

Typical experimental procedures are described below. No differences in product yield or composition were observed when diethyl ether was replaced by tetrahydrofuran. Similarly, it did not matter if the reagents were added alternately in small portions or consecutively in one portion each. An attempt to improve the yield by making fluoride ion more readily available as pyridine hydrofluoride was unsuccessful.

1-Bromo-2-fluoro-1-hexene.—Anhydrous hydrofluoric acid (50 g, 2.5 mol) was condensed into a 500-ml polyethylene bottle and the bottle was cooled to -78° . To the cooled acid was added ether (120 ml), N-bromoacetamide (34.5 g, 0.25 mol), and 1-hexyne (20.5 g, 0.25 mol). The pale yellow slurry so produced was stirred at -78° for 3 hr; then, after overnight storage at -20° , it was poured slowly into a mixture of sodium carbonate (250 g), water (200 ml), ice (200 g), and ether (60 ml). The ether layer was separated and the residue was extracted with ether (three 50-ml portions). The combined ether extracts were washed with nitrous acid solution to destroy any residual acetamide, washed with sodium carbonate solution and then with water, dried, and distilled. There was obtained 10.8 g (47.9%) of 1-bromo-2-fluoro-1-hexene, bp 34° (12 mm), n_D^{25} 1.4361. The product was characterized by elemental analysis (Table I), a C=C stretching frequency in the infrared spectrum (Table II), and by nmr spectroscopy. Infrared spectroscopy also revealed the presence of C—F stretching frequencies at 1144 and 1079 cm^{-1} . The original 1-hexyne does not have any bands in this region.

3-Bromo-4-fluoro-3-hexene.—Anhydrous hydrogen fluoride (80 g, 4.0 mol) was condensed into a 500-ml polyethylene bottle cooled to -78° . Cold tetrahydrofuran (200 ml) was added together with pyridine (2 ml). N-bromoacetamide (70 g, 0.508 mol) and 3-hexyne (32.8 g, 0.4 mol) were added alternately in small portions over a 20–30-min period. The mixture was stirred at -78° for 2 hr, then at 0° for 3 hr. The pale yellow solution was poured onto a mixture of sodium carbonate (300 g, 2.8 mol), water (300 ml), ice (300 g), and methylene chloride (100 ml). The aqueous layer was extracted with a further 100 ml of methylene chloride. The organic extracts were washed with water, nitrous acid, and finally with water. After drying and distillation, 20.2 g (27.9%) of 3-bromo-4-fluoro-3-hexene was obtained. The product was characterized as described above.

Silver Fluoride-Bromine Procedure.—Silver fluoride (14 g, 0.11 mol) was finely ground and added to dry acetonitrile (25 ml) in a 100-ml, three-necked flask. 1-Hexyne (8.29 g, 0.1 mol) was added in one portion. Some heat was evolved. Bromine (16 g, 0.1 mol) in acetonitrile (20 ml) was added very slowly, with stirring, through a dropping funnel. Complete addition required 1.5 hr. The solution was pale yellow and contained a yellow-gray sludge. The solid was removed by filtration and the acetonitrile was removed from the product by water washing. The residue was dried and distilled. Unreacted 1-hexyne (2.5 g) was recovered together with a fraction boiling at $52-53^{\circ}$ (29 mm). Nmr examination showed that there was a trace of the BrF addition product, but that the major product was 1-bromo-1-hexyne. A similar reaction with 3-hexyne gave only 3,4-dibromo-3-hexene.

Registry No.— $\text{BrC}\equiv\text{CCOOCH}_3$, 23680-40-2; bromine monofluoride, 13863-59-7.

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Mesomorphic Properties of Alkoxybenzylideneaminoacetophenones

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Compounds of the alkoxybenzylideneaminoacetophenone series are of special interest, as many of them

have a wide range of smectic phase A below 130° . Four homologs of this series with C_1 , C_2 , C_4 , and C_8 in the n -alkoxy chain length have been reported by Castellano, *et al.*¹

Their observation of a nematic phase in 4- n -octyl-oxylidene-4'-aminoacetophenone we believe to be in error. The only phase we observe between the melt and the isotropic liquid is a smectic phase. The possibility of a nematic phase in the aforementioned compound is, further, ruled out because no nematic phase is observed in the lower homolog with C_7 in the chain length. The absence of the nematic phase in these two compounds is further confirmed by our optical and differential thermal analysis studies.

