Monoethylation was the chief reaction when 50 g. of sodium cyclohexanebutyrate was heated at 150-250° with 10 g. of sodamide under 75 atm. initial ethylene pressure (expt. 29).  $\alpha$ -Ethylcyclohexanebutyric acid was isolated in 31% yield and  $\alpha, \alpha$ -diethylcyclohexanebutyric in 14% yield.

When 10 g. of a 50% dispersion of sodium in mineral oil was used as catalyst for the ethylation of the 50 g. of sodium cyclohexanebutyrate in the presence of heptane as diluent, the diethylated compound was obtained in 19% yield (expt. 30). An unexpected by-product, triethylacetic acid, was obtained in 16% yield based on the cyclohexanebutyrate charged. Its formation seems to indicate the intermediate formation of sodium acetate or, more probably, sodium butyrate during the reaction, the latter being formed by cleavage of the salt. Alternatively, cleavage may have occurred after mono- or diethylation. Cleavage at a cyclohexane ring is, however, not an anticipated reaction.

# Experimental

Procedure B .--- The mixture of salt and catalyst (and diluent, when used) in a glass liner was sealed into an Ipatieff-type rotating autoclave of, usually, 850-ml. capacity. Ethylene was charged to a pressure of about 50 atm. The autoclave then was rotated while being heated from 150 to  $250^\circ$  during 4 or 5 hours. The autoclave was pernitted to cool overnight, the pressure was released, and the autoclave was opened. The product was carefully added to ice-water (or to alcohol when unconverted sodium or potassium was present). The resulting solution was ex-tracted with ether to remove alkali-insoluble material (e.g., amides, nitriles, polymer or diluent) and the alkaline aqueous solution was acidified with dilute hydrochloric acid. The acidified solution was extracted with ether and the extract was dried over sodium sulfate, and distilled.

**Procedure T.**—The salt, catalyst and diluent were sealed into an autoclave equipped with an efficient stirrer (a "turbomixer"<sup>s</sup> of about 1-liter capacity), the autoclave was heated with stirring to about  $180^{\circ}$  and ethylene was admitted to bring the total pressure to about 130° and ethylene was admitted to bring the total pressure to about 40 atm. The temperature usually was increased gradually to about 200 or 250°, more ethylene being added if the pressure dropped to about 10–15 atm. The product was worked-up in the manner described above.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY, EAST LANSING, MICH.]

# The Decomposition of Cyclopropaneacetyl Peroxide<sup>1,2</sup>

## By HAROLD HART AND ROMEO A. CIPRIANI<sup>3</sup>

RECEIVED MAY 29, 1962

Cyclopropaneacetyl peroxide has been obtained crystalline at  $-20^{\circ}$ , and its decomposition rates and products in carbon tetrachloride re-examined. Reproducible first-order kinetics were obtained on 0.02-0.09 N solutions, induced decomposition being demonstrably insignificant at these concentrations. The peroxide decomposes approximately 55 times faster than cyclohexaneacetyl peroxide, and with an activation energy of 26.3 kcal./mole, about 2 kcal. less than for cyclohexaneacetyl peroxide. The major product, in 56% yield, is cyclopropylmethyl cyclopropaneacetate; little, if any, chlorine abstraction product is obtained. The decomposition is unaffected by weak carboxylic acids, but is catalyzed by trichloroacetic acid, the rate increase being proportional to the acid concentration. In addition to the usual ester, an ester of trichloroacetic acid, the rate increase being proportional to the acid concentration. acid is now a major product.

In the decomposition of diacyl peroxides the nature of the R group affects both the rates and products of decomposition. For example, peroxides

in which R is a secondary alkyl group decompose faster than when R is primary.<sup>4</sup> When R is cycloalkyl the decomposition rate depends upon the ring size, the rate in carbon tetrachloride at 70° for R = cyclohexyl being at least 76 times faster than for  $R = cyclopropyl.^5$  Peroxides in which the free radical R is stabilized (benzyl,<sup>6</sup> trichloromethyl,7 triphenylmethyl8) are particularly thermally labile. Phenylacetyl peroxide, which affords

(3) Monsanto Chemical Co. Fellow, 1958-1959.

