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.[6] To check this possibility, we have performed the reaction sequence with optically active 1-pentyne-3-diazotate (**6**, R = CH_2CH_3). The corresponding amine was resolved with tartaric acid, its maximum rotation, $[\alpha]^{20}D$ 16.1°, determined by F nmr of the α-methoxy-α-trifluoromethylphenylacetamide,[7] and the absolute configuration of the (−) amine was established as *S* by ozonolysis of the acetamide to (−)-(*S*)-α-acetaminobutyric acid.[8] (*R*)-**6** (R = C_2H_5) afforded (+)-(*S*)-methyl α-methylbutyrate (**13**, R = C_5H_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 π 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 α-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.[6]

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Wolfgang Kirmse,* Axel Engelmann, Joachim Heese
Abteilung für Chemie der Ruhr-Universität
463 Bochum, Germany

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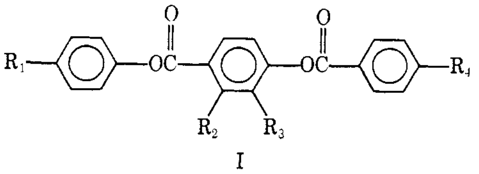
Low-Melting Liquid Crystalline Phenyl 4-Benzoyloxybenzoates

Sir:

The preparation of liquid crystalline compounds with nematic ranges spanning room temperature is of great technological importance.[1] Recent successes in this area include *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline,[2] *dl*-4-(2-methylhexyl)-4′-ethoxy-α-chloro-*trans*-stilbene,[3] and *p*,*p*′-di-*n*-butylazoxybenzene.[4] These materials have several disadvantages which include 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[5] 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.[6] 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.[7]



I

The substituted phenyl 4-benzoyloxybenzoates (Table I) were prepared by the reaction of the substituted 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.[8]

Table I. Substituted Phenyl *p*-Benzoyloxybenzoates

Compd no.	R_1	R_2	R_3	R_4	Nematic range, °C
1	C_5H_{11}	H	H	C_5H_{11}	78–179.5
2	C_5H_{11}	Cl	H	C_5H_{11}	39–122
3	C_5H_{11}	H	Cl	C_5H_{11}	67–130
4	C_5H_{11}	H	Cl	C_7H_{15}	55–119
5	C_5H_{11}	H	Cl	OC_5H_{11}	70–151
6	C_8H_{17}	Cl	H	C_7H_{15}	39–104.5
7	C_8H_{17}	H	Cl	C_7H_{15}	70–106

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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The lowest C–M transition temperature reported by Steinsträsser was 89° for *p-n*-butylphenyl *p-n*-butylbenzoyloxybenzoate. We have been able to obtain liquid crystals with C–M transition temperatures as low as 39° (compound **2**, Table I) as a result of a lateral chloro substituent. The nematic range (83°) for compound **2** is the largest range yet obtained for a single component with a C–M transition temperature below 40°. The most effective location for the lateral substituent in terms of lowering the C–M transition temperatures appears to be ortho to the carbonyl group of the ester linkage (compare compounds **2**, **3**, and **6**, **7** in Table I).

The preparation of additional liquid crystals in the phenyl *p*-benzoyloxybenzoate system is in progress and will be reported later.

J. P. VanMeter,* B. H. Klanderman
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650

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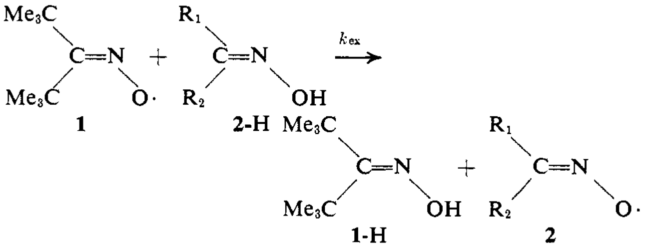
The Oxime–Iminoxy Radical Reaction[1]

Sir:

As part of our work on the free radical di-*tert*-butyliminoxy[2] (**1**), we have studied the exchange reaction between this radical and some oximes.



a, $R_1 = R_2 = Me$
b, $R_1 = Ph$; $R_2 = H$
c, $R_1 = Me_3C$; $R_2 = Me_2CH$

Benzene solutions of **1** (10^{-3} *M*) and **2a**-H or **2b**-H (0.1 *M*) displayed only a well-resolved epr spectrum of **1** that decayed with half-lives of 1 or 2 hr at room temperature. With **2a**-H the decomposition of **1** followed first-order kinetics over a tenfold concentration range. Between 25 and 51° the observed rate constant for decay could be represented by

$$k_{obsd} = 1.2 \times 10^9 \exp(-17{,}900 \text{ (cal mol}^{-1})/RT) \text{ sec}^{-1}$$

Comparable results were obtained in 95% ethanol. With **2b**-H the radical decayed by half after 1.2 hr, but the rate accelerated with time. We had not anticipated such slow reactions. The iminoxy radical **2a** decays rapidly with first-order kinetics($k_{decay}{}^{25°} = 0.04$ sec^{-1}) when generated photochemically under similar conditions.[3] Radical **2b** decays rapidly but with second-order kinetics ($k_{decay}{}^{25°} = 9 \times 10^7\ M^{-1}$ sec^{-1}).