Of the 11 compounds synthesized by us in this series, the lowest homolog with C_1 in the alkyl chain shows no liquid crystalline phase. A nematic phase is observed in compounds with n -alkoxy chain lengths of C_3 , C_4 , C_5 , and C_6 only. All other compounds from C_8 to C_{10} , C_{12} , and C_{14} show an enantiotropic smectic 1 phase. Monotropic smectic 2 is observed in compounds with chain lengths of C_3-C_9 . A plot of phase transition temperatures *vs.* the number of carbon atoms in the alkyl chain is shown in Figure 1. For comparison, the data of Castellano, *et al.*,¹ is shown by dotted lines.

Smectic 1 shows the focal-conic texture typical of smectic A of Sackmann and Demus.² Monotropic smectic 2 appears to be identical with smectic 1, and it is not possible to distinguish this phase from smectic 1 by optical methods.

In Figure 1, one observes an unusually marked alternation of the nematic-isotropic transition temperatures for odd and even numbers of carbon atoms in the alkyl chain of this homolog's series. The plot for even carbon chain homologs lies above that for odd carbon chain members. Further, this extent of alternation decreases as the chain length increases. The alternation of nematic-isotropic transition temperatures in such a series is similar to that found by Gray³ in alkoxybenzoic acids and alkoxy Schiff bases.

The nematic-isotropic transition curve (Figure 1) for both odd and even alkyl chain homologs appears to merge with the rising smectic-nematic transition curve at a point which lies below the point for the homolog with C_7 in the alkyl chain. When such a merging of the nematic-isotropic and smectic-nematic curves takes place, then it is well known that all other higher homologs above the merger do not show a nematic phase. This behavior is indeed observed in 4- n -heptyloxybenzylidene-4'-aminoacetophenone which does not exhibit a nematic phase but has only one enantiotropic smectic mesophase which passes directly into the isotropic liquid. Hence, on this basis, it is unlikely for C_8 to have a nematic phase when its predecessor homolog does not show such a phase.

The absence of a nematic phase in C_8 is further confirmed by our differential thermal analysis (DTA) of this compound. In Figure 2, the thermograms of homologs with alkyl chain length of C_6 , C_7 , and C_8 are shown. An examination of these establishes one enantiotropic liquid crystal phase between the melt and

(1) J. A. Castellano, J. E. Goldmacher, L. A. Barton, and J. S. Kane, *J. Org. Chem.*, **33**, 3501 (1968).

(2) H. Sackmann and D. Demus, *Mol. Cryst.*, **2**, 81 (1966).

(3) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, London and New York, 1962, p 197.

