# The Stereochemistry of the Methylketene β-Lactone Dimer[1]

JOHN E. BALDWIN

*Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois*

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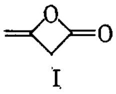
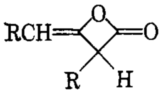
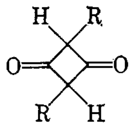
The stereochemistry of the methylketene β-lactone dimer has been deduced from dipole moment data. Carbon atoms 2 and 5 of the dimer are *trans*, as in formula VI. This assignment of stereochemistry has been confirmed by n.m.r. spectral comparisons between the methylketene β-lactone dimer and the intramolecular condensation product of tetramethylenediketene, 8-oxo-9-oxabicyclo[5.2.0]nonene-1.

Structure I for diketene is now generally accepted.[2] Aldoketenes (II) form both neutral dimers, having structures (III) analogous to that of diketene (I),[3-7] and acidic dimers that are derivatives (IV) of cyclobutane-1,3-dione.[8]


I

RCH═C═O
II


III

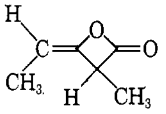

IV

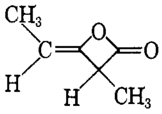
The stereochemistry about the *exo*-cyclic double bond in the neutral aldoketene dimers (III) has not been established. That there may be two neutral methylketene dimers[8] and that two geometrical isomers are possible for structure III[7] have been recognized for some time, but no one has isolated two geometrical isomers of an aldoketene β-lactone dimer or suggested the geometrical disposition of substituents about the *exo*-cyclic double bond in the dimers III that can be prepared. The neutral methylketene dimer has been the subject of an electron diffraction study,[9] but the analysis did not afford an assignment of stereochemistry. Chemical approaches to the geometry of these dimers are rendered difficult by the lability of the lactone ring toward cleavage, which usually leads to stereochemically uninformative products.

Investigation of the β-lactone dimers from methylketene and phenylketene by n.m.r. spectroscopy has shown that they are not mixtures of geometric isomers and probably have the same geometry.[10] No assignment of this stereochemistry, however, was possible.

## Calculations and Results

The experimental data which make recognition of the stereochemistry of the methylketene β-lactone dimer possible are the electric dipole moments of diketene and the neutral methylketene dimer, 3.23 and 3.30 D., respectively.[3] To facilitate calculations based on the two possible geometrical isomers of the methylketene β-lactone dimer, V and VI, the following assumptions are made: V and VI have the same skeletal geometry as diketene[11]; they are planar; both C–C–H angles at C-4 are 120°; the C–C–H angle at C-2 is 114°; the methyl group at C-4 has a dipole moment of 0.35 ± 0.1 D.[12]; the methyl group at C-2 has a moment of 0.03 ± 0.03 D.[12]; and the dipole moments of the dimers may be approximated by a vector sum of bond and molecular electric dipole moments.[13]


V


VI

Let the oxygen and carbon atoms of the carbonyl groups of I, V, and VI define the positive $x$-axis, the lactone oxygen be on the plus $y$-axis, and $\theta$ designate the orientation of the dipole moment of diketene in this coordinant system. While $\theta$ is unknown, it should be small and positive; the carbonyl group must be the dominant polar influence in diketene.

Simple trigonometry and the assumptions set forth above lead to the equations

$$(3.30)^2 = [3.23 \cos \theta_{\text{V}} + (0.35 \pm 0.1) \cos 42° + (0.03 \pm 0.03) \cos 57° \sin 13.5°]^2 + [3.23 \sin \theta_{\text{V}} + (0.35 \pm 0.1) \sin 42° + (0.03 \pm 0.03) \cos 57° \cos 13.5°]^2 + [(0.03 \pm 0.03) \sin 57°]^2$$

$$(3.30)^2 = [3.23 \cos \theta_{\text{VI}} + (0.35 \pm 0.1) \cos 78° + (0.03 \pm 0.03) \cos 57° \sin 13.5°]^2 + [3.23 \sin \theta_{\text{VI}} - (0.35 \pm 0.1) \sin 78° + (0.03 \pm 0.03) \cos 57° \cos 13.5°]^2 + [(0.03 \pm 0.03) \sin 57°]^2$$

which have the solutions $\theta_{\text{V}} = 127 \pm 9°$ and $322 \pm 5°$, and $\theta_{\text{VI}} = 3 \pm 6°$ and $203 \pm 6°$. Only the calculation based on structure VI gives a plausible value for the orientation of the dipole moment of diketene. This result is sufficiently insensitive to reasonable variations in the initial assumptions and parameters for the group moments of the two methyl groups in the methylketene β-lactone dimer that the conclusion seems secure: the neutral methylketene dimer has the stereochemistry of formula VI, and in all probability, the other known aldoketene β-lactone dimers have the same geometry.

Independent evidence to corroborate this deduction of stereochemistry was sought.

Suberyl dichloride may be converted to cycloheptanone, presumably through the intermediates, tetramethylenediketene (VII) and the β,γ-unsaturated β-lac-

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

[2] *Cf.*, V. V. Perekalin and T. A. Sokolva, *Usp. Khim.*, **25**, 1351 (1956).

[3] J. D. Roberts, R. Armstrong, R. F. Trimble, Jr., and M. Burg, *J. Am. Chem. Soc.*, **71**, 843 (1949).

