B.—A solution of **9** (0.41 g, 1.0 mmole) in acetic acid (9.0 ml) and water (1.0 ml) was allowed to stand for 24 hr, then diluted to 100 ml with water. The resulting solid (0.33 g, mp 139–141°, 98% yield) was identified by mixture melting point and qualitative thin layer chromatographic and infrared spectral comparisons with **11** prepared by the other method.

3-Methoxy-17-(3-oxo-1-propynyl)estra-1,3,5(10)-trien-17α-ol (12).—A solution of **10** (0.62 g, 1.5 mmole) in acetic acid (13.5 ml) and water (1.5 ml) was allowed to stand for 24 hr at room temperature, then diluted to 100 ml with water. The resulting solid (0.51 g, 100% yield, mp 93–98°) crystallized from acetonitrile as colorless microscopic crystals, 0.37 g, 73% yield, mp 94–98°, $[\alpha]^{25}D$ +75.5°. Its infrared spectrum showed absorption bands at 4.55 and 6.03 μ.

Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 78.36; H, 7.50.

Registry No.—**4**, 1624-62-0; **5a**, 2848-92-2; **6**, 13491-22-0; **7**, 3966-17-4; **8**, 1035-77-4; **9**, 13389-55-4; **10**, 13389-56-5; **11**, 13389-57-6; **12**, 13389-58-7.

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The Preparation of α-Ketoaldehyde Derivatives from β-Keto Sulfoxides

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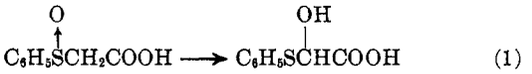
A novel preparation of α-keto acetals and α-ketoaldehyde hydrates from β-keto sulfoxides is described. Excellent yields of aliphatic as well as aromatic α-keto acetals are obtained by refluxing β-keto sulfoxides with 1 equiv of iodine in methanol. The rearrangement of β-keto sulfoxides to α-keto acetals occurs readily with a large variety of acid catalysts, but an equilibrium mixture of products is obtained (*cf.* eq 3) which strongly resists resolution into individual components by the usual methods of separation. Iodine forces the equilibrium toward the α-keto acetal by converting methyl mercaptan to dimethyl disulfide, removing it from the equilibrium system. Thus, iodine serves both as a source of acid catalyst (hydrogen iodide) and as an oxidant to remove methyl mercaptan. Support for an enolization mechanism is also presented.

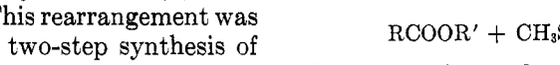
The action of acidic reagents on aromatic α-sulfinyl carboxylic acids to form hemithioacetals or other derivatives of glyoxylic acid was first reported by Pummerer[2] (eq 1). The reaction has been generalized by other



$$C_6H_5\overset{\uparrow}{\underset{O}{S}}CH_2COOH \longrightarrow C_6H_5S\overset{|}{\underset{OH}{C}}HCOOH \qquad (1)$$

workers[3,4] to include β-carbethoxy sulfoxides, β-keto sulfoxides, and β-disulfoxides. This rearrangement was also the key step in the elegant two-step synthesis of ninhydrin.[5]

No definitive study of the mechanism of the Pummerer reaction has been presented. It has been suggested[3] that a multistep dissociation–recombination mechanism initiated by attack of a proton on sulfur occurs, while several authors have suggested an intramolecular transfer of hydroxyl from sulfur to oxygen.[4-6] Evidence has been presented for an intermolecular attack of solvent or other nucleophile on a reactive intermediate[7,8] and for a carbonium ion mechanism.[9] It appeared to us that, if this reaction could be generalized for aliphatic as well as aromatic β-keto sulfoxides, it would represent a very valuable synthetic procedure for preparation of α-ketoaldehydes or their derivatives. There are few good general syntheses of α-ketoaldehydes; a good but more complex reaction sequence utilizing α-diazo ketones has recently been summarized.[10] The preparations of aliphatic[11] and aromatic[4] β-keto sulfoxides in good yield from reaction of the methylsulfinyl carbanion with the corresponding esters (eq 2) have been recently reported.



