximately 18,000 cm^{-1} from 2700 Å) is several times the C=C stretching frequency.

(9) Private communication from R. G. Bennett, Radiation Physics Laboratory, Engineering Department, E. I. du Pont de Nemours and Co., Experimental Station, Wilmington 98, Del.