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[2+2]-CYCLOADDITIONS OF CYCLOPENTYNE [1)]

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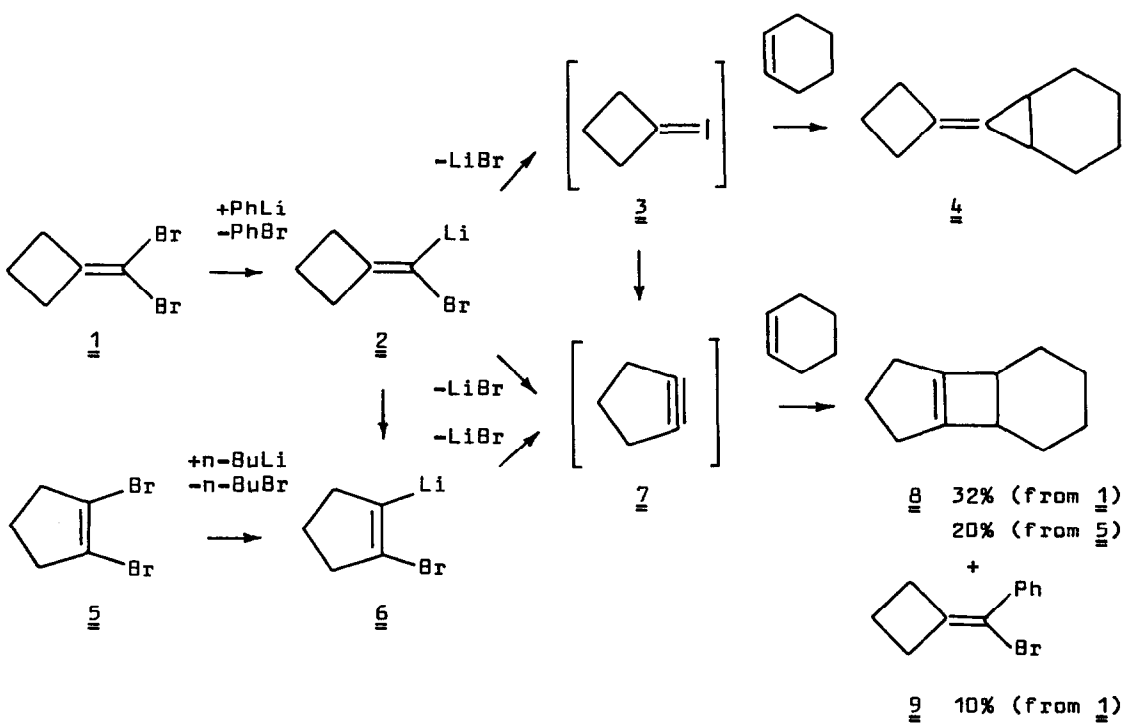
Summary: Cyclopentyne, as generated from dibromomethylenecyclobutane, a formerly unknown cyclopentyne source, undergoes [2+2]-cycloadditions with various substituted olefins yielding bicyclo[3.2.0]hept-1(5)-ene derivatives.

Out of the short-life cycloalkynes [2)], cyclopentyne 7 is one of the most reactive, but one of the least explored. The only reactions studied so far, are polar additions [3)] and [2+4]-cycloadditions with reactive dienes such as 1,3-diphenylisobenzofurane [4)] and tetracyclone [4c)].

We have now found, that cyclopentyne 7, as generated from dibromomethylenecyclobutane 1 [5)], a formerly unknown cyclopentyne source, undergoes [2+2]-cycloadditions with various substituted olefins, yielding bi- and tricyclic systems with bicyclo[3.2.0]hept-1(5)-ene partial structures (see table).



We made this finding in an attempted preparation of 7-cyclobutylidenebicyclo[4.1.0]heptane 4 by reacting dibromomethylenecyclobutane 1 [5] (2.0 mmol) with phenyllithium (1.45 ml (2.0 mmol) of a 1.4 m solution in benzene/ether (70/30)) in cyclohexene (10.0 mmol) for 15 min at -40°C and 45 min at +20°C. Instead of the expected 4, thought to be formed by [1+2]-cycloaddition of cyclobutylidenecarbene 3 with cyclohexene [7], we actually isolated the isomeric tricyclo[6.3.0.0^{2,7}]undec-1(8)-ene 8, a [2+2]-cycloadduct of cyclopentyne 7. (1-Bromo-1-phenylmethylene)cyclobutane 9 was also found and identified by independent synthesis [8].