$$RCOOR' + CH_3SO\bar{C}H_2 \longrightarrow R\overset{\|}{\underset{O}{C}}CH_2\overset{\uparrow}{\underset{O}{S}}CH_3 \qquad (2)$$

Consequently we have investigated the scope of the Pummerer reaction and the conditions necessary to direct it to formation of single products in good yields.

Results

The β-keto sulfoxides were prepared by standard methods.[4,11] Structure determinations of the new compounds were based on their chemical analysis (Table I) and their infrared and nmr spectra (the methylene protons between ketone and sulfoxide in the aliphatic β-keto sulfoxides usually exhibited nonequivalence in nonpolar solvents, appearing as an AB quartet centered at τ 6.22).

Various acids in aqueous solvent systems cause the rearrangement. However, in contrast to the cases where R is aromatic and a crystalline product can be isolated, the variety of products (eq 3) possible in this equilibrium system are oils when R is aliphatic. No specific member of the equilibrium is formed exclusively and separation is very difficult. The mercaptal sulfur could not be completely removed by any of several pro-

(1) Virginia State College, Norfolk, Va. 23504.

(2) R. Pummerer, *Ber.*, **42**, 2282 (1909); **43**, 1401 (1910).

(3) W. J. Kenney, J. A. Walsh, and D. A. Davenport, *J. Am. Chem. Soc.*, **83**, 4019 (1961); D. Walker, *J. Org. Chem.*, **31**, 835 (1966).

(4) H-D. Becker, G. J. Mikol, and G. A. Russell (*J. Am. Chem. Soc.*, **85**, 3410 (1963)) describe the preparation of aromatic β-keto sulfoxides and their rearrangement in hydrochloric acid at room temperature to give good yields of the hemithioacetals of the corresponding α-ketoaldehydes.

(5) H-D. Becker and G. A. Russell, *ibid.*, **28**, 1896 (1963).

(6) D. Walker and J. Leib, *Can. J. Chem.*, **40**, 1242 (1962).

(7) S. Oae, T. Kitao, S. Kawamura, and Y. Kitaoka, *Tetrahedron*, **19**, 817 (1963).

(8) H-D. Becker, *J. Org. Chem.*, **29**, 1358 (1964).

(9) W. E. Parham and M. D. Bhausar, *ibid.*, **28**, 2686 (1963); W. E. Parham and S. H. Broen, *ibid.*, **30**, 728 (1965).

(10) F. Weygand and H. J. Bestmann in "Newer Methods of Preparative Organic Chemistry," Vol. III, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1964, p 451.

(11) E. J. Co rey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1639 (1964).

TABLE I

β-KETO SULFOXIDES, $RCOCH_2\overset{O}{\overset{\uparrow}{S}}CH_3$, FROM CONDENSATION OF ESTERS WITH METHYLSULFINYL CARBANION

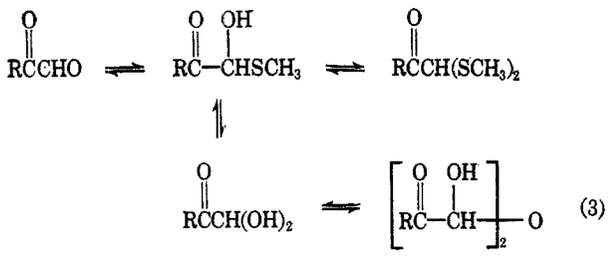
Compd no.	Structure, R	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Calcd, % S	Calcd, % O (direct)	Found, % C	Found, % H	Found, % S	Found, % O (direct)
2	n-C_9H_{19}	77–78	85	62.2	10.4	13.7	13.7	62.5	11.2	13.3	13.8
3	n-$C_{13}H_{27}$	88–89	93	66.6	11.2	11.1	11.1	66.7	11.2	11.1	11.5
4	CH_2=$CH(CH_2)_8$	73–74	90	63.9	9.90	13.1	13.1	63.9	9.90	13.1	12.9
5	cis-$C_8H_{17}CH$=$CH(CH_2)_7$	54–55	78	70.1	11.2	9.3	9.3	70.8	11.8	9.4	9.2
6	C_6H_5	88–89	70	59.3	5.53	17.5		59.4	5.55	17.4	

