Thermal [2 + 2] Cycloaddition of Cyclopropylethylene with Tetracyanoethylene[1]

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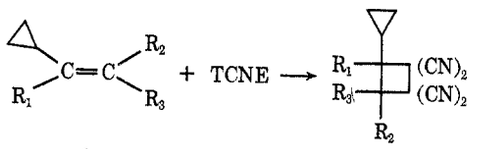
A number of ethylenes substituted by cyclopropyl group(s) (**1a–1k**) are found to undergo thermal [2 + 2] cycloaddition with tetracyanoethylene under mild conditions. Among the olefins studied, 1,1-dicyclopropylethylene (**1a**) was the most reactive while 1,2-dicyclopropylethylene (**1d** and **1e**) were the least reactive; namely, geminal cyclopropyls greatly enhanced the reactivity of ethylene. It was noted that the rate of reaction is influenced by solvent polarity; in other words, the reaction proceeds rapidly in a polar solvent: k_2 (acetonitrile)/(ethyl acetate) = 10^3. Further, the cycloaddition was found to be more than 90% stereospecific. It was surmised that the present cycloaddition should be a donor–acceptor cycloaddition of tetracyanoethylene with cyclopropylethylene, which is highly electron rich.

Tetracyanoethylene (TCNE)[2] has been known not only as a very reactive dienophile[3] but also as an activated olefin which is capable of undergoing [2 + 2] cycloaddition[4] with some conjugated olefins and with electron-rich olefins.[2,5,6] Interestingly, it reacts also with cyclopropylethylenes[7] in a [2 + 2] manner under mild conditions.[1] Recently, Effenberger and Podszun[8] and Barton and Rogido[9] also demonstrated the high reactivities of 1,1-dicyclopropylethylene and 2-cyclopropylpropene in a [2 + 2] cycloaddition with isocyanates.



1 **2**

a, R_1 = c-C_3H_5; R_2 = R_3 = H
b, R_1 = c-C_3H_5; R_2 = CH_3; R_3 = H
c, R_1 = c-C_3H_5; R_2 = $CH(CH_3)_2$; R_3 = H
d, R_1 = R_2 = H; R_3 = c-C_3H_5
e, R_1 = R_3 = H; R_2 = c-C_3H_5
f, R_1 = CH_3; R_2 or R_3 = c-C_3H_5; R_3 or R_2 = H
g, R_1 = R_2 = c-C_3H_5; R_3 = H
h, R_1 = R_2 = R_3 = H
i, R_1 = CH_3; R_2 = R_3 = H
j, R_1 = c-C_3H_5; R_2 = C_6H_5; R_3 = H
k, R_1 = c-C_3H_5; R_2 = R_3 = CH_3

Results

Structure and Reactivity of Olefins.—Various mono-, di-, and tricyclopropylethylenes (**1a–1k**) produce [2 + 2] cycloadducts in their reaction with TCNE (Table I). Among olefins, the most reactive ethylene is 1,1-dicyclopropylethylene (**1a**). The rate of reaction was so rapid that the color developed and disappeared at once, and immediate evaporation of the solvent gave the adduct **2a** in a quantitative yield. The reaction was somewhat slower with 1,1-dicyclopropylpropene (**1b**) and much slower with 1,1-dicyclopropyl-3-methyl-1-butene (**1c**). The reactivity sequence observed here, **1a** > **1b** > **1c**, can be interpreted as the result of steric hindrance of the reaction caused by substitution at the 2 position.

On the other hand, *trans*- and *cis*-1,2-dicyclopropylethylene (**1d** and **1e**) exhibit the lowest reactivity. Under standard conditions (see Experimental Section), **1d** and **1e** produce blue solutions, respectively, but the color remained unchanged even after a lapse of 2 months in both cases. In a polar solvent at an elevated temperature, however, the same reaction took place, and the adducts **2d** and **2e** were isolated as crystalline products. The nmr analyses of the crude adduct fraction show that the adduct was not contaminated by its stereoisomer in both cycloadditions. Thus, it was concluded that the cycloaddition proceeds with a stereospecificity of more than 90%.[10]

Introduction of a methyl group on one of the olefinic carbons makes **1f** much more reactive than the parent **1d** or **1e**. The color faded in this case after *ca.* 5 hr under standard conditions. The third cyclopropyl group also brings about a reactivity increase, as seen in the reaction time of **1g**.

