Vinyl Cations. 14.[1] Preparation and Solvolysis of (Bromomethylene)cyclopropanes. The Generation of Stabilized Vinyl Cations

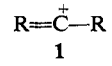
Michael Hanack,* Tilman Bässler, Wolfgang Eymann, William E. Heyd, and Richard Kopp

Contribution from the Fachbereich 14, Organische Chemie, Universität des Saarlandes, D 6600 Saarbrücken, Germany. *Received February 11, 1974*

Abstract: (1-Bromomethylene)cyclopropane (**8**), (1-bromo-1-methylmethylene)cyclopropane (**9**), (1-bromo-1-phenylmethylene)cyclopropane (**10**), and (1-bromo-1-cyclopropylmethylene)cyclopropane (**11**) are synthesized, and their solvolysis rates and the resulting products in various solvents are determined. The relative rates (k_{rel}) in 80% ethanol (100°) are: **8**, $k_{rel} = 1$; **9**, $k_{rel} = 1 \times 10^3$; **10**, $k_{rel} = 2.5 \times 10^3$; **11**, $k_{rel} = 1 \times 10^5$. The solvolysis products are dependent on the substituent in 1 position of the (bromomethylene)cyclopropane. While **8** and **9** rearrange almost completely with the formation of the cyclobutane derivatives **20**, **24**, and **25**, respectively, **10** and **11** yield mostly the nonrearranged cyclopropyl ketones **33** and **35**. The kinetic data and the product analyses show that stabilized cyclopropylidenemethyl cations (**3**) are intermediates in the solvolysis reactions of the (bromomethylene)cyclopropanes **8**–**11**.

Recently, through extensive experiments it has been shown that the generation of vinyl cations through solvolysis of simple vinyl derivatives is possible.[2]

Vinyl cations **1** can be generated as reactive inter-



1

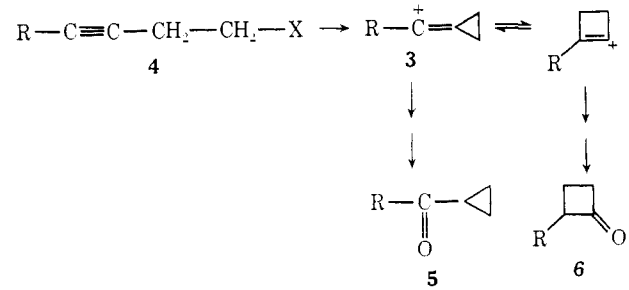
mediates through solvolysis reactions of simple vinyl derivatives when the following conditions are met. For solvolysis, particularly favorable leaving groups should be employed such as the trifluoromethanesulfonate anion (triflate)[2a,3] or the still faster reacting nonafluorobutanesulfonate anion (nonaflate).[4] When poorer leaving groups, that is, those less inclined to undergo SN1 reactions are employed, *e.g.*, tosylate or halogenide (chloride, bromide, or iodide), the vinyl compounds will undergo heterolysis of the carbon–halogen bond only when the resulting vinyl cation is stabilized by suitable neighboring groups with electron-donating abilities.

For vinyl cations **1** it is important whether a substituent R is attached to the positively charged center through a single or a double bond. All electron donors that have been effective in stabilizing saturated (trisubstituted) carbenium ions are suitable for vinyl cations too.

Vinyl cations can be stabilized especially well by the cyclopropyl group, as was first shown by Hanack and Bässler[5] and Sherrod and Bergman,[6] respectively. There are two possibilities for utilizing the high stabilizing effect of a cyclopropane ring on a positive charge. A cyclopropane ring bonded singly produces the secondary vinyl cation **2**, while if the β-carbon atom is in the cyclopropane ring, then one has the cyclopropylidenemethyl cation **3**. The particular stability of the cyclopropylidenemethyl cation, **3**, arises from its special geometry. The electron-donating cyclopropane, because of the short C–C distance of the double bond, is closer to the positive center with the axis of the vacant orbital of the vinyl cation and the plane of the three-membered ring being parallel. In that way there is a particularly favorable geometry for overlap of the participating orbitals. The high stability of **3** was confirmed by MO calculations.[7]

2 **3**

Cyclopropylidenemethyl cations **3** were first proposed by us[8] as intermediates in the homopropargyl rearrangement in which, during solvolyses, reactive homopropargyl derivatives, **4**, can be rearranged with formation of cyclopropylalkyl ketones, **5**, and cyclobutanones, **6**.



4 **3** **5** **6**

Recently we reported on two examples of the generation of cyclopropylidenemethyl cations,[9,10] **3**, through

(1) Part 13: K. Subramanian and M. Hanack, *Tetrahedron Lett.*, 3365 (1973).

(2) (a) M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970); (b) G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, **9**, 185 (1971); (c) P. J. Stang, *Progr. Phys. Org. Chem.*, 10, 205 (1973); (d) L. R. Subramanian and M. Hanack, *J. Chem. Educ.*, in press.

(3) W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *J. Amer. Chem. Soc.*, **93**, 1513 (1971).

(4) L. R. Subramanian and M. Hanack, *Chem. Ber.*, **105**, 1465 (1972).

(5) M. Hanack and T. Bässler, *J. Amer. Chem. Soc.*, **91**, 2117 (1969).

(6) S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 2115 (1969).