TABLE II

α-KETO ACETALS, $RCOCH(OMe)_2$, FROM REARRANGEMENT OF β-KETO SULFOXIDES IN METHANOL

Compd no.	Structure, R	Bp, °C (mm)	Yield, %	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Derivatives, mp, °C: Di-DNP	Dioxime	Bisulfite	Disemicarbazone
7	C_9H_{19}	85 (0.15)	85	67.8	11.3	67.8	11.3	171	93.5–94.5	175 dec	230–230.5
8	$C_{13}H_{27}$	120 (0.15)	87	71.3	11.9	71.2	11.5	161–164	120–121	158 dec	
9	CH=$CH(CH_2)_8$	95 (0.10)	92	69.4	10.8	69.3	10.7	139–142			
10	cis-$C_8H_{17}CH$=$CH(CH_2)_7$		100[a]					134–138			
11	C_6H_5	74 (0.25)	88	66.7	6.7	66.5	6.6	276–278			

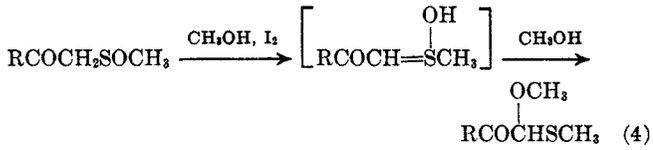
[a] Yield appeared quantitative but the product could not be readily purified.



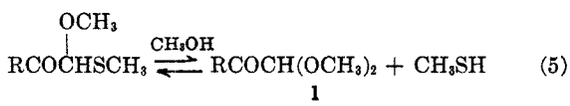
(3)

cedures which included heating under vacuum with dilute aqueous acid or dilute acid in aqueous dimethyl sulfoxide, heating with aqueous or alcoholic mercuric salts, or refluxing in acidic methanol to form the acetal.

In contrast to the above procedures, the use of iodine in aqueous or alcoholic solvent to bring about the Pummerer transformation results in clean formation of the corresponding α-ketoaldehyde hydrate or α-keto acetal **1**. The iodine serves a dual function in the reaction; it acts as a source of acid to catalyze the rearrangement and it removes methyl mercaptan from the equilibrium system by oxidizing it to dimethyl disulfide. Equations 4–6 are formulated in methanol solvent presuming an enolization mechanism to occur.



(4)



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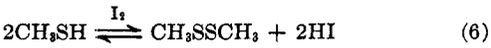
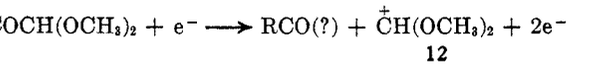


(6)

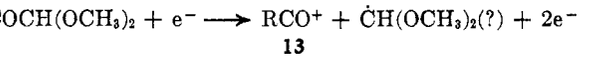
The hydrogen iodide formed from mercaptan oxidation is a very effective catalyst for the first step, so that the reaction becomes autocatalytic. The course of the reaction may be followed roughly by titrating the hydrogen iodide potentiometrically. The reaction is essentially complete after refluxing for 1 hr in methanol. The results and some properties of the acetals are summarized in Table II.

