Thermal and Photochemical α-Carbon–Carbon Cleavages in Imines

By **Joseph H. Boyer** * and **K. G. Srinivasan,** Department of Chemistry, University of Illinois, Chicago Circle Campus, Chicago, Illinois 60680, U.S.A.

Autoxidation produced cyclohexyl isocyanide and benzoic acid from *N*-cyclohexyl-1,3-diphenylpropan-2-imine (16b), and 6-cyclohexylaminodibenzo[*a,c*]cyclohepten-5-one (24) from *N*-cyclohexyl-5,7-dihydrodibenzo[*a,c*]-cyclohepten-6-imine (17b). The α,α-cleavage required for the formation of the isocyanide was attributed to a ready fragmentation of the intermediate 4-cyclohexylimino-3,5-diphenyl-1,2-dioxolan-3-ol (22).

Photolysis of 3,4-dihydro-3-imino-1,9-di-t-butyl-1,4-ethenonaphthalen-2(1*H*)-ones (14) and of 3-imino-2,2,4,4-tetramethylcyclobutanones (15) resulted in extrusion of isocyanides and carbon monoxide. Other products included 1,3-di-t-butylnaphthalene from (14), tetramethylethylene from (15), an adduct (38) of tetramethylcyclopropanone and furan (solvent) from (15b and c) and 2-isopropylidene-4,4-dimethyl-3-phenylimino-oxetan (39) from (15c). Irradiation at 254 nm transformed the imine (16b) into 1,2-diphenylethane and *N*-cyclohexyl-2-phenylvinylideneamine (43) but had no effect on the *N*-cyclohexylthujan-3-imine (18) in cyclohexane or isopropyl alcohol. The *N*-unsubstituted five- and seven-membered ring α-cyanocycloalkanimines were inert to irradiation at 254 nm.

Reactions in the mass spectrometer correlated with thermal and photolytic extrusion of the C_2O_2 bridge from 1,4-dihydro-1,9-di-t-butyl-1,4-ethenonaphthalene-2,3-dione (9), with photolytic extrusion of the RNC_2O bridge from the corresponding monoimines (14), and with the photolysis of the imine (16b) to give the vinylideneamine (43). An intense $M^+ - CO$ peak was also obtained for the diketone (9). Isocyanides were detected as RNC^+ from the imines (14a—e), (15b), (17b), and (18b).

EXTRUSION of carbon monoxide from a carbonyl compound and an isocyanide from an imine occurs readily when α-cleavage is accelerated by relief of strain in a small ring.[1] α-Cleavage in a carbonyl compound is also facilitated by an attached acyl,[2] ethynyl,[2] or cyano-group;[3] an α-substituent capable of stabilising an adjacent positive charge;[4] a β-cyclopropyl group;[2,5] βγ-unsaturation;[2,5] and a βγ-peroxy-function.[6] Homoconjugation [7a] presumably assisted the photoextrusion of acetonitrile from *N*-(α-methylbenzylidene)benzylamine [7b] and the thermal extrusion of an isocyanide from a 1,4-dihydro-9-phenylimino-1,4-methanonaphthalene.[8]

The photoelimination of an isocyanide from a 3-iminoazetine [9] (1) and from a tetramethylcyclobutane-1,3-di-imine [10] (2), and both the proposed [11] photo-ring-expansion of a 4-imino-Δ²-azetine (3) into an imidazole and the thermal ring expansion [12a] of a 4-alkylimino-Δ²-azetine into an imidazole with expulsion of an olefin corresponding to the alkyl substituent can proceed by an α-cleavage at an imine carbon atom. To explain the photoisomerisation of diaminofumaronitrile (4) into 4-amino-5-cyanoimidazole (8), ring expansion of an undetected 4-imino-Δ²-azetine (5) was invoked;[11] however, the formation of the imidazole (8) can also be accounted for by the release of hydrogen isocyanide (cyanide) from 4-amino-3-imino-2-cyanoazetine (6) [tautomeric with (4) and (5)] followed by recombination of the resulting nitrogen ylide with hydrogen cyanide and cyclisation of the adduct (7). An alternative mode of formation of (7) by photocycloreversion of (6) is closely related to similar photoisomerisations of an azetinone [12b] and an azetidinedione.[12c]

The present work was undertaken to investigate structural assistance for the rarely encountered elimination of an isocyanide by α,α-cleavage of C–C bonds.

Preparation of the Imines.—The imines (14)—(18) were selected for study since the corresponding ketones (9)—(13) were either known to extrude carbon monoxide or found to do so.[13–17] Condensations between these ketones and amines gave the expected monoimines.[17–22]

[1] I. Lengyel and J. C. Sheehan, *Angew. Chem. Internat. Edn.*, 1968, **7**, 25; H. Quast and W. Risler, *ibid.*, 1973, **12**, 414; K. Bott, *Annalen*, 1972, **755**, 58; D. Seyferth and R. Demrauer, *Tetrahedron Letters*, 1966, 189; I. Haller and R. Srinivasan, *Canad. J. Chem.*, 1965, **43**, 3165; B. P. Stark and A. J. Duke ' Extrusion Reactions, Pergamon, Elmsford, New York, 1967.

[2] (*a*) R. C. Fuson, ' Reactions of Organic Compounds, Wiley, New York, 1962, pp. 662—671; (*b*) M. Mousseron-Canet and J.-C. Mani, ' Photochemistry and Molecular Reactions,' trans. J. Schmorak, Israel Program for Scientific Translations, Jerusalem, 1972, pp. 138—167.

