[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS CO., DES PLAINES, ILL.]

Condensation of Salts of Saturated Carboxylic Acids with Ethylene in the Presence of Alkaline Catalysts[1]

BY LOUIS SCHMERLING AND W. G. TOEKELT

RECEIVED MAY 4, 1962

Ethylation occurs when a dry mixture of a salt of a saturated carboxylic acid which contains at least one hydrogen atom attached to the α-carbon atom and an alkali metal catalyst is heated at 150–250° under ethylene pressure. Thus, the reaction of potassium acetate in the presence of sodamide yields a mixture of potassium di- and triethylacetate. Similarly, ethylation occurs at the α-carbon atom of sodium propionate, sodium isobutyrate, sodium pelargonate, sodium laurate and sodium stearate. The catalytic nature of the reaction was established by showing that 4.2 moles of sodium propionate and 7.8 moles of ethylene per mole of sodamide were involved in an experiment which yielded 11% of 2-methylbutyric acid and 71% of 2-methyl-2-ethylbutyric acid. The ethylation of sodium cyclopentanepropionate in the presence of sodamide produces a mixture either of α-ethyl- and α,α-diethylcyclopentanepropionic acid or of α-ethyl- and α,α-diethylcyclopentanepropionitrile, depending on the ratio of salt to catalyst. The reaction of sodium cyclohexanebutyrate in the presence of sodamide yields the mono- and diethylated acids; use of sodium as catalyst yields the diethylated acid together with a product due to a cleavage reaction, triethylacetic acid. The mechanism of the ethylations is discussed.

This communication describes a novel catalytic reaction for the synthesis of trialkylacetic acids, the reaction consisting of the condensation of ethylene with salts of carboxylic acids in the presence of alkali metal catalysts. For example, when a dry mixture of potassium acetate and sodamide powders is heated to 250° under 50 atm. initial ethylene pressure in a rotating autoclave, absorption of the olefin occurs and potassium triethylacetate is produced in 25% yield (expt. 1). A similar reaction occurs with sodium acetate (expt. 4). It is somewhat surprising that the solid compounds react with gaseous ethylene in the absence of a solvent for at least one of the reactants. Potassium acetate is reported to melt at 292°, sodium acetate at 324°, and sodamide at 210°. It seems probable that some liquefaction of the salt mixture occurs during the reaction.

The reaction presumably involves a carbanion chain mechanism. Replacement of one of the hydrogen atoms attached to the α-carbon atom occurs in the initiating step

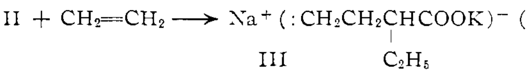
$$CH_3COOK + NaNH_2 \longrightarrow Na^+(:CH_2COOK)^- + NH_3 \quad (1)$$

The potassium sodioacetate adds to ethylene to yield potassium γ-sodiobutyrate, which rearranges to the more stable (but more reactive) α-sodio isomer

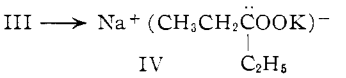
$$Na^+(:CH_2COOK)^- + CH_2{=}CH_2 \longrightarrow \underset{\mathrm{I}}{Na^+(:CH_2CH_2CH_2COOK)^-} \quad (2)$$

$$\mathrm{I} \longrightarrow \underset{\mathrm{II}}{Na^+(CH_3CH_2\ddot{C}HCOOK)^-} \quad (3)$$

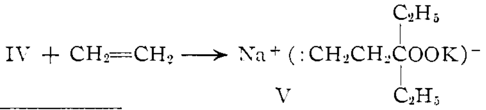
Further reaction of II with ethylene leads to the formation of potassium triethylacetate as end-product

 (4)

$$\mathrm{II} + CH_2{=}CH_2 \longrightarrow \underset{\mathrm{III}}{Na^+}(:CH_2CH_2\underset{C_2H_5}{\underset{|}{C}}HCOOK)^- \quad (4)$$