(7) H. Fischer, K. Hummel, and M. Hanack, *Tetrahedron Lett.*, 2169 (1969).

(8) M. Hanack, J. Herterich, and V. Vött, *Tetrahedron Lett.*, 3871 (1967).

(9) A. Ghenciulescu and M. Hanack, *Tetrahedron Lett.*, 2827 (1970).

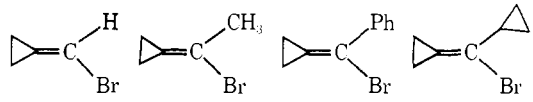
(10) T. Bässler and M. Hanack, *Tetrahedron Lett.*, 2171 (1971).

solvolysis reactions of the methylenecyclopropane derivatives **7** and **8** whereby the especially unstable primary

7 **8**

vinyl cation can be stabilized in the form of a cyclopropylidenemethyl structure. As yet only those (halomethylene)cyclopropanes were investigated whose solvolysis gave the aforementioned primary vinyl cation **3** with R = H.[9,10] An additional stabilization should then be obtained when **3** is a secondary vinyl cation, that is, when R is either an alkyl or an aryl group.

In the following we report on the syntheses and the solvolysis reactions of the (halomethylene)cyclopropanes **8**, **9**, **10**, and **11**.



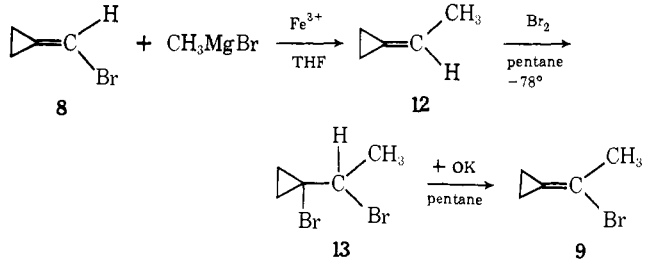
8 **9** **10** **11**

Synthesis of the (1-Bromomethylene)cyclopropanes 8–11

For the synthesis of (1-bromomethylene)cyclopropane (**8**)[10] methylenecyclopropane,[11,12] which is easily accessible from methallyl chloride, was brominated at −78° in pentane, and the resulting 1-bromomethyl-1-bromocyclopropane was dehydrobrominated with KOH. The purification of **8** was done by preparative gas chromatography.

The synthesis of (1-bromo-1-methylmethylene)cyclopropane (**9**) is shown in Scheme I.

Scheme I



8 **12** **13** **9**

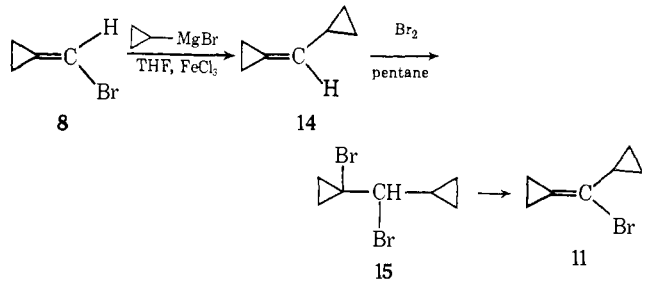
When the dehydrobromination of **13** is carried out in pentane as a solvent[13] **9** is the principal product. This is presumably because isomerization of the double bond into the energetically more favorable position β to the cyclopropane ring is prevented by the two-phase system potassium *tert*-butoxide–pentane. **9** could be separated from unidentified by-products by preparative gas chromatography.

The synthesis of (1-bromo-1-phenylmethylene)cyclopropane (**10**) has already been reported elsewhere.[14]

Scheme II illustrates the synthesis of (1-bromo-1-cyclopropylmethylene)cyclopropane (**11**).[15]

(11) P. Caubère and G. Coudert, *Bull. Soc. Chim. Fr.*, 2234 (1971).
(12) R. Köster, S. Arora, and P. Binger, *Justus Liebigs Ann. Chem.*, 1219 (1973); *Synthesis*, 322 (1971); *Angew. Chem., Int. Ed. Engl.*, 8, 205 (1969).
(13) W. Schoberth and M. Hanack, unpublished results.
(14) J. L. Derocque, F. B. Sundermann, N. Youssif, and M. Hanack, *Justus Liebigs Ann. Chem.*, 419 (1973).
(15) W. E. Heyd and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, 12, 318 (1973).

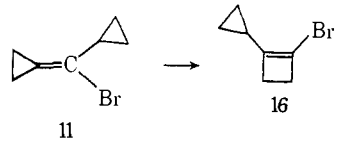
Scheme II



8 **14** **15** **11**

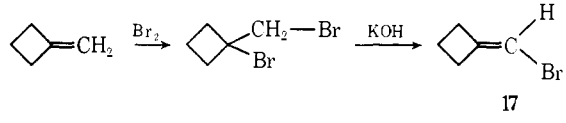
The desired (1-bromo-1-cyclopropylmethylene)cyclopropane (**11**) could be isolated through purification by preparative gas chromatography.

(1-Bromo-1-cyclopropylmethylene)cyclopropane (**11**) is an extraordinarily labile vinyl bromide[15] as will be shown below by its solvolysis reactions. If **11** is purified by preparative gas chromatography and the column temperature is above 120°, a practically quantitative rearrangement to 1-bromo-2-cyclopropylcyclobutene-1 (**16**) may occur which is dependent on the solid support.



