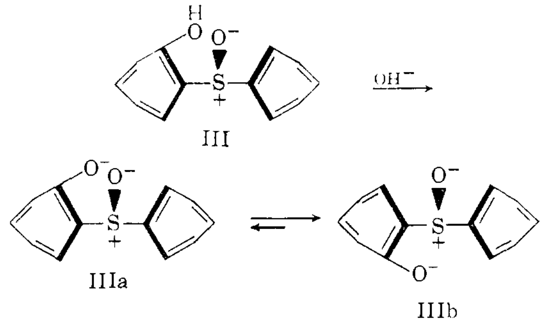
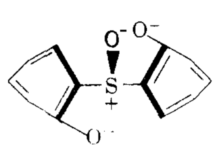


III

IIIa

IIIb



IV

but, in so doing, becomes stabilized by the positive field of the sulfur atom. Moreover, a stable conformation is retained (*cf.* IIIa and IIIb).[10] The dianion (IV) of the 2,2′-di-OH sulfoxide also exhibits this type of internal stabilization. This sulfoxide is more acidic than the corresponding sulfone even though the negative-field influence of the sulfinyl oxygen is now effective in reducing the net acidity, *viz.*, it is less acidic than the 4,4′-di-OH sulfoxide.

This paradox, in which a sulfinyl group effects a greater acidity than does a sulfonyl group, is exhibited also by the corresponding 2-OH compounds and arises, apparently, from the opposite field-effect influence exerted in the two systems. This is better illustrated by a comparison of the 4′-NO_2-substituted compounds in which the positive charge at the sulfur atom of both groups is increased[11]: in the sulfoxides the effective positive field is directly enhanced; in the sulfones the effective negative field is indirectly diminished. This is reflected by the larger difference in acidity between the 2- and 4-OH sulfoxides, but smaller difference between the corresponding sulfones, when a 4′-NO_2-group is introduced.

The behavior of other sulfone and sulfoxide systems may be accounted for on the basis of the type of field effects described here.[12]

[10] One cannot rule out the possibility that the undissociated phenol (III) may be already in the conformation denoted by IIIb. This will be considered in a forthcoming publication.

[11] C. Y. Meyers, G. Moretti and L. Maioli, in ref. 1 (*cf.* H. H. Szmant and G. Suld, Table I, ref. *a*).

[12] C. Y. Meyers, *Tetrahedron Letters*, in press.

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RECEIVED AUGUST 16, 1962

HOMOENOLATE ANIONS

Sir:

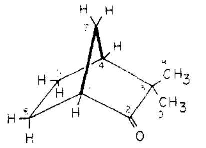
A hydrogen *alpha* to a carbonyl group is acidic and its abstraction by alkali leaves an enolate anion whose charge is stabilized by conjugation with the neighboring pi electrons. We now present evidence that removal of a hydrogen more remote from a carbonyl group can be facilitated by homoconjugation and can lead to a corresponding *homoenolate* anion.

Optically active camphenilone (I, m.p. 38–38.5°, α + 69°; semicarbazone m.p. 224.5–225.5°, α + 255°),[1] which has no ordinarily enolizable hydrogens, was heated at elevated temperature with potassium *t*-butoxide in *t*-butyl alcohol. The ketone was recovered (usually in about 80% yield), was identified by its infrared spectrum and by gas chromatography, and was converted to its semicarbazone. The specific rotation of the purified derivative was recorded to determine its optical purity. The results in Table I are typical and show that (+)-camphenilone is *racemized by the alkaline treatment.* The last run, in which the butoxide was omitted, establishes that the loss of optical activity is not the result of the thermal treatment alone.