[3] J. Kooi and J. H. Boyer, *J.C.S. Perkin I*, 1975, 1743.

[4] F. D. Lewis, C. H. Hoyle, J. G. Magyar, H.-G. Heine, and W. Hartmann, *J. Org. Chem.*, 1975, **40**, 488; F. D. Lewis, R. T. Lauterbach, H.-G. Heine, W. Hartmann, and H. Rudolph, *J. Amer. Chem. Soc.*, 1975, **97**, 1519.

[5] J. E. Starr and R. H. Eastmann, *J. Org. Chem.*, 1966, **31**, 1393.

[6] D. A. Mayers and J. Kagan, *J. Org. Chem.*, 1974, **39**, 3147.

[7] (*a*) R. G. Warren, Y. Chow, and L. N. Ferguson, *Chem. Comm.*, 1971, 1521; (*b*) H. Ohta and K. Tokamuru, *Chem. Letters*, 1974, 1403.

[8] R. S. Atkinson and M. J. P. Harger, *J.C.S. Perkin I*, 1974, 2619.

[9] K. Burger, W. Thenn, and E. Muller, *Angew. Chem. Internat. Edn.*, 1973, **12**, 149.

[10] J. J. Worman and E. A. Schmidt, *Proc. South Dakota Acad. Sci.*, 1973, **52**, 257.

[11] J. P. Ferris, J. E. Kuder, and A. W. Catalano, *Science*, 1969, **166**, 765; J. P. Ferris and J. E. Kuder, *J. Amer. Chem. Soc.*, 1970, **92**, 2527.

[12] (*a*) Louis deVries, *J. Org. Chem.*, 1974, **39**, 1707; (*b*) G. Kretschmer and R. N. Warrener, *Tetrahedron Letters*, 1975, 1335; (*c*) F. Compernolle and F. de Schryver, *J. Amer. Chem. Soc.*, 1975, **97**, 3909.

[13] R. H. Hasek, E. V. Elam, and J. C. Martin, *J. Org. Chem.*, 1961, **26**, 4340.

[14] W. K. Robbins and R. H. Eastman, *J. Amer. Chem. Soc.*, 1970, **92**, 6076, 6077.

[15] K. Mislow and A. J. Gordon, *J. Amer. Chem. Soc.*, 1963, **85**, 3521.

[16] R. H. Eastman, J. E. Starr, R. St. Martin, and M. K. Sakata, *J. Org. Chem.*, 1963, **28**, 2162.

[17] W. Ried and T. S. Eng, *Annalen*, 1969, **727**, 219.

[18] F. D. Popp, *J. Heterocyclic Chem.*, 1974, **11**, 79; H. W. Rothkopf, D. Woehrle, R. Mueller, and G. Kossmehl, *Chem. Ber.*, 1975, **108**, 875; T. Takaji, K. Aida, H. Segawa, and H. Nagai, *Japan. Kokai*, 74 127 921 (*Chem. Abs.*, 1975, **83**, 38,111z). N. V. Lopaeva and L. Yu. Pinegina, *Tr. Perm. Sel.-Khoz. Inst.*. 1971, 3 (*Chem. Abs.*, 1973, **78**, 3886q).

[19] R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *Proc. Chem. Soc.*, 1964, 144.

[20] H. U. Hostetler, *Helv. Chim. Acta*, 1966, **49**, 2417.

[21] R. A. Clark and D. C. Parker, *J. Amer. Chem. Soc.*, 1971, **93**, 7257.

[22] H. Ahlbrecht and S. Fischer, *Tetrahedron*, 1970, **26**, 2837.

Although a quinoxaline was obtained from the diketone (9) and o-phenylenediamine[17] and both monoimines and pyrazines were obtained from the condensation of 1,2-diketones with diaminomaleonitrile,[18] the monoimine

