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UNSATURATED HETEROCYCLIC SYSTEMS. XXXVI. REACTIONS OF TROPONES WITH ACTIVATED ISOCYANATES[1]

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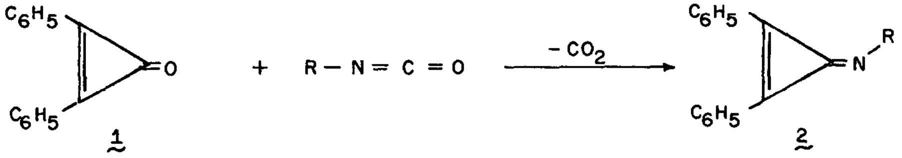
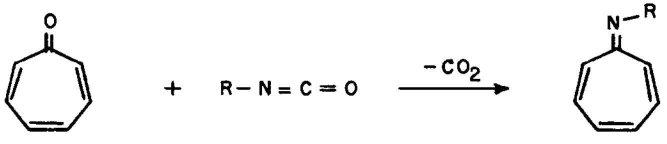
In an earlier publication from this laboratory, diphenylcyclopropenone (1) was shown to react readily with a variety of activated isocyanates to evolve carbon dioxide and give rise in good yield to iminocyclopropenes (2).[3] These transformations were formulated as in-



volving nucleophilic attack of the cyclopropenone oxygen atom at the isocyanate carbon with subsequent cyclization to 1,3-oxazetidin-2-ones and rapid expulsion of carbon dioxide from the latter intermediates. Because this mechanism implies that the reaction may be generally applicable to highly polarizable carbonyl compounds, an extension to tropones suggested itself, and in this communication we describe the results of this study.

Dropwise addition of a solution of 0.01 mole of trichloroacetyl isocyanate in 25 ml. of dichloromethane to a cold (-78°) solution of 0.01 mole of tropone (3) in 30 ml. of the same solvent over a 1 hr. period, followed by warming to room temperature (ca. 1 hr.), resulted in gradual CO_2 evolution. Passage of the reaction mixture through a column of Florisil,[4] elution with CH_2Cl_2, and trituration of the evaporated eluate with hexane afforded crystals of 4a, m.p. 60-61.5°,[5] in 60% yield; $\nu_{max}^{CHCl_3}$ 1670 and 1635 cm.$^{-1}$; $\lambda_{max}^{CH_3CN}$ 244, 247 sh, 252 sh, 318 sh, and 330 mμ (log ε 4.00, 3.97, 3.94, 3.58, and 3.50); $\delta_{TMS}^{CDCl_3}$ 7.18 (multiplet, 6H, vinyl protons).

In similar fashion, exposure of 3 to an equimolar amount of chlorosulfonyl isocyanate



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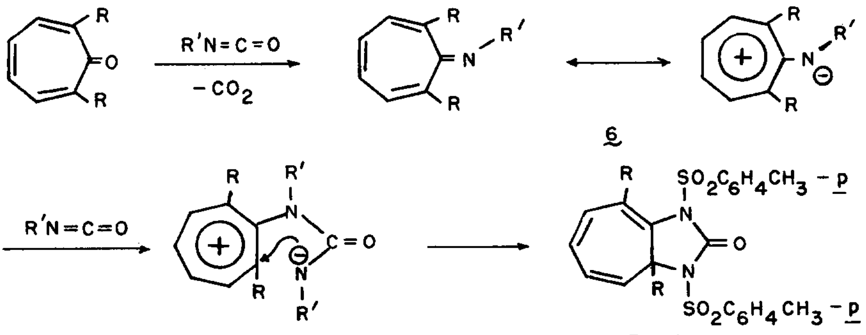
4a , R = $COCl_3$

b , R = SO_2Cl

in CH_2Cl_2 solution led to the ultimate isolation of troponimine 4b, m.p. 168-169°,[5] in 57% yield; $\nu_{max}^{CHCl_3}$ 1640 cm.$^{-1}$; $\lambda_{max}^{CH_3CN}$ 234, 237, 246 sh, and 323 mμ (log ε 3.61, 3.61, 3.38, and 3.32); $\delta_{TMS}^{CDCl_3}$ 7.17 (multiplet, 6H, vinyl protons).

