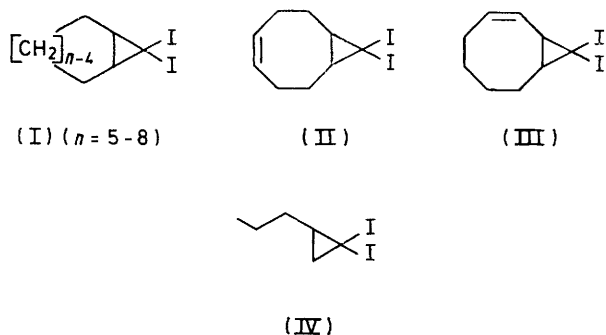


Iodocyclopropanes. Part I. Di-iodocarbene Adducts of Some Cyclic Olefins

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Di-iodocarbene adducts of cycloalkenes undergo thermal reaction more readily than the corresponding dibromides, but their stability increases with the ring size of the alkene from cyclopentene to cyclo-octene, and they may be isolated readily and in several cases distilled unchanged.

THERE are numerous reports concerning the addition of dibromocarbene to olefins, but the corresponding reactions of di-iodocarbene have received little attention. It was reported that this carbene, generated by the reaction of iodoform with potassium *t*-butoxide, gave adducts with some simple acyclic olefins which were too unstable to be isolated at ambient temperature, but which could be reduced to more stable monoiodides.¹ A more recent paper has suggested that some monocyclic adducts are far more stable than earlier thought, often surviving distillation, but decomposing at temperatures up to 130 °C.² It was however stated² that 7,7-diiodobicyclo[4.1.0]heptane (I; $n = 6$) was unstable even in solution.³



We now report the preparation of di-iodocarbene adducts of a number of cyclic olefins [(I; $n = 5-8$), (II), and (III)], and of the monocyclic adduct (IV). All

¹ J. P. Oliver and U. V. Rao, *J. Org. Chem.*, 1966, **31**, 2696.

² R. Mathias and P. Weyerstahl, *Angew. Chem. Internat. Edn.*, 1974, **13**, 132.

³ See also W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 1954, **76**, 6162.

these compounds, including (I; $n = 6$), were readily isolated and in several cases were distilled unchanged. We have already reported the use of the adducts (I; $n = 7$) and (II) in the preparation of 1-substituted *trans*-cycloalkenes,⁴ where the corresponding dibromides were not suitable; other di-iodocarbene adducts discussed here may also prove synthetically useful.

The adducts were prepared by addition of potassium *t*-butoxide in *t*-butyl alcohol to a stirred suspension of iodoform in the olefin and light petroleum at -10 to -20 °C. The system was allowed to warm to ambient temperature, and a slightly exothermic reaction then occurred, the temperature reaching 35–40 °C. The progress of the reaction was easily followed by observing the disappearance of the solid iodoform. The products were pale orange to dark brown oils; those that could be distilled afforded pale red liquids, which soon became very dark brown. Apart from the adducts (I; $n = 5$) and (II) (see below) they were all kept at 0 °C for long periods without change in n.m.r. spectrum.

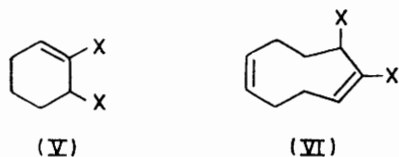
For dibromo- and dichloro-carbene adducts of cycloalkenes, the thermal stability increases with the ring size of the cycloalkene.⁵ In addition, the dichlorides are more stable than the corresponding dibromides.⁵ We now find that the di-iodides show the same effect of ring size and, as expected, react more readily than the dibromides. Thus whereas 6,6-dichloro- and 6,6-dibromo-bicyclo[3.1.0]hexane rearrange to the corresponding 2,3-dihalogenocyclohexenes (V; X = Cl or Br) in 90 min at 170 °C and 60 min at 120°, respectively, the di-iodide (I; $n = 5$) rearranges to 2,3-diiodocyclohexene (V;

⁴ M. S. Baird, *J.C.S. Chem. Comm.*, 1974, 196.

⁵ M. S. Baird, D. G. Lindsay, and C. B. Reese, *J. Chem. Soc. (C)*, 1969, 1173; M. S. Baird and C. B. Reese, *ibid.*, p. 1803.

X = I) either during 5 days at 0 °C or on refluxing for 1 h in acetone (b.p. 56°).