The least substituted ethylene, *i.e.*, vinylcyclopropane (**1h**), reacted fairly slowly, but the adduct **2h** was isolated in 63% yield after 28-hr reflux in methylene dichloride. Again, the substitution of C-1 hydrogen by a methyl markedly increased the reactivity of **1i**.

2,2-Dicyclopropylstyrene (**1j**), in which the substituent at the 2 position is phenyl, has a relatively low reactivity. Under standard conditions, it re-

(1) Preliminary communications: (a) S. Nishida, I. Moritani, and T. Teraji, *Chem. Commun.*, 501 (1970); (b) *ibid.*, 36 (1971).

(2) For a leading reference on the chemistry of polycyano olefins, see E. Ciganeck, W. J. Linn, and O. W. Webster in "The Chemistry of Cyano Group," Z. Rappoport, Ed., Interscience, New York, N. Y., 1970, Chapter 9.

(3) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967).

(4) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 2 (1962).

(5) (a) A. T. Blomquist and Y. C. Meinwald, *J. Amer. Chem. Soc.*, **79**, 5316 (1957); (b) A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959); (c) J. K. Williams, *ibid.*, **81**, 4013 (1959); (d) K. Hafner and J. Schneider, *Justus Liebigs Ann. Chem.*, **624**, 37 (1959); (e) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **1**, 519 (1962); (f) C. A. Stewart, Jr., *J. Amer. Chem. Soc.*, **84**, 117 (1962); (g) C. A. Stewart, Jr., *J. Org. Chem.*, **28**, 3320 (1963); (h) R. C. Cookson, J. Dance, and J. Hudec, *J. Chem. Soc.*, 5416 (1964); (i) C. A. Stewart, Jr., *J. Amer. Chem. Soc.*, **87**, 4021 (1965); (j) J. J. Eisch and G. R. Husk, *J. Org. Chem.*, **31**, 589 (1966).

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(7) (a) S. Nishida, I. Moritani, E. Tsuda, and T. Teraji, *Chem. Commun.*, 781 (1969); (b) T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc. C*, 3252 (1971).

(8) F. Effenberger and W. Podszun, *Angew. Chem., Int. Ed. Engl.*, **8**, 976 (1969).

(9) T. J. Barton and R. J. Rogido, *Chem. Commun.*, 878 (1972).

(10) Nmr spectra of **2d** and **2e** differ at several points in that the mutual contamination of the isomeric adduct can be detected by an nmr examination when more than 10% of the isomer is present in the sample.

TABLE I

CYCLOADDITION REACTIONS OF CYCLOPROPYLETHYLENE WITH TCNE

			Reaction conditions					
Ethylene[a]	Compd	CT_{max}, nm, in CH_2Cl_2	Solvent	Temp,[b]	Time, sec[c]	Product[h]	Mp, °C	Yield, %[d]
1,1-(c-C_3H_5)$_2$	**1a**	...[e]	CH_2Cl_2	rt	1–2	**2a**	167–168	87
1,1-(c-C_3H_5)$_2$-2-CH_3	**1b**	(540)[e]	CH_2Cl_2	rt	150	**2b**	153–155	81
1,1-(c-C_3H_5)$_2$-2-$CH(CH_3)_2$	**1c**	550	CH_2Cl_2	rt	25,000	**2c**	136–137	81
trans-1,2-(c-C_3H_5)$_2$	**1d**	549	CH_3NO_2	100	9,000	**2d**	159–160.5	11[f]
cis-1,2-(c-C_3H_5)$_2$	**1e**	549	CH_3NO_2	100	9,000	**2e**	165–167	25[f]
1,2-(c-C_3H_5)$_2$-1-CH_3[g]	**1f**	602	CH_2Cl_2	rt	17,000	**2f**	97–98.5	58
1,2,3-(c-C_3H_5)$_3$	**1g**	635	CH_2Cl_2	rt	900	**2g**	161–162.5	76
c-C_3H_5	**1h**	420	CH_2Cl_2	Reflux	100,000	**2h**	124–125	63
1-c-C_3H_5-1-CH_3	**1i**	448	CH_2Cl_2	rt	1,400	**2i**	108–109.5	35
1,1-(c-C_3H_5)$_2$-2-C_6H_5	**1j**	400, 600	CH_3CN	rt	430,000	**2j**	160.5–161.5	74
1,1-(c-C_3H_5)$_2$-2,2-$(CH_3)_2$	**1k**	580	CH_2Cl_2	rt	140,000	**2k**	148–149	70