 (5)

$$\mathrm{III} \longrightarrow \underset{\mathrm{IV}}{Na^+}(CH_3CH_2\underset{C_2H_5}{\underset{|}{\ddot{C}}}OOK)^- \quad (5)$$

 (6)

$$\mathrm{IV} + CH_2{=}CH_2 \longrightarrow \underset{\mathrm{V}}{Na^+}(:CH_2CH_2\overset{C_2H_5}{\overset{|}{\underset{C_2H_5}{\underset{|}{C}}}}OOK)^- \quad (6)$$

$$\mathrm{V} + CH_3COOK \longrightarrow (C_2H_5)_3CCOOK + Na^+(:CH_2COOK)^- \quad (7)$$

The final step occurs because the hydrogen atoms of potassium acetate are more acidic than are those attached to the γ-carbon atom of the potassium diethylbutyrate.

The rearrangements of eq. 3 and 5 may involve interaction of the intermediate γ-sodio compound (or corresponding carbanion) with potassium acetate, potassium butyrate or potassium α-ethylbutyrate; *i.e.*, the rearrangements may be intermolecular rather than intramolecular; the reaction of eq. 3 may be written

$$\mathrm{I} + CH_3COOK \longrightarrow \underset{\mathrm{VI}}{CH_3CH_2CH_2COOK} + Na^+(:CH_2COOK)^- \quad (8)$$

$$\mathrm{VI} + Na^+(:CH_2COOK)^- \longrightarrow \underset{\mathrm{II}}{Na^+(CH_3CH_2\ddot{C}HCOOK)^-} + CH_3COOK \quad (9)$$

The first of these reactions (eq. 8) proceeds because the hydrogen atoms in sodium acetate are more acidic than those attached to the γ-carbon atom of sodium butyrate. The second reaction presumably occurs because the hydrogens on the α-carbon atoms in potassium butyrate are more acidic than those in sodium acetate.

Experimental evidence in support of a carbanion chain mechanism for ethylation was obtained by heating sodium α-sodioacetate to 250° under ethylene pressure. When *n*-heptane or cyclohexane was used as diluent, sodium triethylacetate was obtained in 25% yield (expts. 8 and 9). When toluene was employed, the triethylacetate was obtained in smaller yield (15%); *n*-propylbenzene, formed by a competitive carbanion-catalyzed chain reaction, side-chain alkylation,[2] was obtained in 5% yield (expt. 10).

The reaction of 2.6 moles of dry sodium propionate and 0.51 mole of sodamide with ethylene at 150–250° and 195 atm. pressure in a rotating autoclave (expt. 12) gave a high yield (71%) of 2,2-diethylpropionic acid (*i.e.*, 2-methyl-2-ethylbutyric acid) together with a smaller amount (11%) of 2-ethylpropionic acid (*i.e.*, 2-methylbutyric acid). This corresponds to the reaction

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[1] Presented at the Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

[2] H. Pines, J. A. Vesely and V. N. Ipatieff, *J. Am. Chem. Soc.*, **77**, 554 (1955).