The structure of the α-keto acetals were determined by chemical analysis and by their infrared, nmr, and mass spectra. The infrared spectra were all characterized by the ketone carbonyl stretch at 1710 cm^{-1} and a strong acetal ether doublet at 1070–1110 cm^{-1}. The nmr spectrum of **7** is clearly characterized by the methinyl singlet at τ 5.77 (area = 1), methoxyl singlet at τ 6.62 (area = 6), and the methylene adjacent to ketone at τ 7.4 (area = 2). The mass spectra of all the α-keto acetals exhibit small molecular ion peaks and all give a base peak at m/e 75 corresponding to cleavage, giving the stable ion **12**. A strong peak corresponding



12

to the acyl carbonium ion **13** was also present in the spectrum of each α-keto acetal.



13

Use of aqueous 1,2-dimethoxyethane as a solvent for the iodine-catalyzed reaction with the β-keto sulfoxide **2** leads to formation of nonvolatile products, probably a mixture of the analogous α-ketoaldehyde, its hydrate, or its dimeric hemihydrate. This crude product not only readily gave the same derivatives as the acetal **7**, but in contrast to **7** easily formed a bisulfite addition salt.

The use of bromine as an oxidant was investigated briefly. Treatment of **2** for 30 min with refluxing methanol containing 1% sulfuric acid as catalyst, followed by addition of 1 equiv of bromine to oxidize the methyl mercaptan, resulted in formation of the keto acetal **7** in 85% yield. The bromine color was discharged very rapidly; however, no attempt was made to determine if the bromine was reacting only with methyl mercaptan from the acetal equilibrium (eq 5) or with some other species in the solutions. Since bromine is more awkward to measure and handle and offers no advantage over iodine, its use in preparation of other keto acetals was not investigated.

The rearrangement can also be directed to formation

of a single product by removing the α-dicarbonyl species from equilibrium (eq 3) with 2,4-dinitrophenylhydrazine or semicarbazide hydrochloride. In fact, treatment of the keto sulfoxide itself, the acid rearrangement mixture prepared by acid treatment without iodine, or the acetal **1** with these reagents produces the same derivative. The acidity of the standard reagents[12] is adequate to bring about rearrangement and to set up equilibrium.

The ester precursors of the compounds listed in Table I were chosen to test the versatility of the overall sequence. The reaction works equally well for aliphatic and aromatic keto sulfoxides. Furthermore, the conditions used in the two-step sequence do not affect olefinic linkages. A variety of strong bases are known to isomerize double bonds;[13] thus the possibility existed that the very strongly basic system methylsulfinyl carbanion in dimethyl sulfoxide (DMSO) might isomerize olefinic systems.[14] Iodine is known to catalyze *cis–trans* isomerization of double bonds by means of a reversible addition of iodine radicals.[15] The infrared and nmr spectra of the unsaturated ester and β-keto sulfoxide precursors to **9** and **10** were identical in the olefin region with those of the product acetals. Thus no rearrangement of the terminal olefin to the more stable internal position occurs in **9**, nor does the *cis*-olefinic linkage of methyl oleate isomerize to the more stable *trans* form in **10**. Only one isomer was detectable by gas chromatography of the product acetal from **9**.

Discussion

A variety of acidic reagents has been used to catalyze the Pummerer rearrangement in aromatic systems. The system described in this report, iodine in protic solvents, could act as an acidic reagent in three ways. Iodine could act as a Lewis-acid catalyst by coordinating with the sulfoxide oxygen to promote enolization, the small concentration of protons contributed from the equilibrium (eq 7) could initiate the reaction, or