(4) Isobutyryl peroxide decomposes 71 times faster than n-butyryl peroxide in isooctane at  $65^{\circ}$ ; calculated from the data of J. Smid, A. Rembaum and M. Szware, J. Am. Chem. Soc., **78**, 3315 (1956); and J. Smid and M. Szwarc, J. Chem. Phys., 29, 432 (1958).
 (5) H. Hart and D. P. Wyman, J. Am. Chem. Soc., 81, 4891 (1959).

- (6) P. D. Bartlett and J. E. Leffler, *ibid.*, **72**, 3030 (1950).
  (7) W. T. Miller, A. L. Dittman and S. K. Reed, U. S. Patent 2.580,

an example of deviation from the usual product distribution, gave very little benzyl chloride (chlorine atom abstraction) when decomposed in carbon tetrachloride<sup>6</sup>; R-Cl is generally a major product for decompositions in this solvent. It is clear that since the nature of R influences the decomposition rates of diacyl peroxides, there must be R-C, as well as O-O, bond stretching in the transition state for the process. 5, 9, 10  $\,$ 

Aliphatic peroxides in which R is a primary alkyl group (methyl,<sup>4</sup> ethyl,<sup>4</sup> n-propyl,<sup>4</sup> δ-phenylbutyl,<sup>10</sup> cyclobutylmethyl,<sup>5</sup> cyclopentylmethyl,<sup>5</sup> cyclohexylmethyl<sup>5</sup>) all decompose at very nearly the same rate in carbon tetrachloride. The diacyl peroxide from cyclopropaneacetic acid (R = cyclopropylmethyl) appears to be an exception.<sup>5</sup> Although its decomposition rate in carbon tetrachloride was erratic, depending upon the particular batch of peroxide used, even the slowest observed rate was at least 10 times faster than that of the next larger ring (R = cyclobutylmethyl). The CO2 yield was low, the ester yield was high, and no product of the R-Cl type was obtained. Stabilization of the cyclopropylmethyl radical in a manner

<sup>(1)</sup> Taken from the Ph.D. thesis of Romeo A. Cipriani, Michigan State University, 1961.

<sup>(2)</sup> Support from the National Science Foundation, G 3289 and G 14289, is gratefully acknowledged.

<sup>358 (</sup>December 25, 1951); C. Zimmerman, U. S. Patent 2,580,373 (December 25, 1951).

<sup>(8)</sup> H. Wieland and G. Rasuwajew, Ann., 480, 157 (1930).

<sup>(9)</sup> For one detailed interpretation of this phenomenon, see M. Szwarc and L. Herk, J. Chem. Phys., 29, 438 (1958)

<sup>(10)</sup> D. F. DeTar and R. C. Lamb, J. Am. Chem. Soc. 81, 122 (1959).



related to that of the cyclopropylmethyl cation<sup>11</sup> was suggested as a possible explanation for the rapid rates.<sup>12,13</sup>

Because the behavior of cyclopropaneacetyl peroxide was reported<sup>5</sup> to be erratic, it was decided to reinvestigate this peroxide, paying special heed to purity of the peroxide, possible catalysis by acid or base, induced decomposition and the energetics of the reaction. The products were also re-examined under kinetically defined conditions. With proper attention to detail it was possible to obtain consistent, reproducible kinetics with cyclopropaneacetyl peroxide, and the results are described in this paper.

### Results

**Preparation and Purity of the Peroxide.**—Cyclopropaneacetic acid was prepared in two steps by the addition of cyclopropyllithium to ethylene oxide, followed by oxidation of the resulting 2cyclopropylethanol with chromic acid in aqueous acetone (over-all yield 40%).<sup>14</sup> The acid chloride, prepared from the acid and thionyl chloride, was converted to the peroxide with sodium peroxide in moist ether by the usual procedure. The peroxide was crystallized from pentane at  $-80^{\circ}$ , and remained crystalline if stored at  $-20^{\circ}$ , but melted when warmed to room temperature.<sup>15</sup> Iodometric titration<sup>16</sup> showed the peroxide content of various batches to be 85-100%, solvent being the major contaminant.<sup>17</sup>

(11) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, J. Am. Chem. Soc., 81, 4390 (1959).

(12) See also C. G. Overberger and A. Lebovits,  $\mathit{ibid.},$  76, 2722 (1954).

