saturated aqueous sodium disulfite (100 mL) and then dried (Na_2SO_4). Removal of the dichloromethane under reduced pressure left a dark liquid which was distilled under reduced pressure to yield 3-iodo-1-(trimethylsilyl)-1-propyne: 6.2 g (52%); bp 42 °C (2 mm); pale yellow liquid; IR 2951 (s, C≡C) cm^{-1}; ^{1}H NMR δ 0.84 [9 H, s, $Si(CH_3)_3$], 3.70 (2 H, s, CH_2); mass spectrum, calcd for C_6H_{11} ISi (M^+) *m/e* 237.9675, found 237.9688; calcd for $C_6H_{11}Si$ (M^+-I) *m/e* 111.0630, found 111.0634.

Method 2. Iodine (5.06 g, 0.02 mol) was added at once to a stirred solution of 3-(trimethylsilyl)-2-propyn-1-ol (2.56 g, 0.02 mol), tri-*n*-butylphosphine (4.06 g, 0.02 mol), and HMPA (7.16 g, 0.04 mol) in ether (20 mL) at 0 °C under nitrogen. After 15 min the mixture was treated with saturated aqueous sodium disulfite (100 mL) and worked up as described above to yield a dark semicrystalline residue which on distillation at reduced pressure afforded the foregoing iodopropyne (2.3 g, 47%). Entrapment and subsequent decomposition of the product by residual tributylphosphine oxide took place during the distillation. The distilled iodopropyne slowly darkenedand was found by ^{1}H NMR to have decomposed to the extent of approximately 20% after 5 days at -10 °C in the dark.

Acknowledgment. We thank the Australian Research Grant Committee for financial support. We are most grateful to Dr. Jacques Nemorin for carrying out the ^{1}H NMR decoupling experiments required for assignment of proton coupling constants to compounds 1–8.

Registry No. 1a, 70597-22-7; **1b**, 74472-75-6; **1c**, 74472-73-4; **1d**, 74472-76-7; **2a** (isomer 1), 78199-65-2; **2a** (isomer 2), 78199-66-3; **2b** (isomer 1), 78199-67-4; **2b** (isomer 2), 78199-68-5; **2c** (isomer 1), 78199-69-6; **2c** (isomer 2), 78199-70-9; **2d** (isomer 1), 78199-71-0; **2d** (isomer 2), 78199-72-1; (*E*)-**3a**, 74472-94-9; (*Z*)-**3a**, 74472-95-0; (*E*)-**3b**, 74472-98-3; (*Z*)-**3b**, 74472-99-4; (*E*)-**3c**, 74472-87-0; (*Z*)-**3c**, 74472-92-7; (*E*)-**3d**, 78199-73-2; (*Z*)-**3d**, 78199-74-3; **4a** (isomer 1), 78199-75-4; **4a** (isomer 2), 78199-76-5; **4b** (isomer 1), 78217-47-7; **4b** (isomer 2), 78199-77-6; **4c** (isomer 1), 78217-48-8; **4c** (isomer 2), 78199-78-7; **4d** (isomer 1), 78199-79-8; **4d** (isomer 2), 78199-80-1; (*E*)-**5a**, 78199-81-2; (*Z*)-**5a**, 78199-82-3; (*E*)-**5b**, 78199-83-4; (*Z*)-**5b**, 78199-84-5; (*E*)-**5c**, 74472-88-1; (*Z*)-**5c**, 74472-93-8; (*E*)-**5d**, 74473-03-3; (*Z*)-**5d**, 74473-04-4; **6**, 77548-22-2; **7** (isomer 1), 78199-85-6; **7** (isomer 2), 78246-83-0; **8**, 78199-86-7; **9**, 78199-87-8; allyl methyl sulfide, 10152-76-8; allyl *tert*-butyl sulfide, 37850-75-2; allyl phenyl sulfide, 5296-64-0; allyl phenyl selenide, 14370-82-2; diphenyl diselenide, 1666-13-3; 3-bromo-1-propene, 106-95-6; 2-cyclopenten-1-one, 930-30-3; hexamethylphosphoramide, 1608-26-0; 3-iodo-1-(trimethylsilyl)-1-propyne, 78199-88-9; [3-(trimethylsilyl)-2-propynyl]-*o*-phenylenephosphite, 78199-89-0; 3-(trimethylsilyl)-2-propyn-1-ol, 5272-36-6.

Base-Catalyzed Reactions of α,β-Unsaturated Esters and Nitriles. 4. Dimerization of β-Alkyl-Substituted Acrylates[1]

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2-Butenoates [$CH_3CH{=}CHCO_2R$ (1), where R = C_1–C_4 alkyl, cyclohexyl, or 1-bornyl] and higher β-alkyl-substituted acrylates [$R'CH{=}CHCO_2C_2H_5$ (2), where R′ = C_2–C_9 *n*-alkyl] undergo highly selective (>95%) dimerization in the presence of promoted potassium or sodium catalysts to yield corresponding 2-alkylidene-3-alkylglutarates (**3**). The reaction involves metalation of the β-alkylacrylate at the C-2 position, followed by addition at C-3 of a second monomeric molecule. Changes in the relative extent of dimerization (K_r) as a function of structural and experimental variables were determined. K_r is strongly dependent upon the inductive and steric characteristics of the alcoholic (R) group and of the β-alkyl substituent (R′). For an *n*-alkyl group as R′ the K_r value increases with increase in chain length from C_1 to C_4 but then decreases for longer substituents (C_5–C_9). Among the two geometric isomers in the dimeric product **3**, the isomer with an α-vinylic hydrogen cis to the carboalkoxy group is predominant in all cases, but its relative concentration decreases with an increase in the size of R′. Branched or cyclic β-substituents in **2** prevent dimerization due to steric hindrance in the rate-determining addition step. Promoted potassium or sodium catalysts show much higher dimerization activity compared to supported alkali metals or to alkoxides. For conversions of up to 60%, K_r values in proton-exchanging alkylbenzene solvents and in nonexchanging alkylcyclohexanes are closely similar, indicating faster abstraction of an α-vinylic hydrogen from the monomer, rather than a benzylic hydrogen from the solvent, in the chain regeneration step of the reaction.

It was shown[2] previously that ethyl crotonate undergoes selective dimerization at 110 °C in the presence of potassium–benzylpotassium as catalyst to give the diethyl ester of 2-ethylidene-3-methylglutaric acid in 90% yield. In the present study the possibility of enlarging the scope of base-catalyzed oligomerization reactions was investigated by determining the approximate relative dimerization rates of higher β-alkyl-substituted acrylates ($R'CH{=}CHCO_2Et$, where R′ = C_2–C_9 alkyl or cycloalkyl). The effect of the alcoholic group in 2-butenoates ($CH_3CH{=}CHCO_2R$, where R = C_1–C_4 alkyl, cyclohexyl or 1-bornyl) was also studied. Another purpose of this investigation was to determine the effect of experimental variables, i.e., the temperature, solvent, and type of base catalyst, upon relative dimerization rate.