[4] C. H. Hurd and C. A. Blanchard, *ibid.*, **72**, 1461 (1950).

[5] R. L. Wear, *ibid.*, **73**, 2390 (1951).

[6] A. S. Spriggs, C. M. Hill, and G. W. Senter, *ibid.*, **74**, 1555 (1952).

[7] J. R. Johnson and V. J. Shiner, Jr., *ibid.*, **75**, 1350 (1953).

[8] R. B. Woodward and G. Small, Jr., *ibid.*, **72**, 1297 (1950).

[9] J. Bregman and S. H. Bauer, *ibid.*, **77**, 1955 (1955).

[10] J. E. Baldwin and J. D. Roberts, *ibid.*, **85**, 2444 (1963); and unpublished data.

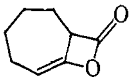
[11] L. Katz and W. N. Lipscomb, *Acta Cryst.*, **5**, 313 (1952).

[12] *Cf.* C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, Chapter IX.

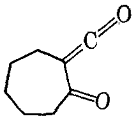
[13] Compare E. J. Corey and R. A. Sneen, *J. Am. Chem. Soc.*, **77**, 2505 (1955); C. F. Wilcox, Jr., *ibid.*, **82**, 414 (1960).

tone VIII.[14] The postulated structure VIII would not be subject to undue steric strain and seems a reasonable conjecture. If this $\beta,\gamma$-unsaturated $\beta$-lactone of unambiguous stereochemistry could be isolated, it would be a valuable molecule for spectral comparisons with the methylene $\beta$-lactone dimer.

$$\underset{\text{VII}}{O{=}C{=}CH{-}(CH_2)_4{-}CH{=}C{=}O}$$



VIII



IX

In the event, VIII was isolated and converted in 71% yield to cycloheptanone 2,4-dinitrophenylhydrazone. The infrared and the n.m.r. spectra [absorptions at 323 c.p.s., $\tau$ 4.62 (skewed triplet with some additional splitting, relative intensity 1); 238 c.p.s., $\tau$ 6.03 (complex multiplet, relative intensity 1); and 140–70 c.p.s., $\tau$ 7.7–8.8 (broad band, relative intensity 8)] of VIII clearly rule out any alternative formulation for the condensation product from VII, such as IX.[15]

The n.m.r. spectrum of VIII contains the desired information relevant to the stereochemistry of the methylketene $\beta$-lactone dimer. The $\alpha$-hydrogen of the neutral methylketene dimer absorbs at 235.5 c.p.s., quite near to the $\alpha$-hydrogen of VIII. But the chemical shift between the vinyl hydrogen of the neutral methylketene dimer (281.5 c.p.s.) and that of VIII is substantial—41.5 c.p.s. This fact suggests that the two vinyl hydrogens are in quite different magnetic environments, and therefore, that they have different stereochemistry.[16] The neutral methylketene dimer is thus VI, not V, in accord with the conclusions based on dipole moment data.

## Experimental[17]

**8-Oxo-9-oxabicyclo[5.2.0]nonene-1 (VIII).**—Suberyl dichloride was dehydrochlorinated with triethylamine in ether.[14] Flash distillation of the filtered reaction mixture at 1 mm. (bath temp., 135°) gave a colorless liquid having $\nu_{\max}^{CCl_4}$ 1890 and 1725 cm.$^{-1}$, strong; 1925, 1855, 1820, 990, 935, 915, and 900 cm.$^{-1}$, medium.

*Anal.* Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.93, 69.75; H, 7.77, 8.15.

The n.m.r. spectrum, described above, was determined with a solution 9.9% by weight in carbon tetrachloride on a Varian A-60 spectrometer. Tetramethylsilane was employed as the internal standard.

**Cycloheptanone from VIII.**—A 30.1-mg. sample of VIII was hydrolyzed with ethanolic potassium hydroxide,[14] cooled, neutralized with sulfuric acid, and diluted with a solution of 2,4-dinitrophenylhydrazine (83 mg.) in 5% ethanolic sulfuric acid. The solid which formed was collected and recrystallized from ethanol-ethyl acetate to give 45.4 mg. (71%) of cycloheptanone 2,4-dinitrophenylhydrazone, m.p. 140–143°, lit.[18] m.p. 147°. The crude derivative was purified by chromatography on Bentonite-kieselguhr[19] and identified by direct infrared spectral, thin layer chromatographic, and mixture melting point comparisons with authentic material (m.m.p. 145–147°).

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[14] A. T. Blomquist and R. D. Spencer, *J. Am. Chem. Soc.*, **69**, 472 (1947); **70**, 30 (1948).

[15] *Cf.* J. C. Sauer, *ibid.*, **69**, 2444 (1947); J. E. Baldwin, *J. Org. Chem.*, **28**, 3112 (1963).

[16] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 119f.

[17] Analyses are by J. Nemeth and associates, Urbana, Ill.

[18] The Merck Index, 7th Ed., Merck and Co., Inc., Rahway, N. J., 1960, p. 309.

[19] J. A. Elridge and M. Whalley, *Chem. Ind.* (London), 589 (1955).