[a] c-C_3H_5 = cyclopropyl. [b] Room temperature (rt) was 20–25°; some experiments were carried out in a thermostat at 25 or 100°. [c] Time required for the completion of color change. [d] Based on the isolated and recrystallized product. [e] Color fading was so rapid that the measurement could not be made. [f] Some TCNE was recovered; yield is based on consumed TCNE. [g] A mixture of geometrical isomers. [h] Satisfactory analytical and osonometric molecular weight data were reported for all products listed in the table: Ed.

quires more than 1 month for the completion of the color change. In acetonitrile, the addition was completed after a lapse of 5 days at room temperature and the [2 +2] cycloadduct **2j** was isolated in a 74% yield.

Effect of Solvent Polarity.—The cycloaddition of **1g** with TCNE was carried out in various solvents and the time required for the completion of the color change was determined at 25°. The results are summarized in Table II. The reaction proceeds quickly in a polar

TABLE II

EFFECT OF SOLVENT POLARITY ON THE RATES OF CYCLOADDITION AT 25°

	1g + TCNE		*p*-Methoxystyrene + TCNE	
Solvent	Time, sec[a]	Yield of **2g**, %	Time, sec[a,b]	Rel rate[c]
CH_3CN	30	80		570
CH_3NO_2	35	80	60	
$CH_3CH_2CH_2NO_2$	240	78		
CH_2Cl_2	600	66		340
$CHCl_3$	1,200	70		
$CH_3COOC_2H_5$	28,000	81	80,000	1.0
C_6H_{12}			2,600,000	0.00091

[a] Time required for the completion of color change of the solution. [b] Reference 6a. [c] Calculated from k_2 (l. mol^{-1} sec^{-1}) obtained by Wiley and Simmons, cited in ref 11a.

solvent such as nitromethane or acetonitrile and slowly in ethyl acetate. The solvent effect observed here is very similar to those reported for the cycloaddition of *p*-methoxystyrene with TCNE.[6a,6d,11]

It will be noteworthy to mention that the products isolated in various solvents are all identical, and no 2:1 cycloadduct has been so far detected.[12] The formation of the same adduct as a single product in a different solvent was also examined in other cases. Moderately reactive **1k** gave the adduct **2k** in acetonitrile (70% yield) or in methanol (23% yield) without any other characterizable adduct. The low yield of **2k** in methanol is due to the consumption of TCNE by methanol (see Experimental Section). Indeed, the highly reactive **1a** gave **2a** in 78% yield in methanol, while the low-reactive **1j** produced **2j** only in a 9% yield. Trapping of a possible intermediate by methanol or of the 2:1 adduct has thus been unsuccessful.