The experimental procedure and analytical methods were similar to those used previously.[1,2]

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(1) Paper 3: J. Shabtai, E. Ney-Igner, and H. Pines, *J. Org. Chem.*, **43**, 4086 (1978).

(2) J. Shabtai and H. Pines, *J. Org. Chem.*, **30**, 3854 (1965).

Table I. Relative Extents of Dimerization (K_r) of 2-Butenoates (Crotonates) as a Function of the Alcoholic (R) Group[a, b]

starting 2-butenoate ($CH_3CH=CHCO_2R$) R	monomer no.	conversion, mol %[c]	K_r
CH_3	1	16.5	1.00
C_2H_5	2	32.0	1.94
$(CH_3)_2CH$	3	56.5	3.42
$(CH_3)_3C$	4	70.0	4.23
c-C_6H_{11}	5	35.5	2.15
1-bornyl[d]	6	10.0	0.60

[a] Catalyst: $K/C_6H_5CH_2K$, prepared from 0.006 mol of potassium metal and 0.0025 mol of *o*-chlorotoluene. [b] In each experiment were used 0.05 mol of monomer, 0.5 mol of toluene as solvent, and 0.01 mol of internal standard (1,2,3,4-tetrahydronaphthalene); reaction temperature 110 °C; reaction time 25 min. [c] Conversion into the corresponding dimer, I. [d] See structure II.


I


II

Table II. Relative Dimerization (K_r) of Ethyl β-Substituted Acrylates ($R'CH=CHCO_2Et$) as a Function of Substituent R'[a, b]

starting monomer ($R'CH=CHCO_2Et$)		catalyst			
		$K/KCH_2C_6H_5$[c]		$Na/NaCH_2C_6H_5$[d]	
R'	monomer no.	conversion, mol %	K_r[e]	conversion, mol %	K_r
CH_3	**2**	32.0	1.00	23.0	1.00
C_2H_5	**7**	68.0	2.06	46.2	2.00
n-C_3H_7	**8**	76.5	2.38	52.4	2.26
n-C_4H_9	**9**	91.5	2.86	58.0	2.54
n-C_5H_{11}	**10**	82.0	2.56	54.2	2.32
n-C_9H_{19}	**11**	60.0	1.87	27.0	1.18
$(CH_3)_2CH$	**12**	<0.1		<0.1	
c-C_6H_{11}	**13**	<0.1		<0.1	

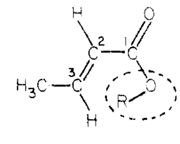
[a] Structure of dimers is given in structure **14** (see text). [b] Experimental conditions: temperature 110 °C; reaction time, 25 min. [c] See Table I, footnote *a*. [d] Prepared as in Table I, footnote *a*, except that 0.006 g of Na metal was used. [e] Some additional experiments indicate that the qualitative order of K_r values for compounds **2** and **7–13** does not change with temperature in the 0–110 °C range; K_r values at 70 °C for compounds **2**, **7**, **8**, **12**, and **13** (relative to that of **2** at 70 °C) are 1.00, 1.96, 2.34, <0.1, and <0.1, respectively; K_r for **7** = 1.91 at 30 °C and 1.89 at 0 °C (relative to K_r for **2** at 30 and 0 °C, respectively).

Results and Discussion

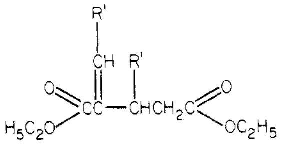
Effect of Alcoholic R Groups. Relative extents of dimerization (K_r) of 2-butenoates ($CH_3CH=CHCO_2R$), where R = CH_3, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$, cyclohexyl, and 1-bornyl, were determined by measurement of monomer conversions under identical experimental conditions (Table I). Due to the high conversions in many experiments the K_r values can be considered only as an approximate, semiquantitative measure of relative dimerization rates. As was seen, K_r increases with an increase in the size of the R group from methyl to *tert*-butyl. However, K_r for cyclohexyl 2-butenoate (**5**) is lower compared to that of isopropyl and *tert*-butyl 2-butenoates (monomer **3** and **4**), and the K_r value reaches a minimum in the case of 1-bornyl 2-butenoate (**6**).

The net effect of the alcoholic R group on the rate of dimerization should depend on the relative importance of its inductive (electron donating) vs. steric effects. The inductive effect (+I) of C_1 to C_4 alkyl groups has been reported to be in the order $(CH_3)_3C > (CH_3)_2CH > CH_3CH_2 > CH_3$.[3] In agreement with the present results, it has been reported that the reactivities of methacrylates for anion addition at the double bond also decreases with the change of the alcoholic alkyl group in the above-indicated order.[4]

For 2-butenoates with bulky R groups, e.g., 1-bornyl, steric effects become relatively more important. Examination of steric models of 1-bornyl 2-butenoate (monomer **6**) shows that rotation of the 1-bornyloxy group around the RO–C(1) bond in the anti conformer may effectively interfere with the approach of a second monomeric unit to the C-3 position[2] (R = 1-bornyl).



Effect of β-Alkyl Substituents. Approximate relative dimerization rates (K_r) of ethyl β-alkyl-substituted acrylates ($R'CH=CHCO_2C_2H_5$, where R' = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *n*-C_5H_{11}, *n*-C_9H_{19}, *i*-C_3H_7, and cyclohexyl) were determined by comparison of monomer conversions under identical experimental conditions with $K/KCH_2C_6H_5$ and $Na/NaCH_2C_6H_5$ as catalysts. The dimeric products formed were identified as substituted ethyl glutarates of the general formula **14**.



14

The results obtained are summarized in Table II. With R' = C_1 to C_4, compounds **2** and **7–9**, monomer conversion increases with an increase in the length of the alkyl group but then gradually decreases with higher (R' ≥ C_5) *n*-alkyl substituents, compounds **10** and **11**. A sharp decrease in dimerization rate is observed for acrylates with branched or cyclic β substituents, i.e., isopropyl or cyclohexyl groups, compounds **12** and **13**. Similar K_r values were obtained with $K/KCH_2C_6H_5$ as with $Na/NaCH_2C_6H_5$ as catalyst, although absolute conversions are considerably higher for all monomers with the potassium-containing catalyst.

The results obtained can be rationalized by considering the inductive and steric effects of the β-alkyl substituents. The increase in the K_r value with an increase in carbon number for compounds **2** and **7–9** indicates that the effect of relatively small *n*-alkyl groups is mostly inductive. Since for monomers with R' = C_1–C_4 the increase in the K_r value parallels the increase in the inductive effect of the *n*–alkyl group, it could be tentatively concluded that the monomeric carbanion addition to the $\Delta^{2,3}$ bond of a second molecule, rather than metalation at C-2, is the rate-determining step of the dimerization process.[2]

For R' (*n*-alkyl) ≥ C_5, monomers **10** and **11**, the steric hindrance effect for addition at the $\Delta^{2,3}$ bond apparently becomes more important, and K_r values decrease with an increase in the chain length of the substituent. Steric hindrance becomes very severe for monomers with a

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(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, NY, 1969, pp 78–95.