When tropone (3) was treated with slightly more than two equivalents of p-toluenesulfonyl isocyanate (CH_2Cl_2, 25°, 16 hrs.), CO_2 evolution was again observed, but the product, m.p. 151-152°, was found to display intense carbonyl infrared absorption ($CHCl_3$) at 1770 cm.$^{-1}$ in addition to the anticipated band at 1645 cm.$^{-1}$. The microanalytical data are clearly consistent with a 1:2 adduct of tropone and the isocyanate less the elements of CO_2 ($C_{22}H_{20}N_2O_5S_2$).[5] Further, the ultraviolet [$\lambda_{max}^{CH_3CN}$ 233, 270, and 278 mμ (log ε 3.36, 3.26, and 3.24)] and nmr spectra of this substance [$\delta_{TMS}^{CDCl_3}$ 7.68 and 7.13 (multiplets, 4H each, aromatic protons), 6.48 (multiplet, 3H, vinyl protons), 6.0 and 5.02 (multiplets, 1H each, vinyl protons), 4.05 (multiplet, 1H, allylic proton), and 2.38 (overlapping singlets, 6H, methyl groups)] are sufficiently revealing to suggest structure 7a.

2,7-Diphenyltropone (5)[6] was also found to undergo reaction with excess p-toluenesulfonyl isocyanate, although somewhat more forcing conditions were required (CH_2Cl_2, reflux,



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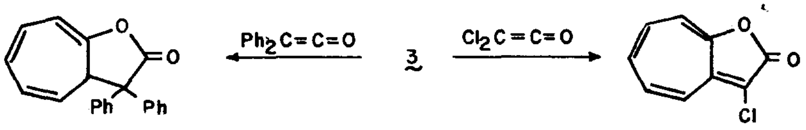
7a , R = H

b, R = C_6H_5

12 hrs.). The resulting solid, m.p. 167.5-169°,[5] exhibited spectral characteristics which likewise strongly support assignment of the cycloheptatriene imidazolone structure 7b; $\nu_{max}^{CHCl_3}$ 1770 and 1645 cm.$^{-1}$; $\lambda_{max}^{CH_3CN}$ 234 and 330 mμ (log ε 3.85 and 3.74); $\delta_{TMS}^{CDCl_3}$ 7.0-7.45 (complex multiplet, 22H, vinyl and aromatic protons), 2.41 and 2.30 (singlets, 3H each, methyl groups).

The mechanism proposed earlier[3] to account for the conversion of diphenylcyclopropenone to iminocyclopropenes in the presence of reactive isocyanates can be extrapolated with little controvertibility to the tropone series. Because troponimines such as 4 and 6 can also be expected to exhibit significant dipolar character, nucleophilic attack of the electron-rich nitrogen center on the electrophilic isocyanate can be envisioned to produce dipolar intermediates which can undergo cyclization (with charge annihilation) to give cycloheptatriene imidazolones. Support for this mechanistic proposal was obtained by monitoring the course of the p-toluenesulfonyl isocyanate-tropone reaction by nmr spectroscopy. With limited quantities of the isocyanate, the troponimine (not isolated in pure form) could be detected; as additional isocyanate was slowly introduced, the concentration of imine gradually diminished and the concentration of 7a increased in proportion.

The reaction of troponimines with isocyanates thus parallels in a mechanistic sense the recently discovered additions of tropone to diphenylketene[7,8] and dichloroketene.[9] Finally, the photochemistry of selected iminocyclopropenes and troponimines is under active investigation and will be reported separately.



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Acknowledgment. Support of this work by the Lilly Research Laboratories is gratefully acknowledged.

FOOTNOTES AND REFERENCES

(1) For previous paper in this series, see L. A. Paquette and L. D. Wise, J. Am. Chem. Soc., 90, in press.

(2) Alfred P. Sloan Foundation Fellow.

(3) L. A. Paquette, T. J. Barton, and N. Horton, *Tetrahedron Letters*, in press.

(4) Florisil is a magnesia-silica gel adsorbent.

(5) All new compounds gave acceptable elemental analyses.

(6) J. Ciabattoni and G. A. Berchtold, *J. Org. Chem.*, **31**, 1336 (1966).

(7) C. Jütz, I. Rommel, I. Lengyel, and J. Feeney, *Tetrahedron*, **22**, 1809 (1966).

(8) A. S. Kende has informed us in a private communication (September 13, 1967) that the 9,9-diphenylbicyclo[5.2.0]nona-3,5-diene-2,8-dione structure assigned by Jütz, et al., to the tropone-diphenylketene adduct is in error and that the product is actually lactone **8** (results of R. Gompper, Munich). Kende's report on the thermal rearrangement of **8** [Tetrahedron Letters, 2661 (1967)] thus, in actual fact, describes the *single* sigmatropic [1,5] shift of its non-vinyl proton.

(9) J. Ciabattoni and H. W. Anderson, *Tetrahedron Letters*, 3377 (1967).