# The Cope Rearrangement of 1-Methoxybicyclo[3.2.0]hepta-3,6-dien-2-ones[1]

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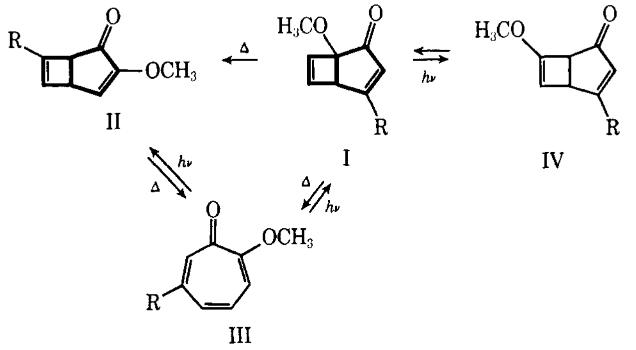
**Abstract:** 1-Methoxybicyclo[3.2.0]hepta-3,6-dien-2-ones (I), upon heating around 200°, were converted into 3-methoxybicyclo[3.2.0]hepta-3,6-dien-2-ones (II) accompanied by 2-methoxytropones (III). The transformation of I to II is a novel thermal rearrangement which has been observed in the bicyclo[3.2.0]heptadienone system. The reaction mechanism of the rearrangement was elucidated by use of deuterium labeling as well as by kinetic studies which support this rearrangement as a concerted [3,3]sigmatropic reaction. The molecular orbital consideration also suggests it to be the first example of the antarafacial–antarafacial Cope rearrangement.

1-Methoxybicyclo[3.2.0]hepta-3,6-dien-2-one derivatives I are one of several types of valence isomers of the corresponding tropolone methyl ethers (III) and they are readily available by irradiation of III[2] in which case photodimers are sometimes formed.[3] Upon prolonged irradiation of III, 1-methoxy compounds (I) first formed undergo further an intriguing photorearrangement to give 7-methoxybicyclo[3.2.0]hepta-3,6-dien-2-ones (IV).[4] Recently Chapman and Lassila have elucidated the mechanism of the photovalence isomerization between I and IV as proceeding through a ketene intermediate.[5a] On the other hand, the thermal rearrangement of the bicyclo[3.2.0]heptadienone system including 1-, 3-, and 7-methoxy derivatives (I, II, and IV) is rather simple and only ring opening takes place at considerably high temperatures (around 400°) to lead to the corresponding tropone derivatives.[3b,4,6] The reason why the ring opening requires such a high temperature is that a thermally allowed conrotatory process is infeasible in the bicyclo[3.2.0]hepta-3,6-dien-2-one system for geometrical reasons. Instead the ring opening must occur by a disrotatory process which is thermally forbidden or a radical mechanism and therefore requires a high-energy process.[7] This is also the case in the pyrolysis of bicyclo[3.2.0]heptadienone itself[8] or bicyclo[3.2.0]heptadiene[9] which provides tropone or cycloheptatriene as a single product.

As reported in our preliminary paper,[2b] however, we have found another type of rearrangement of the bicyclo[3.2.0]heptadienone system takes place in addition to the reorganization to tropones when pyrolysis of 1-methoxy derivatives I is carried out at a temperature lower than 200°. In this rearrangement, the methoxy group at the $C_1$ position and a substituent at the $C_4$ position migrate to the $C_3$ and $C_7$ positions, respectively, as shown in Scheme I. In general, most of the tropolone methyl ethers III, upon irradiation, afforded only valence isomers I,[10] although the formation of other isomers II was suggested on the basis of theoretical considerations.[11] Therefore, this thermal transformation of I to II is a useful method for the synthesis of 3-methoxybicyclo[3.2.0]heptadienones (II).

**Scheme I**



a, R = H
b, R = $i$-$C_3H_7$
c, R = $C_6H_5$

The mechanism of the thermal reaction had been studied using three derivatives, Ia (R = H), Ib (R = $i$-$C_3H_7$), and Ic (R = $C_6H_5$), and a possible mechanism was proposed for the thermal rearrangement of I to II. When Ia, Ib, or Ic was heated in a sealed tube under the conditions shown in Table I, the 3-methoxy isomer IIa,

Table I. Reaction Conditions of the Pyrolysis of I and Yields of the Products (II and III)

| | | Reaction conditions | | | Yield of products, % | |
|---|---|---|---|---|---|---|
| Compd | R | Temp, °C | Solvent | Time, min | II | III |
| Ia | H | 189 | Chloroform | 60 | 56.0 | 31.2 |
| Ib | $i$-$C_3H_7$ | 191 | Chloroform | 60 | 68.0 | 14.7 |
| Ic | $C_6H_5$ | 189 | Methanol | 150 | 72.0 | 14.5 |

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(1) Organic Thermal Reactions. X. Preceding paper in this series: T. Fukunaga, T. Mukai, Y. Akasaki, and R. Suzuki, *Tetrahedron Lett.*, 2975 (1970).

(2) (a) O. L. Chapman, "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience, New York, N. Y., 1963, p 323; D. J. Pasto, "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 155; (b) T. Miyashi, M. Nitta, and T. Mukai, *Tetrahedron Lett.*, 3433 (1967).

(3) (a) T. Mukai, T. Miyashi, and M. C. Woods, *ibid.*, 433 (1967); (b) T. Mukai and T. Shishido, *J. Org. Chem.*, **32**, 2744 (1967).

(4) W. G. Dauben, K. Koch, O. L. Chapman, and S. L. Smith, *J. Amer. Chem. Soc.*, **83**, 1768 (1961); W. G. Dauben, K. Koch, S. L. Smith, and O. L. Chapman, *ibid.*, **85**, 2616 (1963).

(5) (a) O. L. Chapman and J. D. Lassila, *ibid.*, **90**, 2449 (1968); (b) O. L. Chapman, M. Kane, J. D. Lassila, R. L. Loeschen, and H. E. Wright, *ibid.*, **91**, 6856 (1969); (c) A. S. Kende, Z. Goldschmidt, and P. T. Izzo, *ibid.*, **91**, 6858 (1969).

(6) T. Mukai and T. Miyashi, *Tetrahedron*, **23**, 1613 (1967).

(7) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(8) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **87**, 1623 (1965).