Discussion

The present cycloaddition behaves like a thermal[13] [2 + 2] cycloaddition of an electron-rich olefin with a strongly electron-demanding TCNE (donor–acceptor cycloaddition). It strongly suggests that the cyclopropylethylene should be a highly electron-rich olefin like vinyl ether.[6] In fact, some representative cyclopropylethylenes have shown extraordinarily low ionization potentials as an alkene.[14] Thus, 8.08 eV was found for the adiabatic ionization potential of **1a**, 7.72 eV for **1d**, 7.70 eV for **1e**, and 7.48 eV for **1g**, respectively. *However, it was not the olefin of lowest ionization potential that shows the highest reactivity in the present cycloaddition.* For example, the most reactive **1a** possessed a rather high ionization potential, while **1g** showed a mere moderate reactivity in the cycloaddition, although its ionization potential was the lowest. Moreover, in a comparison of three dicyclopropylethylenes, the ionization potentials of 1,2-dicyclopropylethylenes (**1d** and **1e**) were considerably lower than that of 1,1 isomer **1a**, but **1d** or **1e** was far less reactive than **1a**. Apparently, the geminal cyclopropyls greatly enhance the reactivity of ethylene.[15] The important factor for the ease of the present cycloaddition, besides a high reactivity of TCNE, will thus be the strong stabilizing interaction of the cyclo-

(11) (a) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965); (b) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, part 1.7.

(12) In some donor–acceptor cycloadditions, a 2:1 cycloadduct has been isolated. See (a) M. E. Kuehne and L. Foley, *J. Org. Chem.*, **30**, 4280 (1965); (b) P. Otto, L. A. Feiler, and R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **7**, 737 (1968); (c) R. Huisgen, B. A. Davis, and M. Morikawa, *ibid.*, **7**, 826 (1968). See also ref 6a.

(13) In complete dark, the reaction of **1g** with TCNE proceeded at the same rate as that under room light. Also, illumination of a blue solution of **1j** with TCNE with a 100-W tungsten lamp resulted in no change either in the reaction rate or in the course of the reaction. Therefore, the reaction is thermal.

(14) S. Nishida, I. Moritani, and T. Teraji, *Chem. Commun.*, 1114 (1972).

(15) Graf also noted in their study on the cycloaddition of *N*-chlorosulfonyl isocyanate with alkenes that the olefin possessing a structure of $R_2C{=}CH_2$ has a much higher reactivity than that of RHC=CHR: R. Graf, *Justus Liebigs Ann. Chem.*, **661**, 111 (1963); *Angew. Chem., Int. Ed. Engl.*, **7**, 172 (1968).

propyl group with an adjacent electron-deficient center[16] in the highly polarized transition state.[17] A methyl substitution at the 1 position of cyclopropylethylene also results in a reactivity increase, but its effect appears to be smaller than that caused by a successive cyclopropyl substitution (**1a**:**1i** and **1g**:**1f**). The methyl group will stabilize the polarized transition state also, but cyclopropyl accomplishes it to a much higher extent.

The substitution by an alkyl at the 2 position results in the reactivity decrease primarily because of the steric hindrance, which can be seen in a reactivity sequence of **1a** > **1b** > **1g** > **1c**. An exception for the trisubstituted ethylene was **1j**, which reacted much more slowly than either one of the trisubstituted cyclopropylethylenes. Its low reactivity may be due to self-quenching of the reaction.[18] To reach the transition state, it may be necessary for the TCNE to form a complex with the double bond to be reacted, but in **1j** the TCNE may primarily form a complex with the extended π-electron system (the styrene moiety) of **1j** and it will be far less effective for the cycloaddition.

The olefin **1k** is tetrasubstituted; thus it should have a considerably large steric hindrance. Yet the same cycloaddition proceeds rather smoothly. Again, the geminal cyclopropyls greatly enhance the reactivity of the ethylene.

Experimental Section

General.—Ir spectra were recorded on either a Hitachi EPI-S2 spectrophotometer or a Hitachi 215 grating infrared spectrophotometer. Electronic absorption spectra were taken on a Hitachi EPS-2U recording spectrophotometer. Nmr spectra were obtained with either a JEOL JNM-4H-100 or a JNM MH-60 spectrometer. Elemental analyses were performed either by the Microanalytical Laboratory, Faculty of Engineering Science, Osaka University, or by the Microanalytical Laboratory, Faculty of Pharmacy, Hokkaido University. Melting points are uncorrected.