(13) J. D. Roberts has offered an explanation in terms of geometry of orbitals, for the lack of cyclopropylmethyl-cyclobutyl interconversion in the radical and anion, as contrasted with the cation (141st National Meeting of the American Chemical Society, Washington, D. C., March 26, 1962).

(14) This method is superior to the previously described<sup>3</sup> catalytic dehydrogenation of 2-cyclopropylethanol to cyclopropaneacetaldehyde followed by silver ion oxidation. Alkaline permanganate oxidation of 2-cyclopropylethanol was unsatisfactory, considerable over-oxidation to cyclopropanearboxylic acid being observed.

(15) This peroxide had not previously? been obtained crystalline.

(16) L. S. Silbert and D. Swern, J. Am. Chem. Soc., 81, 2365 (1959)

 $(17)\,$  1t was necessary that all unreacted acid chloride be removed by sodium carbonate washing, as this impurity markedly accelerated the peroxide decomposition.

**Kinetics.**—The decompositions were carried out in 0.02–0.09 N solutions of peroxide in purified<sup>18</sup> carbon tetrachloride. Rates were followed by disappearance of the 5.62  $\mu$  peroxide carbonyl band in the infrared, and checked in a few instances by a titrimetric method.<sup>16</sup> For reference, cyclohexaneacetyl peroxide was prepared and its decomposition rates measured. The results on the latter peroxide agreed well with previous<sup>5</sup> measurements. Rate constants were calculated from the least squares slopes of plots of log (optical density) vs. time.

The kinetic results are given in Table I. Comparison of experiments 26 and 27 with 14 and 15 illustrates that the infrared and titrimetric procedures for following disappearance of peroxide give the same rate constants. Experiments 16– 19 show that the rate constant is independent of initial peroxide concentration over a 5-fold range (0.018-0.092 N). Induced decomposition is further shown to be unimportant by the negligible effect of iodine (as scavenger) on the rate constants; for cyclopropaneacetyl peroxide, compare experiments 23 and 24 with 20–22; and for cyclohexaneacetyl peroxide, compare experiments 37 and 38.

DECOMPOSITION RATES OF C	CLOPROP	ANEACETYL AND							
Cyclohexaneacetyl Pe	ROXIDES	in Carbon							
TETRACHLORIDE									
Temp	Init. ner-	$k_1 \times 10^5$ .							

TABLE I

		Temp.,	Init, per-	$k_{1} \times 10^{5}$ ,		
R =	Expt.	°C.	oxide, $N$	sec. ~1		
	14	44.0	0.06	$5.30 \pm 0.30$		
CH2-	15	44.0	.06	$5.07 \pm .21$		
C .	26	44.5	a	$5.03 \pm .24$		
	26	44.5	a	$4.93 \pm .12^{b}$		
	27	44.5	a	$5.07 \pm .32^{b}$		
	16	49.8	0.018	$11.1 \pm .2$		
	17	50.8	.046	$12.4 \pm .4$		
	18	50.8	.055	$13.0 \pm .6$		
	19	50.8	.092	$12.3 \pm .7$		
	20	56.7	.09	$25.8 \pm 1.8$		
	21	56.7	.09	$25.7 \pm 2.4$		
	22	56.5	.09	$27.8 \pm 0.3$		
	23	56.5	$.09^{\circ}$	$29.4 \pm 1.2$		
$\frown$	24	56.5	$.05^{d}$	$28.0 \pm 2.6$		
	36	54.4	.06	$0.308 \pm 0.008$		
	37	64.3	.06	$1.14 \pm .05$		
	38	64.3	$.06^{e}$	$1.23 \pm .04$		
	39	71.8	.06	$2.95 \pm .11$		

<sup>a</sup> Initial concentration was not determined. <sup>b</sup> Followed by iodometric titration<sup>18</sup>; all others were followed by the infrared method. <sup>c</sup> Solution was 0.07 N in iodine. <sup>d</sup> Solution was 0.18 N in iodine.

An Arrhenius plot (Fig. 1) of the data for cyclopropaneacetyl peroxide leads to activation parameters of 24.3 kcal./mole for  $\Delta H^{\pm}$  and 3.1 cal./ degree mole for  $\Delta S^{\pm}$ .

