($CDCl_3$) δ 1.30 (t, J = 7 Hz, 3 H), 4.28 (q, J = 7 Hz, 2 H), and 6.63 (broad s, 1 H).

The other *N*-chloroamides listed in Table I were prepared in the same way but on a smaller scale (from 10 to 100 mmol), the excess of amide varying from 1 to 2%. With amides very insoluble in water, a larger reaction time was needed (up to 30 min) with a few milliliters of methylene chloride being added to speed up the reaction. When working on a 10–40-mmol scale, acidifications were carried out with 1 *N* H_2SO_4. Because of the higher solubility of *N*-chlorocarboxamides in water, four to ten extractions with methylene chloride were performed. The ir spectra (CCl_4) of the *N*-chlorocarbamates **2–6** are quite similar to that of ethyl *N*-chlorocarbamate (**1**) and they all show a band in the following regions: 3400 (free NH), 3200–3180 (broad, associated NH), 1770 (C=O), 1740–1730 (C=O), 1710–1700 (C=O), 1410–1380, 1350–1330, 1200 (ester), and 1080–1000 cm^{-1} (ester).

Typical Procedure for the Monobromination of Carbamates and Carboxamides. Preparation of Ethyl *N*-Bromocarbamate (17). To 4.43 g (43 mmol) of NaBr was added 53.4 ml of NaOCl solution (0.75 mmol/ml, 40 mmol). The mixture was stirred for 15 min at room temperature. The deep yellow hypobromite solution was cooled in an ice bath and 3.60 g (40.4 mmol) of ethyl carbamate was added. The reaction mixture was stirred until it became pale yellow (almost colorless). Methylene chloride (50 ml) was added followed by the dropwise addition of 41 ml (47 mequiv) of 1.15 *N* H_2SO_4 with vigorous stirring. The addition took 1.5 hr. The reddish organic phase was decanted and the aqueous layer was extracted with methylene chloride (3 × 15 ml). The combined extracts were dried (Na_2SO_4) and the solvent was removed on the rotatory evaporator to yield 5.71 g of **17** as a yellow oil (see Table I): ir (CCl_4) 3400, 3200 (broad), 1720 (broad, strong), 1415, 1375, 1330, 1220, 1190 (shoulder), and 1065 cm^{-1}, and weak bands at 3500 and 1590 cm^{-1} due to the presence of ethyl carbamate; nmr (CCl_4) δ 1.28 (t, J = 7 Hz, carbamate CH_3) and 1.33 (t, J = 7 Hz, *N*-bromo- and *N,N*-dibromocarbamate CH_3), 4.17 (q, J = 7 Hz, carbamate CH_2) and 4.28 (q, J = 7 Hz, *N*-bromo- and *N,N*-dibromocarbamate CH_2), 5.41 (broad s, carbamate NH_2), and 6.55 (broad s, *N*-bromocarbamate NH) with the following relative integrations—7.7 (the two overlapping triplets), 5.0 (the two overlapping quadruplets), 1.0, and 1.6.

The other *N*-bromoamides listed in Table I were prepared in exactly the same way except that for water-insoluble amides, longer reaction time was needed (up to 30 min) for the reaction with NaOBr. The ir and nmr absorptions of the crude *N*-bromocarbamates **18** and **19** are given below.

Crude **18**: ir ($CHCl_3$) 3400, 3200 (broad), 1745 (broad, strong), 1390, 1325, 1230, 1185, 1110, and 1045, and weak bands at 3530 and 1585 cm^{-1} (nonbrominated carbamate); nmr (CCl_4) δ 4.75 (s, carbamate CH_2), 4.81 (s, *N*-bromo- and *N,N*-dibromocarbamate CH_2), 5.60 (broad s, carbamate NH_2), 6.40 (broad s, *N*-bromocarbamate NH) with a relative integration of 1.9:8.7:1.0:4.6.