(4) H. Yuki, K. Hatada, K. Ohta, and Y. Okamoto, *J. Macromol. Chem.*, 9 (6), 983 (1975).

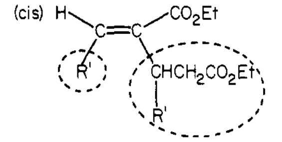
Table III. Relative Activities of Alkali Metal Catalysts for Dimerization of Cyclohexyl 2-Butenoate (13)[a]

catalyst	conversion of 13, mol %	rel dimerization,[g] K_r
$K/KCH_2C_6H_5$ [b]	35.5	1.00
$Na/NaCH_2C_6H_5$ [c]	21.5	0.61
$Li/LiCH_2C_6H_5$ [d]	2.1	0.06
$Li/LiCH_2C_6H_5$ [e]	15.0	
Na/Al_2O_3 [f]	12.3	0.35[h]

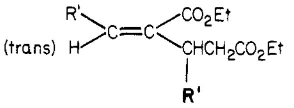
[a] For experimental conditions, see Table I, footnote *b*. [b] See Table I, footnote *a*. [c] See Table II, footnote *d*. [d] Prepared from 0.006 g of Li and 0.0025 mol of *o*-chlorotoluene. [e] A 10-fold amount of $Li/LiCH_2C_6H_5$ catalyst was used in this experiment. [f] Catalyst was prepared in situ by using 0.5 g of Na and 3 g of Alcoa 100-mesh Al_2O_3 (grade F-1), dried at 300–320 °C. The mixture was heated with stirring at 140 °C for 20 min until a black powder was obtained.[6] [g] Dimer: dicyclohexyl 2-ethylidene-3-methylglutarate. [h] Due to differences in the dispersion of this catalyst, as compared with the other catalysts, this result is only approximate.

branched or cyclic R′ group, e.g., isopropyl, **12**, and cyclohexyl, **13**, and addition at the C-3 position is sterically prevented as evidenced by the absence of dimerization in such cases.

The dimeric products of the general formula **14** are composed of two stereoisomers, **14a** and **14b**, in which the vinylic hydrogen is "cis" or "trans" relative to the carboalkoxy group, respectively.



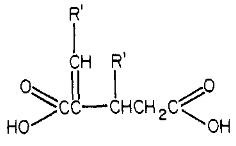
14a



14b

The ratios of the two isomers for all dimeric products obtained from monomers described in Table II were determined by a combination of gas chromatography on a capillary column and by quantitative NMR analysis. In all the cases the cis stereoisomer predominates, cis/trans ratios being in the range of 2.35–4.26. This ratio was found to decrease with increase in the size of the R′ substituent, aparently as a result of increased steric interference between the two cis groups indicated with broken circles in **14a**.

Hydrolysis of the dimeric esters obtained by dimerization of ethyl β-alkylacrylates produces quantitatively the corresponding dicarboxylic acids of the general formula **15**, the cis/trans isomer ratios in this case being in the range of 2.30–4.55 (see Experimental Section).



15

The dimerization–hydrolysis sequence therefore provides a convenient high-yield method for synthesis of various 2,3-disubstituted glutaric acids.

Relative Activities of Alkali Metal Catalysts. Comparative dimerization experiments with promoted potassium, sodium, and lithium catalyst systems were performed by using cyclohexyl 2-butenoate (**5**) as the monomer (Table III).

The relative catalytic activity, as reflected in the K_r values, decreases with a decrease in the electropositivity of the alkali metal used, K > Na > Li. This is in agreement with the behavior observed in the dimerization of acrylates[1] and also in other base-catalyzed carbon–carbon addition reactions.[5]

Table IV. Effect of Temperature upon Relative Dimerization Rate (K_r) of Ethyl 2-Butenoate[a]

temp, °C	conversion,[b] mol %	K_r
140[c]	20.0	1.00
110	32.5	1.60
70	34.0	1.70
30	80.0	4.00
0	75.0	3.75
−20	36.0	1.80

[a] The catalyst and experimental conditions are the same as in Table I, footnotes *a* and *b*. [b] Conversion into diethyl 2-ethylidene-3-methylglutarate. [c] Solvent was *m*-xylene.

The supported Na/Al_2O_3 catalyst, which is a very active catalyst for double bond isomerization of olefins,[6] appears to be less active, $K_r \approx 0.35$, for dimerization of **5** as compared to $Na/NaCH_2C_6H_5$, $K_r = 0.61$, under otherwise identical conditions.

Effect of Temperature upon Dimerization. The effect of temperature upon the dimerization of ethyl 2-butenoate is summarized in Table IV. The results obtained indicate that the optimal temperature range is between 0 and 30 °C, although the reaction proceeds at a reasonable rate even at −20 °C. On the other hand, at higher temperatures, e.g., 70–140 °C, K_r decreases. For clarification of the reason for this behavior, a separate experiment was performed at 140 °C by using the pure dimer, diethyl 2-ethylidene-3-methylglutarate (**14-2**), as the starting material. It was found that the final product contained 46.1% of monomer **2** and 53.9% dimer **14-2**; no other products were detected. This demonstrates that with an increase in reaction temperature, the equilibrium monomer $\rightleftharpoons$ dimer is gradually displaced in the direction of the free monomer.

Effect of Solvent. In order to determine the possible effect of solvents, we studied the dimerization of cyclohexyl 2-butenoate (**5**) catalyzed by $K/KCH_2C_6H_5$ using various alkylbenzenes, as well as methylcyclohexane. The results obtained (Table V) show that essentially no difference in relative dimerization rate is observed in experiments with toluene or methylcyclohexane as solvents, under otherwise identical experimental conditions. This is in agreement with previous observations[7] that sodium-catalyzed dimerization of β-methylstyrene to 1,5-diphenyl-4-methyl-1-pentene proceeds smoothly both in nonexchanging (alkylcyclohexane) and exchanging (alkylbenzene) solvents. Further, there are only minor differences in the conversion of **5** in different alkylbenzene solvents, e.g., toluene, *p*-xylene, and 1,2,4-trimethylbenzene. This indicates that at conversions of up to ~60% the relative dimerization rate (K_r) does not depend to any appreciable extent on the number of exchangeable benzylic hydrogens in the solvent molecule. On the other hand, experiments 5 and 6, in which the reaction time was extended for an additional 30 min after completing the monomer addition, indicate that under these conditions, resulting in overall increased conversions, the relative extent of dimerization is higher

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(5) H. Pines and W. M. Stalick, "Base-Catalyzed Reactions of Hydrocarbons and Related Compounds", Academic Press, New York, 1977.

(6) (a) W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 387 (1960). (b) J. Shabtai and E. Gil-Av, *J. Org. Chem.*, **28**, 2893 (1963).