TABLE I

CONDENSATION OF ETHYLENE WITH ACETATES

Expt.	Procedure	RCOOM Kind	RCOOM Mole	Catalyst Kind	Catalyst Mole	Diluent	*T*, °C.	Press., atm. Init.,[d] r.t.[e]	Press., atm. Max. at *T*	Press., atm. Final r.t.[e]	Chief products, % Et_2-CHCOOH	Chief products, % Et_3COOH	Chief products, % Other
1	B	AcOK	0.31	$NaNH_2$	0.26	None	22–250	54	183	50	22	25	
2	B	AcOK	.31	$NaNH_2$	.26	*n*-C_7H_{16}	24–250	53	200	45	33	14	
3	B	AcOK	.31	NaH[a]	.22	None	150–250	50	103	33	20	34	
4	B	AcONa	.37	$NaNH_2$	.26	None	225–300	55	253	58	9	10	
5	B	AcONa	.37	$NaNH_2$	.26	*n*-C_7H_{16}	24–250	53	214	6[b]	9	17	
6	T	AcONa	.61	$NaNH_2$	.26	C_6H_6	160–258	41	107	40	18	19	7[f]
7	T	AcONa	.61	NaH[a]	.33	C_6H_6	180–254	41[c]	48	1	18	19	9[f,g]
8	B	$NaCH_2COONa$	.19			*n*-C_7H_{16}	22–250	51	142	48		25	
9	B	$NaCH_2COONa$	.19			*c*-C_6H_{12}	21–250	52	178	45		25	
10	B	$NaCH_2COONa$	.19			$C_6H_5CH_3$	20–230	50	125	30		15	5[h]

[a] Dispersion of 53.6% sodium hydride in mineral oil (Metal Hydrides). [b] Low pressure apparently due to leak. [c] Pressure to which ethylene was charged at lower end of the temperature range shown. Additional ethylene was charged to 600 p.s.i. (41 atm.) twice at intermediate temperatures in the range when the pressure fell to about 30 atm. [d] Ethylene charge. [e] Room temperature. [f] Butyric acid. [g] Also 3 g. of higher acids. [h] *n*-Propylbenzene.

TABLE II

CONDENSATION OF ETHYLENE WITH SODIUM PROPIONATE

Expt.	Procedure	EtCOONa, moles	Catalyst Kind	Catalyst Mole	Diluent	*T*, °C.	Press., atm. Init.,[l] r.t.[m]	Press., atm. Max. at *T*	Press., atm. Final r.t.[m]	Chief products, % EtCHMe-COOH	Chief products, % Et_2CMe-COOH	Chief products, % Higher acids, g.
11	B	0.32	$NaNH_2$	0.26	None	160–250	54	171	54		69	
12	Ba	2.60	$NaNH_2$	.51	None	150–250	60	195	58	11	71	
13	T	0.52	$NaNH_2$	.26	C_6H_6	145–195	41	80	23		88	
14	T	.52	$NaNH_2$	.13	$C_{10}H_{18}$[b]	167–179	7[c]	7	3[d]	21	11	
15	T	.52	NaH[e]	.67	C_6H_6	180–224	41[c]	41	..[d]	5	14	15
16	B	.32	K	.05[f]	None	150–250	50	100	39	34	44	
17	B	.32	Na	.13[g]	None	150–250	50	116	49	44	7	
18	B	.32	HSS[h]	.10	None	150–250	50	100	34	63	22	
19	B	.32	HSS	.10	C_6H_6	150–250	50	98	37	28	60	
20	T	.52	HSS	.08[f]	C_6H_6	176–260	41[c]	46	9[d]	4	75	5
21	B	.32	Li[i]	.43	C_6H_6[j]	150–250	50	158	44	19	15	
22	B	.32	BuLi[k]	.05	*n*-C_7H_{16}	140–206	40	55	20	47	42	

[a] Carried out in glass liner in rotating autoclave of 3600 ml. capacity. [b] Decahydronaphthalene. [c] Pressure to which ethylene was charged at lower end of the temperature range shown. [d] Recharged to original pressure 2 to 4 times as pressure dropped 10–15 atm. (2–3 atm. in expt. 14). [e] Dispersion of 53.6% of sodium hydride in mineral oil (Metal Hydrides). [f] Also 1 g. of anthracene. [g] Also 0.5 g. of anthracene. [h] "High surface sodium" (16% dispersion of sodium on alumina). [i] Dispersion of 30% lithium in mineral oil (69%) and oleic acid (1%). [j] Also 5 g. of benzyl chloride. [k] 15.5% Butyllithium in 2/3 pentane and 1/3 heptane (Foote Mineral). [l] Ethylene charge. [m] Room temperature.

of 4.2 moles of sodium propionate and 7.8 moles of ethylene per mole of sodamide and definitely confirms the catalytic nature of the reaction.