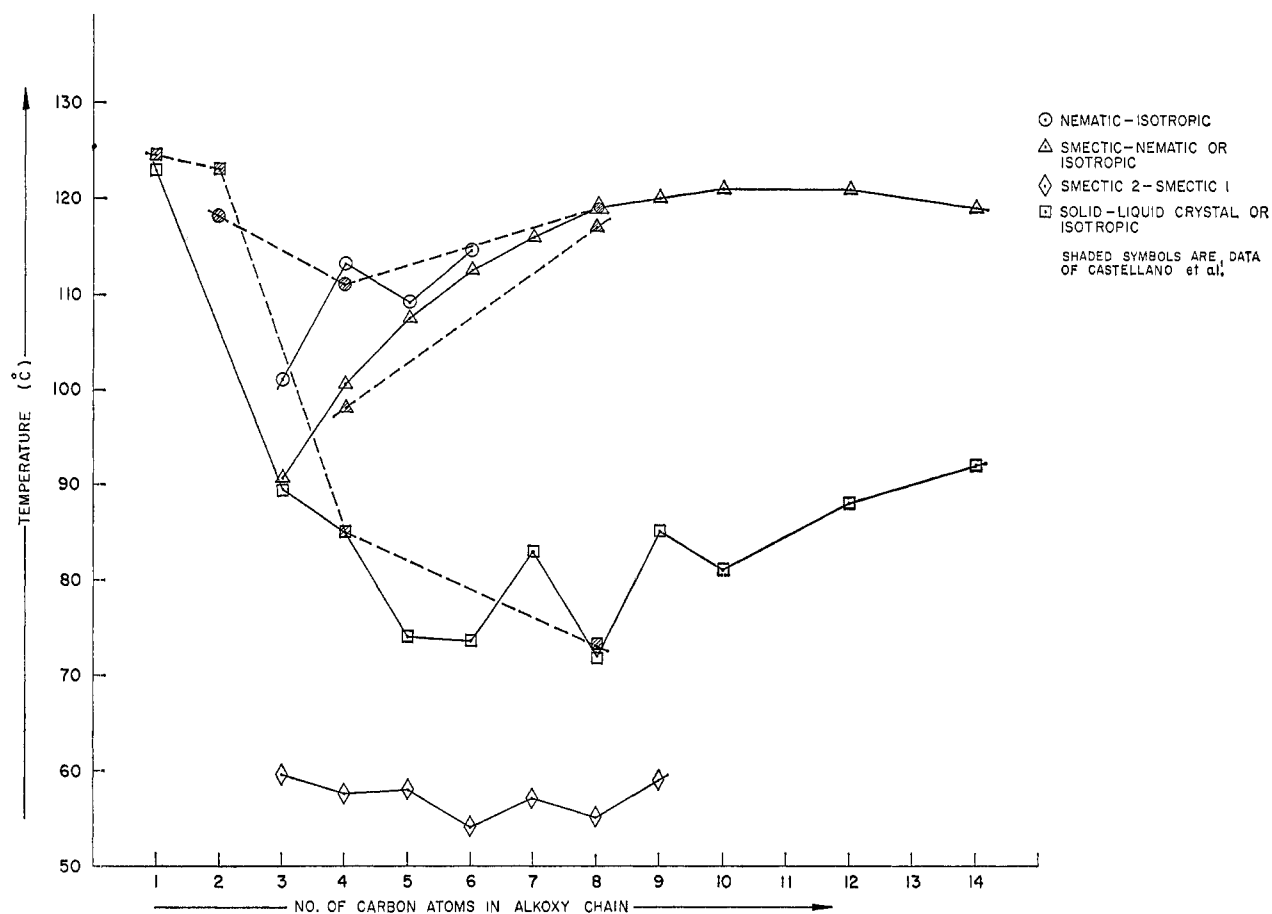


Figure 1.

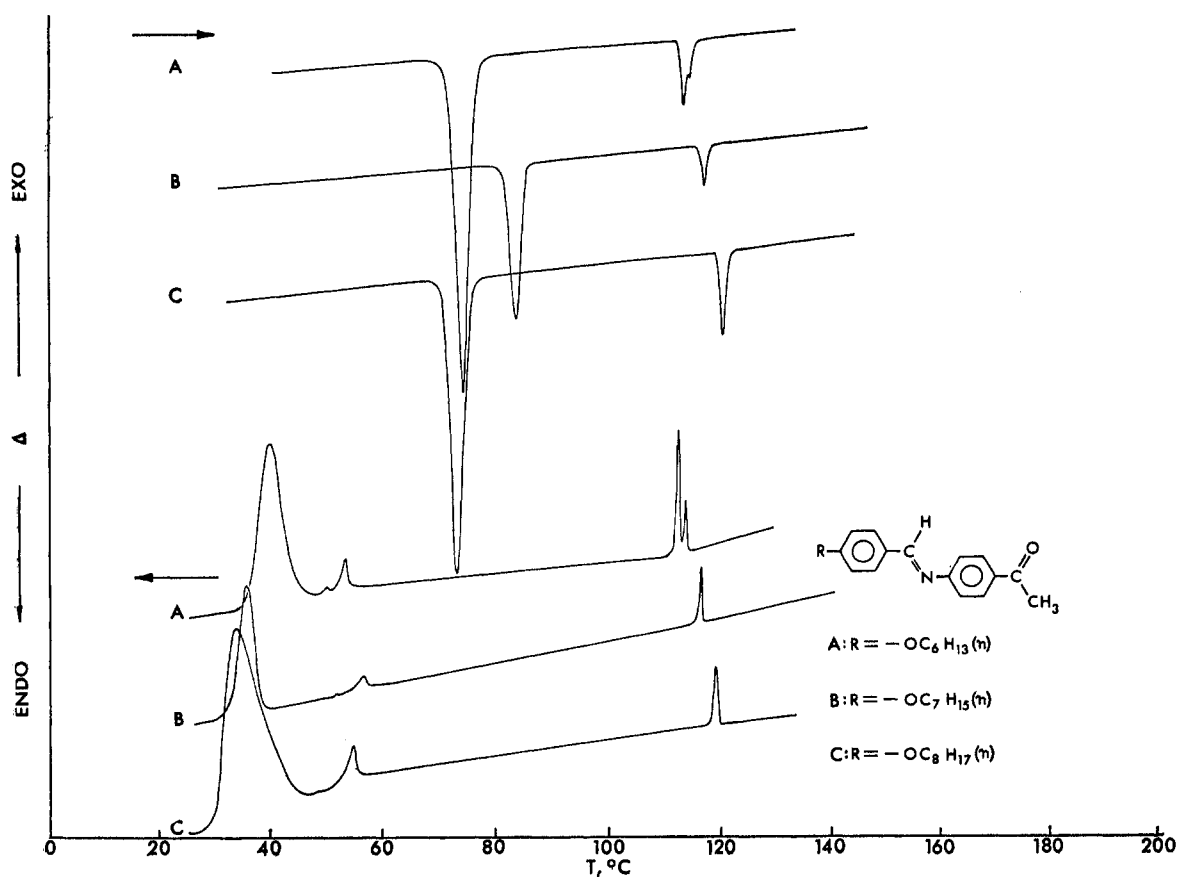
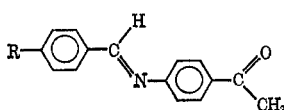