(9) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(10) Irradiation of some tropolone methyl ethers afforded, however, 3-methoxy derivatives as an initial photoproduct, *cf.* ref 2b, 3, and 6.

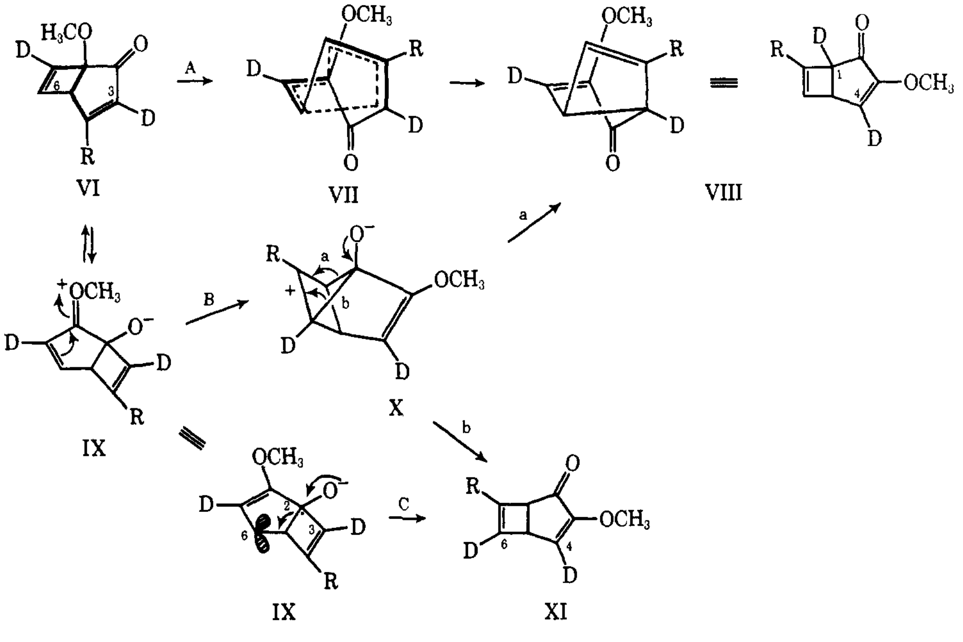
(11) J. P. Malrieu, *Photochem. Photobiol.*, **5**, 301 (1966).

**Table II.** Nuclear Magnetic Resonance Spectra[a]

| Compd | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ |
|---|---|---|---|---|---|---|---|
| Ia | 6.74<br>($OCH_3$) | | 4.33 (d)<br>$J_{34} = 6.0$ | 2.75 (q)<br>$J_{45} = 2.0$ | 6.40 | 3.68<br>$J_{67} = 4.0$ | 3.90 |
| Ib | 6.62<br>($OCH_3$) | | 4.18 (d)<br>$J^* = 1.8$ | 8.80 (d)<br>($CH_3$) | 6.17 (d)<br>(broad) | 3.19 (q)<br>$J_{56} = 1.2$ | 3.64 (q)<br>$J_{67} = 3.0$ |
| Ic | 6.53<br>($OCH_3$) | | 3.53 | 2.20∼<br>2.60 (Ph) | 5.78 (t)<br>$J_{56} = 1.0$ | 3.16 (q)<br>$J_{67} = 2.4$ | 3.56 (q)<br>$J_{57} = 1.0$ |
| IIa | 6.16 (m)<br>$J_{17} = 1.8$ | | 6.32<br>($OCH_3$) | 3.57 (d)<br>$J_{45} = 3.2$ | 6.55 (m) | 3.40 (q)<br>$J_{56} = 1.0$ | 3.56 (q)<br>$J_{67} = 3.0$ |
| IIb | 6.49 (m) | | 6.33<br>($OCH_3$) | 3.57 (d)<br>(broad)<br>$J_{45} = 3.4$ | 6.49 (m) | 3.85 (d)<br>(broad)<br>$J^* = 1.4$ | 9.03 (d)<br>8.91 (d)<br>($CH_3$) |
| IIc | 6.13 (q).<br>$J_{16} = 1.0$ | | 6.38<br>($OCH_3$) | 3.58 (d)<br>$J_{45} = 3.6$ | 6.32 (m)<br>$J_{15} = 3.6$ | 3.36 (q)<br>$J_{56} = 1.2$ | 2.30∼<br>2.80 (Ph) |
| VI | 6.62<br>($OCH_3$) | | D | 8.80<br>($CH_3$) | 6.17 (d)<br>$J_{56} = 1.2$ | 3.19 (d) | D |
| VIII | D | | 6.33<br>($OCH_3$) | D | 6.49<br>(broad) | 3.85 (q)<br>$J_{56} = 1.0$<br>$J^* = 1.4$ | 9.30 (d)<br>8.91 (d)<br>($CH_3$) |
| XII | | 6.18<br>($OCH_3$) | D | 3.11 (d)<br>$J_{45} = 11.5$ | 3.42 (d) | 8.80 (d)<br>($CH_3$) | D |

[a] All spectra were measured on a Varian A-60 in $CDCl_3$ containing TMS as internal reference. Chemical shifts are given as $\tau$ values and coupling constants (hertz) are assumed to be approximately equal to the splittings: d = doublet, t = triplet, q = quartet, m = multiplet, $J^*$ = coupling constant between isopropyl methine and ring proton. D indicates deuterium situated.

**Scheme II**



R = $i$-$C_3H_7$

IIb, or IIc was isolated accompanied by the corresponding tropolone methyl ether (IIIa, IIIb, or IIIc) in the yield shown. Progress of the reaction could be followed by vapor phase chromatography and nmr spectroscopy. The structures of the products (IIa, IIb, and IIc) could be determined from their nmr spectra (see Table II) and ir and uv spectra (see Experimental Section).