$$I_2 + CH_3OH \rightleftharpoons CH_3OI + HI \qquad (7)$$

trace quantities of any reducing agents that might be present in the reaction mixture could react with iodine to provide sufficient hydrogen iodide to start the reaction. In any event, hydrogen iodide produced by the mercaptan oxidation is undoubtedly the principal acid catalyst for the bulk of the reaction. That iodine in methanol reacts with neither the incipient aldehyde in the equilibrium system (eq 4–6) nor with the starting sulfoxide to form sulfone is evidenced by the fact that no acidic products or sulfones were isolated from the reactions and by the fact that the acetals were isolated in very high yield. The increased oxidation potential of α-ketoaldehydes over simple aldehydes has been noted;[16] this undoubtedly works in favor of high yields of aldehyde derivatives. Theoretically, any other system embodying an acid catalyst and a properly selective oxidizing agent should function in the same manner. A single attempt to use 1 equiv of nitrate ion and 2 equiv of mineral acid in 25% aqueous methanol gave the expected acetal in 24% yield. Carboxylic acids were also formed, however, and not all the mercaptal sulfur was removed. No effort was made to optimize the yield from the nitric acid reaction. It is not surprising that the α-keto acetal should be formed in aqueous methanol since attempted recrystallization from methanol of independently prepared hydrate resulted in complete conversion to the α-keto acetal.

The reaction of mercaptans with iodine is known to be reversible in organic solvents and is often carried to completion by extraction of the hydrogen iodide into an aqueous phase.[17] Apparently in our case the high solvating power of methanol lowers the reducing potential of the hydrogen iodide sufficiently that the reverse reaction is not significant.

If the reaction with iodine is interrupted in its midstages (*e.g.*, about 20 min), the reaction mixture contains no starting keto sulfoxide, but rather acetal **1** and the mixed thioacetal **14**. Structure determination of the mixed thioacetals is based on their nmr spectra. The spectra are very similar to that of the acetal **7** except for the SCH_3 singlet at τ 7.9 (area = 3). If the reaction is terminated in less than 3 min, the reaction mixture consists of unreacted keto sulfoxide, some **1**, and mostly **14**. The fact that **14** is formed as an inter-

$$RCOCH(OCH_3)SCH_3$$
14

mediate in the presence of an excess of iodine argues that at no time in the reaction does a dissociation–recombination step involving free methyl mercaptan occur. The free mercaptan would be expected to be rapidly oxidized out of the aldehyde–thioacetal equilibrium system.[17] This would thus argue against the mechanism of Kenney, Walsh, and Davenport.[3] When the reaction is carried out in the absence of a nucleophile (for example, in anhydrous 1,2-dimethoxyethane), only resinous materials are formed. If an intramolecular rearrangement were the first step of this sequence, it should not matter if an external nucleophile were not present. This further supports the enolization mechanism (eq 4) which requires a nucleophile to attack the reactive intermediate.

Experimental Section

The β-keto sulfoxides described in this report were all prepared by addition of the appropriate esters to a solution of methylsulfinyl carbanion in dimethyl sulfoxide at room temperature. The dimethyl sulfoxide in all cases was dried by passage through a column of 4-A molecular sieve pellets, followed by storage over fresh molecular sieve. We could not obtain good yields of the aromatic sulfoxide **6** by this technique; therefore we used the procedure of Becker, Mikol, and Russell[4] for preparation of **6**. Except for the last-described experiment, the rearrangement procedure was the same for all sulfoxides and will be described in detail for only one case. Nuclear magnetic resonance spectra were obtained on a Varian A-60 spectrometer using deuterated

(12) (a) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 111; (b) p 218.

(13) (a) H. Pines and L. A. Schapp, *Advan. Catalysis*, **12**, 118 (1960); (b) A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **84**, 3164 (1962), and references therein; (c) F. Asinger, B. Fell, and G. Collin, *Chem. Ber.*, **96**, 716 (1963).

(14) E. C. Steiner and J. M. Gilbert (*J. Am. Chem. Soc.*, **85**, 3054 (1963)), C. C. Price and W. H. Snyder (*ibid.*, **83**, 1773 (1961)), and D. J. Cram, B. Rickborn, and G. R. Knox (*ibid.*, **82**, 6412 (1960)) have reported unusually high rates for base-catalyzed reactions in DMSO.