Good yields of the ethylation products were also obtained when sodium propionate was heated with ethylene in the presence of sodium or potassium without diluents (expts. 17 and 16) or of butyllithium with benzene as diluent (expt. 22). Use of lithium dispersed in mineral oil and benzene gave fair yields (19 and 15%, respectively) of the mono- and diethylated products (expt. 21).

Use of better mixing than is possible in a rotating autoclave gave high yields of alkylate at much lower pressures. When a mixture of sodium propionate and high surface sodium (16% sodium dispersed on alumina), in the presence of anthracene as promoter and benzene as diluent, was heated with ethylene at a maximum pressure of 46 atm. in a stirred autoclave (a "turbomixer"[3]), there was obtained a 4% yield of 2-ethylpropionic acid, a 75% yield of 2,2-diethylpropionic acid and a small amount of higher molecular weight acids (expt. 20). This corresponds to the reaction of 4.9 moles of sodium propionate and 9.5 moles of ethylene per gram atom of sodium.

A larger amount of the higher molecular weight alkylation product was obtained when sodium hydride was used as catalyst. Formation of the polyalkylated product depended on avoiding relatively long contact between the sodium hydride and the ethylene before the reaction temperature was reached, and also in avoiding overheating during the reaction. A mixture of 50 g. of sodium propionate, 30 g. of a 53.6% dispersion of sodium hydride in mineral oil, and 200 g. of benzene was stirred in the turbomixer (expt. 15) which was heated to 180° before ethylene was charged to 41 atm. The temperature was raised to 224° during 1.5 hours, ethylene being recharged to 41 atm. when the pressure dropped below about 25–30 atm. Work-up of the product gave 2.5 g. (4.8%), 9.3 g. (13.8%) and 14.7 g., respectively, of mono-, di- and polyethylated propionic acid. There was also obtained 16 g. of oily ethylene polymer.

It is interesting to note that the original reaction product in the experiments in which polyalkylation

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(3) G. L. Hervert, U. S. Patent 2,377,937.

TABLE III

CONDENSATION OF ETHYLENE WITH VARIOUS SALTS

Expt.	Procedure	RCOOM Kind	RCOOM Mole	Catalyst Kind	Catalyst Mole	Diluent	T, °C.	Press., atm. Init.,^{b} r.t.^{c}	Press., atm. Max. at T	Press., atm. Final r.t.^{c}	Chief products Kind	Chief products Yield, %
23	B	$Me_2CHCOONa$	0.09	$NaNH_2$	0.20	None	150–250	54	182	45	$Me_2CEtCOOH$	38
24	B	$C_8H_{17}COONa$	.30	$NaNH_2$	.26	None	150–250	50	106	48	$C_7H_{15}CHEtCOOH$	19
											$C_7H_{15}CEt_2COOH$	34
											$C_7H_{15}CEt_2CN$	10
25	B	$C_{11}H_{23}COONa$	.14	$NaNH_2$	.26	None	150–250	50	150	50	$C_{10}H_{21}CEt_2COOH$	52
26	B	$C_{17}H_{35}COONa$	.20	$NaNH_2$	.26	None	150–250	65	235	71	$C_{16}H_{33}CEt_2COOH$	38
27	B	c-$C_5H_9CH_2CH_2COONa$	.18	$NaNH_2$	.26	None	150–254	50	115	46	c-$C_5H_9CH_2CHEtCOOH$	27
											c-$C_5H_9CH_2CEt_2COOH$	9
28	B	c-$C_5H_9CH_2CH_2COONa$	.12	$NaNH_2$	.51	None	143–248	60	140	58	c-$C_5H_9CH_2CHEtCN$	22
											c-$C_5H_9CH_2CEt_2CN$	23
											c-$C_5H_9CH_2CHEtCONH_2$	2
29	B	c-$C_6H_{11}(CH_2)_3COONa$	.26	$NaNH_2$	.26	None	150–250	75	225	70	c-$C_6H_{11}CH_2CH_2CHEtCOOH$	31
											c-$C_6H_{11}CH_2CH_2CEt_2COOH$	14
30	B	c-$C_6H_{11}(CH_2)_3COONa$	.26	Na^a	.22	n-C_7H_{16}	150–250	70	206	46	c-$C_6H_{11}CH_2CH_2CEt_2COOH$	19
											Et_3CCOOH	16