7,7-Di-iodobicyclo[4.1.0]heptane (I; $n = 6$), contrary to the earlier report,² is stable for long periods at 0 °C, can be distilled unchanged at 110–112° and 0.5 mmHg, and is unaffected by heating for 1 h at 95–100 °C alone or by refluxing for 1 h in diethyl ketone (b.p. 101°). At higher temperatures a vigorous exothermic decomposition does occur, giving no identified product; however, in the presence of quinoline, the adduct (I; $n = 6$)



is converted into a mixture of 1- and 2-iodocyclohepta-1,3-dienes in 60 min at 155 °C. The iodides were identified by comparison of their spectra with those of the corresponding bromides obtained analogously from 7,7-dibromobicyclo[4.1.0]heptane.⁶

The adducts (I; $n = 7$) and (I; $n = 8$) were correspondingly more stable. On heating in quinoline they reacted completely in 60 min at 145–155 °C and 100 min at 160–170 °C, respectively. The only volatile product in each case was a diene (cyclo-octa-1,3-diene and cyclonona-1,3-diene, respectively); the origin of these two compounds is not clear. The adduct (II), however, rearranged to the diene (VI; X = I) in 21 days at ambient temperature in the dark. The product was identified by comparison of its spectra with those of the corresponding dibromide (VI; X = Br), which had earlier been obtained under relatively mild conditions, by heating 9,9-dibromobicyclo[6.1.0]non-4-ene in quinoline for 30 min at 150–155 °C.⁷ The adduct (II) also rearranged to (VI; X = I) during several months at 0 °C or on refluxing for 1 h in diethyl ketone. The isomeric iodide (III) reacted completely on heating for 80 min at 155 °C in quinoline, but no identified product was obtained; on heating alone at 100 °C compound (III) apparently decomposed without giving any identified product. The corresponding dibromide is known to rearrange thermally to 9,9-dibromobicyclo[3.3.1]non-2-ene.⁸

The monocyclic derivative (IV) was also relatively stable to heat, but at higher temperatures it decomposed to an intractable residue and in the presence of quinoline also gave no identified product.

EXPERIMENTAL

I.r. spectra were recorded for liquid films or KBr discs; n.m.r. spectra were obtained for solutions in CCl₄ with tetramethylsilane as internal standard.

Preparation of Di-iodocarbene Adducts.—The carbene additions were carried out by stirring the olefin (0.15–0.25 mol) with light petroleum (b.p. 30–40°; 100 ml) and iodo-

⁶ D. G. Lindsay and C. B. Reese, *Tetrahedron*, 1965, **21**, 1673.

⁷ M. S. Baird and C. B. Reese, *J. Chem. Soc. (C)*, 1969, 1808; C. B. Reese and A. Shaw, *Chem. Comm.*, 1970, 1365.

form (25 g), which was only partially soluble, at –10 to –20 °C. Potassium *t*-butoxide [130 ml; from potassium (22 g) in *t*-butyl alcohol (700 ml)] was added over *ca.* 5 min. The solution generally became cloudy and pale brown. On allowing the reactants to reach ambient temperature a slightly exothermic reaction occurred, increasing the temperature to *ca.* 35°, and, over about 0.5–1 h, the solid iodoform disappeared. The products were stirred for 16 h and the solution was then washed with water (5 × 100 ml) and dried (MgSO₄); the solvent and starting material were removed at 14 mmHg and then 1 mmHg. The remaining oily di-iodides showed n.m.r. spectra almost identical with those of the corresponding dibromides. When the di-iodides were distilled, pale red oils were generally obtained; their n.m.r. spectra were identical with those of undistilled materials, and they became very dark in colour over several hours.

6,6-Di-iodobicyclo[3.1.0]hexane (I; $n = 5$), undistilled yield 50% (Found: M , 333.8721. C₆H₈I₂ requires M , 333.8719), showed τ 7.5–8.4 (complex, with maxima at 7.9 and 8.5); ν_{\max} 730s, 990s, 1 115s, and 1 165s cm⁻¹.

7,7-Di-iodobicyclo[4.1.0]heptane (I; $n = 6$), b.p. 110–112° at 0.5 mmHg, yield 34% (Found: M , 347.8868. C₇H₁₀I₂ requires M , 347.8876), showed τ 7.4–9.0 (complex); ν_{\max} 690s, 1 020s, and 1 450s cm⁻¹.

8,8-Di-iodobicyclo[5.1.0]octane (I; $n = 7$), b.p. 108–110° at 0.8 mmHg, yield 40% (58% undistilled) (Found: C, 26.55; H, 3.05%; M , 361.9031. C₈H₁₂I₂ requires C, 26.55; H 3.3%; M , 361.9032), showed τ 7.4–9.4 (complex); ν_{\max} 690s, 960s, 1 120s, 1 470s, and 2 950s cm⁻¹.