In contrast to the facile rearrangement of the 1-methoxy derivatives I, the 3-methoxybicyclo[3.2.0]-heptadienones (IIa, IIb, and IIc) obtained here were unchanged when heated further at the reaction temperature, whereas above 230° IIa, above 250° IIb, and above 400° IIc decomposed to IIIa, IIIb, and IIIc with low conversion without the reverse rearrangement to Ia, Ib, and Ic. In addition, although being stable even at 250°, the same trend has been observed in the pyrolyses of 7-methoxy-4-phenylbicyclo[3.2.0]heptadienone (IVc) and the 7-methoxy-3-phenyl isomer (V)[12] which possess no methoxy group at the $C_1$ position. Thus it should be noted from these facts that the thermal rearrangement of I to II proceeds irreversibly and the existence of the methoxy group at the $C_3$ or $C_7$ position has no effect on the rearrangement. Furthermore, the results in Table I suggest that substitution of the $C_4$ hydrogen by a phenyl or an isopropyl group results in an increase in the formation of the rearranged product II, although the effect is not so large as to decide the reaction path. On the basis of these facts, we would like to propose tenta-

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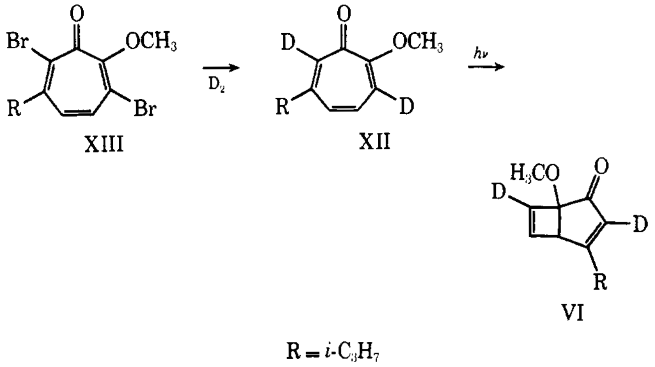
[12] T. Miyashi and T. Mukai, unpublished results. 7-Methoxy-3-phenylbicyclo[3.2.0]hepta-3,6-dien-2-one (V) was obtained in good yield when 2-methoxy-7-phenyltropone was irradiated in methanol.

tively three reaction paths shown in Scheme II for the rearrangement of I to II. In order to make later discussion easier, 3,7-dideuterio-4-isopropyl-1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (VI) was picked as a starting material in Scheme II.

Path A is the concerted Cope type rearrangement[13] *via* a twisted transition state such as VII in which case the product should be only the 1,4-dideuterio-7-isopropyl-3-methoxy derivative VIII. On the other hand, paths B and C are stepwise *via* the dipolar (or radical) intermediate IX which is formed by an acyloin-type rearrangement of VI. In path B, a bond formation between the $C_3$ and $C_6$ position provides a symmetrical intermediate X, which should afford the 1,4-dideuterio compound VIII and the 4,6-dideuterio compound XI in the same ratio, *i.e.*, 50% of each, by cleavage of the a or b bond of X. The integrated nmr absorption for olefinic, methine on ring, and methoxyl protons in the labeled 3-methoxy compound obtained by path B is expected to be a 1:3:6 ratio. This path is supported by the effects of $C_4$-substituents on I (Table I), because the stabilization of the intermediate X could be expected from the substituent effect. In path C, as shown in formula IX, 1,3-migration of the $C_2$–$C_3$ bond to the vacant p orbital at the $C_6$ position, which is located almost parallel to the $C_2$–$C_3$ bond, takes place to lead to the formation of only the 4,6-dideuterio compound XI. In order to determine the real reaction mechanism, the thermal reaction of the 3,7-dideuterio derivative VI was carried out. As shown in Scheme III, VI could be synthesized by irradiation of 3,7-dideuterio-6-isopropyl-2-methoxytropone (XII) which was obtained from the corresponding 3,7-dibromotropone (XIII) by catalytic reduction with deuterium.[14] The integrated nmr absorptions of VI for olefinic, methine, and methoxy protons were in a 1:1:3 ratio as expected. After heating neat VI at 190°, the ratio of these protons in the integrated nmr spectrum of the separated 3-methoxybicyclo compound was found to be 1:1:3. This indicates that the reaction mixture contains only the 1,4-dideuterio compound VIII, and no 4,6-dideuterio compound XI at all. 2-Methoxytropone XII was obtained as a minor product. The structure of the deuterated compounds VI and VIII was confirmed using mass and nmr spectroscopy (Table II). This result establishes that the thermal rearrangement of I to II proceeds through path A, and consequently paths B and C can be discarded.

**Scheme III**



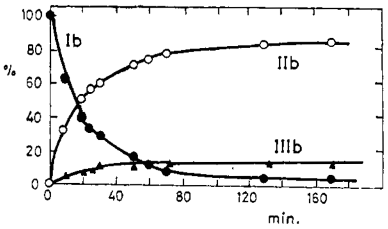
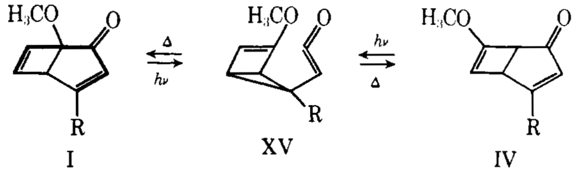


Figure 1. Depletion of Ib and formation of IIb and IIIb during heating of Ib.

There exist two diallylic systems fixed rigidly in the bicyclo[3.2.0]heptadienone system, *i.e.*, a transoid $C_3{=}C_4C_5C_1C_7{=}C_6$ and a cisoid $C_4{=}C_3C_2C_1C_7{=}C_6$. Path A was considered to be a Cope rearrangement arising from the transoid diallylic system. On the other hand, if the Cope rearrangement takes place in the cisoid system, 7-methoxybicyclo compounds IV would be formed *via* bicyclo[2.1.0]pentenylketenes (XV).[5] However, neither IVc nor methyl ester XIV was formed by the thermal reaction of Ic carried out in a methanolic solution. The transformation of I to IV, as mentioned already, was observed by Chapman and Lassila[5a] in the case of the photochemical reaction of Ia. The contrast between the thermal and photochemical transformation of I is intriguing on comparison of the reactions of ground states with those of excited states.