[a] Dispersion of 50% sodium in mineral oil (Gray). [b] Ethylene charge. [c] Room temperature.

TABLE IV

PHYSICAL PROPERTIES OF PRODUCTS

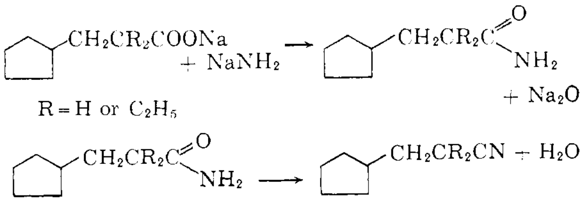
Compound	B.p., °C.	Press., mm.	Atm. B.p., °C.^{a}	$n^{20}D$	Mol. wt. Found^b	Mol. wt. Calcd.	Found, % C	Found, % H	Calcd., % C	Calcd., % H
$EtCHMeCOOH^c$	50–52	0.7								
$Et_2CHCOOH^c$	92–92	12.8			118	116	62.04	10.41	62.55	10.63
$EtCMe_2COOH^c$	103–104	28								
$Et_2CMeCOOH^c$	64–65	0.7	200–202		132	133				
Et_3CCOOH^c	81–82	1.2	220–221^d		143	144				
$C_7H_{15}CHEtCOOH$	148–149	7.2	271–273	1.4355			70.96	11.87	70.91	11.90
$C_7H_{15}CEt_2COOH$	127–127	1.0	285–287	1.4447			73.89	12.37	72.84	12.22
$C_7H_{15}CEt_2CN$	196–196	130	255–256	1.4388			79.45	13.08	79.93	12.90
$C_{10}H_{21}CEt_2COOH$	158–159	0.9					75.45	12.64	74.94	12.58
$C_{16}H_{33}CEt_2COOH$	198–200	0.7	380–382^e		333	341	77.92	13.06	77.59	13.02
c-$C_5H_9CH_2CHEtCOOH$	124–124	2.8	263–264	1.4584	170	170	70.73	10.39	70.55	10.66
c-$C_5H_9CH_2CEt_2COOH$	133–134	2.7		1.4690	194	198	71.89	10.84	72.68	11.18
c-$C_5H_9CH_2CHEtCN$	91–92	6.0		1.4568			79.48	11.31	79.41	11.33
c-$C_5H_9CH_2CEt_2CN$	106–107	5.5		1.4602			80.13	11.65	80.38	11.81
c-$C_5H_9CH_2CHEtCONH_2$			.....^{f}				71.06	11.16	70.96	11.31
c-$C_6H_{11}CH_2CH_2CHEtCOOH$	160–162	7.7	280–282	1.4634						
c-$C_6H_{11}CH_2CH_2CEt_2COOH$	140–142	0.8	309–311	1.4692	236	226	74.56	11.40	74.28	11.58

[a] Determined by boiling sample in test-tube at atmospheric pressure. [b] Determined from neutral equivalent. [c] "Beilstein," Vol. II. [d] M.p. 39–40°. [e] M.p. 42–43°. [f] M.p. 84°.

occurred was completely liquid; that is, it was apparently a colloidal suspension of the salt in the benzene diluent. On contact with air, sufficient benzene evaporated to result in the formation of a "skin" on the liquid.