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# The Acylation of Ketones with Methyl Dichlorofluoroacetate and Certain Related Reactions[1]

RICHARD A. MOORE[2] AND ROBERT LEVINE

*Department of Chemistry, University of Pittsburgh, Pittsburgh 13, Pennsylvania*

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Several $\beta$-diketones of the type $RCOCH_2COCFCl_2$ have been prepared by the reaction of the appropriate ketones with methyl dichlorofluoroacetate in the presence of sodium methoxide. While 7-chloro-7-fluoronorcarane was obtained from the reaction of a mixture of cyclohexene and sodium methoxide with methyl dichlorofluoroacetate and *sym*-difluorotetrachloroacetone under appropriate conditions, a similar reaction with methyl dichlorofluoromethyl ketone gave a mixture of this chlorofluoronorcarane and methyl acetoacetate. A small amount of methyl oxalate and no 7,7-difluoronorcarane were obtained from a similar reaction with methyl chlorodifluoroacetate.

In a previous paper,[3] we reported the preparation of a series of $\beta$-diketones of the type $RCOCH_2COCF_2Cl$ in high yields by the acylation of a number of methyl ketones with methyl chlorodifluoroacetate. We now report the results of a study of the acylation of several methyl ketones with methyl dichlorofluoroacetate (I). Apparently there are no reported syntheses of $\beta$-diketones containing the dichlorofluoromethyl group.

$$\underset{\text{I}}{CCl_2FCO_2CH_3} + \underset{\text{II}}{C_6H_5COCH_3} \xrightarrow{NaOCH_3} CH_3OH + \underset{\text{III}}{C_6H_5COCH_2COCCl_2F}$$

The sodium methoxide-effected acylation of acetophenone (II) with I was studied first. When an ether solution of 1 equiv. of I was added rapidly (10 min.) at room temperature to a suspension of 1 equiv. of sodium methoxide in ether followed by 1 equiv. of II (standard addition, the ester is added to the methoxide followed by the ketone), only a 14% yield of the $\beta$-diketone, benzoyldichlorofluoroacetylmethane (III), was obtained after a 20-hr. reaction time. It was felt that the low yield of III might be due to the possibility that some of I was decomposed by reaction with sodium methoxide. Accordingly, in an attempt to minimize the exposure of the ester to excess sodium

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[1] This work was performed under Contract No. AT(30-1)-670 between the U. S. Atomic Energy Commission and the University of Pittsburgh.

[2] This paper is based on part of a thesis presented by R. A. M. to the graduate faculty of the University of Pittsburgh in partial fulfillment of the requirements of the Ph.D. degree.

[3] R. A. Moore and R. Levine, *J. Org. Chem.*, **29**, 1439 (1964).

TABLE I

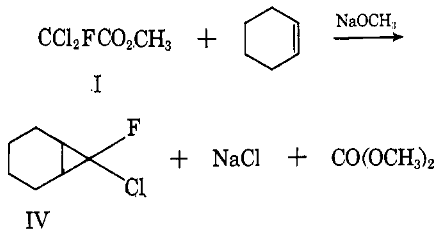
SYNTHESIS OF β-DIKETONES, $RCOCH_2COCFCl_2$, FROM METHYL KETONES AND METHYL DICHLOROFLUOROACETATE

| R | Reaction time, hr. 0° | Reaction time, hr. 25° | Procedure | Yield, % | B.p., °C. | mm. | $n^{25}D$ | Copper salt, m.p., °C. | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_6H_5$ |  | 20 | S.A.[a] | 14 | 129–131 | 4 |  | 265–266.5 dec.[g] | $C_{10}H_7Cl_2FO_2$ | 48.22 | 48.33 | 2.83 | 2.88 |
|  |  |  |  |  | 34–35 (m.p.)[f] |  |  |  |  |  |  |  |  |
|  |  | 24[b] | I.A.[a] | 30 |  |  |  |  |  |  |  |  |  |
|  |  | 18[c] | I.A. | 54 |  |  |  |  |  |  |  |  |  |
|  | 5[c] | 18 | I.A. | 74 |  |  |  |  |  |  |  |  |  |
| $CH_3$ | 5[c] | 18 | I.A. | 65 | 82.0–82.3 | 31 | 1.4810 | 181–182[f] | $C_5H_5Cl_2FO_2$ | 32.11 | 32.41 | 2.70 | 2.45 |
| $i$-$C_3H_7$ | 5[e] | 18 | I.A. | 18 | 102.0–103.0 | 33 | 1.4762 | 108–112 dec.[f] | $C_7H_9Cl_2FO_2$ | 39.09 | 39.21 | 4.22 | 4.19 |
|  | 8[d] | 16 | S.A. | 20 |  |  |  |  |  |  |  |  |  |
| Cyclopentanone | 5[c] | 18 | I.A. | 20 | 87.0–87.5 | 2.75 | 1.5080 | 175–179 dec.[f] | $C_7H_7Cl_2FO_2$ | 39.46 | 39.55 | 3.31 | 3.25 |
|  | 8[d] | 16 | S.A. | 48 |  |  |  |  |  |  |  |  |  |
| 2-$C_4H_3S$[e] | 8[d] | 16 | S.A. | 71 | 100–102 | 0.4 |  |  |  |  |  |  |  |
|  |  |  |  |  | 57.6–58.6 (m.p.)[h] |  |  | 238.5–239.5[f] | $C_8H_5Cl_2FO_2S$ | 37.66 | 37.30 | 1.98 | 2.07 |