11 **16**

(1-Bromomethylene)cyclobutane (**17**)[16] which was



17

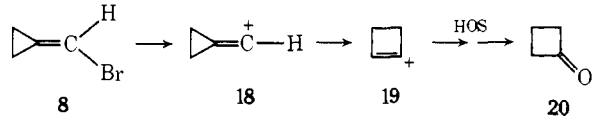
needed for comparison purposes was prepared from methylenecyclobutane through a bromination–dehydrobromination sequence, similar to that used for the 1-bromomethylenecyclopropane derivatives.

Results and Discussion

The (bromomethylene)cyclopropanes **8–11** were solvolyzed in solvents of different nucleophilicity and ionizing power, the resulting reaction products identified, and the solvolysis rates measured.

If we propose a vinyl cation mechanism for the solvolysis of (1-bromomethylene)cyclopropane (**8**), a primary vinyl bromide, then the reaction path given in Scheme III is possible.

Scheme III



8 **18** **19** **20**

Solvolysis of **8** at 140° in 50% aqueous methanol in the presence of 1.2 mol equiv of triethylamine gave cyclobutanone (**20**) as the only solvolysis product detectable by gas chromatography.

The determination of the solvolysis rate of (1-bromomethylene)cyclopropane (**8**) in 60 and 80% aqueous ethanol at 130, 140, and 150° was done by following by

(16) K. L. Erickson, J. Markstein, and K. Kim, *J. Org. Chem.*, 36, 1024 (1971).

gas chromatography the disappearance of the starting material **8** with respect to time.

In order to determine the independence of the reaction rate on the concentration of added base all rates were measured in the presence of 1.1 or 3.0 mol equiv of triethylamine.

The rate constants in Table II show clearly that, in contrast to other unstabilized vinyl halides, (bromomethylene)cyclopropane (**8**) is an appreciably reactive system under solvolytic conditions.[2] The rate constants are almost independent of the concentration of the added base, whereby the possibility of an acid-catalyzed addition–elimination mechanism can be excluded.[17] The *m* value of the Winstein–Grunwald equation[18] was determined to be 0.53 which does not contradict a vinyl cation mechanism, that is, the solvolyses proceed through a SN1 reaction.

The formation of cyclobutanone (**20**) as product of the solvolysis indicates that the intermediate primary vinyl cation, **18**, rearranges to the cyclobutenyl cation, **19** (*cf.* Scheme III), from which cyclobutanone (**20**) is formed. As we have recently shown, cyclobutenyl cations such as **19**, in contrast to other cyclic vinyl cations, are stabilized through a nonclassical interaction between the positive charge and the C-2–C-3 bond, so that the formation of **19** is relatively easy.[7] The ready formation of the cyclobutenyl cation can be shown through the comparatively high solvolysis rates of cyclobutenyl derivatives. The solvolysis of, for example, 1-cyclobuten-1-yl nonafluorobutanesulfonate (nonaflate)[19] in ethanol–water and 2-methyl-1-cyclobuten-1-yl nonaflate[1] shows approximately the same rate as 1-cycloocten-1-yl nonafluorobutanesulfonate in which the resulting vinyl cation can approach the energetically favorable linear geometry.[3]

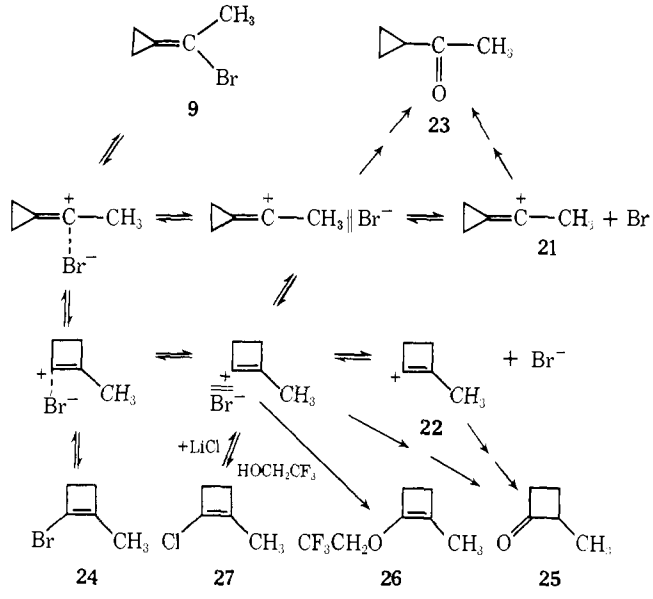
The comparatively high reactivity of (1-bromomethylene)cyclopropane (**8**) can be explained by the stabilizing effect of the cyclopropane ring, which upon formation of the intermediate cyclopropylidene cation, **18**, is especially large (*vide supra*).