and in the imines (14), but in the similar group at C-1 non-equivalent sets in the ratios of 2 : 1 for (9) and 1 : 1 : 1 for (14) revealed restricted rotation.[23] A buttressing effect of the C-3 substituent is greater in the imine than
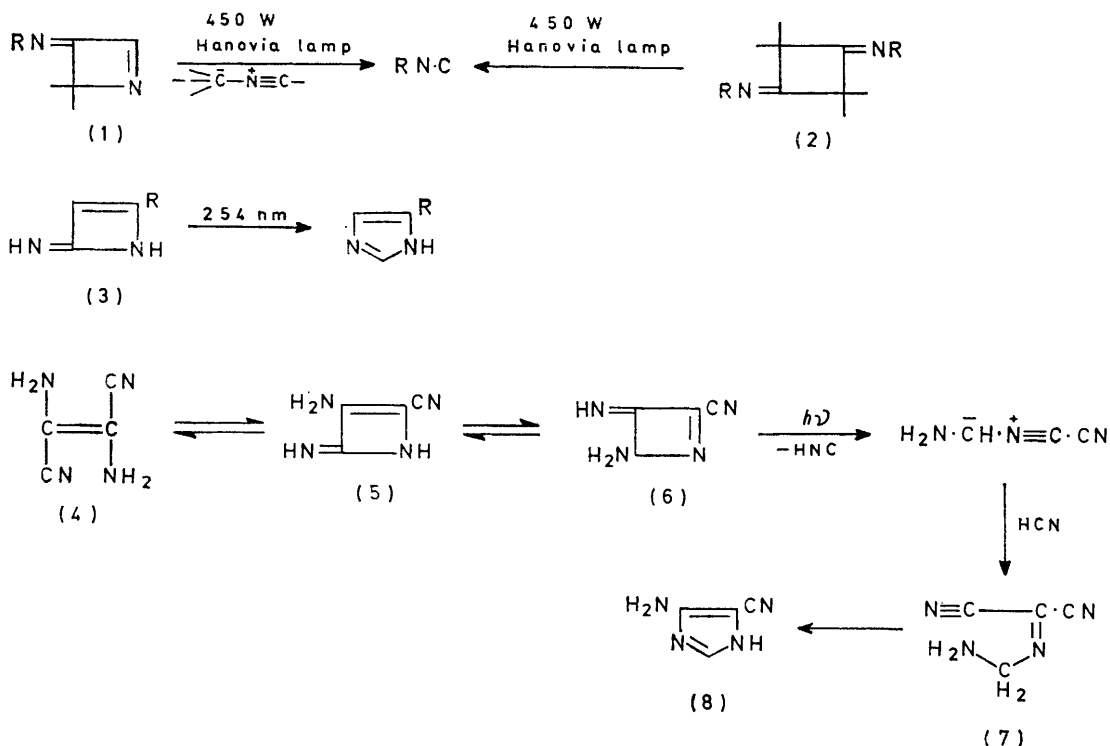
(14e) from diaminomaleonitrile and the diketone (9) could not be transformed into pyrazines. Since steric hindrance from the C-1 t-butyl group can inhibit condensation if the carbonyl group is at C-2 in the

in the ketone, and helps to inhibit condensations at the C-2 carbonyl group.
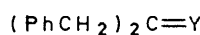
Autoxidation.—The imines (14), (15), (18), and (19) did not react with oxygen at 25 °C but an uncatalysed
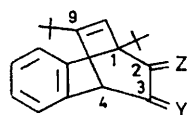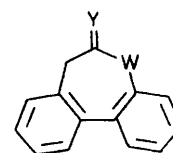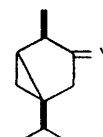

(9)-(13) Y = Z = O, W = CH₂
(14)-(18) Y = NR, Z = O, W = CH₂
(19) Y = NH, W = CH·CN

a; R = Pr^n
b; R = cyclo-C₆H₁₁
c; R = Ph
d; R = p-MeC₆H₄
e; R = H₂N·C(CN):C(CN)
f; R = OH

monoimine (14e), the imino function can be assigned to C-3, thereby correcting its earlier assignment to C-2.[23] A similar location of function in other monoimines (14) was assumed. Magnetically equivalent protons were found in the t-butyl group at C-9 in the diketone (9)

ready autoxidation produced cyclohexyl isocyanide, cyclohexylamine, benzoic acid, and dibenzyl ketone from the imine (16b), and produced 6-cyclohexylamino-dibenzo[a,c]cyclohepten-5-one (24) from the unisolated imine (17b) as it was formed.[24] The formation of

[23] J. H. Boyer and K. G. Srinivasan, *J.C.S. Chem. Comm.*, 1973, 699; 1975, 838.

[24] K. G. Srinivasan and J. H. Boyer, *J.C.S. Chem. Comm.*, 1974, 399.

compound (24) and of other α-oxo-enamines [25] by autoxidation of the corresponding imine supports the intermediacy of an anil (20) of 1,3-diphenylpropane-1,2-dione in the autoxidation of (16b).

A free-radical chain process initiated by transfer of an electron from an enamine tautomer of the Schiff base to cyclohexylamine; and fragmentation of the peroxy-β-lactol form (22) of the hydroperoxide derived from the enamine (21) tautomer of (20) accounted for cyclohexyl isocyanide, benzoic acid, and benzaldehyde, which was autoxidised to benzoic acid. [Benzaldehyde, found as a trace impurity in (11),[27] is slowly formed by autoxidation

SCHEME

an oxygen molecule was proposed [26] to explain the formation of an unsaturated 1,4-diketone by autoxidation of a Schiff base of an αβ-unsaturated ketone. A similar process can account for the autoxidation of the imines (16b) and (17b) and for the inertness of the imines (14) and (15), but not for the inertness of the imines (18), (19), (29) and 2-cyanocyclopentanimine.

of benzyl ketones.[28]] A stream of oxygen through a mixture of cyclohexylamine and dibenzyl ketone also gave cyclohexyl isocyanide and cyclohexylammonium benzoate.

This new formation of an isocyanide by spontaneous α,α-elimination from an intermediate assigned the 4-imino-1,2-dioxolan structure (22) is reminiscent of the

The greater reactivity of (16b) and (17b) can be partially attributed to greater resonance stabilisation of the zwitterionic form of the enamine tautomer. The autoxidation of (16b) to (20) is shown in the Scheme.

Hydrolysis of (16b) accounted for the ketone (11) and

fragmentation of a 1,2-dioxolan-3,4-dione into carbon monoxide, carbon dioxide, and a ketone.[6] Bond cleavage at an imine carbon atom in one and at a carbonyl carbon atom in the other is facilitated by the presence of the βγ-peroxy-function.

[25] E. G. E. Hawkins, *J. Chem. Soc.* (C), 1971, 160.
[26] S. K. Malhotra, J. J. Hostynek, and A. F. Lundin, *J. Amer. Chem. Soc.*, 1968, **90**, 6565.