(7) J. Shabtai and H. Pines, *J. Org. Chem.*, **29**, 2408 (1964).

Table V. Dependence of Cyclohexyl 2-Butenoate (5) Dimerization upon the Proton-Exchange Capacity of the Solvent[a,b]

expt	solvent	no. of benzylic hydrogens	conversion of 5,[c] mol %	rel dimerization, K_r
1	methylcyclohexane	0	61.0	1.00
2	toluene	3	60.0	0.98
3	*p*-xylene	6	60.0	0.98
4	1,2,4-trimethylbenzene	9	58.0	0.95
5[d]	methylcyclohexane	0	63.0	(1.03)
6[d]	toluene	3	75.0	(1.19)

[a] In each experiment were used 0.1 mol of 5, 1 mol of solvent, 0.018 mol of potassium, and 0.008 mol of *o*-chlorotoluene. [b] The total reaction time was 45 min, and the reaction temperature was 110 °C. [c] Conversion into dicyclohexyl 2-ethylidene-3-methylglutarate. [d] In experiments 5 and 6, the reaction time was extended for an additional period of 30 min.

Table VI. Relative Activity of *t*-BuOK/*t*-BuOH-Solvent Systems for Dimerization of Cyclohexyl 2-Butenoate (5) as a Function of the Type of Solvent[a]

catalyst (solvent) system[b]	time[c]	conversion of 5,[d] mol %	rel extent of dimerization[e]
t-BuOK/*t*-BuOH (100% toluene)	0.42	<0.1	
	10	<0.1	
	20	ca. 0.2	
	27	3.5	1.0
t-BuOK/*t*-BuOH (10% Me_2SO + 90% toluene)	0.42	<0.1	
	10	1.6	0.46
	20	6.8	1.94
	27	7.3	2.09
t-BuOK/*t*-BuOH (30% Me_2SO + 70% toluene)	0.42	3.2	0.91 (0.09)[f]
	10	8.3	2.37
	20	20.2	5.77
	27	28.0	8.12
t-BuOK (30% Me_2SO + 70% toluene)	0.42	3.2	0.91 (0.09)[f]
	10	9.1	2.60
	20	20.6	5.89
	27	29.0	8.26

[a] In each experiment were used 0.05 mol of monomer 5, 0.5 mol of solvent, and 0.01 mol of tetrahydronaphthalene as an internal standard. [b] The amount of *t*-BuOK/*t*-BuOH catalyst used in each experiment was 0.0126 mol. [c] Reaction time in hours. [d] Conversion into dicyclohexyl 2-ethylidene-3-methylglutarate. [e] Relative to that with the *t*-BuOK/*t*-BuOH-100% toluene system after 27 h. [f] Value in parentheses, relative to that with $K/C_6H_5CH_2K$ as catalyst, under otherwise identical experimental conditions (see Table III).

in toluene than in methylcyclohexane. The above observations can be explained by assuming a fast and, consequently, not rate-determining protonation step, which at conversions of up to ca. 60% involves preferential abstraction of an α-vinylic hydrogen from the monomer, rather than a less acidic benzylic hydrogen from the solvent. At extended contact time, viz., at higher conversion, there is a gradual decrease in the concentration of unreacted monomer molecules and, consequently, proton abstraction from the alkylbenzene solvent becomes more important.

In several separate experiments HMPA and Me_2SO, in respective concentrations of 5–30% and 5–15%, in toluene were used as solvents. The reactions were carried out under conditions described in the footnotes of Table V. After a reaction time of 25 min practically none of monomer **5** underwent dimerization. It has been reported that potassium dissolved in either HMPA or Me_2SO is an effective catalyst for the isomerization of alkenes.[8,9] The detrimental effect of these solvents upon the dimerization activity of $K/KCH_2C_6H_5$ requires further investigation, but it is probably due to interaction of the solvents with the metallic component of the catalyst.[10-12]

Potassium *tert*-Butoxide and Magnesium Oxide as Catalysts. The relative dimerization activities of *t*-BuOK–solvent systems, at different levels of solvent polarity, were also investigated. Results are given in Table VI.

The dimerization activity of the *t*-BuOK/BuOH–solvent system is much lower compared to that of $K/KCH_2C_6H_5$ (footnote *f*), and is considerably influenced by the polarity of the solvent used. Whereas in pure toluene dimerization is very slow, i.e., only 3.5% conversion in 27 h, the extent of reaction is increased eightfold in the presence of 30% Me_2SO in toluene as a solvent. A pure *t*-BuOK (free of *t*-BuOH) catalyst in the latter solvent shows approximately the same activity as that of the *t*-BuOK–*t*-BuOH system.

For the purpose of comparison the dimerization activity of a magnesium oxide catalyst was also examined. Reactions with **5** as substrate were performed by using the catalyst in the form of a fixed bed in a conventional flow system. It is found that at 110 °C and LHSV = 0.6 h^{-1} the conversion of **5** is ca. 7%. Although no direct comparison with experiments in Tables III and VI is possible, because of the much shorter contact times used with the MgO catalyst, it is indicated that the latter could be an efficient catalyst for dimerization of β-alkyl-substituted acrylates in a continuous-flow system, especially if the contact time is appropriately extended and/or the reaction temperature increased.

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(8) C. Cerceau, M. Laroche, A. Pazdzerski, and B. Blouri, *Bull. Soc. Chim. Fr.*, 921 (1969).

(9) S. Bank, *J. Org. Chem.*, **37**, 114 (1972).

(10) G. Fraenkel, S. H. Ellis, and D. T. Dix, *J. Am. Chem. Soc.*, **87**, 1406 (1965).

(11) H. Normant and M. Larcheveque, *C. R. Hebd. Seances Acad. Sci.*, **260**, 5062 (1965).

(12) D. Martin and H. G. Hauthal, "Dimethyl Sulfoxide", Wiley, New York, 1975, pp 350–351.

Table VII. Some Properties of β-Alkyl-Substituted Acrylate Monomers

monomer structure	bp, °C (torr)	MS, m/e (M^+)	elemental analysis
$CH_3CH=CHCO_2Et$ (2)	138 (760)	114	calcd: C, 63.13; H, 8.83
			found: C, 63.40; H, 8.56
$CH_3CH_2CH=CHCO_2Et$ (7)	77-79 (30)	128	calcd: C, 65.60; H, 9.44
			found: C, 65.25; H, 9.24
$CH_3(CH_2)_2CH=CHCO_2Et$ (8)	82-83 (30)	142	calcd: C, 67.62; H, 11.80
			found: C, 67.42; H, 11.90
$CH_3(CH_2)_3CH=CHCO_2Et$ (9)	98-99 (20)	156	calcd: C, 69.20; H, 10.30
			found: C, 69.42; H, 10.24
$CH_3(CH_2)_4CH=CHCO_2Et$ (10)	115-116 (20)	170	calcd: C, 70.50; H, 10.66
			found: C, 70.42; H, 10.48
$CH_3(CH_2)_8CH=CHCO_2Et$ (11)	188-192 (20)	226	calcd: C, 74.28; H, 11.56
			found: C, 74.40; H, 11.20
$(CH_3)_2CHCH=CHCO_2Et$ (12)	90-92 (35)	142	calcd: C, 65.60; H, 9.44
			found: C, 65.40; H, 9.54
c-$C_6H_{11}CH=CHCO_2Et$ (13)	138-142 (20)	182	calcd: C, 73.08; H, 9.84
			found: C, 73.40; H, 9.90