Crude **19**: ir (CCl_4) 3400, 3240 (broad), 1720 (broad, strong), 1395, 1325, 1210, 1180 (shoulder), and 1050, and weaker bands at 3500 and 1590 cm^{-1} (nonbrominated carbamate); nmr (CCl_4) δ 5.05 (s, carbamate CH_2), 5.85 (s, *N*-bromocarbamate CH_2), 5.35 (broad s, carbamate NH_2), 6.48 (broad s, *N*-bromocarbamate NH), 7.30 and 7.33 (s, aromatic H of the carbamate and the *N*-bromo derivative) with a relative integration of 1.0:2.3:1.1:1.2:7.7.

Registry No.—**1**, 16844-21-6; **2**, 52175-97-0; **3**, 52175-98-1; **4**, 30830-84-3; **5**, 30830-85-4; **6**, 30830-47-8; **7**, 52175-99-2; **8**, 598-49-2; **9**, 36448-95-0; **10**, 52176-00-8; **11**, 35070-76-9; **12**, 35070-77-0; **13**, 35077-08-8; **14**, 35077-09-9; **15**, 35077-10-2; **16**, 52176-01-9; **17**, 52176-02-0; **18**, 52176-03-1; **19**, 52176-04-2; **20**, 3699-17-0; **21**, 3699-20-5; **22**, 52176-05-3; **23**, 52176-06-4; **24**, 35077-11-3; **25**, 36015-63-1; **26**, 52259-82-2; **27**, 35077-12-4; **28**, 359-45-5; **29**, 627-12-3; **30**, 1616-88-2; **31**, 2114-18-3; **32**, 107-69-7; sodium hypochlorite, 7681-52-9; sodium hypobromite, 13824-96-9.

Supplementary Material Available. Characteristic ir absorptions (position of the NH and C=O bands) of the *N*-chlorocarboxamides **9–16** and of the *N*-bromocarboxamides **20–26**, and the nmr absorptions of these *N*-haloamides and of the *N*-chlorocarbamates **2–6** will appear in Table II (ir) and Table III (nmr) following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3136.

References and Notes

(1) (a) Supported by a grant from the National Research Council of Canada; (b) Arts Council of Canada Predoctoral Fellow, 1969–1971; (c) NRCC Postdoctoral Fellow, 1968–1970; (d) France-Quebec Predoctoral Fellow, 1970–1972.
(2) (a) J. Lessard and J. M. Paton, *Tetrahedron Lett.*, 4883 (1970); (b) J. Lessard and H. Driguez, *ibid.*, 4887 (1970); (c) H. Driguez and J. Lessard, *unpublished work.*
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(6) A. Kergomard, *Bull. Soc. Chim. Fr.*, 2360 (1961).
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(15) Commercial hypochlorite solutions from other sources were also used but were found to give less satisfactory results.
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Liquid Crystals. V. Molecular Structural Effects on the Mesomorphism of Phenylene Esters[1]

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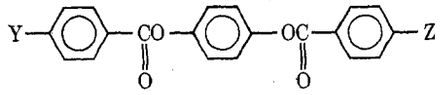
In an earlier paper,[1b] we reported the effects on the mesomorphism (liquid crystallinity)[2-4] of terminally substituted *p*-phenylene dibenzoates (**1**) caused by changing the



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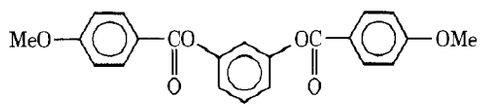
end groups. It was shown that this molecular system has a marked tendency to exhibit nematic mesomorphism, which survives major variations of Y and Z. Since then, we have investigated the effects of more drastic alterations in structure: halogen and methyl substituents on the central phenylene ring, methyl substituents in the 3 and 5 positions of the benzoyl groups, replacement of the central *p*-phenylene with *m*-phenylene and of benzoyl with cinnamyl, and the combination of central chloro substitution with dissimilar acyl groups.

The esters that were prepared have the following structures.