The reaction of dry sodium pelargonate, sodium laurate or sodium stearate with ethylene in the presence of sodamide in the rotating autoclave under standard conditions (50 atm. initial ethylene pressure; 150–250°) resulted in the production of 2,2-diethylalkanoic acids as the major products (expts. 24, 25 and 26, respectively). Similar treatment (expt. 23) of the 2-methylalkanoate, sodium isobutyrate, yielded ethyldimethylacetic acid (*i.e.*, 2,2-dimethylbutyric acid).

A mixture of ethylation products, apparently α-ethyl- together with a smaller amount of α,α-diethylcyclopentanepropionic acid, was isolated in about 35% yield from the product of the reaction of sodium cyclopentanepropionate and sodamide with ethylene (expt. 27). When a higher mole ratio of sodamide to salt (4.2:1 instead of 1.4:1) was used, the product consisted chiefly of α-ethylcyclopentanepropionitrile and α,α-diethylcyclopentanepropionitrile (expt. 28). Formation of these compounds probably involved the intermediate formation of the corresponding amides from the acids and their subsequent dehydration



R = H or C_2H_5

$$Na_2O + H_2O \longrightarrow 2NaOH$$

Isolation of a small amount of crystalline α-ethylcyclopentanepropionamide from the residue from the distillation of the nitriles may be taken as confirmation of this mechanism.

In an analogous manner, production of nitrile accompanied the reaction of sodium pelargonate with ethylene in the presence of sodamide (expt. 24). 2,2-Diethylpelargonitrile was obtained in 10% yield.

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). α-Ethylcyclohexanebutyric acid was isolated in 31% yield and α,α-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° during 4 or 5 hours. The autoclave was permitted 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 extracted 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"[3] of about 1-liter capacity), the autoclave was heated with stirring to about 180° 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[1,2]

BY HAROLD HART AND ROMEO A. CIPRIANI[3]

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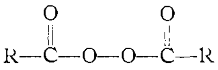
Cyclopropaneacetyl peroxide has been obtained crystalline at −20°, and its decomposition rates and products in carbon tetrachloride re-examined. Reproducible first-order kinetics were obtained on 0.02–0.09 *N* solutions, induced decomposition being demonstrably insignificant at these concentrations. 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 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



$$R-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-R$$

in which R is a secondary alkyl group decompose faster than when R is primary.[4] 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,[6] trichloromethyl,[7] triphenylmethyl[8]) are particularly thermally labile. Phenylacetyl peroxide, which affords an example of deviation from the usual product distribution, gave very little benzyl chloride (chlorine atom abstraction) when decomposed in carbon tetrachloride[6]; 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,[4] ethyl,[4] *n*-propyl,[4] δ-phenylbutyl,[10] cyclobutylmethyl,[5] cyclopentylmethyl,[5] cyclohexylmethyl[5]) all decompose at very nearly the same rate in carbon tetrachloride. The diacyl peroxide from cyclopropaneacetic acid (R = cyclopropylmethyl) appears to be an exception.[5] 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 CO_2 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

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[1] Taken from the Ph.D. thesis of Romeo A. Cipriani, Michigan State University, 1961.

[2] Support from the National Science Foundation, G 3289 and G 14289, is gratefully acknowledged.

[3] Monsanto Chemical Co. Fellow, 1958–1959.

[4] Isobutyryl peroxide decomposes 71 times faster than *n*-butyryl peroxide in isoöctane at 65°; calculated from the data of J. Smid, A. Rembaum and M. Szwarc, *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 2,580,358 (December 25, 1951); C. Zimmerman, U. S. Patent 2,580,373 (December 25, 1951).

[8] H. Wieland and G. Rasuwajew, *Ann.*, **480**, 157 (1930).

[9] For one detailed interpretation of this phenomenon, see M. Szwarc and L. Herk, *J. Chem. Phys.*, **29**, 438 (1958).

[10] D. F. DeTar and R. C. Lamb, *J. Am. Chem. Soc.*, **81**, 122 (1959).