Figure 2.

TABLE I
 4-*n*-ALKOXYBENZYLIDENE-4'-AMINOACETOPHENONES


Compd	Substituents, R	Transition temperatures, °C, from solid or preceding liquid crystal state to			Calcd, %			Found, %		
		Smectic 1	Nematic	Isotropic	C	H	N	C	H	N
1	H ₃ CO ^d			123 124.5 ^a	75.87	5.97	5.53	75.65	5.93	5.50
2	H ₅ C ₂ O			123 ^a (118) ^a						
3	H ₇ C ₃ O	89.5 59.5 ^b	90.5	101	76.84	6.81	4.98	76.81	6.80	5.01
4	H ₉ C ₄ O	85 85 ^a 57.5 ^b	100.5 98 ^a	113 111 ^a	77.26	7.17	4.74	77.17	7.12	4.47
5	H ₁₁ C ₅ O	74 58 ^b	107.5	109	77.64	7.49	4.53	77.97	7.70	4.61
6	H ₁₃ C ₆ O	73.5 54 ^b	112.5	114.5	77.99	7.79	4.33	78.32	7.55	4.43
7	H ₁₅ C ₇ O	83 57 ^b		116	78.30	8.06	4.15	78.43	8.07	4.20
8	H ₁₇ C ₈ O	72 73 ^a 55 ^b	117 ^{a,c}	119 119 ^a	78.60	8.32	3.98	78.49	8.51	4.08
9	H ₁₉ C ₉ O	85 59 ^b		120	78.87	8.55	3.83	78.83	8.53	3.77
10	H ₂₁ C ₁₀ O	81		121	79.11	8.76	3.70	79.04	8.77	3.63
11	H ₂₃ C ₁₂ O	88		121	79.56	9.15	3.44	79.71	9.25	3.38
12	H ₂₅ C ₁₄ O	92		119	79.95	9.49	3.22	80.04	9.49	3.14

^a Transition temperatures reported by Castellano, *et al.*¹ Value in parentheses is the monotropic nematic. ^b Transition from monotropic smectic 2. ^c Transition temperature for smectic 1-nematic by Castellano, *et al.*¹ and is wrong because no nematic phase is observed in this compound. ^d DTA shows an apparent monotropic nematic phase at 98° but this phase is not observable microscopically.

isotropic liquid for C₇ and C₈. However, two enantiotropic mesophases are evident for C₆. Optical studies of these two mesophases indicate that the lower temperature phase is smectic and the higher temperature phase, nematic. Further, these two liquid crystal phases are separated from one another by a very narrow range. Optical studies of the single enantiotropic mesophase observed for C₇ and C₈ show this phase to be smectic A as defined by Sackmann and Demus.² In sum, our observations do not show a nematic phase for C₃ as reported by Castellano, *et al.*¹