The effect of acids on the decomposition rate was examined, and the results are given in Table II. It is clear (expt. 30, 31) that weak carboxylic acids have little effect, but that the strong acid, trichloroacetic acid, markedly accelerates, in proportion to its concentration, the decomposition of cyclopropaneacetyl peroxide (expt. 33-35). Fur-

(18) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath Co., Boston, Mass., 1941, p. 365.

#### TABLE II

# THE EFFECT OF ACIDS ON THE DECOMPOSITION RATES OF CYCLOPROPANEACETVL AND CYCLOHEXANEACETVL PEROXIDES IN CAREON TETRACHLORIDE

R =	Expt.	Init. per- oxide, N	Acid	, N	$k_1  imes 10^5$ , sec. $^{-1}$	,
<sup>a</sup> → CH <sub>2</sub> -	15 30 31 33 34 35 37	$\begin{array}{c} 0.06 \\ .042 \\ .048 \\ .061 \\ .061 \\ .061 \\ .06 \end{array}$	A, <sup>c</sup> TMA, <sup>d</sup> TCA, <sup>e</sup> TCA, TCA,	0.014 .043 .061 .031 .015	$5.07 \pm 0.4.65 \pm4.65 \pm65-80$ 33 1.14 ± 0.	21 18 14 05
$\smile$	41	.06	TCA,	0.068	$4.47 \pm$	

<sup>a</sup> All experiments at  $44.5^{\circ}$ . <sup>b</sup> Both experiments at  $64^{\circ}$ . <sup>c</sup> A = acetic acid. <sup>d</sup> TMA = trimethylacetic acid. <sup>e</sup> TCA for trichloroacetic acid.

thermore, the rate enhancement is much larger than is observed (expt. 41) with cyclohexaneacetyl peroxide.

**Products.**—The nature and amounts of products were determined under kinetic concentrations, but the temperature was higher in order to complete the decompositions more quickly. After 3 hours at 78°, a 0.049 M solution of cyclopropaneacetyl peroxide in carbon tetrachloride showed (infrared) no remaining peroxide. The major products, averages of several experiments and given as moles per mole of peroxide, were carbon dioxide (1.32), ester (0.56)and acid (0.07). Carbon dioxide was determined gravimetrically, ester and acid determined by quantitative infrared using bands at 5.75 and 5.87  $\mu$ , respectively. A careful search was made for R-Cl type product. After 96 ml. of 0.076 N peroxide was decomposed at reflux for 3 hours, careful in vacuo distillation of the carbon tetrachloride showed small amounts of C--H containing material in the distillate. The amount, estimated using the C-H stretching frequency in the infrared, was about 0.17 mole per mole of peroxide, if assumed to be a C<sub>4</sub> chloride; but the compound may have been of the R-R type. This minor product did not show a double bond band in the infrared.

The three major products account for 97.5% of the initial carboxyl function and 59.5% of the alkyl portion of the peroxide. The latter may be augmented to 68% if R-Cl type product is included. Distillation of the ester and acid fractions left a tarry residue which may account for the missing balance of the alkyl groups.

The ester, which was the major organic product, was isolated from larger scale experiments. It had no carbon-carbon double bond absorption in the infrared. Its infrared spectrum, v.p.c. retention time and refractive index were identical with those of authentic cyclopropylmethyl cyclopropaneacetate. Cyclobutyl cyclopropaneacetate, prepared for reference, had the same retention time, but the other properties were distinguishing.<sup>19</sup>

The products from the trichloroacetic acidcatalyzed decomposition of cyclopropaneacetyl peroxide were examined by decomposing a carbon tetrachloride solution  $0.062 \ M$  in peroxide and  $0.125 \ M$  in trichloroacetic acid for 3 hours at  $76^{\circ}$ .

(19) We are indebted to Dr. Frank J. Chloupek for these results.

In addition to carbon dioxide (1.22 moles per mole of peroxide) two esters, absorbing at 5.76  $\mu$  (0.30 mole) and 5.67  $\mu$  (0.58 mole), were obtained. Their identity is discussed below.

# Discussion

The reason for prior erratic results with cyclopropaneacetyl peroxide did not specifically emerge from the present work, but two possible catalysts for its decomposition, strong acids or unconverted acid chloride, may have been the cause of the difficulty. In any event, consistent kinetics were obtained in the present work.