[a] S.A. = standard addition; *i.e.*, the ester is added to sodium methoxide followed by the ketone. I.A. = inverse addition; *i.e.*, the ketone is added to sodium methoxide followed by the ester. [b] The ester is added over a 25-min. period. [c] The ester is added over a 2-hr. period. [d] The ester is added over a 15-min. period. [e] 2-$C_4H_3S$ is the 2-thienyl radical. [f] Recrystallized from aqueous methanol. [g] Recrystallized from aqueous acetone. [h] Recrystallized from $n$-pentane.

methoxide, a reaction was effected in which the order of addition of the ester and ketone to sodium methoxide was reversed, the ester being added last (inverse addition, the ketone is added to the methoxide followed by the ester) over a more extended period of time, *i.e.*, 25 min. In this reaction the yield of III was increased to 30%. In addition, the hydrolysate (the reaction had been quenched with water) contained chloride ion, which indicates that the ester had been decomposed to some extent. When the last reaction was repeated except that the addition time of the ester was increased to 2 hr., the yield of III was raised to 53.5%.

Since the chlorine atoms of I appear to be labile and since Parham and Schweizer[4a] reported that dichlorocarbene is formed by the interaction of ethyl trichloroacetate with sodium methoxide, it was felt that a carbene might be formed in the methyl dichlorofluoroacetate–sodium methoxide system. Therefore, a reaction between I, sodium methoxide, and cyclohexene was performed using the procedure similar to that employed previously[4] in the analogous reaction with ethyl trichloroacetate. A mixture of equivalents of sodium methoxide and I in excess cyclohexene was stirred for 8 hr. at 0° in an ice bath. Then, the ice bath was removed with the intention of allowing the reaction mixture to stand overnight (16 hr.) at room temperature. However, after the reaction mixture had warmed to about 15°, an exothermic reaction ensued and the mixture refluxed without external heating for about 0.5 hr. After the mixture had cooled to room temperature it was allowed to stand for 16 hr. From the reaction mixture there was isolated a 35% yield of 7-chloro-7-fluoronorcarane (IV), whose properties are identical with those of the material prepared by Parham and Twelves[4b] by the reaction of dichlorofluoromethane with cyclohexene in the presence of potassium $t$-butoxide. A 43% yield of IV was obtained by maintaining the reaction mixture at 30–40° for 45 min. followed by 23 hr. at room temperature.



To show that chlorofluorocarbene is formed when the Claisen condensation is effected between I, II, and sodium methoxide at room temperature, this reaction was repeated under standard addition conditions except that cyclohexene was added as a chlorofluorocarbene trap. In this way, there was obtained IV (27%) and III (9%) in addition to recovered I (10%) and II (81%).

A method was devised for minimizing carbene formation when the reaction of the ester (I) with sodium methoxide in cyclohexene indicated that the formation of chlorofluorocarbene seems to be temperature-dependent. It appears that if, after exposing I to sodium methoxide for 8 hr. at 0°, enough of I remained so that when the temperature was raised to 15° an exothermic reaction developed (*vide supra*), then at 0° the rate of carbene formation is probably very slow. Thus, it seemed possible that by lowering the reaction temperature, better yields of the β-diketone (III) might be obtained by slowing down or eliminating the competing carbene-forming reaction. Some support for this argument was obtained by performing a reaction between I, II, and sodium methoxide at 0°. The ketone (II) was added to a suspension of sodium methoxide in ether and then the mixture was cooled to 0° in an ice bath. The ester (I) was then added at 0° over a 2-hr. period and stirring was continued for an additional 3 hr. at 0°. The ice bath was removed and

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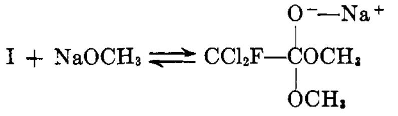
(4) (a) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959); (b) W. E. Parham and R. R. Twelves, *ibid.*, **22**, 730 (1957).

the mixture was allowed to stand for 18 hr. at room temperature and subsequently processed to give 73.5% yield of the β-diketone (III).

The same conditions were employed between I, acetone, and sodium methoxide to give a 65% yield of 1,1-dichloro-1-fluoroacetylacetone. However, when the same cooling period (5 hr.) was used in similar reactions between I and methyl isopropyl ketone, and between I and cyclopentanone, yields of only 18 and 20% of the respective β-diketones were obtained. When these last two reactions were repeated except that the standard addition method was used and the cooling period was extended to 8 hr. followed by 16 hr. at room temperature, there were obtained 20 and 48%, respectively, of dichlorofluoroacetylisobutyrylmethane and 2-dichlorofluoroacetylcyclopentanone. Similarly, 2-acetylthiophene gave a 71% yield of dichlorofluoroacetyl-2-thenoylmethane. The results of the experiments described above appear in Table I.