Mechanism of Dimerization. The results obtained show that the products formed from the dimerization of β-alkyl-substituted acrylates consist exclusively of the diesters of α-alkylidene-β-alkylglutaric acid (14). This finding indicates that the α-vinylic (C-2) hydrogen in β-alkyl-substituted acrylates is considerably more acidic that the allylic methyl (or methylene) hydrogens and that dimerization is most likely initiated by preferential metalation at the C-2 position. This is in accordance with similar observations when acrylates[1], ethyl crotonate,[2] and 2-butenenitrile[13] were submitted to di- and trimerization in the presence of potassium-benzylpotassium catalyst; metalation occurred exclusively at the α-vinylic position. On the other hand, with the same catalyst, β-methylstyrene is metalated preferentially at the allylic position.[7] The difference is probably due to the stronger electron-withdrawing effect of an ester or nitrile group as compared with that of a phenyl group, resulting in higher acidity of the C-2 hydrogen in $\Delta^{2,3}$-unsaturated esters and nitriles.

The indicated mechanism of dimerization of β-alkyl-substituted acrylates is similar to that described for ethyl crotonate.[2] The first step is metalation of the α-vinylic carbon, followed by addition of the carbanion formed to the double bond of another monomeric molecule. At moderate conversions the resulting dimeric carbanion is converted to 14 by preferential abstraction of the C-2 hydrogen from unreacted monomer, with regeneration of the monomeric carbanion (A^-; see Scheme I).

In the case of promoted metals, the initiating step involves reaction of the monomer with benzyl anion derived from o-chlorotoluene, which is employed in the preparation of the catalyst.

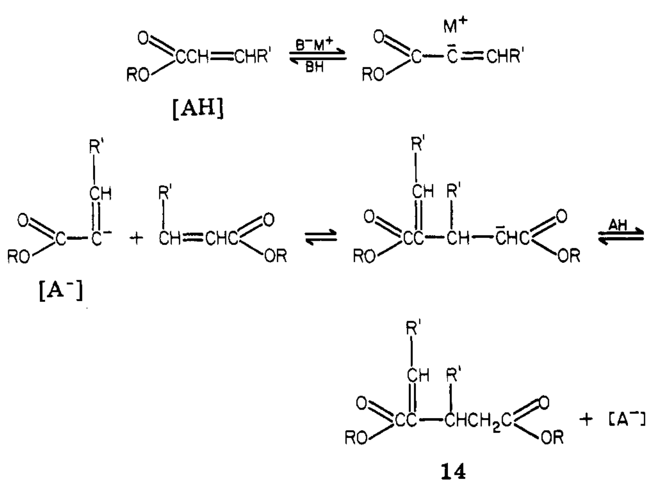
The present study shows that dimerization of β-alkyl-substituted acrylates in the presence of promoted potassium or sodium catalysts is a very selective and versatile reaction, which can be conveniently used for synthesis of a variety of branched glutaric acids and esters.

Experimental Section

Apparatus, Catalysts, and Experimental Procedure. Unless otherwise indicated the apparatus and the experimental procedures were similar to those described in the preceedng paper of this series.[1] Detailed procedures for preparing alkali-benzylalkali metal catalysts and supported Na/Al_2O_3 have been described previously.[1,2,6,13] Other catalysts were obtained as follows.

(a) The t-BuOK-t-BuOH catalyst was prepared from 125 mL of absolute *tert*-butyl alcohol and 6.8 g of freshly cut potassium metal, according to a previously described method.[14]

Scheme I[a]



[a] AH = monomer; B^- = chain initiator.

(b) The t-BuOK (alcohol free) catalyst was prepared from 100 mL of *tert*-butyl alcohol and 22.7 g of potassium metal. The alcohol was brought to reflux, and the potassium was added in small pieces, followed by another 50 mL/of alcohol. The reaction mixture was allowed to reflux for 16 h to complete the reaction, and the excess of alcohol was removed at 120 °C (1 mm). The product obtained was further purified by vacuum sublimation at 220 °C (1 mm).

(c) Magnesium oxide (Harshaw Catalysts, $^1/_8$-in-pellets) was preactivated at 400 °C for 16 h. Experiments with MgO as catalyst were performed as follows. A portion of the MgO (8.2 g) was placed in a flow reactor, i.e., a vertically mounted 60 cm × 17 mm Pyrex glass tube. The reactor was equipped with a thermoregulated cylindrical glass furnace, a flowmeter for controlling the flow rate of the carrier gas, and a calibrated syringe pump for introduction of the reactant. The outlet of the tube was connected to a cooled receiver for quantitative collection of the product. The catalyst fixed bed was activated at 390 °C for an additional 1.5 h under a stream of Drierite-dried nitrogen. The desired reaction temperature in the range of 150-250 °C was then adjusted, and the liquid feed, consisting of 0.025 mol of monomer dissolved in 0.25 mol of toluene, was then introduced into the reactor at a rate of 0.23 mL/min. A slow nitrogen stream was maintained throughout the experiments.

Preparation of Starting Materials. The different α,β-unsaturated esters were prepared by the following methods.

Methyl 2-Butenoate (1). Methanol (3 mol), concentrated sulfuric acid (5 mL), and crotonic acid (0.56 mol) were heated under reflux for 12 h. The mixture was then cooled, water was added, and the ester formed was separated and dissolved in ether.

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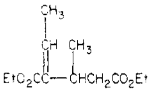
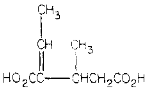
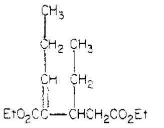
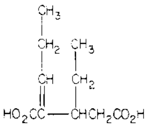
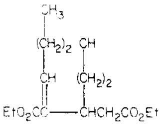
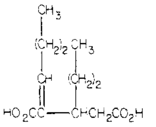
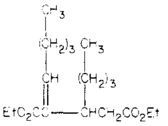
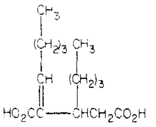
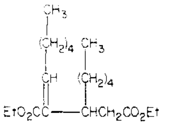
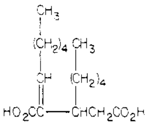
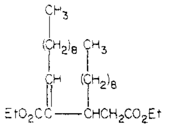
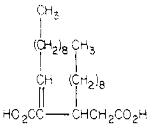
(13) J. Shabtai, E. Ney-Igner, and H. Pines, *J. Org. Chem.*, 40, 1158 (1975).