A comparison with the homologous (1-bromomethylene)cyclobutane[16] (**17**) is well suited to show how much the reactivity of a vinyl bromide is increased through the neighboring group effect of the cyclopropane ring in **8**. In a solvolysis attempt in 70% methanol at 180° in the presence of triethylamine the bromide **17** was recovered unchanged after 21 days. The latter indicates the low reactivity of "normal" vinyl bromides.[20]

(17) M. Hanack, Z. Rappoport, and T. Bässler, *J. Amer. Chem. Soc.*, **92**, 4985 (1970).
(18) S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, **73**, 2700 (1951).
(19) L. R. Subramanian and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, **11**, 714 (1972).
(20) A referee suggested that a major contribution to the rate enhancement of **8** and **9** is the relief of strain going from **18** to **19**, since cyclobutene is more than 10 kcal/mol more stable than methylenecyclopropane [*cf.* P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970)]. Accordingly the ions **18** and **21**, respectively, might not be formed at all during the solvolyses of **8** and **9**. That **8** and **9** solvolyze with formation of the ions **18** and **21** first has been demonstrated with the (*Z*)- and (*E*)-1-bromomethylene-2-methylcyclopropanes. Both isomers in a solvolysis reaction show a rate enhancement which is typical for a methyl group in a cyclopropane ring of a cyclopropylcarbinyl system. In addition both isomers solvolyze with complete rearrangement; the rearranged products are formed from the *Z* and *E* isomer in exactly the same ratio. This excludes a synchronous ring opening, without the intermediacy of a cyclopropylidenemethyl cation (≙ **8** or **9**) [G. Hammen, T. Bässler, and M. Hanack, *Chem. Ber.*, 107, 1676 (1974)].

If one adds a methyl group to (1-bromomethylene)cyclopropane (**8**), the resulting (1-bromo-1-methylmethylene)cyclopropane (**9**) is distinguished by a noticeably increased reaction rate (*cf.* Table II). The solvolysis rate, measured in 80% ethanol, is a factor of 10^3 higher than that of (1-bromomethylene)cyclopropane (**8**) by which a higher stabilization of the intermediate vinyl cation **21** is indicated (Scheme IV).[20] The

Scheme IV



m value[18] of 0.64 is in good agreement with a vinyl cation mechanism.

Of special interest are the solvolysis products of **9**. For the product studies (1-bromo-1-methylmethylene)cyclopropane (**9**) was solvolyzed in different solvent systems in the presence of triethylamine. Gas chromatographic analysis showed that methylcyclopropyl ketone (**23**), 2-methylcyclobutanone (**25**), and a product of further rearrangement which was identified as 1-bromo-2-methyl-cyclobutene-1 (**24**) were produced. The exact product ratios are shown in Table I.

Table I. Yields[a] of the Solvolysis Products of **9** after 4 Days in Different Solvent Systems at 90° with 2.5 equiv of NEt_3 Buffer

Solvent	Salt (added)	Products, % 23	25	24	27	26	9
60% EtOH		<1	35	65			0
80% EtOH		<1	30	70			0
50% TFE		<1	27	65		8	0
80% TFE		<1	15	65		20	0
SO_2 (20°, 45 days)[b]				32			18
100% EtOH	$ZnCl_2$ (30 equiv)		Trace	50	50		0
100% DMF	$ZnCl_2$ (30 equiv)		Trace	55	45		0
50% TFE	LiCl (20 equiv)	<1	10	60	15	15	0
50% DMSO	LiCl (20 equiv)	<1	20	55	25		0

[a] Relative yields measured by gas chromatography. [b] Two unidentified components (12 and 38%).

A surprising result was the formation of the rearranged product 1-bromo-2-methylcyclobutene (**24**) which in all solvolysis reactions of **9** was the main product (see Table I). A rearrangement in this manner, which can

Table II. Solvolysis Rates of the (Bromomethylene)cyclopropanes **8–11**

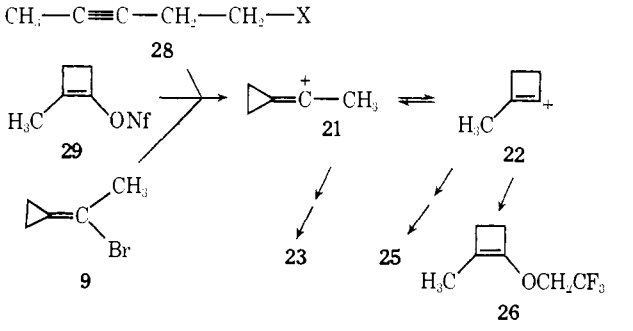
Compd	Solvent, % EtOH	Triethylamine, equiv	Temp, °C	Method[a]	k, sec^{-1}	k_{rel} (approx.)
8	60	3.0	130	A	5.73×10^{-6}	
	80	3.0	130	A	1.44×10^{-6}	
	60	1.1	140	A	1.35×10^{-5}	
	60	3.0	140	A	1.29×10^{-5}	
	60	1.1	150	A	3.41×10^{-5}	
	60	3.0	150	A	2.97×10^{-5}	
	80	3.0	100	B	7.1×10^{-8}	1
9	80	1.5	101	A	6.6×10^{-5}	1×10^{3}
	60	1.5	101	A	3.5×10^{-4}	
	60	2.5	101	A	3.1×10^{-4}	
	50		75.9	C	1.42×10^{-4}	
	50		60.9	C	3.5×10^{-5}	
10	80	1.2	100	A	1.54×10^{-4}	2.5×10^{3}
11[b]	50		29.9	C	2.3×10^{-4}	
	50		48.8	C	1.82×10^{-3}	
	50		67.3	C	9.94×10^{-3}	
	80		48.8	C	6.2×10^{-5}	
	80		74.4	C	7.4×10^{-4}	
	80		100	B	6.35×10^{-3}	1×10^{5}