The cycloaddition was carried out by mixing the two components in an appropriate solvent. Standard reaction conditions are set as 0.05 *M* for both reactants in methylene dichloride at room temperature. When the reaction was carried out in acetonitrile or in methanol, the concentrations of the two reactants increased up to 0.5 mol/l. The time required for the completion of the color change was determined as a measure for the reaction rate.[6a]

After the color change was completed, the product was isolated and characterized in the usual manner. In the following section, experiments of some representative ethylenes with TCNE are described.

Reaction of 1,1-Dicyclopropylethylene (1a) with TCNE. In Methylene Dichloride.—To a solution of 640 mg (5.00 mmol) of TCNE in 100 ml of methylene dichloride, 550 mg (5.10 mmol) of **1a** was added in one portion. A reddish brown color developed instantly but the solution became colorless after 1 or 2 sec. The solvent was evaporated immediately, and the residual solid, mp 164–167°, was recrystallized from the chloroform–carbon tetrachloride (1:2) mixture; 1026 mg (87%) of **2a** was obtained. Pure crystals melted at 167–168°. The high melting point and ir of the crude product were strong evidence supporting the fact that the cycloaddition was proceeding quantitatively.

In Methanol.—A solution of 642 mg (5.02 mmol) of TCNE in 8 ml of absolute methanol was made at 25°, and 541 mg (5.01 mmol) of **1a** was added to it in one portion. An orange-red color developed but it faded after *ca.* 10 sec. Solvent evaporation and recrystallization gave 917 mg (78%) of pure **2a**. A comparison run on mixture melting point and ir confirmed the identity of the two samples.

Reactions of β,β-Dicyclopropylstyrene (1j) with TCNE.—A dark violet solution (λ_{max} 376 and 545 nm) of 321 mg (2.43 mmol) of TCNE and 465 mg (2.53 mmol) of **1j** in 5 ml of acetonitrile was kept at room temperature. The absorption maximum at 545 nm decreased in intensity with the lapse of time and two new absorptions appeared at 387 and 415 nm. After 5 days, the color of the solution became yellow and no more change was observed. Therefore, the solution was concentrated under reduced pressure and the resultant residue was recrystallized from benzene. The adduct **2j** was isolated as colorless needles, 581 mg (74%). Analytically pure material melted at 160.5–161.5° dec. The yellow product, which appears to be the cause for two absorptions at 387 and 415 nm, which formed was so small in quantity that the product could not be characterized.

In methanol, under an argon stream, the same adduct **2j** was isolated in 9% yield after 9 days of reaction. When TCNE (320 mg) alone was dissolved in 5 ml of methanol, it reacted with the solvent at room temperature and the recovered TCNE after 24 hr was a mere 14 mg (4% recovery).

A blue solution (λ_{max} 400 and 600 nm) of 323 mg (2.52 mmol) of TCNE and 4662 mg (25.3 mmol) of **1j** in 100 ml of methylene dichloride was irradiated with a 100-W tungsten lamp from the bottom of the reaction flask. The mixture refluxed gently during the illumination. After 40 hr, it became light green, and it was yellow after 53.5 hr. The solution was concentrated under reduced pressure and the residue was washed with petroleum ether (bp 30–60°), mp 156–157° dec, 739 mg (94%). The ir spectrum of the present sample was superimposable on that of pure **2j** obtained before.

In a separate flask, a mixture very similar to the above was refluxed gently without illumination. The solution became light green after 35 hr and light brown after 41.5 hr.

Spectroscopic Data.—In ir spectra, all adducts exhibited the C≡N stretching vibration at 2240–2260 and cyclopropyl vibrations at 3010–3110 and 1015–1025 cm^{-1}. In the nmr (Table III), signals due to cyclobutane ring protons, methyl, isopropyl, and phenyl appeared at reasonable positions with reasonable splittings. Cyclopropyl protons appeared, in general, as two to four groups of complex multiplets with varying signal areas. The total numbers of cyclopropyl protons were, of course, those deduced from the [2 + 2] cycloadducts. In cycloadditions of tetracyclopropylethylene with TCNE and 1,1-dicyclopropyl-2,2-diphenylethylene dith TCNE,[1b] [2 + 2] cycloadducts were not produced but TCNE was cycloadded to one of the cyclopropane ring. Thus, in these adducts, additional signals due to cyclopentyl ring protons appeared at lower fields. Comparisons of these nmr spectra with those of the present adducts confirm the structure of the present products as [2 + 2] cycloadducts.