It is not known with certainty why the formation of chlorofluorocarbene in the methyl dichlorofluoroacetate–sodium methoxide system is temperature dependent. The intermediate involved in these reactions is undoubtedly the adduct V, which is formed by the addition of sodium methoxide across the carbonyl group of I. This adduct is similar to that which Perham and Schweizer[4a] suggest as an intermediate when dichlorocarbene is formed in the ethyl trichloroacetate–sodium methoxide system.



$$I + NaOCH_3 \rightleftharpoons CCl_2F{-}\overset{O^-{-}Na^+}{\underset{OCH_3}{C}}OCH_3$$

V

Then, chlorofluorocarbene (VI) could be formed from V by a concerted elimination of sodium chloride and methyl carbonate (route I) or by a two-step mechanism involving the intermediate formation of the dichlorofluoromethyl anion (route II).[5]

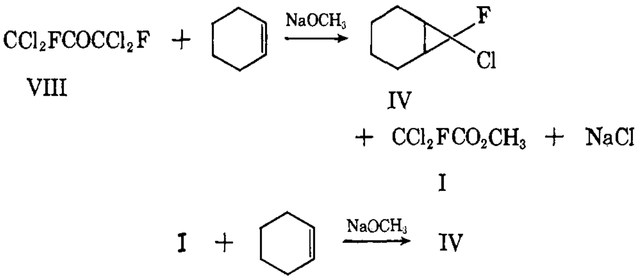
Route I $V \longrightarrow Na^+Cl^- + CO(OCH_3)_2 + :CFCl$ VI

Route II $V \longrightarrow Na^+CFCl_2^- + CO(OCH_3)_2$ VII

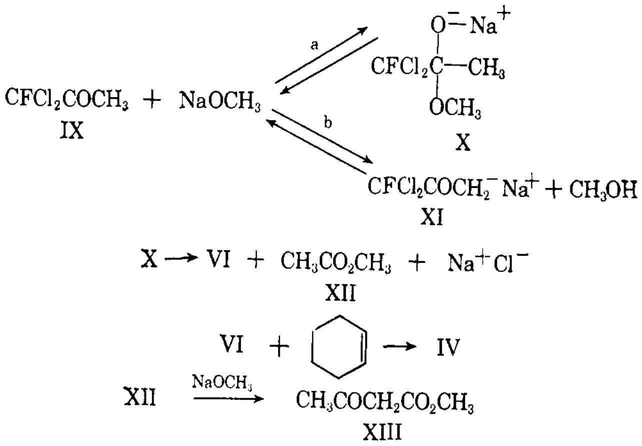
$VII \longrightarrow Na^+Cl^- + VI$

Regardless of whether route I or II operates in the methyl dichlorofluoroacetate–sodium methoxide system, the ease of carbene formation from V appears to be related to the ease of rupturing the carbon to carbon bond between the dichlorofluoromethyl group and the adjacent potential carbonyl carbon atom. Evidently the bond breaking step is thermally sensitive with the intermediate (V) being comparatively stable at 0° but unstable at room temperature. It is interesting to note that in the ethyl trichloroacetate–sodium methoxide system, the intermediate comparable to V must be unstable even at 0° since an 88% yield of 7,7-dichloronorcarane[4a] was obtained when ethyl trichloroacetate was treated at 0° with sodium methoxide in excess cyclohexene.

Since methyl dichlorofluoroacetate (I) has been shown to be a carbene source when treated with sodium methoxide, it was of interest to see whether other systems containing the dichlorofluoroacetyl and also the chlorodifluoroacetyl groups could give rise to carbenes. Three additional reactions were studied which might give rise to chlorofluorocarbene. When *sym*-difluorotetrachloroacetone (VIII) was treated with sodium methoxide in cyclohexene, chlorofluorocarbene was formed as indicated by the isolation of IV in 38% yield.[6] It is suggested that the reaction takes place by the following scheme which suggests that part of IV may arise from the reaction of I with sodium methoxide and cyclohexene, a reaction which we have shown takes place.



However, when sodium dichlorofluoroacetate was treated with sodium methoxide in refluxing cyclohexene none of the norcarane was obtained. In addition, it was found that the reaction of methyl dichlorofluoromethyl ketone (IX), sodium methoxide, and cyclohexene gave a low yield (3.4%) of norcarane IV and a trace of methyl acetoacetate (XIII). The origin of IV and XIII can be rationalized according to the following scheme.



It is suggested that sodium methoxide can react with IX by (a) addition across the carbonyl group to give the adduct X and (b) by abstraction of an α-hydrogen atom to give the ketone anion XI, a reaction which apparently does not occur to an appreciable extent. Then, X may decompose to give VI, sodium chloride, and methyl acetate (XII). The carbene (VI) then reacts with cyclohexene to give IV and XII is self-condensed by sodium methoxide to give XIII.

Three reactions were also attempted as possible routes to difluorocarbene. Thus, methyl chlorodi-

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(5) Route II appears to be more reasonable than route I since it has been shown that VI is formed in a two-step process involving the prior formation of the dichlorofluoromethide ion in both the basic hydrolysis of dichlorofluoromethane [J. Hine and N. W. Burske, *J. Am. Chem. Soc.*, **78**, 337 (1956)] and in the decarboxylation of the dichlorofluoroacetate ion [J. Hine and D. C. Duffey, *ibid.*, **81**, 1129 (1959)].