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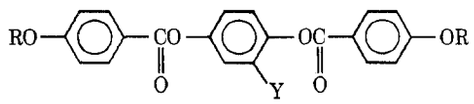
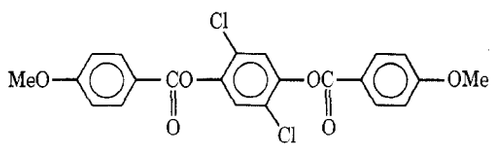


3a, R = Me; Y = Me
b, R = Me; Y = Cl
c, R = Me; Y = Br
d, R = n-C_6H_{13}; Y = Cl



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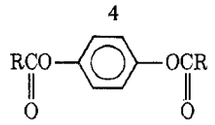
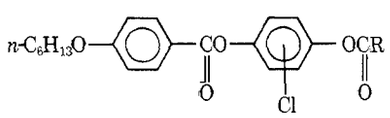
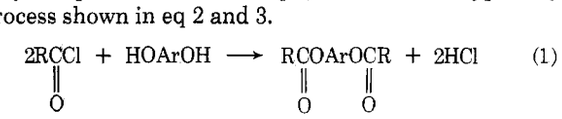


5a, R = 3,4-$Me_2C_6H_3$
b, R = 3,5-$Me_2C_6H_3$
c, R = 4-$MeOC_6H_4CH{=}CH$



6a, R = 4-n-$C_4H_9C_6H_4$
b, R = 4-n-$C_8H_{17}OC_6H_4$
c, R = 3,5-$Me_2C_6H_3$
d, R = 4-$MeOC_6H_4CH{=}CH$

Esters with two identical acyl groups (**2–5**) were synthesized by the process shown in eq 1, and esters of type **6** by the process shown in eq 2 and 3.



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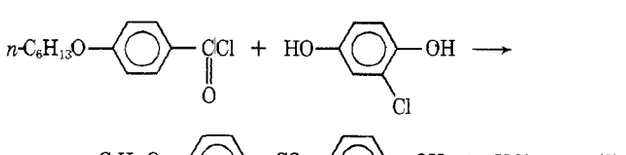

(2)

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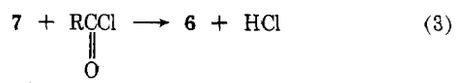


(3)

Experimental Section

Substituted Benzoic and Cinnamic Acids. 4-n-Hexyloxy-, 4-n-octyloxy- (Frinton), 3,4-dimethyl- (Eastman), and 3,5-dimethylbenzoic acid (Aldrich) and *trans*-4-methoxycinnamic acid (Aldrich) were purchased. 4-n-Butylbenzoic acid was prepared by hydrolysis of the corresponding nitrile with NaOH in EtOH–H_2O. After recrystallization from EtOH–H_2O, the product had mp 98°, N–I point[5] 112° (lit. 98°, 112°;[6] 102°, 112° [7]). 4-n-Butylbenzonitrile was obtained by the Sandmeyer method[8] from 4-n-butylaniline (Eastman).

Acyl Chlorides. 4-Anisoyl chloride was a commercial product (Eastman). The others were made from the corresponding acids by treatment with $SOCl_2$ at reflux in the presence of pyridine. Excess $SOCl_2$ was distilled to give the acid chlorides as residues.

Diphenols. Hydroquinone (Matheson Coleman and Bell), resorcinol (Fisher), and methyl-, chloro-, and 2,5-dichlorohydroquinone (Eastman) were purchased. Bromohydroquinone, mp 112° (lit.[9] mp 111°), was synthesized by bromination of hydroquinone with dioxane dibromide[9] when attempts to purify a commercial material (Eastman, practical grade) were unsuccessful.

