JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 1, 281–285 (1988)

EXTRUSIONS OF DIBROMOCARBENE UNDER NEUTRAL CONDITIONS

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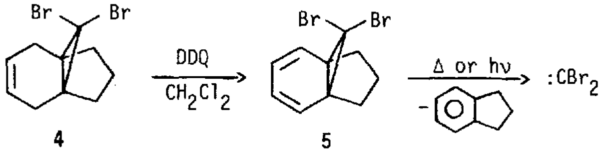
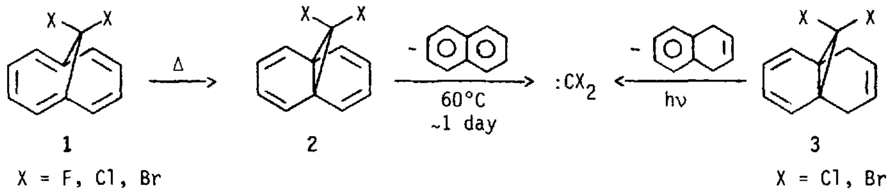
ABSTRACT

The thermal and photochemical decompositions of **5** have been studied. Both reactions lead to CBr_2 transfer in good to high yields. With the 2-pentenes as substrates, CBr_2 transfer is stereospecific in the classical singlet carbene manner.



The generation of free dibromocarbene (CBr_2) under neutral conditions is a long-standing problem. The Seyferth method is flawed, in that organometallic complexes may complicate the observed chemistry.[2] The diazo route is essentially precluded due to instability, [3] and the diazirine is unavailable. Vogel reported[4] the mild thermal extrusion of CX_2 from **1**, but for $X = Cl$ or Br the preparative yields of **1** were too low to be generally useful. Recently, Jones, Jr. and Moss[5] described the photochemical extrusion of CX_2 from **3**, itself prepared from a mono-dehydrogenation of the corresponding 11,11-dihalo[4.4.1]-propella-3,8-diene. The selectivity of the CBr_2 generated from **3** is somewhat different from that of CBr_2 from KOtBu/18-C-6; the source and significance of this difference is currently unknown.



In the course of our studies of bridgehead alkenes,[6] we had occasion to synthesize **5** from **4**.[7] Unlike the synthesis of **3**, the **4** to **5** conversion offers no opportunity for over-oxidation. With no original mind to the extrusion of CBr_2, we were intrigued to observe the formation of indan when **5** was heated at 100°C in HOAc/NaOAc. We thus turned our attention to the question of

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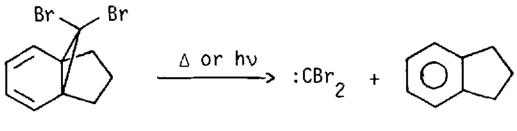
0894–3230/88/050281–05$05.00

Received 30 November 1987
Revised 8 March 1988

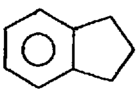
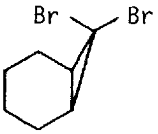


5

thermal CBr_2 extrusion under neutral conditions. (Note that in footnote 10 of reference 4 it is reported that the dichloro analog of **5** transfers CCl_2 to alkenes at temperatures above 150°C.)

When **5** was heated in cyclohexene solution, indan and 7,7-dibromonorcarane[8] were formed in amounts which were temperature and time dependent (see Table 1). In order to probe the question of stereospecificity, we repeated the thermolysis at 147°C, this time with the 2-pentenes as the recipient alkenes. The products and yields are given in Table 3. Dibromocyclopropanes **6** and **7** were independently synthesized via the standard $CHBr_3$/KOtBu procedure. The thermal CBr_2 transfer reported herein was stereospecific.