A kinetic study of the rearrangement (I → II) was carried out in the temperature range from 158 to 183°[15] to establish if it is a concerted multicenter reaction. As a typical example, the depletion of Ib and the formation of IIb and IIIb are shown in Figure 1, when neat Ib was heated at 187° in a sealed tube. The figure was drawn by measuring the proton area of the methoxyl signal of Ib, IIb, and IIIb in their nmr spectra. The plots of the logarithm of the concentration of unchanged Ib against the reaction time were linear. At each temperature, 158, 170, and 183°, the mean value of a ratio of the formation of IIb to IIIb was found to be 4.6, 4.9, and 4.7, respectively. If these ratios can be considered as almost equal within the experimental error, then the value of 4.7 is assigned for the ratio of the rate constants of the two reactions, $k_1/k_2$, independent of the reaction temperature. Therefore, the third reaction from IIb to IIIb ($k_3$) should be negligible. This implies that the two reactions ($k_1$ and $k_2$) take place competitively *via* essentially the same transition state. The rate constants thus obtained are shown in Table III. An Arrhenius plot of the data shown in Table III provides an

$$\begin{tikzcd}
\mathrm{Ib} \arrow[rr, "k_1"] \arrow[dr, "k_2"'] & & \mathrm{IIb} \arrow[dl, "\cancel{k_3}"] \\
& \mathrm{IIIb} &
\end{tikzcd}$$

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(13) S. J. Rhoads, "Molecular Rearrangement," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Part 1, p 684.

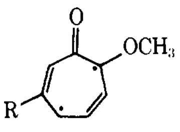
(14) S. Ito, J. Tsunetsugu, T. Kanno, H. Sugiyama, and H. Takeshita, *Tetrahedron Lett.*, 3659 (1965).

(15) This temperature range was selected in order to avoid an unessential pyrolysis of IIb to IIIb and simplify the reaction scheme.

Table III. The First-Order Rate Constants ($\text{Sec}^{-1}$)

| Temp, °C | $10^5(k_1 + k_2)$ | $10^5 k_1$ | $10^5 k_2$ |
|---|---|---|---|
| 158 | 5.50 | 4.52 | 0.982 |
| 170 | 15.8 | 13.1 | 2.68 |
| 183 | 47.6 | 39.1 | 8.35 |

excellent straight line, from which the activation energy and a preexponential factor for the overall reaction and each step was calculated as follows: $k_1 + k_2 = 10^{12.74} \exp(-33{,}500/RT)\ \text{sec}^{-1}$, $k_1 = 10^{12.65} \exp(-33{,}500/RT)\ \text{sec}^{-1}$, $k_2 = 10^{11.98} \exp(-33{,}500/RT)\ \text{sec}^{-1}$. The preexponential factors obtained, $10^{12.65}$ and $10^{11.98}$, correspond to a negative entropy of activation, *i.e.*, $-6.0$ and $-9.1$ eu (at 170°, respectively). They are considerably smaller than that for the thermal isomerization of cyclobutene to butadiene ($A = 10^{13.26}$)[16] and for the isomerization of bicyclo[3.2.0]heptadiene to cycloheptatriene ($A = 10^{14.0}$).[17] These values suggest that the transition state for the rearrangement of Ib to IIb and IIIb requires more steric rigidity than those for the thermal ring opening of cyclobutene and bicyclo[3.2.0]heptadiene. Thus the favorable transition state should be a rigid one such as VII, but not a diradical such as XVI.



XVI, R = *i*-$C_3H_7$

On the other hand, it should be noted that the preexponential factor for the rearrangement *via* VII is rather large as compared with the value for the normal Cope rearrangement of usual noncyclic hexa-1,5-dienes.[18] This may be ascribed to the fact that structural change between the reactant VI and the transition state VII is smaller than that in the case of the Cope rearrangement of the noncyclic hexa-1,5-dienes. Furthermore, the preexponential factor ($A = 10^{12.9}$) for the degenerate Cope rearrangement of bullvalene,[19] in which case there is almost no structural change between the reactant and the transition state, is a little larger than the value obtained for the rearrangement of Ib leading to IIb. Therefore, the preexponential factor, $10^{12.62}$, is reasonable for the Cope rearrangement of a cyclic hexa-1,5-diene such as VI.

The activation energy for the rearrangement, 33.5 kcal/mol, is intermediate between that of the Cope rearrangement of aliphatic hexa-1,5-dienes[18] and that of the vinyl allyl ether rearrangement.[18] Although this value seems to be rather high as compared with the activation energy of the multicyclic Cope rearrangement of bullvalene (12.8 kcal/mol)[19] and *cis*-1,2-divinylcyclobutane (22.4 kcal/mol),[20] whose stereochemistry is especially suitable for the transition state, this is not necessarily imcompatible with the concerted mechanism. This can be attributed to the fact that the diallylic system of I is geometrically more disadvantageously transoid and the resulting transition state is an unusual twisted one.

The irreversibility of the isomerization, *i.e.*, II $\not\rightarrow$ I, and the role of the methoxy group in the Cope rearrangement is of interest. In the case of thermal isomerization of the cyclobutene system, Frey pointed out the reducing and enhancing effects on an activation energy by substituents located in the ring.[21] Because the same trend of the substitution effect should exist in the bicyclo[3.2.0]heptadienone system, a difference of activation energy (6 kcal/mol) between Ib and bicyclo[3.2.0]hepta-3,6-diene (39.5 kcal/mol)[17] would result mainly from the total reducing effect by the methoxy group located at the $C_1$ position and by the carbonyl group at the $C_2$ position. It is, however, difficult to estimate the stabilization effect of the $C_2$-carbonyl group, because of no available data. Since only the $C_1$-methoxy group is strongly responsible for the facile Cope rearrangement among the methoxy groups located at the $C_1$, $C_3$, and $C_7$ positions, the irreversibility of the rearrangement might be explained by reducing effect on an activation energy with this methoxy group. This seems to be the steric repulsion between the $C_1$ methoxy group and the $C_5$ hydrogen atom in Ib, which brings about a twisting of the cyclobutene in the transition state VII to assist a simultaneous bond formation between the $C_3$ and $C_6$ positions as well as a stretching of the $C_1$–$C_5$ bond. As a result an unusual Cope rearrangement of the bicyclo[3.2.0]heptadienone system takes place in spite of the geometrical disadvantage of the transoid diallylic system.

The kinetic data obtained above, *i.e.*, the first-order kinetics, a reasonably low activation energy, and a negative entropy change, in addition to the chemical evidence using the labeled compound should characterize the stereospecific rearrangement of I to II as the concerted Cope rearrangement *via* the cyclic twisted transition state VII.