[27] P. S. Engel, *J. Amer. Chem. Soc.*, 1970, **92**, 6074.
[28] A. G. Pinkus, M. Z. Haq, and J. G. Lindberg, *J. Org. Chem.*, 1970, **35**, 2255.

The aminotropone (24), the preferred tautomer of the α-imino-ketone (23), was stable relative to a non-aromatic zwitterionic form and resisted autoxidation.

Thermolysis and Photolysis.—Thermal elimination [23] of the dicarbonyl bridge in the diketone (9) at 170—180 °C gave 1,3-di-t-butylnaphthalene (26) in 51% yield, but similar treatment of a monoimine derivative (14) led to an intractable mixture. Photochemical conversion [23] gave the naphthalene (26) in 91% yield from (9) and in 47—78% yield from the imines (14) along with an isocyanide (27) in 49—63% yield. Although lack of detection did not preclude the initial formation of ethylenedione (28a) from (9) and its monoimine (28b) from (14), a Norrish type I cleavage at the carbonyl group with simultaneous or subsequent cleavage of two bonds can also account for the products. A preference for initial bond cleavage at a C-2 carbonyl rather than at a C-3 imine carbon atom has indirect support in the photochemical and thermal inertness of the imine (29) and the di-imine (30).[29] Although rotamerisation and recyclisation of a diradical intermediate accounted for the photoisomerisation of the ketone (33) into the keten (34), the corresponding 'ketens' (31) and (32) from (9) and (14) were not detected.

(26)   O=C=C=P   (35)
        (28a) P = O
        (28b) P = NR
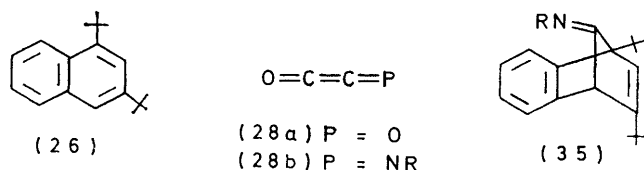
An initial extrusion of carbon monoxide from the imines (14) leaving the imine (35), followed by ready

extrusion was not concerted was indicated by the failure to detect 2,3-dicyano-5-hydroxypyrazine from an expected ring closure of the hypothetical adduct of carbon monoxide and amino(isocyano)maleonitrile (36). Both dissociation of the adduct into carbon monoxide and the isocyanide (36) and stepwise extrusion of these molecules from (14e) are unlikely, since 4,5-dicyanoimidazole, a stable product from the expected ready ring-closure isomerisation of (36), was not detected. Breakdown of the dicyanovinylamine before and/or with extrusion, followed by recombination to give an intractable mixture resembling the black amorphous 'azulmic acid' from polymerisation of hydrogen cyanide is proposed. Ring-closure isomerisation of (14e) can give a 4-imino-Δ²(or Δ¹)-azetine but a 3-imino-Δ¹-azetine isomer of (14e), *cf.* (6), is not available. The inability of (14e) to isomerise into an imino-derivative (37) of 4-amino-5-cyanoimidazole (8) tends to discredit the proposed ring-enlargement isomerization of 3-amino-2-cyano-4-imino-Δ²(or Δ¹)-azetine into (8) in favour of initial extrusion of hydrogen isocyanide from the 3-iminoazetine tautomer followed by recombination and cyclization (see above).

Irradiation of the imines (15a—c) in cyclohexane led to nearly complete recovery of starting material and no product was detected. The imines (15a and b) in furan underwent photoextrusion of isocyanide in 30% yield and gave lesser amounts of the known adduct (38) from furan and tetramethylcyclopropanone. Similar treatment of the monoanil (15c) in anhydrous furan gave phenyl isocyanide (27c), the adduct (38), and 2-iso-propylidene-4,4-dimethyl-3-phenylimino-oxetan (39), isolated as its adduct (40) with water after chromatography on silica gel. When an equimolar mixture of

(14e)