TABLE III

NMR SPECTRA OF THE ADDUCT[a]

Adduct	Nmr signals, τ
2a	7.88 (s, 2 H), 8.85–9.95 (m, 10 H)
2b	7.48 (q, 1 H, *J* = 7 Hz), 8.72 (d, 3 H, *J* = 7 Hz), 8.2–10.3 (m, 10 H)
2c	7.7 (m, 2 H), 8.92 (d, 3 H, *J* = 6 Hz), 9.03 (d, 3 H, *J* = 6 Hz), 8.4–9.7 (m, 10 H)
2d	7.6 (m, 2 H), 8.7–9.7 (m, 10 H)
2e	7.45 (m, 2 H), 8.35–9.75 (m, 10 H)
2g	7.67 (d, 1 H, *J* = 10 Hz), 8.2–9.9 (m, 15 H)
2h	7.1 (m, 3 H), 8.8–9.6 (m, 5 H)
2i	7.25 (s, 2 H), 8.45 (s, 3 H), 8.6–9.8 (m, 5 H)
2j	2.25 (s, 5 H), 4.20 (s, 1 H), 8.1–9.9 (m, 10 H)
2k	8.35 (s, 6 H), 8.7–9.4 (m, 10 H)

[a] In $CDCl_3$ except **2g**, which was recorded in CD_3COCD_3.

(16) C. D. Poulter and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2297 (1972), and references cited therein.

(17) R. Huisgen, R. Grashey, and J. Sauer, in "The Chemistry of Alkenes," Vol. 1, S. Patai, Ed., Interscience, New York, N. Y., 1964, p 787; see also ref 2, 6, 9, 11, and 12.

(18) The cycloaddition was effectively slowed down by an addition of an equimolar quantity of nonreacting aromatic hydrocarbon. Thus in the presence of various aromatics, the following time was necessary for the reaction of **1b** with TCNE under standard conditions: mesitylene, 27 min; *p*-xylene, 19 min; toluene, 11.5 min; benzene, 5.5 min; and cyclohexane, 2.5 min. Thus, the complexed TCNE with a nonreacting aromatic hydrocarbon is no more reactive, or at least far less reactive, than the free TCNE.

Registry No.—**1a**, 822-93-5; **1b**, 18738-69-7; **1c**, 38868-43-8; **1d**, 10359-44-1; **1e**, 23510-65-8; **1f**, 27847-24-1; **1g**, 23603-63-6; **1h**, 693-86-7; **1i**, 4663-22-3; **1j**, 23772-96-5; **1k**, 27720-84-9; **2a**, 26047-84-7; **2b**, 38858-55-8; **2c**, 38858-56-9; **2c**, 27926-30-3; **2e**, 27829-87-4; **2f**, 27847-26-3; **2g**, 27847-25-2; **2h**, 38858-59-2; **2i**, 27847-27-4; **2j**, 38858-61-6; **2k**, 31776-08-6; TCNE, 670-54-2.

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Secondary Deuterium Isotope Effects in the Solvolysis of Cyclobutyl and Cyclopropylcarbinyl Methanesulfonates

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Deuterated cyclobutyl methanesulfonates **1a–d** and cyclopropylcarbinyl methanesulfonates **2a–d** were prepared and their solvolysis rates were measured in 60% aqueous diglyme. With cyclobutyl methanesulfonates, a reduced α effect, an inverse β effect, and a rather large normal γ effect were observed. These results indicate a strong 1–3 interaction in the transition state. The isotope effects found in solvolysis of cyclopropylcarbinyl methanesulfonates are inconclusive with respect to a possible bridging in the transition state. A degenerate internal rearrangement of cyclopropylcarbinyl methanesulfonate was demonstrated to occur during acetolysis.