Table 1. Yields of thermal CBr_2 transfer to cyclohexene

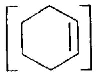
		% Yields		
Temperature (°C)	Reaction time (h)			Recovered **5**
120	6	9	10	>90
120	19	18	20	74
135	6	23	27	70
135	12	47	50	53
147	6	56	53	21
147	12	64	56	9

(It is worthwhile to note that thermolysis of **5** in 10 equiv. *trans*-stilbene (147°C, 12 h) led to a 42% yield of indan, but no dibromocyclopropane adduct. We have otherwise noticed the reluctance with which *trans*-stilbene accepts CBr_2 under normal (e.g. $CHBr_3$/base) conditions. However, the thermolysis of **5** is apparently subject to solvent effects. Thus heating **5** with 10 equiv. *trans*-stilbene in cyclohexane as solvent (147°C, 10 h) led to a 74% yield of indan (again without any CBr_2 plus stilbene adduct).)

As mentioned above, **5** gave indan without formation of a CBr_2 adduct, which led us to think that the CBr_2 extrusion was unimolecular. A more quantitative test of this hypothesis was realized by following the loss of **5** under pseudo-first order conditions in cyclohexene or cyclohexene/cyclohexane solution. The derived pseudo-first order rate constants (Table 2) are unchanged over an eight-fold change in [cyclohexene]. This clearly illustrates the unimolecular nature of the thermal CBr_2 extrusion from **5**.

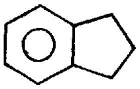
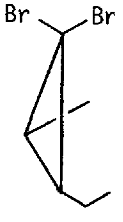
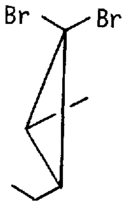
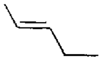
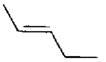
The room temperature photochemical extrusion of CBr_2 was also investigated, with the results shown in Table 3. The yield of dibromocyclopropanated product was at least as good as

Table 2. Kinetics of thermal decomposition of 5[a]

 , M	$k \times 10^5$ (s^{-1})
9·6[b]	2·8 ± 0·1
4·8[c]	3·0 ± 0·1
1·2[d]	2·9 ± 0·2

[a] In each case, $[5]_0 = 0{\cdot}16$ M; T = 134° ± 1°C.
[b] Pure cyclohexene
[c] 50% cyclohexene/50% cyclohexane.
[d] 12·5% cyclohexene/87·5% cyclohexane.

Table 3. Products and yields from CBr_2 extrusions in 2-pentenes

		Products[b]			
Starting[a] Materials	Decomposition Conditions		 6	 7	Recovered 5
5+ 	147°C, 8·5 h	65%	40%	—	20%
5+ 	147°C, 8·5 h	87%	—	55%	24%
5+ 	hv (254 nm), 18·5 h	90%	90%	2·7%[c]	51%
5+ 	hv (254 nm), 18·5 h	75%	—	75%	52%

[a] In each case the molar ratio of 5 to alkene was 1:161.
[b] Yields based on unrecovered 5.
[c] Average of 3 GC analyses of the same sample.

that reported from **3**.[5] The small amount of **7** formed from *cis*-2-pentene may be misleading, in that 1–2% of **7** was also formed from *cis*-2-pentene and $CHBr_3$/KOtBu. In any event, photolysis of 4.5mg **5** in 0·2 ml *cis*-2-pentene/1 ml pentane for 9 h led to a 75% yield of indan, a 63% yield of **6**, but *no trans isomer*. **7**. Attempts to observe a direct photoisomerization of **6** (in *cis*-2-pentene) to **7** led to possibly 0·5% isomerization after 18·5 h.

In summary, **5** is a readily available source of CBr_2. In addition, this approach to CBr_2 represents a paradigm for other carbenes; we are pursuing such possibilities.

EXPERIMENTAL SECTION

General

NMR spectra were recorded on a Nicolet 300 MHz instrument; IR spectra were recorded on Beckman IR-18A and IR-4250 spectrophotometers; mass spectra were obtained on Finnegan 4023 quadrupole GC/MS and Kratos MS-50 high resolution MS instruments. Product yields were determined by internally standardized (mesitylene) capillary GC analysis on a Hewlett-Packard 5890 machine. Under standard temperature programming conditions (80°C for 2 min, then 80°-300°C at 20°C/min.), the following retention times were observed: **5**: 8·69 min.; **6**: 4·47 min.; **7**: 4·17 min.; indan: 4·04 min. Melting points are uncorrected. A medium pressure Hanovia lamp was used for photolyses.