The decomposition rate, although not as rapid as previously observed,<sup>5</sup> was nevertheless appreciably greater than that for higher cycloalkaneacetyl peroxides. Cyclopropaneacetyl peroxide decomposed approximately 55 times faster than cyclohexaneacetyl peroxide. This is comparable in magnitude to the enhancement found by Overberger and Lebovits<sup>12</sup> for structurally related azobisnitriles. The rate increase is due predominantly to an approximately 1.5–2.0 kcal. per mole decrease in activation energy, and may be interpreted to mean that the cyclopropylmethyl radical, through an electron delocalization process, is more stable than the cyclohexylmethyl radical, for which such delocalization is not possible.

That radicals are in fact produced by the decomposition of cyclopropaneacetyl peroxide was demonstrated by the observation that at  $60^{\circ}$  it initiates the polymerization of styrene, although less efficiently than benzoyl peroxide.

The major organic decomposition product was the ester, cyclopropylcarbinyl cyclopropaneacetate; although the yield (56%) was not as large as previously observed,<sup>5</sup> it was still much greater than for other cycloalkaneacetyl peroxides (20-30%). Consistent with this was the lower (66% vs. 88%) CO<sub>2</sub> yield. The yield of R-Cl type product, if indeed any was produced at all, was no greater than 8-9%, whereas with cyclohexaneacetyl peroxide a 66% yield of cyclohexylmethyl chloride was obtained. This means either that not many free cyclopropylmethyl radicals were produced or that, if formed, they reacted by other (presumably lower energy) paths rather than abstract chlorine atoms from the solvent. The material balance for the carboxyl moiety of the peroxide was fine (97.5%) but a major part of the alkyl moiety (32-40%) went to unidentified products, possibly polymer.

Trichloroacetic acid markedly accelerated the decomposition of cyclopropaneacetyl peroxide, the increase being approximately 15-fold for equimolar acid at 44.5°. The acceleration was proportional to the amount of acid (Table II, expt. 33–35) and was very much smaller for cyclohexaneacetyl peroxide. The yield of cyclopropylcarbinyl cyclopropaneacetate was decreased and replaced by another ester with absorbtion at 5.67  $\mu$ , undoubtedly a trichloroacetate. Cyclopropylmethyl trichloroacetate shows carbonyl absorption at 5.67  $\mu$ . In view of the propensity for cyclopropylmethyl nethyl cation formation, it appears likely that trichloroacetic acid accelerates the decomposition by an ionic mechanism.



## Experimental

Cyclopropaneacetic Acid. A. 2-Cyclopropylethanol.— 2-Cyclopropylethanol was prepared from a cyclopropylorganometallic and ethylene oxide according to Hart and Wyman<sup>5</sup> except that important modifications were used to prepare cyclopropyllithium or cyclopropylmagnesium chloride. Because these procedures may be generally useful, they are described here. Cyclopropyllithium was prepared by adding to 7.3 g. of a fine lithium sand in 250 ml. of anhydrous ether a solution of 46.3 g. of cyclopropyl chloride in 150 ml. of anhydrous ether, at a temperature of 0-10° (3 hours). After standing an additional hour the cyclopropyllithium was ready for use and gave a 66% yield of 2-cyclopropylethanol on reaction with ethylene oxide. Cyclopropylmagnesium chloride was prepared by using tetrahydrofuran as solvent, benzyl bromide (20 mole per cent. of the amount of cyclopropyl chloride) and reflux for 18 hours (1.6 mole scale) to complete formation of the Grignard reagent. The yield of 2-cyclopropylethanol, after reaction in the usual way with ethylene oxide, was 42%. B. Oxidation with Chromium Trioxide–Sulfuric Acid.—

B. Oxidation with Chromium Trioxide-Sulfuric Acid.— To a well stirred solution of 39.5 g. (0.46 mole) of 2-cyclopropylethanol in 92.5 ml. of acetone was added, over a period of 13 hours with the temperature never being allowed to exceed 30°, a solution of 61.5 g. (0.615 mole) of chromium trioxide and 98.5 g. (1.04 moles) of sulfuric acid in 405 ml. of water. Water (100 ml.) was added and the mixture stirred for an additional hour. The layers were separated and the water layer extracted with ether. The ether extracts were added to the organic layer and the solvents removed by distillation (steam-bath). To the residue was added 300 ml. of 4 N sodium hydroxide and the mixture was refluxed for 5 hours. After cooling, the alkaline mixture was extracted with ether; this extract, on work-up, gave 6 g. of unoxidized 2-cyclopropylethanol.

