



methyl isobutyrate with the deuterium label exclusively in one of the methyl groups, as shown by pmr (clean quartet of H-2 in the deuterium-decoupled spectrum) and mass spectrometric evidence ( $M - 15$ ,  $M - 18$ ).

The question that remains to be examined is how the hypothetical product of propargyl diazotate cyclization, the methyleneoxadiazoline **8**, is transformed into the cyclopropanone **11**. Loss of nitrogen might afford the oxyallyl cation **9** which is thought to be in equilibrium with or equivalent to the cyclopropanone.<sup>6</sup> To check this possibility, we have performed the reaction sequence with optically active 1-pentyne-3-diazotate (**6**,  $R = \text{CH}_2\text{CH}_3$ ). The corresponding amine was resolved with tartaric acid, its maximum rotation,  $[\alpha]^{20\text{D}} 16.1^\circ$ , determined by F nmr of the  $\alpha$ -methoxy- $\alpha$ -trifluoromethylphenylacetamide,<sup>7</sup> and the absolute configuration of the (-) amine was established as *S* by ozonolysis of the acetamide to (-)-(*S*)- $\alpha$ -acetaminobutyric acid.<sup>8</sup> (*R*)-**6** ( $R = \text{C}_2\text{H}_5$ ) afforded (+)-(*S*)-methyl  $\alpha$ -methylbutyrate (**13**,  $R = \text{C}_5\text{H}_5$ ) with 88% inversion of configuration (12% racemization). This result eliminates the planar oxyallyl cation **9** as a major intermediate. The cyclopropanone must arise by back-side displacement of nitrogen, either by the lone pair of the methyleneoxadiazoline anion **7** (producing the enolate **10** of cyclopropanone **11**), or by the  $\pi$  electrons of the methyleneoxadiazoline **8**. We are not aware of an experiment which would determine the sequence of protonation and displacement of nitrogen.

The present study provides stereochemical information which is not available from the Favorskii rearrangement of  $\alpha$ -halo ketones. The high stereospecificity of the overall reaction—including formation and cleavage of a cyclopropanone intermediate—is of obvious significance to the oxyallyl cation problem.<sup>6</sup>

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## Low-Melting Liquid Crystalline Phenyl 4-Benzoyloxybenzoates

Sir:

The preparation of liquid crystalline compounds with nematic ranges spanning room temperature is of great technological importance.<sup>1</sup> Recent successes in this area include *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline,<sup>2</sup> *dl*-4-(2-methylhexyl)-4'-ethoxy- $\alpha$ -chloro-*trans*-stilbene,<sup>3</sup> and *p,p'*-di-*n*-butylazoxybenzene.<sup>4</sup> These materials have several disadvantages which in-

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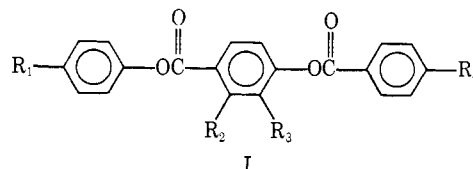
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clude chemical or photochemical instability and/or a yellow color which is objectionable in certain display applications. In an effort to prepare nematic liquid crystalline compounds which are both colorless and more stable than the above materials, we have been preparing liquid crystals with the ester functionality as the central linkage.

A recent publication by Steinsträsser<sup>5</sup> concerning para,para'-disubstituted phenyl *p*-benzoyloxybenzoates (**I**) has prompted us to give a preliminary account of our



work on the same system. We have chosen this system for investigation since the unsymmetrical nature of the central linkage may lead to lower melting materials than those obtained from hydroquinone or terephthalic acid.<sup>6</sup> The high thermal stability of the mesophase, as indicated by the high nematic-to-isotropic transition temperature, for the corresponding symmetrical materials indicated that liquid crystals derived from **I** could accommodate lateral substituents with only a moderate reduction in the mesomorphic thermal stability.<sup>7</sup>

The substituted phenyl 4-benzoyloxybenzoates (Table I) were prepared by the reaction of the substituted

Table I. Substituted Phenyl *p*-Benzoyloxybenzoates

Compd no.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	Nematic range, °C
1	C <sub>5</sub> H <sub>11</sub>	H	H	C <sub>5</sub> H <sub>11</sub>	78–179.5
2	C <sub>5</sub> H <sub>11</sub>	Cl	H	C <sub>5</sub> H <sub>11</sub>	39–122
3	C <sub>5</sub> H <sub>11</sub>	H	Cl	C <sub>5</sub> H <sub>11</sub>	67–130
4	C <sub>5</sub> H <sub>11</sub>	H	Cl	C <sub>7</sub> H <sub>15</sub>	55–119
5	C <sub>5</sub> H <sub>11</sub>	H	Cl	OC <sub>3</sub> H <sub>11</sub>	70–151
6	C <sub>5</sub> H <sub>17</sub>	Cl	H	C <sub>7</sub> H <sub>15</sub>	39–104.5
7	C <sub>5</sub> H <sub>17</sub>	H	Cl	C <sub>7</sub> H <sub>15</sub>	70–106

benzoyl chloride with the substituted phenyl 4-hydroxybenzoate in pyridine solution at room temperature. The substituted phenyl 4-hydroxybenzoates were prepared by the acid-catalyzed esterification of phenols following the procedure of Lowrance.<sup>8</sup>

The crystal-to-mesophase transition temperatures for the unsymmetrical materials were significantly lower than the corresponding symmetrical derivatives, whereas the mesophase-to-isotropic transition temperatures varied only slightly for  $R = R'$ . For example, the nematic range of 4-*n*-pentylphenyl (4-*n*-pentylbenzoyloxy)benzoate is 78–179.5°, compared to 123–185.5° for *p*-phenylene bis(*p*-*n*-pentylbenzoate) and 152–178° for bis(*p*-*n*-pentylphenyl) terephthalate.

In contrast to the work of Steinsträsser, we have employed the use of lateral substituents as a means of increasing the dissymmetry of the liquid crystal molecule in order to obtain a further reduction in the crystal-to-mesophase (C–M) transition temperature (see Table I).

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