10,10-Dibromo[4.3.1]propella-2,4-diene (5)

A solution of **4**[7] (2·4 g, 8·3 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 4·2 g, 18 mmol) in 10 ml CH_2Cl_2 was heated at 75°C for two days in a sealed tube. The cooled tube was opened, and the filtered greenish solid washed with hexane. Subsequent chromatography on alumina gave colorless crystals of **5** (0·8 g, 35%), mp 72°–73°C. IR (CCl_4): 3040, 2970, 2940, 2870, 1445, 1170, 1155, 1040, 635 cm^{-1}; the ^1H-NMR, UV and exact mass have been reported.[6b]

(Z)-1,1-Dibromo-2-ethyl-3-methylcyclopropane (6).

Addition of $CHBr_3$ to a mixture of *cis*-2-pentene (Aldrich) in pentane, and KOtBu at −20°C was effected in the standard fashion.[7] The *cis*-cyclopropane (**6**) was purified by distillation, bp 25°-26°C/0·05 Torr. ^1H-NMR ($CDCl_3$): δ 1·03 (t, 3H), 1·08 (d, 3 H), 1·3–1·7 (m, 4 H); ^{13}C-NMR ($CDCl_3$): δ 38·6, 35·0, 28·1, 20·2, 12·6, 11·1; IR (neat): 2966, 2932, 2876, 1456, 1381, 1126, 737 cm^{-1}. Analysis calculated for $C_6H_{10}Br_2$: *m/e* 241·9129. Found: *m/e* 241·9132.

(E)-1,1-Dibromo-2-ethyl-3-methylcyclopropane (7).

trans-2-Pentene (Aldrich) was used to prepare **7** by exactly the same procedure used for **6**; **7** had the same bp as **6**. ^1H-NMR ($CDCl_3$): δ 0·9–1·2 (m, 2 H), 1·04(t, 3 H), 1·4 (d, 3 H), 1·5–1·6 (m, 2 H); ^{13}C-NMR ($CDCl_3$): δ 39·9, 39·3, 31·4, 26·1, 17·4, 12·6; IR (neat): 2964, 2932, 2876, 1458, 1381, 1138, 825, 756, 737 cm^{-1}. Analysis calculated for $C_6H_{10}Br_2$: *m/e* 239·9149, Found: *m/e* 239·9153. Under our GC conditions, **7** has a retention time between indan and **6**.

Thermolysis of 5 in cyclohexene.

Solutions of **5** (0·15 g , 0·5 mmol) in cyclohexene (0·4 g, 5 mmol) were sealed in tubes and immersed in an oil bath at the temperature and for the times indicated in Table 1. The cooled tubes were then opened, and the solutions diluted with $CHCl_3$ to appropriate analytical GC concentrations. After 15 μl of mesitylene had been added, GC analyses were performed. Correction factors were obtained using commercial indan (Aldrich) and independently prepared 7,7-dibromonorcarane.[8] The results are given in Table 1.

For the kinetic runs (Table 2), five sealed tubes with identical contents were immersed simultaneously in an oil bath held at 134° ± 1°C. One tube each was withdrawn after 3, 6, 12, 24, and 48 h, and the cooled solutions analyzed by GC with internal mesitylene standards. The rate constants were calculated by the standard method for first order reactions.

Thermolysis of 5 in 2-pentenes.

A solution of **5** (9 mg, 0·03 mmol) in either *cis*- or *trans*-2-pentene (0·35 g, 5 mmol) was sealed in a pyrex tube and immersed in an oil bath at 147°C for 8·5 h. The cooled tube was opened, the contents diluted, mesitylene added, and the mixture analyzed by capillary GC. The results are given in Table 3.

Photolysis of 5 in 2-pentenes.

Exactly the same sealed solutions as described above were irradiated in a Rayonet reactor for 18·5h. The opened samples were analyzed as above to give the data shown in Table 3.

ACKNOWLEDGEMENT

We are grateful for support of this work by the National Science Foundation (CHE-8416728).

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