9,9-Di-iodobicyclo[6.1.0]nonane (I; $n = 8$), undistilled yield 65%, b.p. 144–146° at 1.0 mmHg (some charring) (Found: C, 28.65; H 3.5%; M , 375.9202. C₉H₁₄I₂ requires C 28.7; H 3.7%; M , 375.9189), showed τ 7.6–9.0 (complex with maximum at 8.5); ν_{\max} 680s, 1 055s, 1 455s, 1 475s, and 2 950s cm⁻¹.

9,9-Di-iodobicyclo[6.1.0]non-4-ene (II), undistilled yield 63% (Found: M , 373.9044. C₉H₁₂I₂ requires M , 373.9032), showed τ 4.58 (2 H, t, J 4 Hz), 7.4–8.2 (8 H, complex), and 8.6 (2 H, complex); ν_{\max} 670s, 740s, 1 085s, 1 440s, 1 490s, 1 655m, 2 950s, and 3 020s cm⁻¹. Attempted distillation of this compound at 1 mmHg caused a very vigorous exothermic reaction with evolution of iodine and formation of a thick gum.

9,9-Di-iodobicyclo[6.1.0]non-2-ene (III), b.p. 136–138° at 1 mmHg (Found: M , 373.9067. C₉H₁₂I₂ requires M , 373.9032), showed τ 4.1 (1 H, d, J 11 Hz, further split), 4.95 (d, J 11 Hz), and 7.5–9.2 (10 H, complex); ν_{\max} 655s, 675m, 715m, 760m, 1 040m, 1 080m, 1 460s, and 2 950s cm⁻¹.

1,1-Di-iodo-2-propylcyclopropane (IV), b.p. 72–76° at 1.5 mmHg, yield 25% (Found: M , 335.8827. C₆H₁₀I₂ requires M , 335.8876), showed τ 8.0–9.2 (complex); ν_{\max} 1 470s, 1 440s, 1 100s, 1 040s, and 995 s cm⁻¹.

Thermal Reaction of Adducts.—The adducts were heated alone, in a solvent, or in the presence of an equal weight of quinoline. Apart from (I; $n = 5$) and (II), none gave an identified product when heated alone, and decomposition occurred at temperatures below those used for their *vacuum* distillation; presumably the vacuum allows removal of HI and I₂, which may promote the exothermic decomposition.

2,3-Di-iodocyclohexene (V; X = I). (a) 6,6-Di-iodobicyclo[3.1.0]hexane (I; $n = 5$) (2 g) was refluxed for 1 h

⁸ M. S. Baird, D. G. Lindsay, and C. B. Reese, *Chem. Comm.*, 1968, 784.

in acetone (15 ml). Charcoal (1 g) was added and the products were refluxed for 5 min; the mixture was filtered and the solvent removed at 14 mmHg and 25 °C. The residue was dissolved in light petroleum (b.p. 30–40°; 5 ml); the solution was filtered through CC-7 silica (5 g) and the column was eluted with more petroleum (50 ml). The eluate was evaporated to leave as a brown free-running oil, 2,3-di-iodocyclohexene (1.46 g, 73%), b.p. 104–106° at 1 mmHg (Found: M , 333.8688. $C_6H_8I_2$ requires M , 333.8719); τ 3.7 (1 H, t, J 4 Hz), 5.0br (1 H, t, J ca. 2 Hz), and 7.5–8.3 (6 H, complex); ν_{max} 730s, 810m, 895s, 940m, 995s, and 1 620m cm^{-1} .

(b) 6,6-Di-iodobicyclo[3.1.0]hexane was kept for 5 days at 0 °C; an n.m.r. spectrum then showed complete rearrangement to 2,3-di-iodocyclohexene.

1,9-Di-iodo-cis,cis-cyclonona-1,5-diene (VI; X = I). (a) 9,9-Di-iodobicyclo[6.1.0]non-4-ene (II) (2.0 g) was refluxed for 1 h in diethyl ketone (10 ml). The mixture was refluxed with charcoal (1 g) for 5 min, filtered, and evaporated. The product crystallised slowly, and was recrystallised from acetone at low temperature; yield 1.4 g (70%), m.p. 58–59° (Found: M , 373.9011. $C_9H_{12}I_2$ requires M , 373.9032); τ 3.5 (1 H, complex), 4.0–4.8 (2 H, complex), 5.2 (1 H, dd, J 3 and 10 Hz, with first and third lines smaller than second and fourth), and 7.3–8.4 (8 H, complex); ν_{max} 735s, 795m, 825m, 857m, and 873s cm^{-1} .