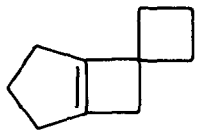
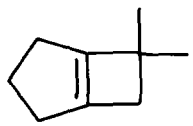
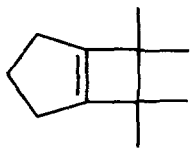
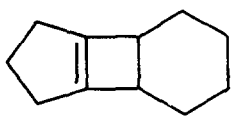
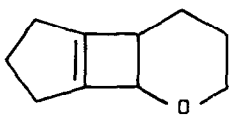
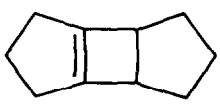
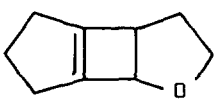
The ^{1}H NMR of 8 (100 MHz, $CDCl_3$) shows an eight proton multiplet at δ 1.20-1.90 (cyclohexane-H), a six proton multiplet at 1.90-2.30 (cyclopentene-H) and a two proton multiplet at 2.80-3.00 (cyclobutene-H) and compares favourably with the data reported for unsubstituted bicyclo[3.2.0]hept-1(5)-ene [10]. The ^{13}C NMR (50.3 MHz, $CDCl_3$) exhibits six lines at δ 18.33 (C-4, C-5), 23.88 (C-3, C-6), 26.33 (C-10), 30.41 (C-9, C-11), 39.23 (C-2, C-7) and 153.24 (C-1, C-8) and is in full accord with the structure given.

The unexpected formation of 8 prompted us, to react 1,2-dibromocyclopentene 5, the most efficient cyclopentyne source known so far [11], with cyclohexene as well. Under appropriate conditions, i.e. by reacting n-butyllithium (1.60 ml (2.0 mmol) of a 1.25 m solution in hexane) with a solution of 1,2-dibromocyclopentene 5 (2.0 mmol) in cyclohexene (20.0 mmol) for 30 min at -78°C and 25 h at +20°C, we obtained the same cycloadduct 8 as formed from 1, albeit in considerably reduced yield (20% vs. 32% from 1). This finding provides evidence, that cyclopentyne 7 is an intermediate in the formation of 8 from both 5 and 1. Concerning the formation of 7 from 1 it remains uncertain, whether it is formed directly from 2 or by way of a cyclobutylidenecarbene-cyclopentyne rearrangement as proposed [4d] for the closely related formation of cyclopentyne 7 from bromomethylenecyclobutane. An intermediacy of 6 may be excluded, as 6 is known [4e] to be rather stable under the conditions employed for the generation of 7 from 1.

In view of the potential preparative value of [2+2]-cycloadditions of cyclopentyne 7 in constructing bi- and tricyclic systems prone to further elaboration [12], we reacted other olefins with cyclopentyne 7 as well. As can be seen from the table, a series of six further [2+2]-cycloadducts of cyclopentyne 7 were obtained by reacting dibromomethylenecyclobutane 1 with solutions of phenyllithium in methylenecyclobutane, isobutylene, tetramethylethylene, 2,3-dihydropyrane, cyclopentene and 2,3-dihydrofurane respectively. All cycloadducts were isolated by preparative glpc and identified on the basis of their IR, ^{1}H NMR (table), ^{13}C NMR (table) and mass spectral data. The ^{1}H NMR data of 14 (table) compare well with those reported for unsubstituted bicyclo-[3.2.0]hept-6-ene [13].