(6) Recently a 36% yield of IV has been reported from the reaction of VII, potassium *t*-butoxide, and cyclohexene [B. Farah and S. Horensky, *J. Org. Chem.*, **28**, 2494 (1963)].

fluoroacetate (XIV) was treated with sodium methoxide in cyclohexene at 40–60° for 34 hr.[7a] However, no 7,7-difluoronorcarane (XVII) was isolated. Instead, there was obtained a small amount of methyl oxalate (XVI) which was probably formed by a nucleophilic displacement of chloride ion on carbon by methoxide followed by hydrolysis. This observation is of interest since Hine and Duffey[7b] noted that oxalic acid is formed

$$\underset{\text{XIV}}{CF_2ClCO_2CH_3} + OCH_3^- \longrightarrow \underset{\text{XV}}{CH_3OCFCO_2CH_3} + Cl^-$$

$$\text{XV} \xrightarrow{H_2O} \underset{\text{XVI}}{(CO_2CH_3)_2}$$

during the decarboxylation of chlorodifluoroacetate ion in aqueous solution.

Although Haszeldine, *et al.*,[8] have obtained an 11% yield of XVII when sodium difluorochloroacetate was thermally decomposed in a mixture of cyclohexene and diglyme, it has now been observed that heating a mixture of this salt and sodium methoxide in refluxing cyclohexene gave none of XVII. In addition, while Grant and Cassie[9] obtained a 59% yield of 7,7-dichloronorcarane from the reaction of hexachloroacetone with cyclohexene in the presence of sodium methoxide for 15 hr. (5 hr. at 0–5° and 10 hr. at 25°), none of XVI was obtained when a similar reaction was performed in the present study except that *sym*-dichlorotetrafluoroacetone was used with a reaction time of 25 hr. and a reaction temperature of 45–50°. A small amount of the starting ketone (20%) was isolated as its hydrate.

## Experimental

**Halogenated Intermediates. A. Methyl Dichlorofluoroacetate.**—A mixture of dichlorofluoroacetic acid (147.0 g., 1.0 mole), absolute methanol (48.0 g., 1.5 moles), and 50 ml. of concentrated sulfuric acid was refluxed for 5 hr. and allowed to stand at room temperature for 17 hr. The crude ester was distilled from the reaction mixture and was washed successively with a saturated sodium carbonate solution, a saturated calcium chloride solution, and finally with water. It was distilled from phosphorus pentoxide to give 145 g. (90%) of methyl dichlorofluoroacetate, b.p. 114.5–115.5° at 732 mm., $n^{25}D$ 1.4024.[10]

**B. Methyl Dichlorofluoromethyl Ketone.**—Dichlorofluoroacetic acid (44.1 g., 0.3 mole) dissolved in 50 ml. of *n*-butyl ether was added, over a 2-hr. period at 0° to a rapidly stirred solution of methylmagnesium iodide (0.9 mole in 400 ml. of *n*-butyl ether). The mixture was stirred at 0° for 6 hr. more and then processed using the earlier procedure[11] for the preparation of ketones containing perhaloalkyl groups to give 16.5 g. (38.0%) of methyl dichlorofluoromethyl ketone, b.p. 94–95° at 744 mm., $n^{25}D$ 1.4025.

*Anal.* Calcd. for $C_3H_3Cl_2FO$: C, 24.85; H, 2.09. Found: C, 24.94; H, 2.03.

**Acylation of Acetophenone with Methyl Dichlorofluoroacetate.**—To commercial (Olin Mathieson) 95% sodium methoxide (6.0 g., 0.105 mole) suspended in 100 ml. of anhydrous ether, acetophenone (12.0 g., 0.100 mole) dissolved in 15 ml. of anhydrous ether was added in 10 min. To the rapidly stirred mixture which was maintained at 0° by an ice bath, methyl dichlorofluoroacetate (16.1 g., 0.100 mole) dissolved in 30 ml. of anhydrous ether was added over a 2-hr. period. After 3 additional hr. of stirring at 0°, the reaction mixture was allowed to stand at room temperature for 18 hr. The reaction was quenched and processed in the customary manner[3] to give 18.3 g. (73.5%) of benzoyldichlorofluoroacetylmethane, b.p. 129–131° at 4 mm.

**Reactions Involving the Formation of Chlorofluorocarbene. A. From Methyl Dichlorofluoroacetate.**—Methyl dichlorofluoroacetate (32.2 g., 0.20 mole) was added all at once to sodium methoxide (12.0 g., 0.21 mole) suspended in 140 ml. of dry cyclohexene and cooled to 0° in an ice bath. The reaction mixture was stirred for 8 hr. at 0° in a nitrogen atmosphere at which time the ice bath was removed. Upon warming to about 15° an exothermic reaction took place and the mixture refluxed for about 0.5 hr. without external heating and then cooled slowly to room temperature. The mixture was allowed to stand for 16 hr. at room temperature and then was quenched by the addition of 200 ml. of water. The phases were separated and the aqueous phase was extracted with two 100-ml. portions of *n*-pentane. The combined organic phases were dried over anhydrous magnesium sulfate. The solvent and the excess cyclohexene were removed at atmospheric pressure and the residue was distilled *in vacuo* to give 10.5 g. (35%) of 7-chloro-7-fluoronorcarane,[6] b.p. 69.5° at 34 mm., $n^{25}D$ 1.4576. The infrared spectrum of the product was superimposable on that of an authentic sample.