The stereochemistry of the transition state VII must be discussed on the basis of the molecular orbital considerations. According to the Woodward–Hoffmann rule, [3,3]sigmatropic reactions like Cope and Claisen rearrangements are allowed to occur in both suprafacial–suprafacial and antarafacial–antarafacial manners.[22] However, a large number of experimental studies[23] as well as of theoretical studies[24] have supported that this kind of [3,3]sigmatropic rearrangement could occur *via* only a chairlike transition state, but not *via* a boatlike transition state, although both are brought about by the suprafacial–suprafacial process. On the other hand, the antarafacial–antarafacial [3,3]sigmatropic rearrangement has been considered not to occur, because the transition state has much strain. However, Hoffmann[25] and Woodward[26] pointed out that the

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(16) W. Cooper and W. D. Walters, *J. Amer. Chem. Soc.*, **80**, 4220 (1958); W. P. Hauser and W. D. Walters, *J. Phys. Chem.*, **67**, 1328 (1963).

(17) M. R. Willcott and E. Goerland, *Tetrahedron Lett.*, 6341 (1966)

(18) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969), and references therein cited.

(19) A. Allerhand and H. S. Gutowsky, *J. Amer. Chem. Soc.*, **87**, 4092 (1965).

(20) G. S. Hammond and C. D. DeBoer, *ibid.*, **86**, 899 (1964).

(21) H. M. Frey, "Advances in Physical Organic Chemistry," Vol. 4, V. Gold, Ed., Academic Press, New York, N. Y., 1966, p 185, and references cited therein.

(22) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 828 (1969), and see also ref 7.

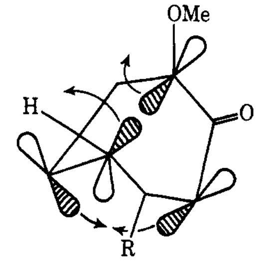
(23) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962); *Angew. Chem., Int. Ed. Engl.*, **2**, 115 (1963); A. Jefferson and F. Scheinmann, *Quart. Rev., Chem. Soc.*, **22**, 391 (1968).

(24) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 4389 (1965).

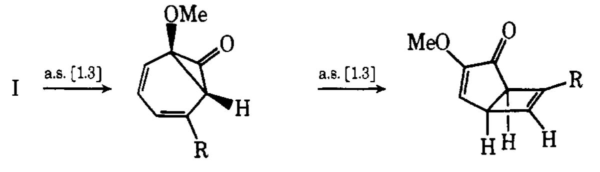
(25) Private communication, March 4, 1968.

(26) R. B. Woodward, plenary lecture presented at the IUPAC Symposium on Valence Isomerization, Sept 1968, at Karlsruhe, Germany.

stereospecific rearrangement found by us would be the first example of the antarafacial–antarafacial Cope rearrangement. Later Schmid and his coworkers discussed it in more detail in their report.[27] Since supports for the concerted process could be obtained as mentioned above, we would stand for the interpretation[28] suggested by Woodward and Hoffmann. The molecular orbitals of the transition state and the manner of the bond formation and the bond fission can be depicted in XVII which corresponds to a twisted boatlike form.



XVII

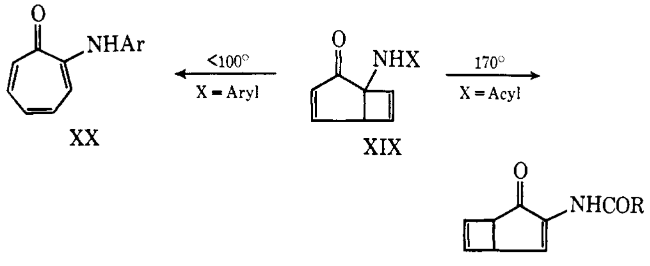


XVIII

II

In addition to the antarafacial–antarafacial [3,3]-sigmatropic process, Schmid and his coworkers proposed another mechanism, which is composed of two subsequent antarafacial–suprafacial [1,3]sigmatropic processes.[27] According to their proposition, a norcaradienone XVIII should be considered as an intermediate. Such valence isomers of tropones are expected to give readily the corresponding tropones or sometimes decarbonylated products.[29] However, this seemed not to be the case in the thermolysis of 1-methoxybicyclo[3.2.0]heptadien-2-ones, when it was carried out at temperatures lower than 200°. Thus we would prefer the [3,3]sigmatropic process to the twofold process of the [1,3]sigmatropic rearrangement, although it is difficult to rule out the latter mechanism based on the concrete evidence.

Furthermore, Baldwin and Kaplan suggested the possibility of other mechanisms for this rearrangement from I to II based on their study in which a degenerate trans–trans Cope rearrangement could not be confirmed in a bicyclo[3.3.0]octa-2,6-diene system.[30] We would emphasize that even derivatives similar to I in the bicyclo[3.2.0]heptadienone system did not always undergo the Cope rearrangement. The essential conditions for the antarafacial–antarafacial Cope rearrangement are not only the moderate molecular strains to make the orbital overlap and the bond cleavage easy in the transition state, but also the existence of the methoxy group at the $C_1$ position and of the carbonyl group at the $C_2$ position which may stabilize the transition state electronically or geometrically. Concerning these points, we should cite the following fact found by Kimura.[31] Upon heating at temperatures lower than 100°, 1-arylaminobicyclo[3.2.0]hepta-3,6-dien-2-one derivatives (XIX) which are isoelectronic with I are readily transformed into the corresponding 2-arylaminotropones (XX), whereas 1-acylamino derivatives around 170° rearranged to 3-acylaminobicyclo[3.2.0]heptadienones (XXI) in good yield, respectively.



XX

XIX

XXI

These are striking examples to show the electronic or geometric effect of the substituent located at the $C_1$ position in the thermal reactions of the bicyclo[3.2.0]heptadienone system.

## Experimental Section[32]

**Preparation of 2-Methoxytropone Derivatives. (a) 6-Isopropyl Derivative (IIIb).**[33] This material was prepared in 80% yield from 3-iodo-6-isopropyl-2-methoxytropone by catalytic reduction in methanol over 5% palladium on carbon: bp 139–140° (2 mm); $\nu_{max}^{liq}$ 1628, 1593, 792, and 676 $cm^{-1}$.

*Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.22; H, 7.76. The picrate of IIIb was obtained as yellow needles by treatment with picric acid in methanol, mp 118°.

*Anal.* Calcd for $C_{17}H_{17}N_3O_9$: C, 50.12; H, 4.21; N, 10.32. Found: C, 50.26; H, 4.36; N, 10.41.