[a] Method A, vpc; B, extrapolation; C, titration. [b] Thermodynamic data: (50% ethanol) $\Delta H^{\ddagger} = 20.0$ kcal/mol, $\Delta S^{\ddagger} = -7.1$ eu; (80% ethanol) $\Delta H^{\ddagger} = 21.0$ kcal/mol, $\Delta S^{\ddagger} = -10.7$ eu.

typically be described as an internal return[21] with simultaneous structural rearrangement, has not to our knowledge been observed up to now in the case of vinyl cations. The rearrangement of **9** to **24** is direct evidence for a vinyl cation mechanism since the formation of **24** by other mechanisms, *e.g.*, the addition–elimination mechanism,[2] is clearly excluded. As is shown in Table I addition of chlorides in the solvolyses causes formation of a considerable amount of 1-chloro-2-methylcyclobutene (**27**) as well as the bromide **24**. The predominance of the rearranged bromide under all solvolysis conditions suggests an ion-pair mechanism.[21] The formation of rearranged chloride **27** in the trapping experiment with lithium chloride shows the presence of solvent separated ion pairs, while the bromide, **24**, should result from tight ion pairs. Scheme IV shows the formation of the individual reaction products with respect to ion-pair formation.

The overwhelming formation of rearranged products in the solvolysis of **9** shows unequivocally that a vinyl cation mechanism is involved and must proceed by a rearrangement reaction through the intermediates **21** and **22**. The formation of 2-methylcyclobutanone (**25**), through the solvolysis of (1-bromo-1-methylmethylene)cyclopropane (**9**), is in agreement with all other investigations which were done with the isomeric "homopropargyl derivatives."[1,2,22] Thus the solvolysis reactions of pentynyl derivatives (**28**, X = $-OSO_2C_6H_4$-*m*-NO_2, $-OSO_2CF_3$) in acidic solvents, *e.g.*, trifluoroacetic acid, formic acid, or the nonacidic solvents such as trifluoroethanol and trifluoroethanol–water gave predominantly methylcyclobutanone (**25**) (Scheme V). As in the solvolysis of the pent-3-ynyl triflate[23] (**28**, X = OTf) the solvolysis of **9** in TFE gave the ether **26**, the formation of which directly implicates an intermediate **22**. **25** is likewise the main product from the solvolysis of the especially fast reacting 2-methyl-

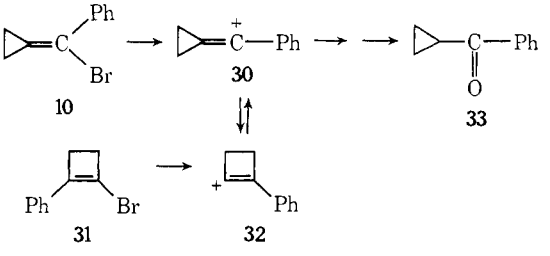
Scheme V



cyclobutenyl nonaflate (**29**).[1] That the isomeric "homopropargyl derivatives" **28**, **29**, and **9** under solvolysis conditions produce almost the same product mixture indicates that in all three cases the reactions proceed through the intermediates **21** and **22**.[8]

As has already been described elsewhere,[14] the substitution of a phenyl group on (1-bromomethylene)-cyclopropane drastically raises the stability of the solvolytic intermediate, the vinyl cation. Thus (1-bromo-1-phenylmethylene)cyclopropane (**10**) solvolyzes 2.5 × 10^3 times faster than the nonsubstituted (1-bromomethylene)cyclopropane (**8**) (80% ethanol at 100°) (see Table II).

The increased stability of intermediate vinyl cations such as **30** is also shown in the product analysis in which **10**, in contrast to the (1-bromomethylene)cyclopropane derivatives **8** and **9**, gives the nonrearranged phenyl cyclopropyl ketone **33** as the main product.[14]



(21) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Amer. Chem. Soc.*, 78, 328 (1956); D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, pp 152–158.

(22) M. Hanack, S. Bocher, J. Herterich, K. Hummel and V. Vött, *Justus Liebigs Ann. Chem.*, 733, 5 (1970), and literature cited therein.

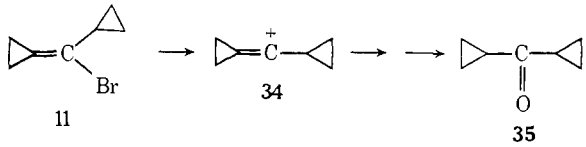
(23) H. Stutz and M. Hanack, *Tetrahedron Lett.*, 2457 (1974).

Phenyl cyclopropyl ketone (**33**) is also obtained as the main reaction product when 1-bromo-2-phenylcyclobutene-1 (**31**) is solvolyzed in various solvent systems and under different conditions.[14] The favored formation of phenyl cyclopropyl ketone (**33**) in the solvolysis of **10** shows directly the increased stability of the intermediate vinyl cation **30**. While in the cyclopropylidenemethyl cation **30** the neighboring phenyl group can stabilize the positive charge directly through a mesomeric effect, the phenyl group in **32** does not contribute to the stabilization of the positive charge. **32** therefore appears to be less favored.