(15) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 302.

(16) H. Adkins, *et al.*, *J. Am. Chem. Soc.*, **71**, 3622 (1949).

(17) (a) J. W. Kimball, R. L. Kramer, and E. E. Reid, *ibid.*, **43**, 1199 (1921); (b) J. R. Sampey and E. E. Reid, *ibid.*, **54**, 3404 (1932); (c) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., New York, N. Y., 1958, p 124.

chloroform solutions unless otherwise specified. Melting points were obtained on a Uni-Melt Hoover capillary melting point apparatus. Mass spectra were obtained on a Bendix Model 12–100 time-of-flight spectrometer.

1-Methylsulfinylundecan-2-one.—A slurry consisting of 8.6 g of sodium hydride (55% mineral oil suspension; 4.8 g, 0.20 mole, of active sodium hydride) in 300 ml of dried dimethyl sulfoxide was heated at 65° under a nitrogen sweep for 2 hr until gas evolution ceased. The solution was cooled to 20° and maintained at that temperature by an ice–water bath while 18.6 g (0.10 mole) of methyl decanoate was added dropwise. The solution was stirred at room temperature for 30 min, then poured onto 300 g of ice and water containing 52.5 g (0.20 mole) of ammonium chloride. The resultant slurry was extracted with three 500-ml portions of chloroform. The chloroform solution was dried over anhydrous magnesium sulfate and the chloroform removed on a rotary evaporator under aspirator vacuum. Residual dimethyl sulfoxide was removed using a vacuum pump. Yield of crude 1-methylsulfinylundecan-2-one was 20.6 g (89%), mp 68–75°. Recrystallization from 300 ml of 60–90° ligroin containing 10 ml of ethanol gave 14.4 g of white crystals, mp 77–78°.

Recrystallized material (0.1 g, 0.00043 mole) was dissolved in 2 ml of ethanol and 8.5 ml (0.00129 mole) of 2,4-dinitrophenylhydrazine reagent solution[12a] was added. The solution was warmed briefly on a steam bath and allowed to cool. The orange precipitate was filtered, washed with 25 ml of ethanol, and air dried, giving 0.16 g of bishydrazone, mp 171°. *Anal.* Calcd for $C_{23}H_{28}N_8O_8$: C, 50,8; H, 4.8; N, 20.7. Found: C, 50.6; H, 4.8; N, 20.7.

Recrystallized sulfoxide (0.1 g, 0.00043 mole) was dissolved in 3 ml of ethanol and about 3 drops of water was added. A 0.142-g (0.00129 mole) quantity of semicarbazide hydrochloride was added and the suspension warmed to reflux. The clear solution was heated at reflux 30 min, then allowed to cool. The precipitate was filtered and washed with 10 ml of water followed by 25 ml of ethanol: yield 0.12 g; mp 230–230.5°. *Anal.* Calcd for $C_{13}H_{26}N_6O_2$: C, 52.5; H, 8.7; O, 10.7. Found: C, 52.6; H, 9.7; O, 11.0.

1,1-Dimethoxyundecan-2-one.—1-Methylsulfinylundecan-2-one (11.6 g, 0.05 mole) was dissolved in 100 ml of methanol containing 8.0 g (0.031 mole) of iodine. The solution was refluxed for 90 min, then allowed to cool. Most of the methanol was removed at room temperature on a rotary evaporator under aspirator vacuum. The dark residual oil was taken up in 50 ml of chloroform and extracted twice with 50-ml portions of saturated sodium thiosulfate solution. The very light yellow chloroform solution was dried with anhydrous magnesium sulfate and solvent removed under vacuum. The residual oil (11.8 g) was subjected to simple distillation through a Vigreux head giving 9.8 g, 85% yield, of a colorless liquid boiling at 85° (0.2 mm). Dimethyl disulfide was identified by its gas chromatographic retention time as the principal component of the lower boiling fraction. Gas chromatography on a 5-ft, $^3/_8$-in. Ucon Polar column showed >95% purity for the keto acetal. Identification by spectral means is described in the Results.