(b) **6-Phenyl Derivative (IIIc).** This material was prepared in 50% yield by methylation of 4-phenyltropolone[34] with the ethereal solution of diazomethane: mp 115°; $\nu_{max}^{KBr}$ 1613, 1592, 780, and 758 $cm^{-1}$; $\lambda_{max}^{MeOH}$ 276, 355, and 370 nm ($\log \epsilon = 4.33$, 3.66, and 3.50).

*Anal.* Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.37; H, 5.56.

**Preparation of 1-Methoxybicyclo[3.2.0]hepta-3,6-dien-2-one Derivatives (I).** (a) **Ia.** This material was prepared by irradiation of 2-methoxytropone (**IIIa**) according to the procedure of Chapman and Dauben.[4]

(b) **4-Isopropyl Derivative (Ib).** A solution of 3 g (17 mmol) of IIIb in 500 ml of cyclohexane was irradiated externally in a Pyrex vessel with a 400-W high-pressure mercury lamp (Toshiba H-400P) under nitrogen atmosphere for 12 hr. After evaporation of the solvent, a residual oil was dissolved in benzene and chromatographed on a column containing 150 g of silica gel. Evaporation of the benzene–ether (25:1) fractions and distillation of the residue obtained here afforded 120 mg (4%) of IIb as a yellow oil: bp 150–155° (bath temperature) (1 mm); $\nu_{max}^{liq}$ 1705, 1608, 795, and 723 $cm^{-1}$; $\lambda_{max}^{MeOH}$ 240 and 265 nm ($\log \epsilon = 3.78$ and 3.78); nmr spectra, see Table II.

*Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.26; H, 7.53.

Distillation of the oil obtained from the benzene–ether (20:1) fractions gave 735 mg of Ib (25%) as a yellow oil: bp 120–125° (bath temperature) (1 mm); $\nu_{max}^{liq}$ 1695, 1595, 750, 712, and 685 $cm^{-1}$; $\lambda_{max}^{MeOH}$ 218 and 244 nm ($\log \epsilon = 4.10$ and 3.94).

*Anal.* Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.34; H, 7.95.

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The same treatment of the benzene–ether (15:1) fractions gave 760 mg (25%) of methyl 2-isopropyl-4-keto-2-cyclopentene-1-acetate (XXII) as a yellow oil: bp 150–155° (bath temperature) (1 mm); $\nu_{max}^{liq}$ 1730, 1695, and 1605 cm$^{-1}$; nmr spectrum (in $CDCl_3$) $\tau$ 4.05 (triplet, $J$ = 1.5 Hz, $C_3$-$H$), 8.85 (doublet, $J$ = 7.0 Hz) and 8.90 (doublet, $J$ = 7.0 Hz) ($CH_3$ of isopropyl group), 7.87 (quartet, $J$ = 19.0 and 2.6 Hz) and 7.30 (quartet, $J$ = 19.0 and 6.0 Hz) ($CH_2$ at C-5), 7.74 (quartet, $J$ = 16.0 and 9.5 Hz), and 7.18 (quartet, $J$ = 16.0 and 4.5 Hz) ($CH_2$ at C-6), 6.34 (singlet, $OCH_3$ of ester).

*Anal.* Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.54; H, 8.29.

The ether fractions gave 710 mg (24%) of a yellow oil which was proved to be identical with the starting material (IIIb).

(c) **4-Phenyl Derivative (Ic).** The irradiation of a solution of 3 g (14 mmol) of IIIc in 300 ml of methanol was carried out as described above for the preparation of Ib. A crude photoproduct (3 g) was dissolved in benzene–petroleum ether (1:1) and chromatographed on a column containing 100 g of neutral alumina (activity III). The benzene–petroleum ether (1:1) fractions afforded 620 mg of pale yellow crystals, which on fractional recrystallization from ethanol gave two kinds of crystals. The sparingly soluble portion (110 mg, 4%) was yellow prisms, mp 172°, which was a photodimer of IIIc.[3a] The compound had $\nu_{max}^{KBr}$ 1681 cm$^{-1}$; $\lambda_{max}^{MeOH}$ 320 nm (log $\epsilon$ = 4.20); mol wt (osmometry), 432.

*Anal.* Calcd for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70. Found: C, 79.21; H, 5.75.

The easily soluble portion (400 mg, 13%) was colorless needles, mp 128°, whose structure was proved to be IIc from the following data: $\nu_{max}^{KBr}$ 1695 cm$^{-1}$; $\lambda_{max}^{MeOH}$ 250 nm (log $\epsilon$ = 4.50); nmr spectrum, see Table II.

*Anal.* Calcd for $C_{14}H_{12}O_4$: C, 79.22; H, 5.70. Found: C, 79.32; H, 5.68.

The benzene fractions gave 930 mg of a reddish yellow oil and the benzene–ether (9:1) fractions afforded 700 mg (23%) of the starting material (IIIc). The former portion (930 mg) was dissolved in benzene and chromatographed again on a column containing 50 g of silica gel. The benzene–ether (20:1) fractions afforded 530 mg of yellow crystals, mp 51–55°, which on recrystallization from cyclohexane gave 460 mg (20%) of Ic as yellow needles: mp 63°; $\nu_{max}^{KBr}$ 1692 cm$^{-1}$; $\lambda_{max}^{MeOH}$ 225 and 300 nm (log $\epsilon$ = 4.20 and 4.31); nmr spectrum, see Table II.

*Anal.* Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.22; H, 5.77.

The benzene–ether (15:1) fractions gave 280 mg of colorless crystals, mp 71–73°, which on recrystallization from cyclohexane afforded 230 mg (10%) of methyl 4-keto-2-phenyl-2-cyclopentene-1-acetate (XXIII) as colorless crystals: mp 76–77°; $\nu_{max}^{KBr}$ 1724 and 1681 cm$^{-1}$; $\lambda_{max}^{MeOH}$ 285 nm (log $\epsilon$ = 4.59); nmr spectrum (in $CDCl_3$) $\tau$ 3.46 (triplet, $J$ = 1.8 Hz, $C_3$-$H$), 6.70–7.60 (complex multiplets), 6.31 (singlet, $OCH_3$ of ester).

*Anal.* Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.21; H, 5.97.