**B. From the Reaction of Methyl Dichlorofluoroacetate with Sodium Methoxide, Acetophenone, and Cyclohexene.**—Methyl dichlorofluoroacetate (48.3 g., 0.300 mole) in 45 ml. of anhydrous ethyl ether was added to a rapidly stirred slurry of 95% sodium methoxide (18.0 g., 0.315 mole), anhydrous ethyl ether (300 ml.), and cyclohexene (300 ml.). Acetophenone (36.0 g., 0.300 mole in 45 ml. of anhydrous ether) was added in 5 min.; the mixture was stirred for 18 hr. at room temperature and processed in the regular manner[3] to give, in addition to the excess cyclohexene solvent, acetophenone (29.0 g., 81%, b.p. 103–112° at 35 mm.), methyl dichlorofluoroacetate (4.8 g., 10%, b.p. 110–120° at 735 mm.), 7-chloro-7-fluoronorcarane (12.0 g., 27%, b.p. 69–75° at 35 mm.), and benzoyldichlorofluoroacetylmethane (8.3 g., 9%, b.p. 131–135° at 4 mm.).

**C. From *sym*-Difluorotetrachloroacetone.**—To a rapidly stirred suspension of 95% sodium methoxide (13.5 g., 0.25 mole) in cyclohexene (82.0 g., 1.0 mole), *sym*-difluorotetrachloroacetone (23.2 g., 0.1 mole) was added over a period of 1 hr. at such a rate that the reaction temperature remained at 35–40°. It was necessary to cool the reaction mixture intermittently for 2 hr. after the addition of the ketone to maintain the reaction temperature at 35–40°. The mixture was stirred for 6 hr. at room temperature and then was allowed to stand for 19 hr. The reaction was quenched as described above for A to give 7-chloro-7-fluoronorcarane (11.3 g., 38%, b.p. 50–54° at 14–16 mm.) in addition to recovered cyclohexene.

**D. From Methyl Dichlorofluoromethyl Ketone.**—To 95% sodium methoxide (13.5 g., 0.25 mole) suspended in cyclohexene (82.0 g., 1.0 mole), methyl dichlorofluoromethyl ketone (14.5 g., 0.10 mole) was added in 45 min. at such a rate that the reaction temperature did not exceed 40°. The mixture was stirred for 10 hr. at room temperature and hydrolyzed with 100 ml. of 10% sulfuric acid. The phases were separated and the aqueous phase was extracted with several portions of ether. The combined organic phases were dried over Drierite and the ether and unchanged cyclohexene were removed at atmospheric pressure. Distillation of the residue gave 1.0 g. of a liquid, b.p. 87–90° at 79 mm., which gave a positive test with alcoholic ferric chloride solution and suggested the presence of a $\beta$-keto ester. The mixture was dissolved in ether and was extracted with 2% sodium hydroxide solution to remove the $\beta$-keto ester. The ether layer was dried and distilled to give 0.5 g. (3.4%) of 7-chloro-7-fluoronorcarane (b.p. 62–62.5° at 24 mm., $n^{25}D$ 1.4572) whose infrared spectrum was superimposable on that of an authentic sample. The basic extract was acidified with dilute sulfuric acid and extracted with ether. The ether extracts were concentrated to give methyl acetoacetate (0.1 g.) which gave a semicarbazone, m.p. 151–152° alone and when mixed with an authentic sample,[12] and whose infrared spectrum was superimposable on that of an authentic sample.

**Reaction of Methyl Difluorochloroacetate, Cyclohexene, and Sodium Methoxide.**—Methyl difluorochloroacetate (36.0 g., 0.25 mole) was added in 10 min. to a rapidly stirred suspension of 95%

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[7] (a) A higher temperature was used than in the analogous reaction with I which gave a 35–43% (*vide supra*) yield of 7-chloro-7 fluoronorcarane, since it was believed that XIV would be more stable than I to cleavage by sodium methoxide; (b) J. Hine and D. C. Duffey, *J. Am. Chem. Soc.*, **81**, 1131 (1959).

[8] J. M. Birchall, G. W. Gross, and R. N. Haszeldine, *Proc. Chem. Soc.*, 81 (1960).

[9] F. W. Grant and W. B. Cassie, *J. Org. Chem.*, **25**, 1433 (1960).

[10] E. Gryszkewiez-Trochimowski, A. Sporzynski, and J. Wnuk, *Rec. trav. chim.*, **66**, 419 (1947).

[11] K. T. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2268 (1956).

[12] H. Staudinger and H. Becker, *Ber.*, **50**, 1021 (1917).

sodium methoxide (17.3 g., 0.32 mole) in 250 ml. of cyclohexene under a nitrogen atmosphere. During the course of the addition of the ester, the reaction temperature rose to 45° and subsequently the reaction mixture assumed a gel-like consistency. The reaction mixture was warmed to about 65° when an exothermic reaction occurred and the mixture refluxed without external heating for about 30 min. After the reaction temperature had dropped to 40°, the reaction was maintained at 40° for 10 hr. by external heating and then the mixture was heated to and maintained at 60° for 24 hr. The reaction was quenched by the addition of 200 ml. of water, the phases were separated, and the organic phase was extracted with three 100-ml. portions of *n*-pentane. The combined organic phases were dried over Drierite. After removing the *n*-pentane and the cyclohexene, a small residue remained, which on distillation gave 0.6 g. (2.4%) of methyl oxalate, b.p. 159–161° at 735 mm., m.p. 53–54°. The infrared spectrum of this ester was superimposable on that of an authentic sample of methyl oxalate.