(b) 9,9-Di-iodobicyclo[6.1.0]non-4-ene was kept in the dark at ambient temperature for 21 days. The n.m.r. spectrum then showed complete disappearance of the starting material, and clean signals due to (VI; X = I). If the adduct (II) was left for ca. 1 year at 0 °C the same result was observed.

Thermolysis of 7,7-di-iodobicyclo[4.1.0]heptane (I; n = 6). (a) *In the presence of quinoline.* 7,7-Di-iodobicyclo[4.1.0]heptane (3.0 g) was heated with quinoline (6 g) at 115–125 °C. After 4 h, the n.m.r. spectrum showed almost complete disappearance of the starting material; the products were warmed to 155 °C for 1 h, poured into 2N-sulphuric acid (100 ml), and extracted with ether (100 ml). The extract was washed with 2N-acid (100 ml) and water (100 ml), dried ($MgSO_4$), and evaporated at 14 mmHg. The n.m.r. spectrum of the crude product showed no changes in the olefinic or higher field regions from those before work-up. The product (0.8 g, 41%) gave one peak on g.l.c. (M^+ 220), which was collected and shown to contain the isomeric 1- and 2-iodocyclohepta-1,3-dienes by comparison with literature data (n.m.r. and i.r.) for the analogous bromides.⁵

(b) *Heating alone.* The di-iodide was heated alone for 10 min at 95–100 °C. The n.m.r. spectrum was identical with that of the starting material. However, on heating for 4 min at 110–115 °C, copious evolution of iodine occurred and only an intractable residue remained.

(c) *Heating in diethyl ketone.* The di-iodide (200 mg) was refluxed for 1 h in diethyl ketone (2 ml). The solvent was

removed and the residue showed an n.m.r. spectrum identical with that of the starting material.

Thermolysis of 8,8-di-iodobicyclo[5.1.0]octane (I; n = 7). (a) *In the presence of quinoline.* The di-iodide (1.9 g) in quinoline (1.9 g) was stirred for 1 h at 145–155 °C. Considerable charring occurred, but the n.m.r. spectrum showed complete disappearance of the starting material and the formation of apparently one product. Flash distillation of the cooled mixture at 1 mmHg gave cyclo-octa-1,3-diene (217 mg, 33%), identical (n.m.r. and i.r.) with an authentic sample. Comparison of the n.m.r. spectrum of the diene with that of the crude mixture showed the diene to be the only major product.

(b) *Heating alone.* The di-iodide was heated for 30 min at 110 °C. Some iodine was evolved and the product was a thick oil, but the n.m.r. spectrum was identical with that of the starting material.

Thermal rearrangement of 9,9-di-iodobicyclo[6.1.0]nonane (I; n = 8). (a) *In the presence of quinoline.* 9,9-Di-iodobicyclo[6.1.0]nonane (3 g) was heated with quinoline (5 g) at 160–170 °C for 100 min. The products were poured into 6N- H_2SO_4 (100 ml) and extracted with ether (50 ml); a black solid formed which was removed by centrifugation. The aqueous layer was washed with ether (50 ml), and the combined organic layers were washed with water (2 × 100 ml), dried ($MgSO_4$), and evaporated at 14 mmHg and 20 °C to give a red oil. G.l.c. showed this to contain a single major volatile product, which was obtained by flash distillation at 20 °C and 1 mmHg and shown (n.m.r., i.r., and mass spectra) to be cyclonona-1,3-diene (350 mg, 36%).

(b) *Heating alone.* No change was observed in the n.m.r. spectrum when the di-iodide was heated alone at 105–110 °C for 75 min. However after 5 min at 130–140 °C complete decomposition had occurred to give a thick tar, together with iodine fumes.

9,9-Di-iodobicyclo[6.1.0]non-2-ene (III). (a) *In the presence of quinoline.* The di-iodide (350 mg) was heated at 155 °C with quinoline (400 mg). After 10 min, the n.m.r. spectrum of a portion showed the presence of starting material. After 80 min, however, the starting material had completely reacted; there were no olefinic signals but only a broad complex signal, τ 7.0–9.5.

(b) *Heating alone.* On heating alone at 100 °C the di-iodide became extremely dark and a considerable amount of intractable material was formed. However the n.m.r. spectrum after 10 min showed no new olefinic signals.

1,1-Di-iodo-2-propylcyclopropane (III). The di-iodide was unchanged on heating at 90–95 °C for 35 min but on heating for 35 min at 110–115 °C in the presence of an equal weight of quinoline, complete reaction occurred to produce a thick tar containing only a trace of CCl_4 -soluble material.

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