(14) A. Zwierzak and H. Pines, *J. Org. Chem.*, 28, 3392 (1963).

Table VIII. Numbers of Starting Monomers and Corresponding Dimeric Esters and Acids

monomer	dimeric ester	no.	corresponding dicarboxylic acid	no.
2	 $EtO_2CC(=CHCH_3)-CH(CH_3)CH_2CO_2Et$	14-2	 $HO_2CC(=CHCH_3)-CH(CH_3)CH_2CO_2H$	15-2
7	 $EtO_2CC(=CHCH_2CH_3)-CH(CH_2CH_3)CH_2CO_2Et$	14-7	 $HO_2CC(=CHCH_2CH_3)-CH(CH_2CH_3)CH_2CO_2H$	15-7
8	 $EtO_2CC(=CH(CH_2)_2CH_3)-CH((CH_2)_2CH_3)CH_2CO_2Et$	14-8	 $HO_2CC(=CH(CH_2)_2CH_3)-CH((CH_2)_2CH_3)CH_2CO_2H$	15-8
9	 $EtO_2CC(=CH(CH_2)_3CH_3)-CH((CH_2)_3CH_3)CH_2CO_2Et$	14-9	 $HO_2CC(=CH(CH_2)_3CH_3)-CH((CH_2)_3CH_3)CH_2CO_2H$	15-9
10	 $EtO_2CC(=CH(CH_2)_4CH_3)-CH((CH_2)_4CH_3)CH_2CO_2Et$	14-10	 $HO_2CC(=CH(CH_2)_4CH_3)-CH((CH_2)_4CH_3)CH_2CO_2H$	15-10
11	 $EtO_2CC(=CH(CH_2)_8CH_3)-CH((CH_2)_8CH_3)CH_2CO_2Et$	14-11	 $HO_2CC(=CH(CH_2)_8CH_3)-CH((CH_2)_8CH_3)CH_2CO_2H$	15-11

The ethereal solution was washed with aqueous 10% sodium carbonate and dried with anhydrous $MgSO_4$, and the solvent was removed. The crude product was distilled to give 99% pure methyl 2-butenoate: bp 118–120 °C (760 mm); 91% yield.

Higher 2-Butenoates (Compounds 2–6). Recrystallized crotonic acid (0.58 mol, mp 72–73 °C), 2.64 mol of the appropriate alcohol, 5 mL of concentrated sulfuric acid, and 60 mL of benzene were introduced in a Soxhlet apparatus containing 20 g of anhydrous $MgSO_4$. The mixture was refluxed overnight and then cooled, and 200 mL of water plus 60 mL of benzene were added to the flask. The mixture was washed with aqueous 10% sodium bicarbonate and with water. The organic layer was dried over anhydrous $MgSO_4$ and then fractionally distilled at reduced pressure to give the pure 2-butenoates in yields of 80–92%. The identity of the products was confirmed by measurement of NMR and mass spectra and by elemental analysis.

β-Alkyl-substituted acrylic acids ($R'CH{=}CHCO_2H$, where $R' = C_2$–C_9 *n*-alkyl) were prepared by modifying and enlarging the scope of a previously reported[15,16] procedure.

To 1.3 mol of pyridine, placed in an ice-water-cooled flask, were added with constant stirring 1 mol of malonic acid and then 1.25 mol of the desired aldehyde. The mixture was left for 2 days at room temperature and then poured into a beaker containing an excess of 50% sulfuric acid. The resulting solution was extracted 6 or 7 times with small portions or ether (50–60 mL), the extract was dried over anhydrous $MgSO_4$, and the solvent was removed by evaporation. The crude product was fractionally distilled at 0.5 mm to give the pure (>98%) β-alkyl-substituted acid in 90–94% yield.

Ethyl β-Alkyl-Substituted Acrylates. A solution consisting of 0.58 mol of β-alkyl-substituted acrylic acid, 2.64 mol of ethanol, 60 mL of benzene, and 5 mL of concentrated sulfuric acid were introduced in a Soxhlet apparatus containing 20 g of anhydrous $MgSO_4$ and esterified as described above for 2-butenoates. The yields of esters 2 and 7–13 were 86–94%. Table VII summarizes some data and the elemental analyses of the purified (>98%) compounds.

Table IX. NMR Spectra and Isomeric Composition of Dimeric Esters (2-Alkylidene-3-alkylglutarates)[a]

ester	chemical shift,[b] δ					"cis"/"trans" isomeric ratio
	HC=C	OCH_2	CH	CH_3 in R'CH= group at C-2	CH_3 in R' group at C-3	
14-2	6.70 (q, 1 H, *J* = 7.2)	4.10 (q, 4 H, *J* = 7.0)	3.0–3.5 (m, 1 H)	1.82 (d, 3 H, *J* = 7.2)	1.23 (d, 3 H, *J* = 6.5)	4.26
14-7	6.78 (t, 1 H, *J* = 7.2)	4.05 (q, 4 H, *J* = 7.0)	3.16–2.70 (m, 1 H)	1.38 (t, 3 H, *J* = 6.5)	1.18 (t, 3 H, *J* = 6.5)	3.18
14-8	6.68 (t, 1 H, *J* = 7.2)	4.05 (q, 4 H, *J* = 7.0)	3.18–2.77 (m, 1 H)	*c*	*c*	2.60
14-9	6.70 (t, 1 H, *J* = 7.2)	4.08 (q, 4 H, *J* = 7.0)	2.22–2.72 (m, 1 H)	*c*	*c*	2.47
14-10	6.69 (t, 1 H, *J* = 7.2)	4.05 (q, 4 H, *J* = 7.0)	3.14–2.66 (m, 1 H)	*c*	*c*	2.46
14-11	6.76 (t, 1 H, *J* = 7.2)	4.10 (q, 4 H, *J* = 7.0)	3.26–2.76 (m, 1 H)	*c*	*c*	2.35

[a] Chemical shifts are given in parts per million (δ); the solvent was CCl_4. [b] In parentheses are given the following: multiplicity, coupling constant, *J* (in hertz), and integration. [c] Broad absorption band due to increased complexity and superposition of adjacent CH_2 group signals.

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(15) S. E. Boxer and R. P. Linstead, *J. Chem. Soc.*, 740 (1931).
(16) A. A. Goldberg and R. P. Linstead *J. Chem. Soc.*, 2343 (1928).