(36)   (14e) ⇌   ... (37)
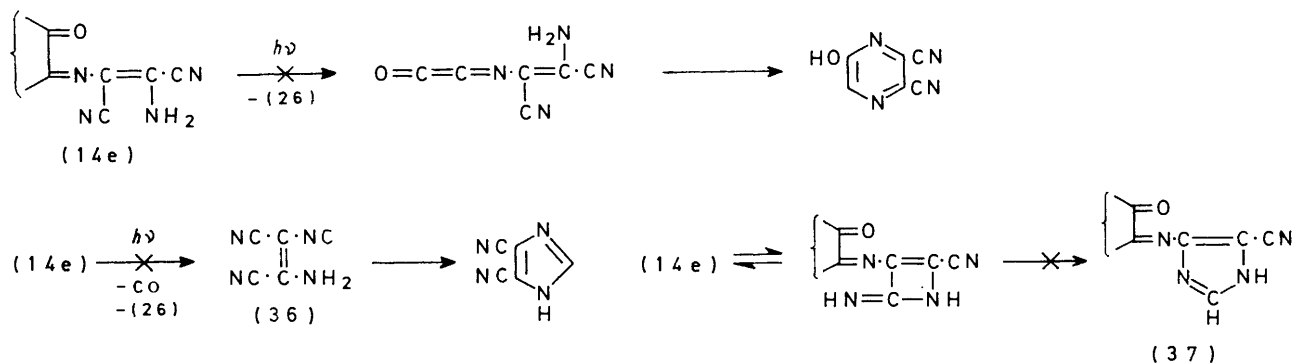
extrusion of an isocyanide, has not been eliminated from consideration; however, since naphthalene and an isocyanide were efficiently produced by thermolysis of similar methanonaphthalenimines at 150 °C,[8] the formation of an intractable mixture from (14) at 170—180 °C reduces the possibility of the intermediacy of (35) during thermolysis of (14).
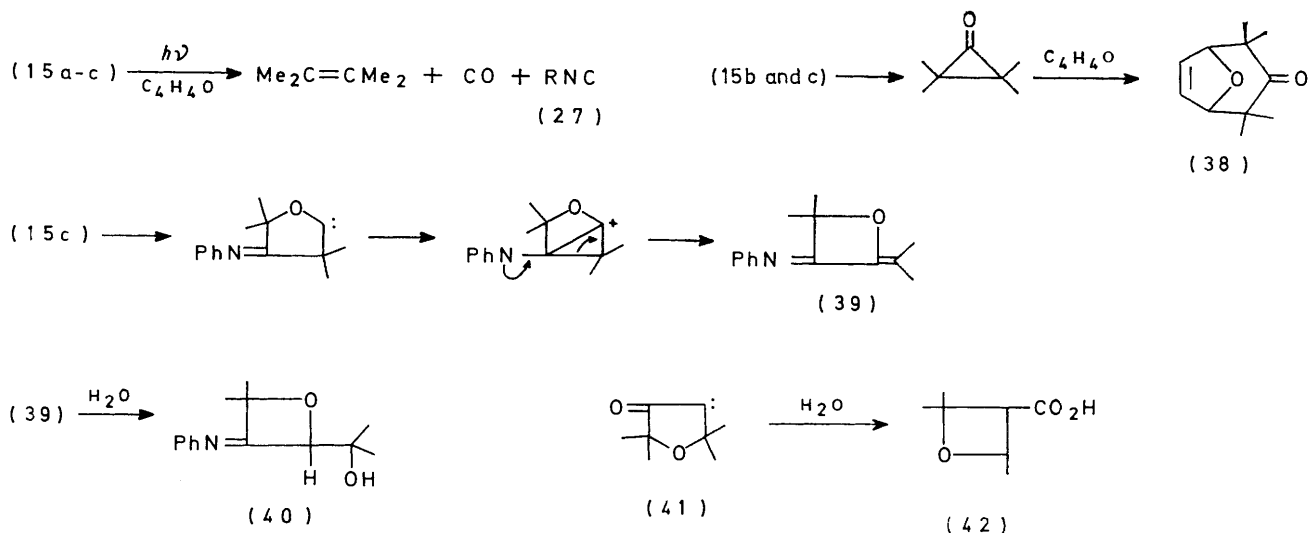
Photoextrusion of the bridge in the imine (14e) gave 1,3-di-t-butylnaphthalene (26) in 63% yield. That the

(15c) and water in furan was irradiated, tetramethyl-cyclobutane-1,3-dione (10) (61% yield) was a major product, which confirmed the formation of (40) after photolysis of (15c). The formation of the oxetan (39) can be explained by ring expansion to an oxacarbene followed by ring contraction assisted by homoconjugation with the β-imino-function, to re-form (15c) or to produce the isomer (39). Photoisomerisation of the diketone (10) into a ketone analogue of the anil (39),[30]

[29] H. Hart, D. L. Dean, and D. N. Buchanan, *J. Amer. Chem. Soc.*, 1973, **95**, 6294; H. Hart and R. W. Pfieffer, *J.C.S. Chem. Comm.*, 1974, 126.

[30] R. C. Cookson, A. G. Edwards, J. Hudec, and M. Kingsland, *Chem. Comm.*, 1965, 98.

and photoexpansion of (15c) [20] and azetidinediones [31] in methanol into five-membered rings are known. The proposed formation of the oxetan (39) by ring-contraction of an α-oxacarbene is related to the similar contraction proposed for other cyclic α-oxacarbenes [32a] and to the formation of an oxetancarboxylic acid (42), explained by contraction of the β-oxacarbene (41).[32b]

An N-cyclohexylimine (18b), obtained from a mixture of α- and β-thujones, was not affected by irradiation (254 nm) in either cyclohexane or in isopropyl alcohol. Similar treatment of an equimolar mixture of thujone and cyclohexylamine brought about decarbonylation [16] and the formation of a small amount of the imine (18b).

Reactions in the Mass Spectrometer.—The assignment

$$(15a-c) \xrightarrow[C_4H_4O]{h\nu} Me_2C=CMe_2 + CO + RNC \quad (27)$$

In contrast with the photoextrusion of carbon monoxide from the ketone (11),[14,27] irradiation of the imine (16b) gave a complex mixture from which 1,2-diphenylethane and N-cyclohexylphenylacetamide (44) were isolated. That cyclohexyl isocyanide was not produced was established by the absence of the characteristic