Finally, from (1-bromo-1-cyclopropylmethylene)-cyclopropane (**11**) an especially high reaction rate and thus an especially stable vinyl cation were expected.[15] The kinetics of the solvolysis of **11** were measured by continuous titration in 50 and 80% aqueous ethanol at various temperatures and pH values. The results are shown in Table II.

The analysis of the reaction products showed that dicyclopropyl ketone was the only product.

Table II shows clearly that the bromide **11** solvolyzes through a SN1 mechanism including the intermediate vinyl cation, **34**. **11** solvolyzes faster in solvents of



11 34 35

higher ionizing power (50% ethanol); the Winstein–Grunwald *m* value[18] of 0.89, determined from rate constants at 48.8°, is the highest reported up to now for a reaction passing through a vinyl cation. The negligible increase in the reaction rate with pH, caused by a small salt effect produced by the added base, eliminates with certainty the possibility of an acid catalyzed addition–elimination mechanism. An additional indication of the unusual stability of the intermediate vinyl cation **34** is shown by the fact that here also no rearrangement to a four-membered ring product occurs.

The high stability of the vinyl cation **34** is also shown by a comparison of the solvolysis rate of **11** with those of other (bromomethylene)cyclopropanes. As can be seen in Table II, **11** solvolyzed 10^5 times faster than (1-bromomethylene)cyclopropane (**8**) and still about 10^2 times faster than **10**.

It is remarkable that the rate ratio between the phenyl and the methyl derivatives **10** and **9** is very low (Table II). This points to a considerable ground-state stabilization of **10** due to conjugation between the phenyl ring and the double bond. To stabilize the positive charge in **30**, the phenyl ring must be rotated around 90° for a favorable overlap of the participating orbitals. The fact that **11** solvolyzes significantly faster than **10**[24] could also be partly explained by ground-state stabilization of **10**, though additional kinetic data of suitable substituted vinyl compounds for comparison are not available at the present time.

Experimental Section

A. Synthesis of the Bromomethylenecyclopropanes 8–11. Synthesis of Bromomethylenecyclopropane (8). Methylenecyclopropane.[11,12] A suspension of 200 g (5.0 mol) of $NaNH_2$[25] in 200 ml of dry di-*n*-butyl ether was treated dropwise at 130° with a solution of 390 ml (3.9 mol) methallyl chloride in 200 ml of di-*n*-butyl ether. The readily volatile products (methylenecyclopropane and 1-methylcyclopropene) were carried by a nitrogen stream to a cold trap (−78°). After the addition was complete, the reaction mixture was stirred for an additional 1–2 hr at 130°. The ammonia was allowed to evaporate from the two-phase condensate at −33°. The volatile products (bp ~5°) were led through dilute H_2SO_4 and then through potassium *tert*-butoxide in DMSO (70°; 11.2 g of base in 50 ml of DMSO) and the methylenecyclopropane (about 100 g, 45–50% yield; pure by nmr) was condensed at −78°; nmr τ 4.67 (m, 2), 8.95 (t, 4).

1-(Bromomethyl)-1-bromocyclopropane. Methylenecyclopropane (108 g, 2.0 mol) in 400 ml of pentane was brominated at −78°.[12] Excess bromine was destroyed with methanol–H_2O and Na_2SO_3. *Caution!*, during the bromination a strong lacrymator is formed [2-(bromomethyl)-3-bromopropene]. The pentane solution was washed with several 100-ml portions of water and dried over $CaCl_2$. Distillation afforded 321 g (1.5 mol, 75%) of dibromide; bp 63–64° (17 Torr); ir $\bar{\nu}$ 957, 1028, 1218, 1237, 1427 cm^{-1}; nmr τ 6.30 (s, 2), 8.6–8.75 (m, 2), 8.8–8.95 (m, 2).

(1-Bromomethylene)cyclopropane (8). 1-(Bromomethyl)-1-bromocyclopropane (62.1 g, 0.29 mol) was added to a mixture of 300 ml of DMSO and 19.3 g (0.34 mol) of crushed KOH and stirred at room temperature for 30 hr. The mixture was poured into 1200 ml of ice–water and extracted with five 100-ml portions of pentane. The combined pentane layers were dried with $CaCl_2$ and concentrated, and **8** was distilled at reduced pressure: bp 53–54° (105 Torr); 15.5 g (40%); ir $\bar{\nu}_{C=C}$ 1755 cm^{-1}; nmr τ 3.65 (quint, 1), 8.4–9.2 (m, 4).

Synthesis of (1-Bromo-1-methylmethylene)cyclopropane (9). (Methylmethylene)cyclopropane (12).[26] The Grignard reagent was prepared from 6.1 g (0.25 mol) of magnesium turnings in 335 ml of dry THF and methyl bromide which was bubbled through the mixture until all of the magnesium was dissolved. A solution of 23.0 g (0.173 mol) of **8** in 60 ml of THF with a catalytic amount of $FeCl_3$ was treated dropwise at 0° with the filtered methyl Grignard solution, the extent of reaction being monitored by gc (2 m × 6 mm 10% Carbowax 20M on 60/80 Chromosorb PAW, col. 100°, 60 ml/min of N_2). (Methylmethylene)cyclopropane (**12**) was distilled from the reaction along with much THF: nmr τ 9.04 (m, 4), 8.24 (m, 3), 4.35 (m, 1).