In compounds with alkyl chain length C₃-C₉, a previously unobserved¹ monotropic smectic 2 phase is observed. This phase is observed in cooling DTA thermograms as shown in Figure 2 for C₆, C₇, and C₈. Since smectic 2 is a supercooled state, it must be carefully distinguished from a transition to a solid. If the transition does represent a mesophase, the transition should be completely reversible. We, therefore, did make thermograms in which, after the smectic 1-smectic 2 transition occurred on cooling, the DTA was reversed and the transition ran through on the heating cycle. In all cases, the transition was still present on heating, confirming our supposition that the transition did not represent crystallization.

Optically, monotropic smectic 2 appears to be identical with smectic 1, that is, smectic A. Within the limits of our optical measuring techniques, we can observe no change at the smectic 1-smectic 2 transition temperature. There does appear to be a difference in viscosity between smectic 1 and smectic 2. If the

relatively viscous smectic 2 is distorted by moving the cover slip, then on reheating there is flow near the smectic 1-smectic 2 transition temperature.

It is interesting to note that smectic 1 and smectic 2 cannot be classified according to the miscibility method of Sackmann and Demus.² Since both phases have identical optical textures, there would be no phase boundary owing to miscibility. We recently encountered a similar situation during our studies on the smectic phases of the homologs of 4-*n*-alkoxybenzylidene-4'-aminopropiophenones⁴ where an explanation is given for the unusual behavior of these apparently identical smectic phases.

Experimental Section

Determination of Transition Temperatures.—The phase transition temperatures were determined both by differential thermal analysis (Du Pont DTA 900) and with a Leitz Panphot polarizing microscope using a Mettler FP-2 heating stage. Melting points (solid-liquid or solid-liquid crystal transition) have been regarded as the transitions with the highest transition energy. These are also always the transitions that can most easily be supercooled, whereas supercooling in the case of liquid crystal transitions is negligible.

Monotropic liquid crystal transition temperatures observed below the melting points during the cooling operation of DTA thermograms were confirmed by reheating of the samples before crystallization. The assignments of the transition temperatures were confirmed by the polarizing microscope, except for the monotropic smectic 2-smectic 1 transitions. The highest tem-

(4) S. L. Arora, T. R. Taylor, and J. L. Ferguson, "Symposium on Ordered Fluids and Liquid Crystals, Sept 1969," American Chemical Society, Washington, D.C., in press.

perature smectic phase is always called smectic 1, the next lower one smectic 2, and so on. The transition temperatures for the various liquid crystal phases are listed in Table I. The error of the temperature measurements is estimated to be smaller than $\pm 2^\circ$.

Preparation of Materials.—4-aminoacetophenone was recrystallized from commercially available material.

4-n-Alkoxybenzaldehydes were prepared from *p*-hydroxybenzaldehyde and various alkyl bromides either according to the method of our earlier publication⁵ or by that of Weygand and Gabler.⁶

Alkoxybenzylideneaminoacetophenones were prepared by refluxing equimolecular quantities of the 4-aminoacetophenone and the appropriate 4-*n*-alkoxybenzaldehyde in absolute alcohol for 5–6 hr. The product after isolation was recrystallized several times from appropriate solvents until the transition temperature remained constant.

The liquid crystal–liquid crystal transitions with the purified compounds were sharp and reversible. Differential thermal analysis gave on heating and on cooling, within a fraction of a degree, equal temperatures for these transitions.

Registry No.—1, 23596-02-3; 2, 17224-17-8; 3, 23596-04-5; 4, 17224-18-9; 5, 23596-06-7; 6, 23596-07-8; 7, 23596-08-9; 8, 17224-19-0; 9, 23596-10-3; 10, 23596-11-4; 11, 23596-12-5; 12, 23596-13-6.

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(5) S. L. Arora, J. L. Ferguson, and A. Saupe, *Mol. Cryst. Liq. Cryst.*, in press.

(6) C. Weygand and R. Gabler, *J. Prakt. Chem.*, **155**, 338 (1940).