1,1-Dimethoxyundecan-2-one (*in Situ* **Rearrangement**).—Methyl decanoate (18.6 g, 0.10 mole) was added dropwise to a solution of 0.20 mole of methylsulfinyl carbanion in 400 ml of dimethyl sulfoxide (prepared as described above) kept at 15–20° by an ice–water bath. The mixture was stirred at room temperature for 0.5 hr; 400 ml of methanol, 9.8 g (0.10 mole) of sulfuric acid, and 14.0 g (0.055 mole) of iodine were added and the solution was warmed to 60° for 1 hr. The solution was cooled and most of the methanol removed under aspirator vacuum. Sodium thiosulfate, 50 g (0.32 mole) dissolved in 500 ml of water, was added and the resulting cloudy solution extracted with three 300-ml portions of chloroform. The chloroform solution was dried over anhydrous magnesium sulfate and the solvent removed under aspirator vacuum. The residual oil was distilled through a simple Vigreux head. That fraction boiling at 85–90° (0.2 mm) was collected and determined by gas chromatography on a 5-ft, $^3/_8$-in. Ucon Polar column to be >98%, 1,1-dimethoxyundecan-2-one: yield 14.5 g (63%) based on methyl decanoate.

Registry No.—**2**, 13133-44-3; **3**, 13133-45-4; **4**, 13133-46-5; **5**, 13133-47-6; **6**, 2813-22-1; **7**, 13133-49-8; **7** (di-DNP), 13133-50-1; **7** (dioxime), 13133-51-2; **7** (disemicarbazone, 13133-52-3; **8**, 13133-53-4; **8** (di-DNP), 13133-54-5; **8** (dioxime), 13133-55-6; **9**, 13133-56-7; **9** (di-DNP), 13133-57-8; **10** (di-DNP), 13133-58-9; **11**, 6956-56-5; **11** (di-DNP), 4881-22-5.

Acknowledgment.—The author wishes to thank Drs. W. I. Lyness, W. W. Bannister, and T. J. Flautt for valuable suggestions and discussions during the course of this work and to acknowledge the technical assistance of R. R. Cvach and J. F. Ward.

Nuclear Magnetic Resonance Spectra of Some Substituted Benzotriptycenes. The Effect of Steric Compression

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The chemical shifts of protons and/or methyl substituents in 5,12-*o*-benzeno-5,12-dihydronaphthacenes (benzotriptycenes) substituted in the 5, 6, 11, and 12 positions with methyl and phenyl groups were determined. The data are interpreted in terms of a steric compression shift by both methyl and phenyl.

The concept of a local magnetic field generated by the interaction of an external magnetic field and the system of π electrons in an aromatic ring has proved very useful in explaining many otherwise anomalous chemical shifts.[1] Some cases exist, however, where the ring current theory fails in even a qualitative sense. For example, the discrepancies between the observed and calculated chemical shifts in the case of 1,4-dialkyl-2,3,9-triphenylanthracenes are approximately 1.5 ppm.[2]

Wilcox and Roberts[3] observed that the bridgehead protons in 2,5-diphenyltriptycene resonate at *lower* field (by 0.3 ppm) than those in triptycene, even though the angle of twist of the phenyl groups was estimated to be such that the ring current theory predicts an *upfield* shift of *ca.* 0.5 ppm. They ascribe this anomaly to the intervention of a "steric" effect previously proposed by Reid[4] and described in more detail by others.[5] An example of this steric effect of classic proportions

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(2) T. H. Regan and J. B. Miller, *J. Org. Chem.*, **32**, 592 (1967).

(3) C. F. Wilcox, Jr., and F. D. Roberts, *J. Org. Chem.*, **30**, 1959 (1965).

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