The relative reactivities of cyclopentyne 7 towards 2,3-dihydropyrane and cyclohexene have been determined by competition experiments and found to be

Table. [2+2]-Cycloadducts of cyclopentyne 7, as generated from dibromomethylene-cyclobutane 1

	cycloadduct[a]	yield[b]	^{1}H NMR[d]	^{13}C NMR[e]
10		28%	1.50-2.80 (m)	16.76, 26.41, 28.85, 30.85, 31.15, 42.57, 49.30, 147.42, 156.16
11		30%	1.20 (s, 6H), 1.90-2.40 (m, 8H)	25.81, 26.13, 28.78, 30.81, 42.83, 43.10, 144.71, 159.16
12		27%	1.06 (s, 12H), 1.90-2.30 (m, 6H)	22.87, 25.88, 27.84, 46.71, 155.40
8		32%[c]	1.20-1.90 (m, 8H), 1.90-2.30 m, 6H), 2.80-3.00 (m, 2H)	18.33, 23.88, 26.33, 30.41, 39.23, 153.24
13		31%	1.30-2.70 (m, 10H), 2.80-3.05 (m, 1H), 3.55-3.85 (m, 2H), 4.40-4.55 (m, 1H)	19.94, 22.92, 26.79, 29.90, 30.39, 40.28, 61.53, 71.38, 153.58, 158.29
14		23%	1.10-1.90 (m, 6H), 1.90-2.30 (m, 6H), 3.24 (d, 2H, J=6Hz)	24.16, 25.82, 25.97, 29.19, 45.92, 150.50
15		35%	1.40-1.80 (m, 2H), 1.90-2.40 (m, 6H), 3.25-3.50 (m, 1H), 3.55-4.25 (m, 2H), 5.00-5.20 (m, 1H)	26.50, 26.62, 29.09, 29.21, 45.76, 66.88, 79.24, 151.13, 154.68

(a) Experimental conditions as described for 8 (see text); correct elemental analyses, IR and mass spectral data were obtained in all cases. (b) All yields are of single run experiments (except 8) and were determined by glpc with n-octane as internal standard; response factors were not determined. (c) Best yield of a series of six runs. (d) 100 MHz, $CDCl_3$, δ (ppm). (e) 50.3 MHz, $CDCl_3$, δ (ppm).

2.9:1 in favour of 2,3-dihydropyrane. This indicates a large reactivity of this electrophilic species.

References and Notes

Dedicated to Professor Georg Wittig on Occasion of His Eightyfifth Birthday

1) Cycloalkynes, part 1.

2) Reviews: R.W.Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, 1967; A.Krebs in "Chemistry of Acetylenes", H.Viehe Ed., Marcel Dekker, New York, 1969; M.Nakagawa in "The Chemistry of Carbon-Carbon Triple Bond", S.Patai Ed., Wiley, New York, 1978.

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5) Dibromomethylenecyclobutane 1 (bp 70°C/12 mm) was obtained in 82% yield after a general procedure of Posner [6] by reacting cyclobutanone with triphenylphosphine/tetrabromomethane in refluxing benzene; ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 13.43, 32.58, 78.95, 146.96.

6) G.H.Posner, G.L.Loomis and H.S.Sawaya, Tetrahedron Lett. 1975, 1373.

7) 1,1-Dibromo-2-methylpropene, an open chain analog of 1, has been reported to give a 41% yield of 7-isopropylidene-bicyclo[4.1.0]heptane by treatment with methyllithium in cyclohexene: H.D.Hartzler, J. Amer. Chem. Soc. 86, 526 (1964).

8) (1-Bromo-1-phenylmethylene)cyclobutane 9 was prepared by bromination of (1-phenylmethylene)cyclobutane [9] with pyridine perbromide in dichloromethane and subsequent dehydrobromination with potassium t-butoxide in benzene/pentane; ^{13}C NMR (50.3 MHz, CDCl3): δ 15.88, 32.35, 113.98, 127.75, 128.05, 137.56, 143.06.

9) H.J.Bestmann and E.Kranz, Chem. Ber. 102, 1802 (1969).

10) W.Kirmse and K.H.Pook, Angew. Chem. Int. Ed. Engl. 5, 594 (1966).

11) Judged from a 30% yield of 1:2 adduct obtained with 1,3-diphenylisobenzofurane as trapping agent (4e).

12) Compare the reactions performed with bicyclo[3.2.0]hept-1(5)-ene (10).

13) O.L.Chapman, D.J.Pasto, G.W.Borden and A.A.Griswold, J. Amer. Chem. Soc. 84, 1220 (1962).

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