Education and to Kyung-Pook National University, Taegu, Korea, for extension of Dr. Lee's leave of absence.

(12) (a) Author to whom correspondence should be addressed at the Department of Chemistry, The University of Oklahoma, 620 Parrington Oval, Room 211, Norman, Okla. 73069. (b) Fulbright International Exchange Fellow, 1966-1968.

> Lynn B. Rodewald,* 12a Hak-ki Lee^{12b} Department of Chemistry, University of Texas at Austin Austin, Texas 78712 Received February 18, 1972

Intramolecular Reactions of Propargyl Diazotates. A Novel Approach to the Favorskii Rearrangement

Sir:

Aliphatic diazotates, generated from nitrosoamides and base, have been trapped by intramolecular reaction with epoxide¹ and allene² groups. We report here on the intramolecular addition of propargyl diazotates to the carbon-carbon triple bond which initiates a reaction sequence closely related to the Favorskii rearrangement.3

N-Nitroso-N-propargylureas and carbamates afford propargyl and allenyl ethers when treated with weakly alkaline methanol.⁴ In 0.5 N NaOCH₃, however, some of the nitrosoamides produce esters in high yield, as shown below.



Ester formation proceeds readily with terminal triple bonds; it is completely eliminated, however, by substitution of the ethynyl hydrogen by methyl (3 reacts to give ethers exclusively). Phenyl substitution, as in 5, causes a decrease but no complete elimination of ester formation. The substituent effects are suggestive of nucleophilic attack on the triple bond as the initial step. The two isomeric phenyl compounds 4 and 5 give rise to the same ester whereas the structurally related α -methyl and α -phenyl compounds (2 and 4, respectively) produce structurally different esters. The pattern of ester structures is rationalized by assuming a cyclopropanone as the immediate percursor of the esters (Scheme I). Both α - and γ -substituted nitroso-Scheme I



amides afford the same cyclopropanone 11. If R stabilizes a neighboring negative charge, as in the case of phenyl,⁵ alkoxide opens the cyclopropanone to give ester 12. If R destabilizes a neighboring negative charge, as in the case of methyl, the result of alkoxide attack is a branched-chain ester 13.

Scheme I is fully confirmed by the distribution of deuterium in methyl propionate obtained from 1-d

$$DC = CCH_2NCONH_2 \xrightarrow{CH_3OD}_{CH_3ONa}$$

$$1-d$$

$$D \longrightarrow CH_2DCD_2CO_2CH_3 + CD_3CH_2CO_2CH_3$$

in CH₃OD. The deuterium-decoupled pmr spectrum of the product mixture displayed sharp singlets for the α and β protons. Obviously, the components of the mixture carry hydrogen either in the α or in the β position, but not in both positions. The integral of the undecoupled spectrum yielded an $\alpha:\beta$ proton ratio of 43:57. The deviation from 50:50 should be attributed to a slow exchange of the α protons of methyl propionate in 0.5 *N*CH₃ONa–CH₃OD rather than to an isotope effect.

Similarly, 2-d in CH₃OD-CH₃ONa was converted to $DC = CCHNHCO_2CH_3$



⁽⁵⁾ Both 1-chloro-1-phenyl-2-propanone and 1-chloro-3-phenyl-2propanone afforded methyl 2-phenylpropionate on treatment with W. D. McPhee and E. Klingsberg, sodium methoxide in methanol: J. Amer. Chem. Soc., 66, 1132 (1944).

⁽¹⁾ A. Padwa, N. C. Das, and D. Eastman, J. Amer. Chem. Soc., 91, 5178 (1969); A. Padwa, P. Cimiluca, and D. Eastman, J. Org. Chem., 37,805(1972).

⁽²⁾ D.J. Northington and W. M. Jones, *Tetrahedron Lett.*, 317 (1971).
(3) Reviews: A. A. Achrem, T. K. Ustynjuk, and J. A. Titov, *Usp. Khim.*, 39, 1560 (1970); A. S. Kende, *Org. React.*, 11, 261 (1960).
(4) W. Kirmse and J. Heese, *Chem. Commun.*, 258 (1971).

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 = C₅H₅) 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

(6) N. J. Turro and W. B. Hammond, Tetrahedron, 24, 6017, 6029 (1968); N. J. Turro, S. S. Edelson, J. R. Williams, T. R. Darling, and W. B. Hammond, J. Amer. Chem. Soc., 91, 2283 (1969); D. B. Sclove, J. F. Pazos, R. L. Camp, and F. D. Greene, *ibid.*, **92**, 7488 (1970). Theory: R. Hoffmann, *ibid.*, **90**, 1475 (1968); N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, ibid., 92, 3854 (1970).

(7) J. A. Dale, D. L. Dull, and H. S. Mosher, J. Org. Chem., 34, 2543 (1969).

(8) R. Marshall, S. M. Birnbaum, and J. P. Greenstein, J. Amer. Chem. Soc., 78, 4636 (1956).

> Wolfgang Kirmse,* Axel Engelmann, Joachim Heese Abteilung für Chemie der Ruhr-Universität 463 Bochum, Germany Received September 29, 1972

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-nbutylaniline,² dl-4-(2-methylhexyl)-4⁷-ethoxy- α -chlorotrans-stilbene,3 p,p'-di-n-butylazoxybenzene.⁴ and 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 Steinsträsser⁵ 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

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

 Table I.
 Substituted Phenyl p-Benzoyloxybenzoates

| Compo no. | i Rı | R ₂ | R₃ | R₄ | Nematic range, °C |
|---------------------------------|--|------------------------------|-------------------------------|--|--|
| 1 2 3 4 5 6 7 | $\begin{array}{c} C_{3}H_{11} \\ C_{3}H_{11} \\ C_{3}H_{11} \\ C_{3}H_{11} \\ C_{5}H_{11} \\ C_{5}H_{11} \\ C_{8}H_{17} \\ C_{8}H_{17} \\ C_{8}H_{17} \end{array}$ | H Cl H H Cl H | H H Cl Cl Cl H | $\begin{array}{c} C_{5}H_{11}\\ C_{5}H_{11}\\ C_{5}H_{11}\\ C_{7}H_{15}\\ OC_{5}H_{11}\\ C_{7}H_{15}\\ C_{7}H_{15$ | 78-179.5 39-122 67-130 55-119 70-151 39-104.5 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.8

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-tomesophase (C–M) transition temperature (see Table I).

⁽¹⁾ J. A. Castellano, RCA Rev., 33, 296 (1972).

⁽²⁾ H. Kelker and B. Scheurle, Angew. Chem., Int. Ed. Engl., 8, 884 (1969). (3) W. R. Young, A. Aviram, and R. J. Cox, J. Amer. Chem. Soc.,

^{94, 3976 (1972).} (4) J. van der Veen, W. H. deJeu, A. H. Grobben, and J. Boven, Mol. Cryst. Liq. Cryst., 17, 291 (1972).

⁽⁵⁾ R. Steinsträsser, Angew. Chem., Int. Ed. Engl., 11, 633 (1972).

⁽⁶⁾ M. J. S. Dewar and R. S. Goldberg, J. Org. Chem., 35, 2711 (1970). (7) S. L. Arora, J. L. Fergason, and T. R. Taylor, *ibid.*, 35, 4055

^{(1970).}

⁽⁸⁾ W. W. Lowrance, Jr., Tetrahedron Lett., 3453 (1971).