N-Ethoxycarbonylazonine[1]

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Summary Direct photolysis (2537 Å) of (**2**) and (**3**) provides *N*-ethoxycarbonylazonine.

PHOTOCHEMICAL rearrangements of some $[CH]_{10}$ and C_9H_{10} hydrocarbons[2] at low temperatures reported recently from this laboratory strongly suggest that *N*-ethoxycarbonylazonine (**1**), azacyclonona-2,4,6,8-tetraene, may be produced by irradiation of nitrogen analogues of C_9H_{10} hydrocarbons, such as (**2**), a nitrene adduct of cyclo-octatetraene, and its thermal product (**3**).[3] We report the photochemical synthesis of (**1**) and present a preliminary account of its chemistry.

A 5 mM-solution of (**2**) or (**3**) in pentane was irradiated at −80° with a spiral low-pressure (2537 Å) mercury lamp (1·8 m., 120 mA) [15 min. for (**2**), 25 min. for (**3**)]. Silicic acid chromatography at 0° followed by vacuum distillation at 0°/0·001 mm. Hg provided a pure isomer (calculated *M* for $C_{11}H_{13}NO_2$, 191·0946; found, *m/e* 191·0944) showed absorption maxima† at λ_{max} (MeOH) 265 (log ϵ 3·53), λ_{min} 353 nm, (3·47) λ_{max} ($CHCl_3$) 3·36m, 5·84s, 6·15sh, 6·75w, 6·80w, 7·11s, 7·23s, 7·28sh, 7·46m, 7·63s, 7·96m, 8·55m, 8·93m, 9·73m, and 10·60w μm. N.m.r. spectra of this compound were temperature-dependent and showed the presence of eight olefinic protons in addition to an ethyl

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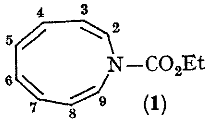
† A general feature of this u.v. spectrum is very similar to that of (*cis*)[4]-cyclononatetraene,[2b] $\lambda_{shoulder}$ (MeOH) 260, 269, and 280 nm. (log ϵ 3·3, 3·2, and 3·0).

group (see below for further discussion). All these spectral data are fully consistent with the assignment of structure (**1**) to this compound.

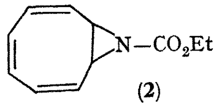
Catalytic hydrogenation of (**1**) with rhodium catalyst under the same condition as that used for [10]annulenes and cyclononatetraenes[2] provided a saturated compound which was found to be identical with *N*-ethoxycarbonylazacyclonone (mass spec., g.l.c., n.m.r., and i.r.). This chemical evidence combined with the above spectral data establishes the structure of (**1**).

Compound (**1**) is not thermally stable and is readily converted (55°, 15 min., $t_{\frac{1}{2}}$ 45 min. at 40°) into its isomer (**4**) which was hydrogenated to provide the corresponding perhydro-compound, which is identical with *N*-ethoxycarbonyl-*cis*-perhydroindole, prepared from *N*-ethoxycarbonylindole. Therefore (**4**) is *N*-ethoxycarbonyl-*cis*-8,9-dihydroindole.

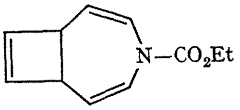
In the 60 MHz. ^{1}H n.m.r. spectra of (**1**), a triplet (−30°) at τ *ca.* 3·4—3·8 (dd, overlap, τ 3·50, 3·60) very likely due to 2-H and 9-H broaden at approximately −5° and are time-averaged (d) at 40°. Similar behaviour is observed for signals at τ *ca.* 4·4—4·9 (3-H and 8-H) and at τ *ca.* 4·0—4·2 (4-, 5-, 6-, 7-H). Presumably the restricted rotation of N–CO_2Et[4] is mainly responsible for the temperature-dependent n.m.r. spectra but conformational changes of the ring cannot be excluded until a precise analysis of these spectra is completed.‡



(**1**)



(**2**)



(**3**)

Comparison of chemical shifts of the ring protons of (**1**) with those of (**3**) and acylpyrroles[4] indicates that *N*-substituted azonines exhibit no significant diamagnetic circulation around the ring system. The similarity of the u.v. spectrum of (**1**) with that of cyclononatetraene and its thermal instability also support the view that (**1**) possesses very little, if any, so-called aromaticity.

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‡ Only a few days before we submitted this manuscript, A. G. Anastassiou and J. H. Gebrian reported a photosensitized rearrangement of (**2**) (*J. Amer. Chem. Soc.*, 1969, **91**, 4011). Therefore, we have summarized our observation without a detailed analysis of spectra and kinetic parameters of the thermolysis.

[1] A. M. Patterson, L. T. Capell, and D. F. Walke, "The Ring Index," 2nd edn., American Chemical Society, 1960, p. 60.

[2] (a) S. Masamune and R. T. Seidner, *Chem. Comm.*, 1969, 542; (b) S. Masamune, P. M. Baker, and K. Hojo, preceding communication; (c) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, 1968, **90**, 5286. Leading references for the chemistry of $[CH]_{10}$ hydrocarbons are quoted therein.

[3] S. Masamune and N. T. Castellucci, *Angew. Chem. Internat. Edn.*, 1964, **3**, 582. The structure of (**3**) was further confirmed by converting it into the corresponding perhydro-compound, which was identical with a sample prepared in an unambiguous manner (S. Masamune and R. T. Seidner, unpublished).

[4] See, *e.g.*, T. Matsuo and H. Shosenji, *Chem. Comm.*, 1969, 501.