2- and 3-Chloro-4-hydroxyphenyl 4-n-Hexyloxybenzoate (7). A mixture of these isomers was prepared by overnight reaction of chlorohydroquinone (0.10 mol) and 4-n-hexyloxybenzoyl chloride (0.017 mol) in 90 ml of dry pyridine at room temperature. The resulting mixture was poured into 300 ml of 2 N aqueous HCl. An oil separated which was washed with aqueous $NaHCO_3$ and then H_2O. Extraction with 95% EtOH left by-product **3d** as the residue. Crude **7** was recovered from the extract by precipitation with H_2O. The precipitate was dissolved in ether, and the solution was washed with aqueous $NaHCO_3$ and treated with Norit. Recrystallization from 90–120° petroleum ether gave a 53% yield of **7**, mp 109–112°. *Anal.* Calcd for $C_{19}H_{21}O_4Cl$: C, 65.41; H, 6.08. Found: C, 65.43; H, 5.94.

Phenylene Diesters. Typically, for the preparation of type **2–5** esters, 1 molar equiv of diphenol and 4 molar equiv of acyl chloride were allowed to react overnight in dry pyridine at room temperature. The mixture was then poured into a large volume of H_2O. The precipitate was removed by filtration, washed with H_2O and aqueous $NaHCO_3$, and recrystallized from a suitable solvent after treatment with Norit. The procedure for preparing **6a–d** was generally similar, using **7** instead of a diphenol. The exception was the reaction of **7** and 4-methoxycinnamyl chloride, which gave a highly colored product by this method, and so was run in benzene rather than pyridine solution. Excess acyl chloride can be recovered (as the acid) by acidification of the alkaline filtrate and/or aqueous $NaHCO_3$ wash liquor with hydrochloric acid.

The results are summarized in Table I.

Table I
Phenylene Diesters[a]

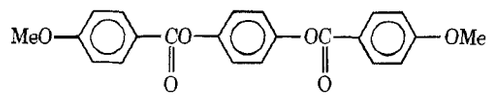
Compd[b]	Recrystn solvent	Yield, %	Melting range, °C	N–I point, °C
2	EtOH	92	137–138	*c*
3a	EtOH–acetone	96	169–170	250[d]
3b	EtOAc	97	165–166.5	254[d]
3c	EtOAc	94	162.5–164, 168.5–170[e]	249.5[d]
3d	EtOH–dioxane	47	89–90	169.5
4	Dioxane	94	234.5–236	(215)[f]
5a	Acetone	16	207–208	*c*
5b	EtOH	73	156–158.5	*c*
	Cyclohexane		170.5–172.5[e]	
5c	Dioxane	64	209–214	>337[g]
6a	Pentane	8	70–78	158
6b	Hexane	52	75–77	161.5
6c	MeOH	30	96.5–102.5	*c*
6d	90–120° petroleum ether	49	119–167	238

[a] Satisfactory analytical data (±0.4% for C and H) were reported for all compounds in the table. [b] **5c** and **6a–d** are believed to be mixtures of isomers. [c] Not mesomorphic. [d] These compounds exhibit monotropic nematic–smectic transitions at 126 (**3a**), 127.5 (**3b**), and 130° (**3c**). [e] Polymorphic. [f] Monotropic transition. [g] Decomposition begins at this temperature.

Analyses. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

As mentioned above, system **1** shows a remarkable propensity toward nematic mesomorphism.[1b] Among esters of type **1**, the di-*p*-anisoate (**8**) displays one of the most stable



8

nematic mesophases (nematic range, 222–300°)[10] and, therefore, in studying the effects of altering the central phenylene ring on the mesomorphism of system **1**, **8** was selected as the reference compound.

The molecular structural criteria for mesomorphism are linearity, rigidity, and polarity. In **2**, the central *p*-phenylene of **8** is replaced by *m*-phenylene. No significant changes in rigidity or polarity should result and, while less linear, the molecule **2** is capable of adopting a configuration that must certainly be considered rod-shaped. Yet **2** melts 84° below **8** and is not liquid crystalline, so that the N–I point has been depressed at least 162°. By contrast, replacement of the central *p*-phenylene in **8** by 1,4-bicyclo[2.2.2]octylene and *trans*-1,4-cyclohexylene only lowers the melting point 37 and 25°, and the N–I point 31 and 105°, respectively.[11] The alicyclic units are less polarizable than phenylene and cyclohexylene is less rigid, but they preserve linearity. These comparisons constitute a striking example of the effects of molecular symmetry on melting point and of molecular linearity on mesomorphism.

