Tetrahedron Letters No. 35, pp 3731 - 3734, 1972. Pergamon Press. Printed in Great Britain.

REACTION OF HYDRAZINE WITH 1,2-DIPHENYL-3-DIBENZOYLMETHYLENECYCLOPROPENE AND 1,2-DIPHENYL-3-DIACETYLMETHYLENECYCLOPROPENE; FORMATION OF PYRIDAZINES

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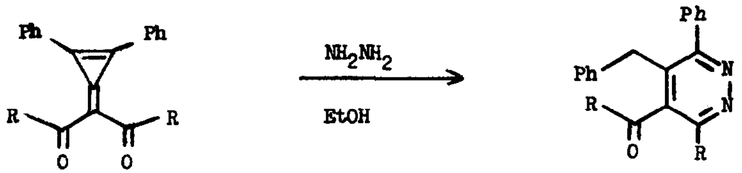
(Received in USA 15 June 1972; received in UK for publication 25 July 1972)

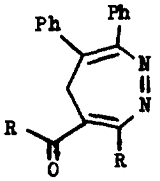
Conjugation of the methylenecyclopropene functionality with carbonyl groups (as in 1a,b) results in a polarized charge distribution similar to that observed in cyclopropenones. Because of this polarization and the tendency of small ring compounds to undergo transformations resulting in the relief of strain, rearrangements and ring opening reactions may be expected in these systems. When 1,2-diphenyl-3-dibenzoylmethylenecyclopropene[2] (1a) and 1,2-diphenyl-3-diacetylmethylenecyclopropene[3] (1b) are allowed to react with hydrazine, 3,6-diphenyl-4-benzyl-5-benzoylpyridazine (2a) and 3-phenyl-4-benzyl-5-acetyl-6-methylpyridazine (2b) are isolated in 68% and 47% yields, respectively. A suspension of 1a (2.3 mmol) in 150 ml abs EtOH is stirred at room temperature and 0.25 ml 85% aq NH_2NH_2 is added. After stirring for 20 min, $MgSO_4$ is added and, after 5 min additional stirring, the drying agent is filtered and the EtOH solution is concentrated at reduced pressure. The pyridazine 2a (mp 202) precipitates as a white solid and is purified by recrystallization from EtOH or by sublimation. The pyridazine 2b, an oil resulting from similar treatment of cyclopropene 1b, is isolated by silica gel chromatography.



1a, R=Ph
1b, R=Me

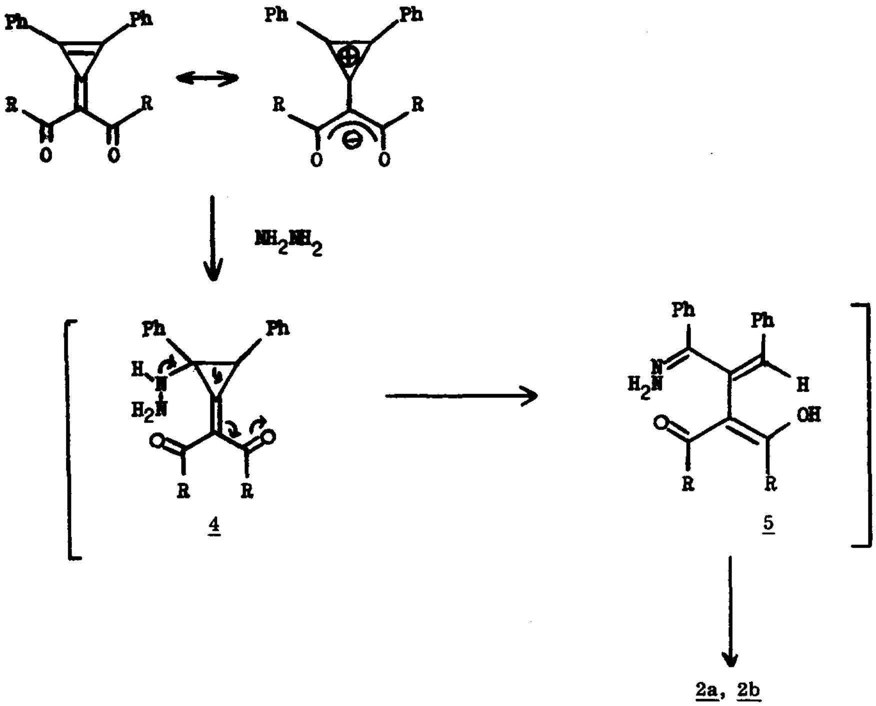
2a, R=Ph
2b, R=Me

The pyridazine structure for 2a and 2b is indicated by spectral data (see Table 1), which are in excellent agreement with reported data for similar systems.[4] Alternate structural possibilities 3a, b are excluded by the finding that such systems are unstable with respect to the corresponding 3,4-diazanorcaradiene, which would have nmr properties widely different from those observed.[5]



3a, R=Ph
3b, R=Me

The pyridazines may result from the series of steps illustrated below. An initial Michael addition to the cyclopropene double bond affords 4. Ring opening with proton transfer yields 5 which can then undergo condensation to the observed products 2a and 2b. Alternatively, 4 may close to the bicyclic intermediate 6, which can undergo a 1-3 proton shift coupled with cyclopropane bond breakage to give 2a and 2b. However, ring opening of 6 might just as likely proceed to a 4H-diazepine, which was not observed. The mechanism of this reaction is presently under consideration.[6]



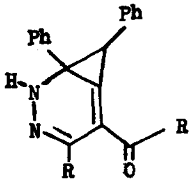


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Table 1

Spectral Properties of 2a, 2b

2a ($C_{30}H_{22}N_2O$)[a]	ir ($CHCl_3$); no NH, OH; 3080(w), 3060(w), 2980(w), 1670(s), 1600(m), 1500(w), 1450(s), 1380(s) cm^{-1} uv(EtOH); λ_{max} 205 (ϵ 49,000), 253 (ϵ 28,500) nm nmr($CDCl_3$); 6.60-7.80 ppm, 20H, m; 4.10 ppm, 2H, s ms, m/e (rel int); 426(55), mol ion; 105(95), 77(100)
2b ($C_{20}H_{18}N_2O$)[b]	ir ($CHCl_3$); no NH, OH; 3080(w), 3060(w), 2940(w), 1705(s), 1500(w), 1455(w), 1390(m) cm^{-1} uv (EtOH); λ_{max} 205 (ϵ 15,800), 235 (sh) (ϵ 5500), 275(sh) (ϵ 1400) nm nmr ($CDCl_3$); 6.72-7.52 ppm, 10H, m; 4.00 ppm, 2H, s; 2.67 ppm, 3H, s; 2.06 ppm, 3H, s ms, m/e (rel int); 302 (11), mol ion; 43(100)

a. determined by analysis

b. determined by high resolution mass spectrum

Acknowledgements: This work was supported by a grant from the Haverford College Faculty Research Fund. The author thanks Dr. Merle Battiste for helpful suggestions. Mass spectra were kindly provided by the laboratory of Dr. K. Biemann, Massachusetts Institute of Technology.

References

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3. For other chemistry of these systems see:
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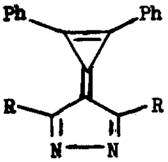
6. The interesting diazacalicene system 7, another potential product of this reaction, was not observed.



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