Table X. IR and Mass Spectral Data on Dimeric Esters (2-Alkylidene-3-alkylglutarates)

ester	bp, °C (torr)	MS, *m/e* (M^+)	IR abs maxima,[a] cm^{-1}	elemental analysis
14-2	80–82 (0.6)	228	2990 (s), 1742 (s), 1720 (s), 1469 (m), 1456 (m), 1390 (w), 1378 (m), 1293 (w), 1263 (s), 1183 (s), 1124 (w), 1040 (s), 950 (w)	calcd: C, 63.13; H, 8.83 found: C, 63.60; H, 8.68
14-7	116–120 (0.8)	256	2970 (s), 2920 (s), 1725 (s), 1700 (s), 1465 (m), 1450 (m), 1395 (w), 1375 (m), 1280 (m), 1140 (s), 1100 (w), 1040 (s), 950 (w)	calcd: C, 65.59; H, 9.44 found: C, 65.68; H, 9.54
14-8	122–126 (0.7)	284	2980 (s), 2940 (s), 2870 (s), 1735 (s), 1630 (m), 1465 (s), 1440 (m), 1390 (w), 1365 (w), 1090 (m), 1030 (m), 960 (w)	calcd: C, 67.62; H, 11.81 found: C, 67.80; H, 11.90
14-9	134–135 (0.7)	312	2980 (s), 2900 (s), 1745 (s), 1720 (s), 1480 (m), 1455 (m), 1395 (w), 1380 (m), 1100 (m), 1040 (s), 980 (w), 940 (w)	calcd: C, 69.19; H, 10.38 found: C, 69.35; H, 10.44
14-10	145–150 (0.7)	340	2980 (s), 2880 (s), 1740 (s), 1720 (s), 1475 (m), 1445 (w), 1375 (m), 1100 (w), 1040 (w), 980 (w)	calcd: C, 70.54; H, 10.66 found: C, 70.30; H, 10.71
14-11	210–212 (0.5)	452	2980 (s), 2860 (s), 1745 (s), 1710 (s), 1475 (m), 1450 (s), 1390 (w), 1040 (w), 980 (w)	calcd: C, 74.28; H, 11.58 found: C, 74.50; H, 11.80

[a] Intensity: s, strong; m, medium; w, weak.

Table XI. NMR Spectra and Isomeric Composition of Dimeric Acids (2-Alkylidene-3-alkylglutaric Acids)[a]

dimeric acid	chemical shift,[b] δ					"cis"/"trans" isomeric ratio
	HC=C	OH	CH	CH_3 in R′CH= group at C-2	CH_3 in R′ group at C-3	
15-2	6.96 (q, 1 H, *J* = 7.2)	11.40 (s, 2 H)	3.00–3.30 (m, 1 H)	1.32 (d, 3 H, *J* = 7.2)	1.23 (d, 3 H, *J* = 6.5)	4.55
15-7	7.05 (t, 1 H, *J* = 7.2)	12.16 (s, 2 H)	3.23–2.90 (m, 1 H)	1.60 (t, 3 H, *J* = 6.5)	1.00 (t, 3 H, *J* = 6.5)	3.76
15-8	7.00 (t, 1 H, *J* = 7.2)	11.42 (s, 2 H)	3.24–2.88 (m, 1 H)	*c*	*c*	3.35
15-9	7.00 (t, 1 H, *J* = 7.2)	11.67 (s, 2 H)	3.29–2.88 (m, 1 H)	*c*	*c*	3.32
15-10	7.00 (t, 1 H, *J* = 7.2)	11.33 (s, 2 H)	3.29–2.88 (m, 1 H)	*c*	*c*	2.82
15-11	7.05 (t, 1 H, *J* = 7.2)	11.87 (s, 2 H)	3.21–2.80 (m, 1 H)	*c*	*c*	2.80

[a] Chemical shifts are given in parts per million (δ); the solvent was CCl_4. [b] In parentheses are given the multiplicity, the coupling constant, *J* (in hertz), and the integration. [c] Broad absorption band due to increased complexity and superposition of adjacent CH_2 group signals.

Isolation and Identification of Reaction Products. Products formed by the dimerization of β-alkyl-substituted acrylates were isolated in a purity of >99% by a combination of fractional distillation and preparative gas chromatography and subsequently identified by measurements of NMR, IR, and mass spectra and by elemental analysis. For simplicity in presentation of data, the numbering of monomers and the corresponding dimeric esters and acids are given in Table VIII. NMR and isomeric composition data on the dimeric esters are summarized in Table IX, while infrared absorption maxima and some other properties are given in Table X.

Examination of the NMR signals due to the α-vinylic proton in diesters **14-7** to **14-11** reveals that in addition to the main triplet, centered at 6.68–6.78 ppm, due to geometric isomer **14a**, there is an additional triplet of lower intensity centered at 5.78–5.97 ppm due to isomer **14b**. The two signals were used to determine the relative concentration of these isomers for each one of the dimeric esters.

It should be noted that in the case of α,β-unsaturated esters and acids the β-carboalkoxy (or carboxylic group) has a deshielding effect on the cis vinylic proton. The differential shielding of the "cis" and "trans" vinylic protons is 0.58 ppm for methacrylic acid and 0.63 ppm for methyl "*cis*"-and "*trans*"-crotonate.[2] The separation of the two signals in the present case is in the range of 0.83–1.00 ppm, allowing for easy determination of the "cis"/"trans" isomer distribution in all diesters (Table IX).

Table XII. IR and Mass Spectral Data on Dimeric Acids (2-Alkylidene-3-alkylglutaric Acids)

dimeric acid	MS, *m/e* (M^+)	IR abs maxima,[a] cm^{-1}
15-2	172	3050 (s), 2990 (s), 2970 (w), 1730 (s), 1525 (m), 1465 (m), 1410 (s), 1390, (w), 1290 (m), 1210 (s), 920 (w)
15-7	200	3050 (s), 3000 (s), 2960 (w), 2910 (w), 1720 (s), 1530 (m), 1470 (m), 1415 (s), 1385 (w), 1285 (m), 1220 (s), 920 (m)
15-8	228	3070 (broad band), 3010 (s), 2980 (m), 2920 (m), 1745 (s), 1720 (s), 1480 (m), 1430 (s), 1397 (w), 1295 (s), 1270 (m), 930 (m)
15-9	256	3070 (broad band), 2990 (s), 3960 (m), 2900 (w), 1722 (s), 1706 (s), 1475 (m), 1420 (s), 1385 (w), 1290 (s), 1260 (s), 920 (m)
15-10	284	3070 (broad band), 2990 (s), 2960 (s), 1725 (s), 1705 (s), 1700 (s), 1475 (m), 1380 (w), 1280 (s), 1250 (m), 920 (m)
15-11	394	3070 (broad band), 2990 (s), 2960 (s), 2880 (m), 1725 (s), 1700 (s), 1475 (m), 1425 (s), 1390 (w), 1270 (s), 1240 (m), 920 (m)

[a] Intensity: s, strong; m, medium; w, weak.

Hydrolysis of 2-Alkylidene-3-alkylglutarates 14 to Corresponding Diacids 15. Diester 14 (1 g) was hydrolyzed by refluxing with 10% aqueous sodium hydroxide (25 mL) for 8 h. The mixture was then cooled to room temperature, acidified with 10% aqueous hydrochloric acid, and continuously extracted with ether for 24 h. The acid obtained was freed from the solvent and identified by measurements of NMR, IR, and mass spectra. The spectral data and the isomeric composition of all diacids are summarized in Tables XI and XII.