of an abundant ion at m/e 240 to 1,3-di-t-butylnaphthalene $(M^+ - 2CO)$ correlated with the predominant thermal and photochemical extrusion of the C_2O_2 bridge from the diketone (9). An alternative major fragmentation $(M^+ - CO)$ was shown by the intense peak at m/e 268 (80%). Since other ethenonaphthalenediones
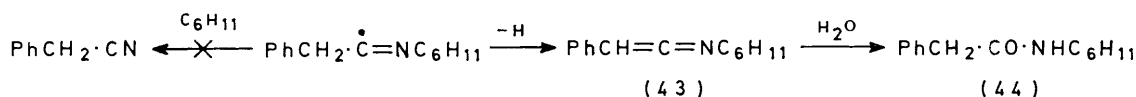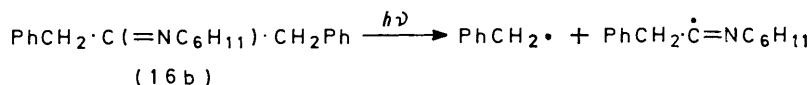
odour (most sensitive test) and confirmed by i.r. spectra and g.l.c. An initial α-cleavage can give benzyl and N-cyclohexylphenylacetimidoyl radicals, in analogy with the photocleavage of the N-(α-methylbenzylidene)benzylamine into benzyl and N-benzylacetimidoyl radicals [7b] (see above). Benzyl dimerisation gave diphenylethane, and loss of a hydrogen atom from the acetimidoyl radical gave N-cyclohexylphenylvinylideneamine (43). Hydration on silica gel produced the amide (44). Although the analogous formation of a keten from a ketone can occur,[33] the photolysis of dibenzyl ketone (11) did not give phenylketen.[14,27]

gave very weak M — CO peaks [34,35] and a methanonaphthalenone was extremely unstable with respect to decarbonylation,[8] an unidentified stabilising rearrangement accompanying monodecarbonylation of (9) was assumed.

The predominant photochemical extrusion of the bridge from the imines (14a—f) corresponded to the process M^+ — RNC — CO, shown by an intense ion at m/e 240. The isocyanide, RNC$^+$, from (14a—e) was responsible for the ions at m/e 69, 109, 103, 117, and 118 respectively but M^+ — RNC was not detected [a possible exception was a very weak peak at m/e 268 from (14a)].

[31] F. Compernolle, J. Schutyser, and F. C. DeSchryver, *Org. Mass Spectrometry*, 1975, **10**, 74.
[32] (a) R. F. C. Brown, F. W. Eastwood, and G. McMullen, *J.C.S. Chem. Comm.*, 1975, 328; (b) I. K. Korobitsyna, L. L. Rodina, and L. M. Stashkova, *Zhur. obshchei Khim.*, 1963, **33**, 3109; *Khim. geterotsikl. Soedinenii*, 1966, **2**, 843.

[33] P. Yates, *Pure Appl. Chem.*, 1964, **16**, 93.
[34] J. Strating, B. Zwannenburg, A. Wagenaar, and A. C. Udding, *Tetrahedron Letters*, 1969, 125.
[35] N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D'Angelo, *J. Amer. Chem. Soc.*, 1965, **87**, 4097.

Since the process $M^+ - CO$ was not general for the imines, the ion m/e 309 from (14a) was assigned to the fragment $M^+ - C_2H_4$ and the ion m/e 358 from (14e) to $M^+ - CH_2N$. The former was accounted for by extrusion of ethylene from a tautomer (45) of (14a) by a process formally related to a Norrish type III [2b] cleavage, and the latter by stepwise extrusion of hydrogen cyanide and a hydrogen atom from (14e).

Cyclohexyl isocyanide was identified as the ion of m/e 109 obtained from (15b), (17b), and (18b) but not from (16b).

(45)

(14e)
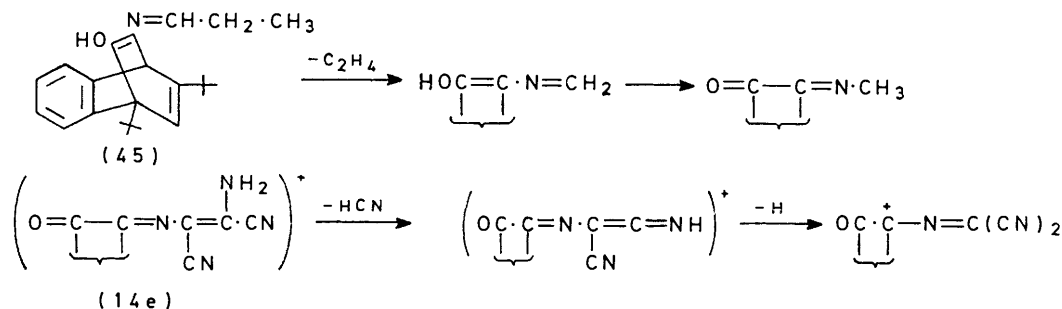
EXPERIMENTAL

Instruments used included a Perkin-Elmer 237B grating i.r. spectrophotometer, Varian A60 and T60 n.m.r. spectrometers, a Cary 14 u.v. spectrophotometer, an A.E.I. MS30 double-beam mass spectrometer, a Varian 1800 gas chromatograph with flame ionization detector, and a Varian 20 recorder with disc integrator. Mass spectra were obtained at 70 eV.