With **2c**-H in benzene, *o*-dichlorobenzene, CCl_4, or 95% ethanol **1** decayed and radical **2c** appeared. An equilibrium was attained within a few *minutes* which favored **1** over **2c**. The equilibrium mixture is stable for hours. The spectra of **1** and **2c** overlap but differ sufficiently for the equilibrium constant to be estimated by double integration of the highest field components of the triplets. In benzene at 25° values of [**1**][**2c**-H]/[**1**-H][**2c**] = $K_{eq}{}^{25°}$ ranged from 130 to 900 depending on the exact procedure used to estimate the concentrations of **1** and **2c**. This equilibrium could be approached from the opposite direction by brief irradiation ($\lambda > 313$ nm) of a degassed benzene solution of **2c**-H (0.1 *M*) and **1**-H (8×10^{-4} *M*) containing di-*tert*-butyl peroxide. The mixture of **1** and **2c** that resulted was initially rich in **2c**. Equilibration again occurred within a few minutes[4] and two determinations gave $K_{eq}{}^{25°} = 380$ and 500 in good agreement with the first method.[5] The free energy for the formation of **2c** from **2c**-H is therefore *ca.* 3 kcal/mol less favorable than that for the formation of **1** from **1**-H.[6]

To determine the exchange rate for the thermoneutral reaction, **1** was isotopically labeled with ^{17}O by photolysis of di-*tert*-butyl peroxide and di-*tert*-butylketimine in benzene in the presence of oxygen[7,8] enriched with ^{17}O. After addition of excess **1**-H to the ^{17}O-labeled **1** [$a(^{17}O) = 22.6$ G[10]], we observed a pseudo-first-order decay of the lowest field satellite of the **1**-^{17}O.

$$(Me_3C)_2C{=}NH \xrightarrow[^{34}O_2,\ h\nu]{Me_3COOCMe_3} (Me_3C)_2C{=}N{-}^{17}O\cdot$$

$$(Me_3C)_2C{=}N{-}^{17}O\cdot + (Me_3C)_2C{=}NOH \xrightarrow{k_{ex}}$$
$$(Me_3C)_2C{=}N{-}^{17}OH + (Me_3C)_2C{=}NO\cdot$$

The average of five determinations gave $k_{ex}{}^{25°} = 1.3 \pm 0.3\ M^{-1}$ sec^{-1} with an activation energy, E_{ex}, of 7 ± 2 kcal/mol from 7 to 37°.

The rate constant for this exchange is very much less and the activation energy is considerably greater than has been found for other hydrogen atom transfers between like oxy radicals[11] and other nearly thermoneutral hydrogen transfers between dissimilar oxy radicals.[14] Hydrogen bond formation probably plays an important role in all these reactions.

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[1] Issued as NRCC No. 13025.

[2] J. L. Brokenshire, G. D. Mendenhall, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 5278 (1971).

[3] J. L. Brokenshire, J. R. Roberts, and K. U. Ingold, *ibid.*, **94**, 7040 (1972).

[4] When generated from **2c**-H and peroxide by photolysis, **2c** [$a_N = 30$ G, $a_H = 5.5$ G (1 H)] is stable for several hours at similar concentrations.

[5] We noted, qualitatively, a reversible decrease in K_{eq} on heating to 50°.

[6] Although intermolecular H bonding of **2a**-H may reduce the rate of the **1**–**2a**-H reaction, such an effect with **2c**-H is much too small to explain the large value of $K_{eq}{}^{25°}$. Thus, the free OH stretching bands of **2c**-H and **1**-H, recorded as 0.01 *M* solutions in CCl_4, are superimposable, yet in this solvent $K_{eq}{}^{25°} \approx 10^3$.

[7] In the absence of oxygen the unstable di-*tert*-butylketiminyl radical is obtained [$a_N = 28.9$ G, $a_H = 2.8$ G (18 H)].

[8] This is the first dialkyliminoxy to be labeled with ^{17}O although $MeCOC({=}N{-}^{17}O\cdot)Me$ has been prepared previously[9] by reaction of 2-butanone with labeled NO_2 (from NO + $^{34}O_2$). However, the NO_2 procedure is limited to compounds of the type $RCOCH_2R'$ and only half the ^{17}O present in the oxygen is incorporated in the radical.

[9] B. C. Gilbert and W. M. Gulick, Jr., *J. Phys. Chem.*, **73**, 2448 (1969).

[10] For comparison,[9] $a(^{17}O) = 22.75$ G for $MeCOC({=}N{-}^{17}O\cdot)Me$.

[11] For example, at room temperature in CCl_4: $k_{ex} \sim 200\ M^{-1}$ sec^{-1} for 2,4,6-tri-*tert*-butylphenoxy;[12,13] $k_{ex} \sim 160\ M^{-1}$ sec^{-1} for di-*tert*-butyl nitroxide;[12] $k_{ex} > 5 \times 10^6\ M^{-1}$ sec^{-1} for diphenyl nitroxide.[12] For these reactions E_{ex} is 0–4 kcal/mol.

[12] R. W. Kreilick and S. I. Weissman, *J. Amer. Chem. Soc.*, **84**, 306 (1962); **88**, 2645 (1966).

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[14] At ambient temperatures k_{ex} values are in the range 10^3–10^6 M^{-1} sec^{-1} for the reactants ROO· + R′OOH,[15] ROO· + ArOH,[16,17] ArO· + ROOH,[17,18] and ArO· + Ar′OH.[19] Activation energies are very low for thermoneutral and exothermic reactions but increase (and k_{ex} becomes smaller) when the exchange is endothermic.

[15] J. A. Howard, W. J. Schwalm, and K. U. Ingold, *Advan. Chem. Ser.*, **No. 75**, 6 (1968).