Substituents on the central *p*-phenylene were also explored. Arora, *et al.*,[12] showed that a methyl group in this position lowers both the melting and N–I point about 40° in the *n*-hexyloxy and higher homologs of **8**. Our results for a similarly placed chloro substituent in the *n*-hexyloxy (**3d**) and *n*-hexyloxy–*n*-octyloxy (**6b**) homologs are much the same. For a methyl (**3a**), chloro (**3b**), or bromo (**3c**) group in **8** itself, the lowering of the transition temperatures is greater (about 50°). Two chloro groups in the 2 and 5 positions of the central ring of **8** (**4**) lower the N–I point almost twice as much as one (85 *vs.* 46°), indicating that the effect is additive.[3] However, the melting point of **4** is 14° higher than that of **8**, probably because of increased polarity and molecular weight with little sacrifice in molecular symmetry.

The lower thermal stability of the nematic mesophase produced by substituents on the central ring seems to be a steric effect, the bulky groups preventing close lateral approach of adjoining parallel molecules and thereby diminishing intermolecular attractive forces.[3] The same effect should also lower smectic mesophase stability and, indeed, Arora, *et al.*,[12] found this to be true. It is well known that smectic behavior is usually enhanced by long *n*-alkyl end groups.[3] For the *n*-hexyloxy and higher homologs of **8**, these workers first encountered smectic mesomorphism in the heptyloxy ester (N–Sm point 110°) on ascending the series. For the analogous esters with a methyl on the central ring, a smectic mesophase did not appear until the undecyloxy compound (N–Sm point 74°). The situation for chloro substitution is similar. The ester **1** (Y = *n*-$C_6H_{13}O$, Z = *n*-$C_8H_{17}O$)[13] is smectic (Sm–N point 107°) whereas its chloro-substituted counterpart (**6b**), mp 77°, is not. Furthermore, the *n*-hexyloxy homolog with the central chloro group (**3d**) is not smectic even when supercooled to 54°. Therefore, our observation of smectic mesomorphism, and at fairly high temperatures (126–130°), in the *methoxy* esters with methyl (**3a**), chloro (**3b**), and bromo (**3c**) groups in the central *p*-phenylene ring came as a surprise.

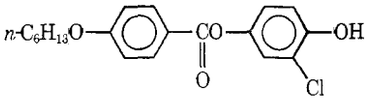
We can only speculate as to the reason for this unusual behavior. Compound **8** and its homologs are compatible structurally with smectic mesomorphism, having the strong dipoles crosswise to the molecular long axis associated with ester linkages, which are often present in smectic compounds.[14] In **3a–c**, these are buttressed by the additional crosswise dipole produced by the substituent on the central ring. Thus, although unexpected, the appearance of a smectic mesophase is not illogical. *n*-Alkyl end groups of intermediate length would further enhance lateral attraction if forced into parallel, extended configurations by close approach of adjacent molecules, but this is hindered by the bulky substituent. In fact, such alkyl groups seem to exert a deleterious effect on smectic mesomorphism, perhaps by assuming random configurations and thus decreasing molecular linearity. For terminal *n*-alkyl chains of great length, the natural extended configuration (as in linear polyethylene) appears to be reachieved and a smectic mesophase is again observed. If this view is correct, the N–Sm point should decrease at first as the homologous series starting with **3a–c** is ascended, then pass through a minimum value, and finally rise again. We intend to prepare the presently missing members of the three series in order to test the hypothesis.