1-(1-Bromocyclopropyl)-1-bromoethane (13). The bromination of **12** was carried out in the same way as in the preparation of **8**. The only gc detectable product **13** was used in the next step without purification. A sample for analysis was purified by gc (2 m × 6 mm 3% SE-30 on voraport 30, 100–120 mesh, col. 100°, 60 ml/min of He): nmr τ 6.33 (quart, 1), 8.16 (d, 3), 8.52–8.75 (m, 2), 8.75–9.00 (m, 2).

(1-Bromo-1-methylmethylene)cyclopropane (9). To a suspension of 10.1 g (0.09 mol) of potassium *tert*-butoxide in 100 ml of pentane at 0° was added a solution of *ca.* 14 g (0.06 mol) of the crude dibromide **13** in 50 ml of pentane. The mixture was stirred for 10 min at room temperature and hydrolyzed with 100 ml of water; the pentane phase was washed three times with 50 ml of water and then dried over Na_2SO_4. After removal of the solvent, **9** was collected in a cold trap (−190°) at low pressure (1 Torr). Pure **9** can be isolated by preparative gas chromatography (2 m × 6 mm 10% UCC W982 on Chromosorb PAW 60/80 mesh, col. 90°, 60 ml/min of N_2). **9** is air sensitive and quickly becomes yellow: ir $\bar{\nu}_{C=C}$ 1788 cm^{-1}; nmr τ 7.63 (m, 3), 8.70 (m, 4); mass spectrum *m/e* 146 and 148 (molecular ion), 67 (vinyl cation); total yield **8** → **9** equals 10%.

Synthesis of (1-Cyclopropyl-1-bromomethylene)cyclopropane (11). (Cyclopropylmethylene)cyclopropane (14).[26] The Grignard reagent was prepared from 2.4 g (99 mmol) of magnesium turnings in 50 ml of dry THF and 10 g (83 mmol) of cyclopropyl bromide in 10 ml of THF. After the Grignard was formed, it was stirred for 30 min at reflux. Then, while cooling with an ice–salt bath, a catalytic amount of $FeCl_3$ was added followed by 4.65 g (35 mmol) of (bromomethylene)cyclopropane (**8**) in 5 ml of THF. The reaction was heated at reflux for 30 min and then stirred at room temperature for 12 hr. After hydrolysis with 100 ml of aqueous NH_4Cl, it was extracted three times with 150 ml of pentane, washed twice with 200 ml of water, and dried over $MgSO_4$. **14** was purified

(24) Compare also H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, **95**, 2400 (1973); G. A. Olah and P. W. Westermann, *ibid.*, **95**, 7530 (1973).

(25) Suspension in toluene, Merck, W. Germany.

(26) M. Tamura and J. Kochi, *Synthesis*, 303 (1971).

by condensation in a cold trap (−78°) at 15 Torr: ir $\bar{\nu}_{C=C}$ 1770 cm^{-1}; nmr τ 4.69 (m, 1), 8.57 (m, 1), 9.00 (d, 4), 9.47 (m, 4).

(1-Bromocyclopropyl)cyclopropylbromomethane (15). **14** was converted to the dibromide in the same way as described for the preparation of **8**. The dibromide was used without further purification: nmr τ 7.00 (d, 1), 8.98 (m, 9).

(1-Cyclopropyl-1-bromomethylene)cyclopropane (11). Pulverized sodium amide (1.95 g, 50 mmol) was washed with pentane and THF, and in 30 ml of dry THF was treated with 1.23 g (16.6 mmol) of *tert*-butyl alcohol in 15 ml of dry THF.[27] After 2 hr of stirring at 40° the reaction was complete. Into this solution was added, dropwise, at 0°, 2.35 g (9.3 mmol) of the dibromide **15** in 10 ml of dry THF. The elimination reaction was complete after 3 hr of stirring at 0°. After hydrolysis with 200 ml of ice–water and extraction with three 50-ml portions of pentane the solution was dried and concentrated. The purification of **11** was achieved by preparative gas chromatography on a 3 m × 6 mm 10% SE-30 on 60/80 Chromosorb PAW at 95°. At temperatures over 120° **11** may rearrange to the isomeric 2-cyclopropylcyclobutenyl bromide (**16**): ir $\bar{\nu}_{C=C}$ 1760 cm^{-1}; nmr τ 8.30 (m, 1), 8.72 (AABB, 4), 9.12 (m, 4); mass spectrum *m/e* 172 and 174.

Synthesis of (1-Bromomethylene)cyclobutane (17).[16] **1-Bromo-1-bromomethylcyclobutane.** Methylenecyclobutane[28] (4.77 g, 10.07 mmol) in 30 ml of dry THF at 0° was brominated with 12 g (0.075 mol) of bromine in 20 ml of CCl_4. Distillation afforded 6.5 g (40%) of the dibromide, bp 80–95° (25 Torr).

(Bromomethylene)cyclobutane (17).[29] Pulverized KOH (3.4 g, 0.06 mol) and 3.2 g (0.014 mol) of the dibromide were mixed in a small flask with 3.4 g of quartz sand. The mixture was heated to 80–90° at 100 Torr and the resulting mixture (1.7 g) collected in a cold trap at −40°. The material was dried over $CaCl_2$; it consisted of 77% **17** and unidentified products: ir $\bar{\nu}_{C=C}$ 1666 cm^{-1}; nmr τ 7.73–8.31 (m, 2), 7.13–7.52 (m, 4), 4.28 (quint, 1, J = 2 Hz).