The alkaline solution was acidified to congo red with 10% sulfuric acid and extracted with ether. After drying and removal of the solvent there was obtained 22.3 g. (57%) based on unrecovered alcohol) of cyclopropaneacetic acid,

b.p. 91° at 15 mm.,  $n^{25}_D$  1.4321, neut. equiv. 100.1 (caled. 100.1).

Cyclopropaneacetyl Peroxide.—To a suspension of 2.0 g. (0.026 mole) of sodium peroxide in 40 ml. of anhydrous ether was added 5.8 g. (0.049 mole) of cyclopropaneacetyl chloride (prepared by refluxing the acid and 10% excess thionyl chloride in chloroform for 4 hours, and then fractional distillation). The reaction was initiated by adding 2 drops of water. Reaction was assumed to be complete when the yellow color of the peroxide had disappeared and the addition of a drop or two of water no longer caused the temperature to rise.

Cold water was added to dissolve the sodium chloride, the layers were separated and the ether layer washed with 10% sodium carbonate, then dried over calcium chloride. The ether was removed (Rinco evaporation, no applied heat), 20 ml. of pentane was added to the liquid residue, and the whole was cooled to Dry Ice temperature in a CO<sub>2</sub> atmosphere. The crystalline peroxide was filtered (sintered glass) and stored in pentane or carbon tetrachloride solution. Titration<sup>16</sup> gave the peroxide content. Infrared spectra in carbon tetrachloride and in carbon disulfide showed no carbonyl-containing impurities in the peroxide.

carbonyl-containing impurities in the peroxide. **Kinetic Procedure.**—The apparatus was similar to those used previously<sup>5,21</sup> with minor improvements. Samples withdrawn periodically were frozen in Dry Ice, and the entire batch of samples for any one run were analyzed at one time. Rates were followed spectrophotometrically using the  $5.62\,\mu$  peroxide band in the infrared. Rate runs checked iodometrically<sup>16</sup> were analyzed as follows: A 1-ml. aliquot of peroxide solution was dissolved in 5 ml. of glacial acetic acid containing 0.0005% ferric chloride hexahydrate. The solution was freed of oxygen by flushing with carbon dioxide, 0.5 ml. of saturated aqueous sodium iodide was added, and the solution was allowed to stand in the dark for 20 minutes. After addition of 5 ml. of water, the solution was titrated with standard thiosulfate, 2 ml. of starch indicator being added shortly before the end-point was reached. Standardization of the thiosulfate using this procedure with benzoyl peroxide gave results identical with those obtained using potassium iodate.

**Products.**—Carbon dioxide, ester and acid were determined using techniques described previously.<sup>5,21</sup> In the case of trichloroacetic acid catalyzed decomposition, the CO<sub>2</sub> was again determined gravimetrically by nitrogen sweep through an Ascarite tube. The cooled reaction solution was then washed with 10% sodium carbonate, which removed both the trichloroacetic acid and any other acidic products (cyclopropaneacetic acid). Aliquots of the remaining dried solution were then analyzed with infrared (at 5.67 and 5.76  $\mu$ ) for the two esters present.

The ester from the decomposition of cyclopropaneacetyl peroxide was isolated as follows. The peroxide (ca. 5 g.) in 100 ml, of carbon tetrachloride was refluxed for 12 hours. After the solvent was removed by careful fractionation  $(600 \times 7 \text{ mm. vacuum jacketed tantalum wire spiral column)}$  the residue boiling at  $80\text{-}110^\circ$  at 15 mm. was collected. This distillate was passed through a Beckman Megachrom vapor phase chromatograph at  $150^\circ$  using four 12', 20% silicone columns in parallel. The ester collected had an infrared spectrum identical with that of authentic<sup>5</sup> cyclopropaneacetate.<sup>10</sup>

(21) H. H. Lau and H. Hart, J. Am. Chem. Soc., 81, 4897 (1959).

<sup>(20)</sup> The alkyl group may also have the cyclobutyl or allylcarbinyl structures on the two structures directly above.