Turning next to variations of the acyl groups in system **1**, in **5a** these are 3,4-dimethylbenzoyl, so that there are two terminal and two lateral methyl substituents. It is convenient to compare nonmesomorphic **5a**, mp 208°, and the corresponding ester without the lateral methyls (**1**, Y = Z = Me), mp 231.5°, N–I point 236°.[1b] Introduction of the side groups lowers the melting point 23.5° and the N–I point at least 28°. In **5b**, the acyl groups are 3,5-dimethylbenzoyl; *i.e.*, there are four lateral methyl substituents. This compound exhibits polymorphism, melting at 158.5° when recrystallized from ethanol and at 172.5° when recrystallized from cyclohexane.[15] It is not mesomorphic so, relative to **1** (Y = Z = Me), the N–I point is lower by at least 77.5°. The decrease in transition temperatures with increasing lateral substitution exemplified by **5a** and **5b** is in accord with generally accepted theory. Bulky side groups inhibit close approach of neighboring molecules and, therefore, diminish intermolecular attraction. In addition, they make the molecule less rod-shaped. In **5c**, mp 209–214°, N–I point >337°, the acyl groups are 4-methoxycinnamyl. This compound is best compared with **8**, from which it differs by insertion of CH=CH between the benzene ring and carbonyl in the acyl groups. The resulting increased molecular length and polarizability are consistent with the significant increase in the N–I point. For the same reasons, one would expect a higher melting point also. The fact that **5c** melts 8° lower than **8**, and over a temperature range, leads us to believe that it is a mixture of geometric isomers, three of which (trans,trans, cis,trans, and cis,cis) are possible. *trans*-4-Methoxycinnamic acid was used in preparing **5c**, but some isomerization could have occurred during the synthesis. Any cis geometry would decrease molecular linearity and, therefore, nematic mesophase stability. In consideration of the high N–I point, it appears that **5c** is mainly the trans,trans isomer.

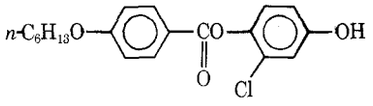
The remaining materials (**6a–d**) represent attempts to prepare low-melting nematic esters of type **1**. Four factors known to contribute to low melting points were employed: mixtures, molecular dissymmetry, a bulky lateral substituent, and a long chain *n*-alkoxy end group. In each instance, the starting material was the phenolic ester **7**, prepared by nucleophilic displacement of chlorine from *p*-*n*-hexyloxybenzoyl chloride by chlorohydroquinone (eq 2). Either of the OH groups in the latter may serve as the nucleophilic center, so that two isomeric products (**7a** and **7b**) are possible. The generally broad melting ranges of **6a–d** suggest that **7** is a mixture of **7a** and **7b**, and that this position isomerism is carried forward into the final products which, as a result, are mixtures. For **6d**, there is the additional

possibility of cis–trans isomerism. The ester molecules are dissymmetric because of the chloro substituent and the two different acyl groups.

Three of the four materials are nematic. The exception is **6c**, demonstrating again the powerful deleterious effect of bulky lateral substituents on mesomorphism. The high melting and N–I points of **6d**, although it is obviously a mixture, suggest that the main components are the *trans*-4-methoxycinnamates of **7a** and **7b**. **6a** and **6b** are the low-

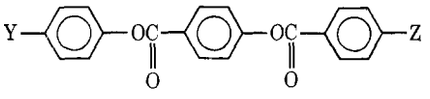


7a



7b

est melting examples of type **1** esters to date. This is consistent with their being mixtures and with their structures. The combination of a chloro substituent on the central *p*-phenylene ring with terminal *n*-alkyl or *n*-alkoxy groups in a very closely related system (**9**) has been shown[16] to result



9

in low-melting (39–70°) (nematic) compounds. The relatively low melting point of **3d** is also consistent with this.

