

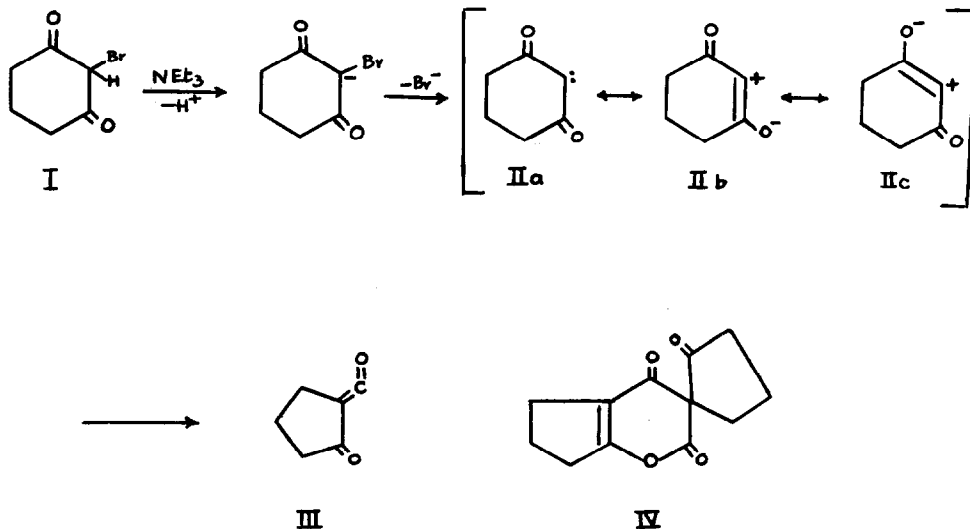
1,4-CYCLOADDITIONS TO A KETOKETENE

R. Selvarajan, K.Narasimhan, & S.Swaminathan,
 Department of Organic Chemistry, University of Madras, Madras-25,
 India.

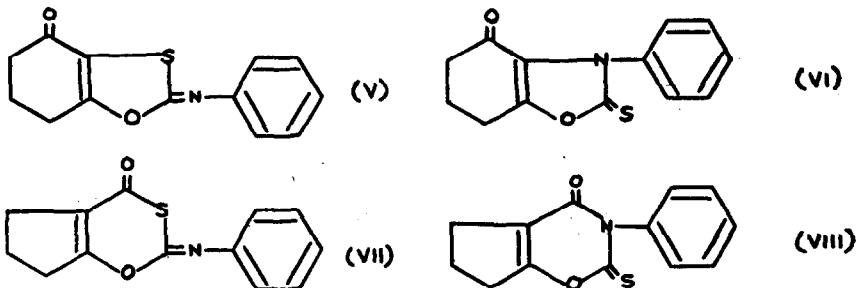
(Received 23 August 1966; in revised form 27 March 1967)

The bromodione¹(I) when reacted with equivalent amounts of triethylamine and phenyl isothiocyanate in benzene furnishes triethylamine hydrobromide almost quantitatively and a crystalline product (VIII), m.p. 184-185.5° in 12% yield in addition to much tar. Analysis and a mass spectrum indicate the molecular formula C₁₃H₁₁NO₂S (i.e. C₆H₆O₂ + C₇H₅NS). Analogous products are obtained with phenylisocyanate (X, m.p.75-75.8°, 25% yield) and with alpha-naphthyl isocyanate (XI, m.p.142-3°, 5% yield).

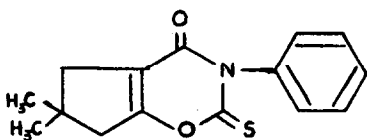
It is obvious that the dione (I) is undergoing α -dehydrobromination to give the dioxocarbene species II a \leftrightarrow IIb \leftrightarrow IIc and subsequent reaction through these species or the ketoketene III resulting from a Wolff rearrangement:



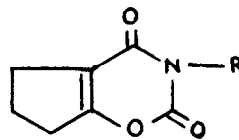
A priori, each of the above reagents can add in a 1,3 fashion to the dipolar species II b \leftrightarrow II c, as has been demonstrated by Huisgen² et al in reactions of the carbene from tetrachlorobenzene - O - diazoxide or in a 1,4 fashion to the ketone III which has been reported³ to be formed and then to dimerise to IV during the pyrolysis of 2-diazocyclohexane-1,3-dione. Four structural possibilities arise in each case depending on whether the cycloadditions are to a C = N or a C = O (or S) present in the reagents used. With phenyl isothiocyanate for example, the possible structures are V to VIII:



The above adduct does not give any 2,4 - DNP derivative and has λ_{max} Nujol 6.21 (m), 6.3 (m), 6.44 (s) and 6.77 μ (v.s.). The lack of absorption at ca 6.0 μ rules out the cyclohexeneone structures. The compound has λ_{max} EtOH 214, 241 and 262 $m\mu$ (ϵ , 14,450, 11090 and 17,380). The absorption at 241 $m\mu$ is absent in the adducts obtained from phenyl and α -naphthyl isocyanates and strongly indicates structure VIII incorporating a thiocarbonyl group known⁴ to absorb in the region. The IR absorptions at 6.21, 6.3 and 6.77 μ provide further support to the above structure and may be assigned⁵ to the tertiary amide carbonyl, phenyl and thiolactam groups respectively. The U.V. maximum at 262 $m\mu$ is also close to those reported² for IV and related compounds (272 to 279 $m\mu$). The NMR spectrum⁶ shows signals at τ 2.1 to 2.8 (5 H, aromatic, m), at τ 7.4 (4H, allylic, t) and τ 7.85 (2H, methylene, q.). The adduct IX, m.p.196-197° obtained in 22% yield by treating similarly 2-bromo-5,5-dimethyl-cyclohexane-1,3-dione⁷ with phenyl isothiocyanate has similar spectral properties; λ_{max} EtOH 212, 241 and 262 $m\mu$ (ϵ , 12,590, 11,030 and 16,020); λ_{max} CHCl₃ 6.2(m), 6.275 (m), 6.43 (s) and 6.71 μ (v.s.) NMR: τ 2.2-2.9 (5H, aromatic, m), τ 7.54 (4H, allylic, s) and τ 8.9 (6H, gem dimethyl, s). The assignment for the allylic protons in VIII is confirmed by comparison with IX where they now show up as a singlet.



IX



X, R = C₆H₅
 XI, R = α-C₁₀H₇

The adducts obtained with phenyl isocyanate and α-naphthyl isocyanate are by analogy formulated as X and XI respectively. Consistent with these structures, adduct X has $\lambda_{\max}^{\text{EtOH}}$ 216 and 275 m μ (ϵ ,15,890 and 32,110); $\lambda_{\max}^{\text{CHCl}_3}$ 6.14 (shoulder), 6.26 (s), 6.45 (s) and 6.69 μ (m); NMR: τ 2.2-2.8 (5H, aromatic, m), τ 7.4 (4H, allylic, t) and τ 7.95 (2H, methylene, q). Adduct XI has $\lambda_{\max}^{\text{EtOH}}$ 228, 264 and 308 m μ (ϵ ,2412, 11,060 and 11,060); $\lambda_{\max}^{\text{CHCl}_3}$ 6.19 (s), 6.25 (s), 6.47 (v.s.) and 6.87 μ (w); NMR: τ 1.8-2.55 (7H, aromatic, m); τ 7.35 (4H, allylic, t) and τ 7.95 (2H, methylene, q).

It is clear that the dioxocarbene II a, though stabilized by resonance with the forms II b and II c is too short lived to be capable of an intermolecular 1,3-dipolar addition. Evidently it prefers to undergo the intramolecular Wolff rearrangement like most monoxocarbenes and then 1,4-cycloaddition.

Acknowledgements: We thank Mr. R. Balasubramanian for microanalyses and IR spectra, Dr. H.A. Lloyd of the National Institute of Health, U.S.A. and Mr. M.W. Klohs of the Riker Laboratories, U.S.A. for NMR and mass spectral data. R.S. thanks the Government of India and K.N. thanks the University of Madras for the award of Fellowships.

References

1. G. Merling, Ann., 278, 42 (1894).
2. R. Huisgen, H. König, G. Binsch and H.J. Sturm, Angew. Chem. 73, 368 (1961)
3. H. Stetter and K. Kiehs, Tetrahedron Letters, 3531 (1964).
4. A.E. Gillam and E.S. Stern, Electronic Absorption Spectroscopy, II Edn., p.263. Edward Arnold (Publishers) Ltd., London (1957).
5. Koji Nakanishi, Infrared Absorption Spectroscopy, p.p.46, 26 and 54, Holden Day Inc., San Francisco (1962).
6. The NMR Spectra for the compounds reported in this paper were obtained in CDCl₃ with a Varian Model A 60 Spectrometer using tetramethyl silane as the internal standard.
7. D. Vorlander and M. Kohlmann, Ann., 322, 248 (1902).