Quantitative Studies in Stereochemistry. XIII. The Peroxide-Induced Pinacolization of Acetophenone. The Thermal Stability of the Acetophenone Pinacols

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The *t*-butyl peroxide induced pinacolization of aryl ketones has been reported to involve a dimerization of ketyl radicals as the final step in the reaction sequence.¹ Similar ketyl radicals are known to be intermediates in electro- and photopinacolization processes. Where the starting ketone (or aldehyde) is unsymmetrical, both *dl* and *meso* forms of the pinacol may be produced. Previous studies involving acetophenone in neutral or acidic media have demonstrated that essentially identical *dl/meso* ratios of diastereomers are produced by both the electrochemical and photochemical techniques.^{2–4} It would be anticipated that a stereochemical study of the peroxide-induced pinacolization should yield this same *dl/meso* ratio of products.

Preliminary studies gave wildly erratic results; it was subsequently realized that the thermal stability of the acetophenone pinacols was an important factor. Tables I and II summarize the pertinent data.

TABLE I
THE PEROXIDE-INDUCED PINACOLIZATION OF ACETOPHENONE

Expt	<i>t</i> -Butyl peroxide, ml	Solvent, ml ^a	Time, hr	Temp, °C	Recovered ketone, % ^b	Pinacols, % ^b	Ratio <i>dl/meso</i>
1	1	4	16	120	8	88	0.89
2	2	4	1	120	32	65	1.05
3	1	4	0.5	160	7	92	1.01
4	1	4	2	160		100	1.00
5	0.5	4	0.5	160	3	95	0.98
6	0.1	4	0.5	160	80	16	0.94
7	0.5	2	5	160		100	0.92
8	0.5	2	24	160	33	58	0.78
9	0.5	2	48	160	18	80	0.79
10	0.5	2	120	160		85	0.50
11	None	4	360	160	70		

^a 2-Pentanol. ^b Based on 500 mg of acetophenone starting material used in all runs.

Results and Discussion

From Table I it may be observed that the highest *dl/meso* ratios correspond to the largest amount of peroxide, the lower temperature, and the shortest periods of time. If peroxide stability is considered,^{5–7} these data, taken collectively, may conveniently be interpreted as reflecting rapid utilization of the peroxide, rapid formation of the pinacols, and a slower interconversion of the pinacols *via* a thermal process. On this basis, expt 2 in Table I would best reflect the nonthermal process, *i.e.*, maximum amount of peroxide at the lower temperature for a period of time short of complete reaction. It will be noted that these conditions gave rise to a *dl/meso* ratio (1.05) which is virtually identical with those observed in the earlier photochemical studies (1.09 ± 0.03)² at room temperature, identical with those observed in the same study at the boiling point of 2-pentanol (1.03–1.05), and the highest ratio observed in the present study.

This excellent correspondence lends additional weight to the general mechanism proposed by Huyser and Neckers¹ and further supports the stereochemical arguments in the related photochemical studies.^{2,4}

The subsequently carried out thermal studies reported in Table II verify and extend this interpretation. Previous studies of the thermal stability of pinacols⁸ have dealt with those derived from symmetrical ketones, and no stereoisomerism would be observed. The present study would appear to constitute the first

(5) *t*-Butyl peroxide has been reported to have a half-life of 19.8 min at 160° in dilute benzene solution, although the decomposition is said to be practically unaffected by its chemical environment. See Lucidol Product Bulletin 7.101. Other selected figures from this source of *t*_{1/2} include 34.0 hr (115°), 6.4 hr (130°), and 1.38 hr (145°).

(6) W. A. Pryor ("Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 84) reports half-lives of 11 years (60°) and 35 sec (180°).

(7) C. S. Huyser and A. A. Kahl [*Chem. Commun.*, 1238 (1969)] describe the accelerated decay of *t*-butyl peroxide in the presence of α -hydroxyalkyl radicals. Since such a condition would prevail in the present studies, the half-lives reported in ref 5 and 6 are correspondingly too long.

(8) D. C. Neckers and D. P. Colenbrander, *Tetrahedron Lett.*, 5045 (1968), and references cited therein.

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(2) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **31**, 3755 (1966).

(3) J. H. Stocker and R. M. Jenevein, *ibid.*, **33**, 294 (1968).

(4) J. H. Stocker, R. M. Jenevein, and D. H. Kern, *ibid.*, **34**, 2810 (1969).