**Thermal Isomerization of Bicyclo[3.2.0]hepta-3,6-dien-2-one Derivatives.** (a) **1-Methoxy Derivative (Ia).** A solution of 350 mg (2.6 mmol) of Ia in 1.5 ml of chloroform was heated at 189° for 60 min in a sealed tube under nitrogen atmosphere. After chloroform had been evaporated, the residue was distilled at 110–120° (bath temperature) *in vacuo* (1 mm) to give 326 mg of a yellow oil. Vapor phase chromatographic analysis showed the distillate was composed of two compounds and one of them was identified as IIIa by its retention time. The distillate could be separated into two fractions by means of preparative scale thin layer chromatography using silica gel and benzene–ether (10:1) used as a developing solvent. Distillation of the extract from the lower fraction gave 109.2 mg (31.2%) of IIIa as a yellow oil. By the same manner the upper fraction afforded 196 mg (56%) of IIa as a colorless oil: bp 85–95° (bath temperature) (1 mm); $\nu_{max}^{liq}$ 1706 cm$^{-1}$; $\lambda_{max}^{MeOH}$ 226 and 265 nm (log $\epsilon$ = 3.72 and 3.85); nmr spectrum, see Table II.

*Anal.* Calcd for $C_8H_8O_2$: C, 70.57; H, 5.92. Found: C, 70.69; H, 5.87.

(b) **4-Isopropyl-1-methoxy (Ib) and 1-Methoxy-4-phenyl Derivatives (Ic).** The thermal isomerization of Ib and Ic and separation of the pyrolysate were carried out essentially in the same manner described in (a). Thus the products shown in Table I could be obtained in the yields as shown there.

(c) **3-Methoxy (IIa), 6-Isopropyl-3-methoxy (IIb), and 3-Methoxy-6-phenyl Derivatives (IIc).** When each compound IIa, IIb, or IIc as neat or in chloroform or methanol solution was heated at 190–200° for 30–60 min under nitrogen atmosphere in a sealed tube, no reaction was observed and each compound IIa, IIb, or IIc was recovered quantitatively. However, heating of IIa at 230° for 40 min or IIb at 250–260° for 50 min resulted in a partial decomposition and nmr spectroscopy showed that the products obtained were composed of 23.5% IIa and 16.5% IIIa or 65% IIb and 35% IIIb, respectively. On the other hand, when a solution of 200 mg (1 mmol) of IIc in 4 ml of benzene was pyrolyzed by passing through a vertical column (8 × 100 mm) packed with Pyrex helices preheated at 300°, IIc remained unchanged, but at 450°, a partial decomposition took place leading to the mixture of 33% IIIc and 50% IIc.

**3,7-Dideuterio-6-isopropyl-2-methoxytropone (XII).** A solution of 8.1 g (24 mmol) of 3,7-dibromo-6-isopropyl-2-methoxytropone[33] in 400 ml of anhydrous dioxane containing 15 ml of deuterium oxide was reduced with deuterium over 5% palladium on carbon in the presence of 4.72 g (58 mmol) of anhydrous sodium acetate at room temperature and ordinary pressure. During the reduction for 8 hr, 1.3 l. (58 mmol) of deuterium was absorbed. After the catalyst had been removed by filtration and the filtrate concentrated, the residual solution was diluted with water and extracted with chloroform. The extract was washed with water, dried on sodium sulfate, and concentrated *in vacuo* to give 4.3 g of an oil. The oil afforded 5.6 g of picrate in methanol, mp 118–119°, which showed no depression of melting point on admixture with picrate of IIIb. Passing a saturated chloroform solution of the picrate through a column containing 50 g of alumina (activity II), evaporation of the chloroform elution and distillation of the residual oil *in vacuo* afforded 2.2 g (49%) of XII as a pale yellow oil: bp 140–143° (2 mm); *m/e* 180 (M$^+$); $\nu_{max}^{liq}$ 1615, 1570, 827, and 747 cm$^{-1}$; nmr spectrum, see Table II.

**3,7-Dideuterio-4-isopropyl-1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (VI).** The irradiation of XII and the separation of the photoproducts were carried out essentially as described above for the preparation of Ib. Thus, 3.5 g (19.5 mmol) of XII afforded 748 mg (21%) of VI as a yellow oil, bp 120–123° (bath temperature) (1 mm) and 477 mg (13.6%) of methyl 3,5-dideuterio-2-isopropyl-4-keto-2-cyclopentene-1-acetate (XXIV) as a yellow oil, bp 150–155° (bath temperature ) (1 mm), with recovery of 484 mg (13.8%) of the starting material (XII). An appreciable amount of VIII could not be isolated. The spectral data of the photoproducts are as follows: VII, $\nu_{max}^{liq}$ 1700, 1580, 794, 725, and 698 cm$^{-1}$; *m/e* 180 (M$^+$); nmr spectrum, see Table II: XXIV, $\nu_{max}^{liq}$ 1730, 1695, and 1605 cm$^{-1}$; *m/e* 198 (M$^+$); the nmr spectrum is very similar to that of XXII except for signals of $C_3$-$H$ and $C_5$-$H$; $\tau$ 8.85 (doublet, $J$ = 7.0 Hz) and 8.90 (doublet, $J$ = 7.0 Hz) ($CH_3$ of isopropyl group), 7.74 (quartet, $J$ = 16.0 and 9.5 Hz), and 7.18 (quartet,