Preparation of Ketones and Imines.—The previously described 1,4-dihydro-1,9-di-t-butyl-1,4-ethenonaphthalene-2,3-dione (9) was obtained as yellow prisms, m.p. 135—136° (lit.,[17] 103°); ν_{max} (CHCl$_3$) 1 740 cm^{-1} (CO); δ(CDCl$_3$) 1.13 (9 H, s, Bu^t), 1.36 (6 H, s, *Me*$_2$CMe), 1.73 (3 H, s, *Me*CMe$_2$), 4.56—4.60 (1 H, d, CH), 6.20—6.22 (1 H, d, C=CH), 7.30—7.40 (3 H, m, C$_6$H$_4$), and 7.75—8.00 (1 H, m, C$_6$H$_4$ *peri*-position); m/e 296 (4%, M^+), 268 (80, M − CO), 240 (80, M − 2CO), 183 (80), and 126 (85) (Found: C, 81.25; H, 8.0. C$_{20}$H$_{24}$O$_2$ requires C, 81.1; H, 8.1%).

5,7-Dihydrodibenzo[a,c]cyclohepten-6-one (12),[36] 9,10-dihydro-9,10-ethanoanthracen-11-one (25),[37] and the known imines (15b and c),[13] (16b),[21] and (19) [38] were prepared according to published directions. Tetramethylcyclobutane-1,3-dione (10), dibenzyl ketone (11), and thujone (13) were commercially available.

Other imines were prepared: (*A*) by heating at reflux an equimolar mixture of the ketone and a primary amine in (*a*) methanol containing (i) a few drops of concentrated hydrochloric acid until the ketone was no longer detected [18] or (ii) a catalytic amount of acetic acid for 1 h [18] or (*b*) benzene or toluene, sometimes with a catalytic amount of toluene-*p*-sulphonic acid; [13] (*B*) by heating at reflux for 40 h an equimolar mixture of the ketone and a primary

amine in anhydrous benzene or xylene, using a Dean–Stark trap packed with molecular sieves (4A) to remove water as formed; [21,29] (*C*) by heating the ketone in dimethyl sulphoxide with 2 equiv. of hydroxylamine hydrochloride in water for 4 h.

The yellow imines (14a—e), the colourless oxime (14f), and the colourless imine (29) were purified by recrystallization; the colourless liquid imines (15) and (18) were purified by distillation. Each gave satisfactory elemental analyses (C, H, and N) and showed i.r., n.m.r., and u.v. absorption in support of the assigned structures. Preparation details are given in Table 1; elemental analyses, u.v.,

n.m.r., i.r., and mass spectral data (Tables 2 and 3) are available in Supplementary Publication No. SUP 21767 (7 pp.).†

N-*Cyclohexyl*-1,3-*diphenylpropane*-2-*imine* (16b), prepared by method *B* in 87% yield, was distilled free of the ketone (as determined by absence of i.r. absorption at 1 715 cm^{-1}) at 242—243 °C and 0.1 mmHg [lit.,[21] b.p. >230° at 0.9 mmHg for a mixture of the imine (92%) and the ketone (8%)] (Found: C, 86.3; H, 8.25; N, 4.45. C$_{21}$H$_{25}$N requires C, 86.55; H, 8.65; N, 4.8%); m/e (20 eV) 291 (M^+, 33), 265 (4), 209 (18), 200 (22), 199 (100), 118 (100), 91 (88), 83 (77), and 54 (33).

Attempts to prepare the N-cyclohexylimine (17b) by method *Ab* in refluxing toluene led to recovery of the ketone (12) and no indication of reaction. When method *Aai* was followed, t.l.c. showed the disappearance of the ketone (12) after refluxing for 3 h. A colourless solid obtained in 60% yield, m.p. 118—119° (from hexane) was identified as 6-*cyclohexylaminodibenzo*[a,c]*cyclohepten*-5-*one* (24); ν_{max}(CH$_2$Cl$_2$) 1 626 cm^{-1} (C=O); δ(CDCl$_3$) 1.20—2.03 (10 H, m) and 3.2 (1 H, m) (C$_6$H$_{11}$), 5.13 [1 H, s, OH (enol) or NH (enamine)], 6.23 (1 H, s, C=CH), and 7.30—8.00 (8 H, m, C$_6$H$_4$) (Found: C, 83.35; H, 6.95; N, 4.5. C$_{21}$H$_{21}$NO requires C, 83.15; H, 7.0; N, 4.65%); m/e 303 (M^+, 85), 260 (50), 206 (75), 178 (40), 165 (95), 103 (100), and 102 (100). Heating the tropone (24) with an excess of hydroxylamine hydrochloride and a drop of pyridine in refluxing ethanol for 2 h gave the dioxime of dibenzo[a,c]-cycloheptene-5,6(7H)-dione as a colourless solid, m.p. 218—219° (from methylene chloride–hexane); yield 70% (Found: C, 71.2; H, 4.95; N, 11.1. Calc. for C$_{15}$H$_{12}$N$_2$O$_2$: C, 71.4; H, 4.8; N, 11.1%). Three of the four geometrical isomers of the dioxime have been previously reported, with m.p. 158—160°,[39] 186—187°,[40] and 212—215°.[41]

† For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1975, Index Issue.