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# Polymeric Peroxide of 2,5-Dimethyl-2,4-hexadiene and a New Selective Reduction of Its Peroxide Linkage

KARL GRIESBAUM,[1] ALEXIS A. OSWALD, AND WALTER NAEGELE[2]

*The Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey*

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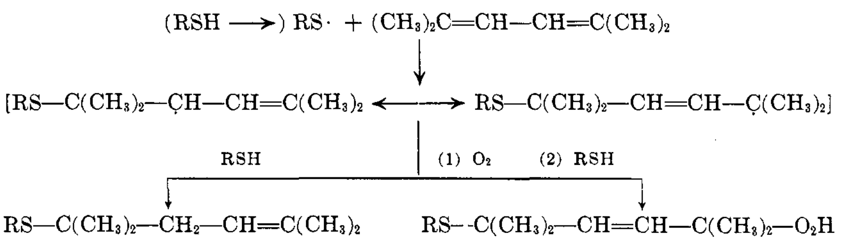
The autoxidation of 2,5-dimethyl-2,4-hexadiene affords in good yield the corresponding *trans*-1,4-polyperoxide as the only detectable product. This appears to be the first completely selective autoxidation of an acyclic conjugated diene. The *trans*-1,4 structure of the polyperoxide was established by infrared and n.m.r. analysis and by the results of reduction reactions. Catalytic hydrogenation of the polyperoxide produced 2,5-dimethylhexane-2,5-diol in high yield. During base-catalyzed reduction with an aromatic thiol, on the other hand, only the peroxide linkages were cleaved to yield *trans*-2,5-dimethyl-3-hexene-2,5-diol in 75% yield. The latter reaction represents a new method for the selective reduction of the O–O bond in polyperoxides containing olefinic linkages.

Previous reports from this laboratory have indicated that there is a correlation between the structure of a conjugated diene and the course of its free-radical reactions.[3] If the initial allylic-radical intermediate enters into a reaction requiring significant activation energy, the thermodynamically more stable products are formed.[4-6] If, on the other hand, the allylic radical undergoes a reaction requiring little or no activation energy, the thermodynamically less stable products are produced.[4,7] Typical examples of this principle are thiol addition and thiol co-oxidation reactions[4] (see Scheme I).

SCHEME I



The autoxidation of conjugated dienes to form polymeric peroxides resembles the above-mentioned co-oxidation reaction in its second propagation step. In both cases, an allylic radical intermediate combines with the oxygen diradical in a step of negligible activation energy. One might therefore anticipate similar product orientations for the two reactions. However, to the best of our knowledge, completely selective autoxidation reactions of acyclic conjugated dienes have never been observed.

In studying the autoxidation of 1,3-butadiene, Handy and Rothrock[8] showed that both 1,2- and 1,4-addition of oxygen occurred. In a series of papers, Kern and co-workers reported the autoxidation of chloroprene,[9,10] isoprene,[11] and 2,3-dimethyl-1,3-butadiene.[11-13] They arrived at the conclusion that isoprene and 2,3-dimethyl-1,3-butadiene each form 1,2-polyperoxides. However, their published data do not prove that these were the sole reaction products. In a later study Kawahara[14] indeed found that the autoxidation of 2,3-dimethyl-1,3-butadiene is a more complex reaction and specifically mentioned that 1,4-addition may also occur.

A polymeric peroxide of 2,5-dimethyl-2,4-hexadiene had also been reported previously by Harper and coworkers.[15] Although these workers suggested a 1,4-

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(1) To whom inquiries should be addressed.

(2) Analytical Research Division.

(3) For a summarized treatment of this subject see A. A. Oswald and K. Griesbaum, "Free Radical Addition of Thiols to Diolefins and Acetylenes," in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., in press.

(4) A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *J. Org. Chem.*, **27**, 2439 (1962).

(5) A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, **84**, 3897 (1962).

(6) A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *J. Org. Chem.*, **28**, 1262 (1963).

(7) A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *ibid.*, **28**, 2355 (1963).

(8) C. T. Handy and H. S. Rothrock, *J. Am. Chem. Soc.*, **80**, 5306 (1958).

(9) W. Kern, H. Jockusch, and A. Wolfram, *Makromol. Chem.*, **16**, 81 (1955).

(10) See also A. L. Klebanskii and R. M. Sorokina, *Zh. Prikl. Khim.*, **35**, 2735 (1962).

(11) W. Kern and A. R. Heinz, *Makromol. Chem.*, **16**, 81 (1955).

(12) W. Kern and J. Stallmann, *ibid.*, **7**, 199 (1951).

(13) W. Kern, A. R. Heinz, and J. Stallmann, *ibid.*, **16**, 21 (1955).

(14) F. K. Kawahara, *J. Am. Chem. Soc.*, **79**, 1447 (1957).

(15) S. H. Harper, H. W. B. Reed, and R. A. Thompson, *J. Sci. Food Agr.*, **2**, 94 (1951).