Acknowledgment. We wish to thank Stephen A. Haut for suggesting the preparation of compound **2.**

Registry No.—**2,** 51933-64-3; **3a,** 51933-65-4; **3b,** 51933-66-5; **3c,** 51933-67-6; **3d,** 51933-68-7; **4,** 51933-69-8; **5a,** 51933-70-1; **5b,** 51933-71-2; **5c,** 51933-72-3; **6a,** 52003-48-2; **6b,** 52003-49-3; **6c,** 52003-50-6; **6d,** 52124-32-0; **7,** 52003-51-7.

References and Notes

(1) (a) This work was supported by a grant from the Research Council of the University of North Carolina at Greensboro. (b) Previous paper in this series: J. P. Schroeder and D. W. Bristol, *J. Org. Chem.*, **38,** 3160 (1973).
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(5) Nematic–isotropic transition temperature. The following abbreviations are used in this note: N = nematic, Sm = smectic, and I = isotropic.
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(14) Reference 3, pp 166 and 188.
(15) Ester **3c** is also polymorphic. Two distinct fusions were seen in the melting point determination (Table I), and a DSC trace gave peaks at 163 and 172°. Cooling and reheating the sample in the DSC gave mainly a peak at 177.5°, which was also the result when the compound was recrystallized from ethanol rather than ethyl acetate.
(16) J. P. VanMeter and B. H. Klanderman, *J. Amer. Chem. Soc.*, **95,** 626 (1973).

A Reexamination of the Effect of α- and β-Methyl Substitution on the Esterification Rates of Saturated Aliphatic Acids

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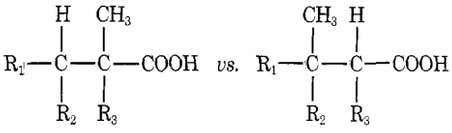
From an examination of his collection of data concerning the hydrogen chloride catalyzed esterification rates in methanol of various aliphatic acids, Newman concluded "... substitution of methyl groups for hydrogen causes a greater decrease in rate when at the beta-carbon than when at the alpha- or gamma-carbon."[1] Essentially the same conclusion was reached by Taft, "In each case methyl substitution is more effective in the beta than in the alpha position,"[2] and by Schulte and Kirschner, "... the influence of the methyl group in the beta position is somewhat greater than in the alpha position."[3] This general conclusion has been widely accepted.[4]

However, by looking at the effect of α- and β-methyl substitution in a much simpler scheme, one not generally carried out by the authors cited, the opposite effect is observed, namely that an α-methyl substitution decreases the rate *more* than a β-methyl substitution. This simple and direct scheme consists of the comparison of the rates of sets of two isomeric acids, differing only in the α or β placement of a methyl group.



α-methyl acid vs. β-methyl acid

The results from ten such sets are given in Table I. Five of the sets of data are from Newman's collection; the remainder were obtained from gas chromatographic analysis of partly esterified mixtures of acids. Details of the gas chromatographic method used for sets 8 and 9 are given in the experimental section. Data in Table II show that this method is capable of considerable precision.

Because of branching, an α-methyl acid may have two β-methyl acids for comparison of rates. In all cases except example number 10 of Table I, the β-methyl acid of the set esterifies faster than the α-methyl isomer. The average for the k_β/k_α ratios in examples 1–9 is 1.8 ± 0.5. Example number 10 consists of a set of much more sterically hindered acids than the others and appears to be the only case where Newman made use of the comparison of such isomers to demonstrate his conclusion. No actual numerical ratio was established by Newman between the rates of these two acids since the rate for the β-methyl acid was considered to be too slow for measurement.

Yufit has apparently taken Newman's data (without crediting him) and developed an empirical method for calculating the esterification rates of the aliphatic acids from their structures.[7] Unfortunately, his calculations for the various acids do not always seem to follow his method as stated; however, for the simple case of placing a methyl group in the α or β position of a normal acid, it can be shown that the general prediction is that the β-methyl acid will esterify (presumably at 40°) ~1.4 times as fast as the α-methyl acid. Thus, from exactly the same body of data entirely different conclusions were reached by the methods of Yufit and Newman.

From an examination of the data in Table I, it seems rea-