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Autoxidation.—A stream of oxygen passing through a neat sample of the imine (16b) for 48 h gave a precipitate of cyclohexylammonium benzoate (38%), m.p. 172.5—173° (Found: C, 70.55; H, 8.75; N, 6.25. Calc. for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.35%), identical with a sample prepared from cyclohexylamine and benzoic acid. At 200 °C the salt gave *N*-cyclohexylbenzamide, m.p. 148—149°.[42] Hexane eluted cyclohexyl isocyanide (8% yield) from the liquid portion of the reaction mixture on a silica gel column. Further elution with hexane–benzene gave the ketone (11) (19%) and intractable mixtures. A separate experiment verified the occurrence of hydrolysis

32; (15c), 2.15 in 500, 40, (27c), 25. The adduct (38), isolated by eluting an alumina column with hexane was identical (i.r. spectra) with an authentic sample and was isolated in 5.2% yield from the anil (15c) and in trace amounts from the imine (15b). Hexane–benzene (9 : 1) next eluted 1-(4,4-*dimethyl-3-phenylimino-oxetan-2-yl*)-1-*methylethanol* (160 mg, 13%), m.p. 92—93°; $\nu_{max.}$(CHCl$_3$) 3 356 (OH) and 1 681 cm^{-1} (C=N); δ(CDCl$_3$) 0.83, 1.00, 1.08, and 1.40 (12 H, 4s, 4 CH$_3$), 2.30 (1 H, s, OH), 3.00—3.30 (1 H, m, CH·OR), and 7.00—7.50 (5 H, m, Ph) (Found: C, 71.7; H, 8.3; N, 5.9. $C_{14}H_{19}NO_2$ requires C, 72.1; H, 8.2; N, 6.00%).

TABLE 1

Preparation of the imines (14a—e), (15), (18), and (29) and the oxime (14f)

	(14a)	(14b)	(14c)	(14d)	(14e)	(14f)	(15a)	(18b)	(29)
Method	*A ai*	*A ai*	*A ai*	*B*	*A aii*	*C*	*A b*	*B*	*A ai*
Time (h)	0.25	2	3	0.66	1	4	10	42	6
Yield (%)	67	50	51	69	49	60	50	73	40
M.p. (°C)	152—153	155—156	85—86	120—121	180 (decomp.)	202—203	*a*	*b*	185—186

a B.p. 84—86 °C at 5.2 mmHg.   *b* B.p. 95—97 °C at 0.5 mmHg.

of the imine (16b) to the ketone (11) on a silica gel column. The same results were obtained when a mixture of cyclohexylamine and dibenzyl ketone was similarly treated with oxygen; however, there was no noticeable reaction when the ketone by itself was treated with oxygen.

Photolysis.—Cyclohexane and furan, used as solvents, were distilled from lithium aluminum hydride. Solutions of the imines were degassed with a stream of nitrogen for 2—4 h prior to being irradiated at 254 nm in a Rayonet RPR 100 photochemical chamber reactor equipped with 16 low-pressure mercury lamps until the monoimine was no longer detected by t.l.c. Concentration left a residue which was chromatographed on a column of silica gel or alumina and eluted with hexane–benzene.

For the imines (14a—e) in cyclohexane (1 g in 500 ml) the results [compound, hours of irradiation, isocyanide, yield (%)] were: (14a), 2, (27a), 57; (14b), 10, (27b), 53; (14c), 13, (27c), 53; (14d), 30, (27d), 49; (14e), 3, —, —. In corresponding yields of 71, 78, 66, 62, and 63%, di-t-butylnaphthalene (26)[43] was isolated by eluting the silica gel column with hexane; in a similar way it was isolated in 47% yield following irradiation of the monoxime (14f). The yield of *p*-tolyl isocyanide is based on its isolation as *p*-tolylformamide, m.p. 53°, after hydration of the isocyanide on the silica gel column.

Comparable irradiations of the imines (15a—c), each in cyclohexane, gave traces of isocyanides detected by i.r. spectroscopy after 8—10 h.

For the imines (15a—c) the results [compound, g in ml of furan, hours of irradiation, isocyanide, yield (%)] were: (15a), 2.0 in 500, 60, (27a), 31; (15b), 1.1 in 500, 24, (27b),

A solution of the imine (16b) (1.46 g, 5 mmol) in freshly distilled furan (300 ml) was purged with a stream of nitrogen for 2 h and irradiated at 254 nm for 72 h. After concentration the residue was placed on a silica gel column. Hexane (400 ml) eluted 1,2-diphenylethane (221 mg, 23%), m.p. 50—51°; δ(CDCl$_3$) 2.85 (4 H, s, CH$_2$) and 7.10 (10 H, s, Ph). More hexane (600 ml) eluted an intractable yellow oil (93 mg). Hexane–benzene (9 : 1; 600 ml) eluted dibenzyl ketone (11) (620 mg, 60%). [An independent experiment confirmed that the imine (16b) was nearly quantitatively hydrolysed to the ketone (11) on a silica gel column.] Hexane–benzene (4 : 1; 600 ml) then eluted an intractable fraction (76 mg), and a 3 : 1 mixture (600 ml) eluted N-*cyclohexylphenylacetamide* (44) (11%), m.p. 144—145°; $\nu_{max.}$(CHCl$_3$) 1 661 cm^{-1} (CO) (Found: C, 77.0; H, 8.55; N, 6.55. $C_{14}H_{19}NO$ requires C, 77.40; H, 8.80; N, 6.45%).

α-Cyano-cycloheptanimine and -cyclopentanimine were not affected by irradiation (254 nm) for 4 days in furan or methylene chloride. The *N*-cyclohexylthujan-3-imine (18b) in cyclohexane, benzene, or isopropyl alcohol was not affected by irradiation (254 nm) for 120 h. When an equimolar solution of thujone and cyclohexylamine in cyclohexane was irradiated (254 nm) for 2 h, carbon monoxide was extruded from the ketone, as shown by the absence of carbonyl absorption at 1 709 cm^{-1}.

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