Registry No. 1, 18707-60-3; **2**, 10544-63-5; **3**, 18060-77-0; **4**, 3246-27-3; **5**, 16491-62-6; **6**, 46472-88-2; **7**, 2445-93-4; **8**, 1552-67-6; **9**, 2351-88-4; **10**, 2351-90-8; **11**, 78217-11-5; **12**, 2351-97-5; **13**, 6048-09-5; (*E*)-**14-2**, 22485-82-1; (*Z*)-**14-2**, 22528-27-4; (*E*)-**14-7**, 78217-12-6; (*Z*)-**14-7**, 78217-13-7; (*E*)-14-8, 78217-14-8; (*Z*)-14-8, 78217-15-9; (*E*)-14-9, 78217-16-0; (*Z*)-14-9, 78217-17-1; (*Z*)-**14-10**, 78217-18-2; (*Z*)-1410, 78217-19-3; (*E*)-**14-11**, 78217-20-6; (*Z*)-**14-11**, 78217-21-7; (*E*)-**15-2**, 78217-22-8; (*Z*)-**15-2**, 78217-23-9; (*E*)-**15-7**, 78217-24-0; (*Z*)-15-7, 78217-25-1; (*E*)-**15-8**, 78217-26-2; (*Z*)-**15-8**, 78217-27-3; (*E*)-**15-9**, 78217-28-4; (*Z*)-**15-9**, 78217-29-5; (*E*)-**15-10**, 78217-30-8; (*Z*)-**15-10**, 78217-31-9; (*E*)-**15-11**, 78217-32-0; (*Z*)-**15-11**, 78217-33-1; crotonic acid, 3724-65-0; malonic acid, 141-82-2.

Kinetic and Thermodynamic Study of the Base-Catalyzed Oxidative Cleavage of 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol

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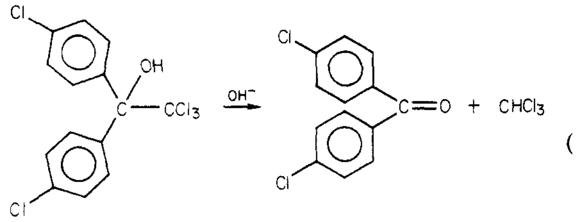
The kinetics and mechanism of the base-catalyzed oxidative cleavage of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (**1a**) and 1,1-diphenyl-2,2,2-trichloroethanol (**1b**) have been studied as a function of base concentration, solvent, and temperature. The pseudo-first-order rate constant for the disappearance of both **1a** and **1b** increases linearly at low base concentration, reaching a plateau at high hydroxide ion concentration. From data obtained in the plateau region values of 18.7 kcal/mol, 21.3 kcal/mol, and 8.8 eu were determined for the free energy, enthalpy, and entropy of activation of **1a**, respectively. The values of the activation parameters for compound **1b** are similar to those described for **1a**. The data obtained are consistent with an ElcB-type mechanism.

It has been recently reported[1] that in the presence of hexadecyltrimethylammonium bromide (CTAB) and hexadecyldimethyl(2-hydroxyethyl)ammonium bromide (CHEDAB) enhancements of 200- and 345-fold of the rate of the base–catalyzed oxidative cleavage of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (**1a**) occurs in aqueous basic solutions (eq 1). Despite the fact that **1a** is a pesticide used on a commercial scale and that it has also been identified as a metabolite in the enzymatic degradation of 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT),[2-4] there is not any detailed study available about the stability, kinetics, and mechanism of its oxidation to 4,4′-dichlorobenzophenone (**2a**) in basic solutions.



(1)

Considering that **1a** has a reasonably acidic proton and a not very labile leaving group, it represents an ideal compound for detection of an ElcB type mechanism similar to the "irreversible" first-order carbanion elimination.[5-7] The decomposition of **1a** has many biological implications. Thus, it appeared of interest to study this reaction in order to obtain information about the mechanism of the base-catalyzed oxidative cleavage and of the kinetic and thermodynamic stability of **1a** in aqueous solutions.

Experimental Section

1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethanol (**1a**) was purchased from Chemical Service, and its purity found to be satisfactory by thin-layer chromatographic, UV, and IR analysis. The compound 1,1-diphenyl-2,2,2-trichloroethanol (**1b**) was prepared by a previously described procedure.[8] Methanol was obtained from Merck Chemical Co., and water was deionized and distilled. The pH of the aqueous solutions was adjusted by the addition of NaOH and determined by means of a Methrohm E-350-B pH meter. Stock solutions of **1a** and **1b** (10^{-3} M) were prepared in methanol and kept in the refrigerator, being stable for several weeks. In solutions with pH >11, the concentration of hydroxide ion was directly determined by titration.

Rates of oxidation of **1a** were determined by following (Shimadzu UV-210-A spectrophotometer for the slower runs and Durrum JASCO stopped-flow instrument for the faster ones) the appearance of 4,4′-dichlorobenzophenone (**2a**) at 263 nm in methanol and at 267 nm in water; for compound **1b** the reaction was monitored at 258 nm. The temperature for the kinetic runs was maintained within ±0.1 °C of the desired value by using a water-jacketed cell. Individual pseudo-first-order rate constants, k_{expt} values, were obtained from linear plots of ln $(A_\infty - A_t)$ vs. time. All of these plots were linear for at least 90% of the reaction, and the correlation coefficients were greater than 0.99.

Chloroform was identified with a Varian 2440-D gas chromatograph by using a 2 m × 3.2 mm column packed with squalane. The temperatures of the column, detector, and injection block were 85, 120, and 125 °C, rspectively. A retention time of 80 s was found. Under our experimental conditions the hydrolysis of chloroform to carbon monoxide and formate ($k_2 = 2.3 \times 10^{-5}$ M^{-1} s^{-1} at 20.0 °C[9]) is not observed.

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(1) Nome, F.; Schwingel, E. W.; Ionescu, L. G. *J. Org. Chem.* **1980**, *45*, 705.

(2) Korte, F.; Klein, W. *Pharma Int., Engl. Ed.* **1971**, *5*, 12.

(3) Kuhr, R. *CHEMTECH.* **1976**, 316.

(4) Khan, M.; Gassman, M.; Haque, R. *CHEMTECH.* **1976**, 62.

(5) Bordwell, F. G.; Knippe, A. C.; Yee, K. C. *J. Am. Chem. Soc.* **1970**, *92*, 5945.

(6) Saunders, W. H., Jr., Cockerill, A. F. "Mechanism of Elimination Reactions"; wiley: New York, 1973.

(7) Saunders, W. H., Jr. *Acc. Chem. Res.* **1976**, *9*, 19.

(8) Bergmann, E. D.; Kaluszyner, A. *J. Org. Chem.* **1958**, *23*, 1306.

(9) Hine, J.; Ehrenson, S. J. *J. Am. Chem. Soc.* **1958**, *80*, 824.

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