Table IV. Product Distribution from Nmr Analysis

| Reaction temp, °C | Reaction time, min | Concentration, % [Ib] | Concentration, % [IIb] | Concentration, % [IIIb] | [IIb]/[IIIb] |
|---|---|---|---|---|---|
| 183 | 10 | 68.8 | 25.6 | 5.6 | 4.6 |
| | 15 | 62.4 | 30.9 | 6.7 | 4.6 |
| | 20 | 47.0 | 43.2 | 9.8 | 4.4 |
| | 30 | 34.0 | 54.5 | 11.5 | 4.7 |
| | 35 | 32.5 | 55.2 | 12.3 | 4.5 |
| | 40 | 29.4 | 58.0 | 12.6 | 4.6 |
| | 50 | 21.4 | 65.0 | 13.6 | 4.8 |
| | 55 | 20.8 | 65.7 | 13.5 | 4.9 |
| | 60 | 20.0 | 66.3 | 13.7 | 4.9 |
| 170 | 40 | 65.0 | 28.8 | 6.2 | 4.7 |
| | 70 | 51.0 | 40.9 | 8.1 | 5.0 |
| | 130 | 28.7 | 59.0 | 12.3 | 4.8 |
| | 160 | 21.8 | 65.0 | 13.2 | 4.9 |
| | 190 | 16.4 | 69.5 | 14.1 | 4.9 |
| | 220 | 13.1 | 72.0 | 14.9 | 4.8 |
| | 253 | 8.5 | 75.5 | 15.9 | 4.7 |
| 158 | 100 | 74.0 | 21.3 | 4.7 | 4.6 |
| | 141 | 63.7 | 29.7 | 6.6 | 4.5 |
| | 180 | 55.2 | 36.4 | 8.4 | 4.4 |
| | 230 | 43.7 | 46.4 | 9.8 | 4.8 |
| | 260 | 42.4 | 47.5 | 10.1 | 4.7 |
| | 310 | 36.2 | 53.0 | 10.8 | 4.9 |
| | 325 | 34.2 | 54.3 | 11.5 | 4.7 |
| | 340 | 29.7 | 59.0 | 11.3 | 5.2 |

$J$ = 16.0 and 4.5 Hz) ($CH_2$ at $C_6$), 6.34 (singlet, $OCH_3$ of ester), 7.87 (broad doublet with small intensity, $J$ = 2.6 Hz, $CH$ at $C_5$).

**Thermal Isomerization of 3,7-Dideuterio-4-isopropyl-1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (VI).** After 200 mg (1.1 mmol) of neat VI was heated at 180° in a sealed tube under nitrogen atmosphere for 135 min, the pyrolysate was dissolved in benzene and the solution was chromatographed on a column containing 10 g of silica gel. The benzene-ether (25:1) fractions afforded 101 mg (51%) of VIII as a yellow oil: bp 95–100° (bath temperature) (1 mm); $\nu_{max}^{liq}$ 1705, 1592, 725, and 685 cm$^{-1}$; $m/e$ 180 ($M^+$); nmr spectrum, see Table II. The ether fractions gave 21 mg (11%) of XII.

**Reaction Rate of the Cope Rearrangement of 4-Isopropyl-1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (Ib).** The material used for this kinetic study was purified by redistillation of the ordinary photoproduct (Ib) described previously using a spinning band column. Vapor phase chromatographic analysis of the distillate, bp 79–80° (1 mm), revealed no evidence of contamination of Ib. The reaction vessel was made of Pyrex tubing, 5 mm o.d. and 60 mm in length, with a thick sphere 6 mm in diameter at the bottom. About 30 mg of the material was introduced into the vessel and it was sealed under a nitrogen stream. Eight reaction tubes and a thermometer were fitted in the necks of a 500-ml flask with nine necks and a reflux condenser, which contained a suitable solvent. Eight vessels were heated at the same time by vapor of the boiling solvent such as cyclohexanol (158°), $p$-dichlorobenzene (170°), or dimethyl sulfoxide (183°). During heating, each vessel was withdrawn from the flask periodically and cooled quickly with ice and a salt bath to quench the reaction. The reaction material was diluted with 0.3 ml of deuteriochloroform and then the nmr spectrum of the solution was measured by a Varian A-60 spectrometer (sweep time 500 sec, sweep width 100 cps). The concentration ratios of the isomerized products IIb and IIIb and of Ib were calculated from the proton area of the signal ascribed to the methoxy group of the corresponding compounds. The results obtained were shown in Table IV.

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# The Michael Reaction in Nonalkaline Media. V. Effect of Structure on the Rate and Mechanism of Addition of 1,1-Dinitrocarbanions to Methyl Acrylate

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**Abstract:** The kinetics of the addition of a series of substituted 1,1-dinitromethide ions to methyl acrylate have been studied in 50% dioxane and in water. The requirement for acid catalysis in these Michael additions has been defined as a lowering of the free energy of the transition state for the reversal of the initially formed carbanion $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$. This can be accomplished by a substituent R which is able to delocalize negative charge by a resonance interaction. For borderline cases, the rate of protonation of the carbanion $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$ may be a deciding factor in effecting a change from an acid catalyzed to an uncatalyzed reaction. A comparison of the specific rate and activation parameters for fluorodinitromethide ion with alkyl, chloro, and hydrogen dinitromethide ions shows that the 2000-fold increase in rate for R = F is due to a 5 kcal mol$^{-1}$ decrease in $\Delta H^*$. This enhanced nucleophilicity is attributed to a destabilization of an sp$^2$-hybridized carbon by an $\alpha$-fluorine substituent.

The addition of substituted 1,1-dinitrocarbanions to acrylic systems, in particular methyl acrylate, is well documented in the literature.$^{1-4}$ Results of previous kinetic studies of Michael additions to acrylic systems$^{5-9}$ suggest the following mechanism for the addition of 1,1-dinitrocarbanions to methyl acrylate. HA is any acid and $A^-$ its conjugate base. When one compares the results obtained in similar buffer solutions with trinitromethane,$^{5-8}$ R = $NO_2$ ($pK \approx 0^{10}$), and 1,1-dinitroethane,$^9$ R = $CH_3$ ($pK = 5.1^{10}$), a change

$$RC(NO_2)_2^- + CH_2{=}CHCO_2CH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{An^-}{RC(NO_2)_2CH_2{}^-CHCO_2CH_3} \quad (1)$$

$$An^- + HA \underset{k_{A^-}}{\overset{k_{HA}}{\rightleftharpoons}} RC(NO_2)_2CH_2CH_2CO_2CH_3 + A^- \quad (2)$$

in the rate-determining step of the reaction is observed. With trinitromethane as the addend, the reaction is subject to general acid catalysis; protonation of the intermediate carbanion $An^-$ is rate determining.$^{11}$ However, with 1,1-dinitroethane as the addend,$^9$ no evidence was found for acid catalysis in phosphate, borate, or carbonate buffers.

To determine if changes in the basicity of the intermediate carbanion $An^-$ caused by varying the substituent R are *solely* responsible for the change in mechanism, we have measured the rates of addition of a

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(11) At high acidities, the rate of protonation is increased to the point where the formation of the intermediate carbanion becomes rate determining.$^{5,8}$