B. Solvolyses. Description of the Gc Kinetics. About 0.2 mmol (30 mg) of the bromide **9** was dissolved in 30 times its volume of the desired solvent, buffered with 1.2–2.5 mol equiv of triethylamine, and after the addition of 4 μl of chlorobenzene as an internal standard, sealed in eight small ampoules. The ampoules were placed in a thermostated bath (±0.1°) at the desired temperature and at successive time intervals removed and placed in an ice bath. From the gas chromatogram one determines a product/standard ratio by comparison of the peak heights. The plot of the logarithm of this ratio as a function of time gives the desired k values. The columns used were 2 m × 6 mm or 3 mm 10% Carbowax 20M on Chromosorb PAW at 100 or 80°. The kinetics for **8**, **9**, and **10**[14] were done in this manner. Additionally, the solvolyses of the bromides **9** and **11** were followed by automatic continuous titration. In this case *ca.* 5 μl of the substance in 30 ml of aqueous ethanol was solvolyzed under the noted conditions (*cf.* Table II).

Description of a Typical Product Analysis. The bromide **9** (30 mg, 0.2 mmol) was dissolved in ten times its volume of aqueous solvent and buffered with 2 mol equiv of triethylamine. The mixture was heated in a sealed ampoule for 4 days at 90°. Part of the products was identified directly by gc–ms (Varian-MAT 311, 2 m × 3 mm 10% Carbowax 20M on Chromosorb PAW, col. 90°, 20 ml/min of He). The remainder of the solvolysis mixture was added to three times its volume of saturated NH_4Cl solution and extracted with three portions of pentane. The pentane phase was worked up by preparative gc (2 m × 6 mm 10% Carbowax 20M on Chromosorb PAW, col. 80–120°, 60 ml/min of He). The separated fractions were trapped in CCl_4 at 0°.

Cyclopropyl methyl ketone (23) could only be identified through comparison of retention times with an authentic sample.

2-Methylcyclobutanone (25) was indicated by mass spectrometry: *m/e* 84 (molecular ion, 49%), 56 (−CO, 100%). The nmr spectrum was identical with that of an authentic sample: nmr (90 MHz) τ 7.0–7.25 (m), 7.65–8.1 (m), 8.3–8.7 (m), 8.75–9.1 (m), 8.83 (d).

2-Methylcyclobutenyl bromide (24):[30] mass spectrum *m/e* 148 and 146 (molecular ions, 18%), 67 (−Br, 100%); nmr τ 7.15–7.3 (m, 2), 7.3–7.62 (m, 2), 8.33 (m, 3).

2-Methyl-1-(2′,2′,2′-trifluoroethoxy)cyclobutene (26):[23] mass spectrum *m/e* 166 (molecular ion, 80%), 151 (−CH_3, 28%), 97 (−CF_3, 32%), 83 (−CH_2CF_3, 20%), 67 (−OCH_2CF_3, 100% vinyl cation). Vpc comparison with an authentic sample was performed.[23]

2-Methylcyclobutenyl chloride (27): mass spectrum *m/e* 104 and 102 (molecular ions, 50 and 21%), 67 (−Cl, 100%, vinyl cation); nmr τ 7.3–7.5 (m, 2), 7.6–7.75 (m, 2), 8.3 (m, 3).

Solvolysis of Bromomethylenecyclopropane (8). In analogy to the solvolysis of **9**, 133 mg (1 mmol) of **8** was heated to 140° for 14 days in 3 ml of 70% methanol in the presence of 110 mg (1.1 mmol) of triethylamine. Upon work-up, the only product found was cyclobutanone which was identified by comparison of its gc behavior and its ir spectrum with those of an authentic sample; ir $\bar{\nu}_{C=C}$ 1790 cm^{-1}.

Solvolysis of (1-Bromomethylene)cyclobutane (17). In analogy to the solvolysis of **8**, 147 mg (1 mmol) of **17** in the presence of 110 mg (1.1 mmol) of triethylamine was heated for 21 days at 180° in a sealed ampoule. Analysis by gc showed that no reaction had taken place; the bromide **17** was recovered unchanged.

Solvolysis of (1-Bromo-1-phenylmethylene)cyclopropane (10). Product studies, solvolysis rates, and further experimental data are published elsewhere.[14]

Solvolysis of (1-Bromo-1-cyclopropylmethylene)cyclopropane (11). A 370-mg (2.14 mmol) sample of **11** in the presence of 1.08 g (10.7 mmol) of triethylamine was heated in 50 ml of 50% EtOH–H_2O for 6 hr. **11** had completely disappeared and dicyclopropyl ketone was the only product found by vpc. A nmr spectrum of the collected peak was identical with an authentic sample.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the VW Foundation. We thank Dr. J. C. Carnahan, Jr., for the help in preparing the manuscript.

(27) P. Caubère and G. Coudert, *Tetrahedron*, 28, 5635 (1972).

(28) Purchased from EGA-Chemie, D-7924 Steinheim/Albuch, W. Germany.

(29) H. Normant and P. Maitte, *Bull. Soc. Chim. Fr.*, 1424 (1960).

(30) *Cf.* Ph.D. Thesis, N. Youssif, Tübingen, 1971.