Since the early work by Bergstrom and Siegel[1] and Roberts, *et al.*,[2] solvolytic rearrangements of cyclopropylcarbinyl and cyclobutyl derivatives remained on the scene of mechanistic chemistry.[3,4] However, even after two decades the exact structure of the solvolytic intermediate(s) is still ambiguous. Recent results[4,5] clearly showed that the cyclopropylcarbinyl → cycloproplycarbinyl, the cyclopropylcarbinyl → cyclobutyl, and the cyclopropylcarbinyl → allylcarbinyl rearrangements are highly stereospecific, the rotation of the methylene group being completely absent during rearrangements. This conclusion has been more recently confirmed by the nmr studies of stable cyclopropylcarbinyl and cyclobutyl cations generated from the corresponding alcohols in SbF_5–SO_2ClF solutions at low temperatures.[6] The nmr spectra showed three signals: two three-proton methylene doublets and a one-proton methine multiplet. Cyclobutyl and cyclopropylcarbinyl derivatives appear to solvolyze by forming in the rate-determining step one and two intimate ion pairs, respectively, which then further ionize to the corresponding equilibrating solvent-separated ion pairs.[7,8] A number of nonclassical structures for the intermediate cations could fit this scheme.

In this paper we wish to report about secondary isotope effect studies in the solvolysis reaction of cyclobutyl and cyclopropylcarbinyl methanesulfonates which lead, *inter alia*, to a reinterpretation of some earlier findings.[9]

(1) C. G. Bergstrom and S. Siegel, *J. Amer. Chem. Soc.*, **74**, 145 (1952).
(2) M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960), and references cited therein.
(3) Reviews: Chapters by H. G. Richey, Jr., and by K. B. Wiberg, B. A. Andes, Jr., and A. J. Ashe in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1971.
(4) Z. Majerski and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 665 (1971), and references cited therein.
(5) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970); **90**, 4195 (1968).
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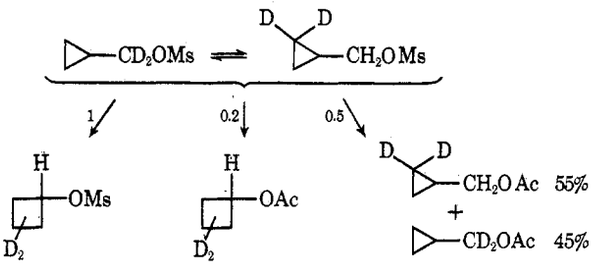
Results

Specifically deuterated cyclobutyl methanesulfonates **1a–d** and cyclopropylcarbinyl methanesulfonates **2a–d** were prepared as described in the Experimental Section.

The acetolysis of the cyclopropylcarbinyl derivatives is known to be accompanied by an internal return to cyclobutyl isomers.[2] Therefore, a degenerate cyclopropylcarbinyl → cyclopropylcarbinyl rearrangement could also be expected. Such an internal return reaction could change the rate constant during the solvolysis of deuterated cyclopropylcarbinyl derivatives because of the label scrambling. In the present work we checked this possibility by following the acetolysis of cyclopropylcarbinyl-*1,1-d*$_2$ methanesulfonate (**2a**) in perdeuterated acetic acid at 37° using the nmr technique. The observed changes of the proton signals are shown in Figure 1. The spectra in Figure 1 clearly demonstrate the occurrence of a degenerate cyclopropylcarbinyl rearrangement reaction as well as the internal return into cyclobutyl methanesulfonate and the formation of two corresponding acetates. The relative rates obtained by integration of the final spectra are given in the scheme below.



These results are in good agreement with previous experimental evidence.[2,8]

Methanesulfonates **1a–d** and **2a–d** were solvolyzed in 60% aqueous diglyme at 40° and the reaction rates were followed by continuous titration of liberated acid by means of an automatic recording titrator. The rate constants and the corresponding kinetic isotope