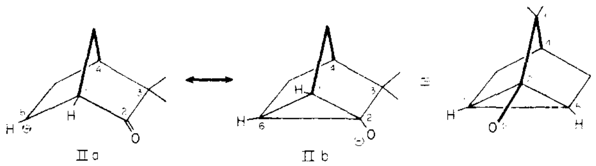
TABLE I[2]

Temp., °C.	Time, hr.	% Racemization
185	12	26
185	36	69
185	48	88
250	4	100
250	113 (alkali omitted)	0

We interpret the racemization as abstraction of a hydrogen from C.6 to form a non-classical anion II, termed a homoenolate anion, whose charge is stabilized by delocalization to the carbonyl group (*cf.* resonance structures IIa and IIb).



I



IIa IIb

Formation of this ion provides an opportunity for the C.2–C.6 bond to become equivalent to the C.2–C.1 bond and hence for the system to lose its optical activity. Recapture of a proton at C.6 regenerates the original (+)-camphenilone, whereas protonation at C.1 leads to the enantiomer.[3]

The mobility of hydrogens in camphenilone was further supported by deuterium-incorporation experiments in which the ketone was heated at 185° with potassium *t*-butoxide in *t*-butyl alcohol-*d*. The deuterium content and the relative distribution of deuterated species in the recovered ketone were determined mass spectroscopically. In separate runs conducted for 12 hr. and for 48 hr. the recovered camphenilone contained mono-, di-

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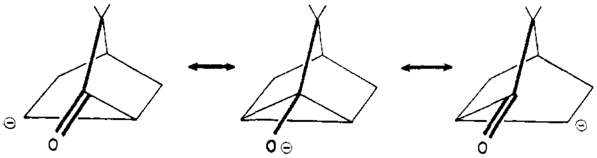
[1] (a) W. P. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); (b) W. Hückel, *Ann.*, **549**, 186 (1941).

[2] In all the runs reported in this paper the concentrations were not the same. Typically, the potassium *t*-butoxide molar ratio ranged from 2–4 and the *t*-butyl alcohol molar ratio ranged from 20–60, relative to camphenilone.

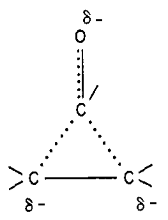
[3] Protonation of a homoenolate ion on oxygen would give the corresponding *homoenol*. In the present case the homoenol is also a cyclopropyl alcohol.

and trideuterated species as well as undeuterated material. After a 100 hr. run there was a slight indication (0.2%) of a tetradeuterated species as well. When the product from the 100 hr. run was treated with potassium *t*-butoxide in fresh *t*-butyl alcohol-*d* for an additional 166 hr., the relative amounts of deuterated species were: 1% (no D), 7% (1D), 26% (2D), 38% (3D), 21% (4D), 6% (5D), 1% (6D). Incorporation of up to three deuterium atoms is understandable in terms of the homoenolate anion II, which could permit exchange of both hydrogens at C.6 as well as of the bridgehead hydrogen at C.1. This latter hydrogen becomes exchangeable as a consequence of the interconversion of positions 1 and 6 in the homoenolate anion. That prolonged treatment eventually produced species with more than three deuterium atoms shows that C.6 is not the only homoenolizable site.

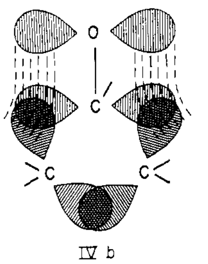
Additional information on the homoenolate ion was obtained by comparison of the extent of racemization of (+)-camphenilone with its extent of deuterium incorporation. Table II shows the results of four runs conducted with *t*-butoxide at 185° in *t*-butyl alcohol-*d*. The deuterium incorporation was assayed mass spectroscopically and the extent of racemization was determined from the optical activity of the derived semicarbazone. In each run the percentage racemization corresponded closely with the percentage of molecules having deuterium.[4] This close correspondence between racemization and deuterium entry reveals (a) that the first hydrogen exchanged is at a location that leads to a racemizable ion (this can only be at C.6); and (b) that the homoenolate ion formed by loss of a C.6 hydrogen racemizes before it can pick up deuterium from the solvent. Consequently, the homoenolate anion either has a symmetrical structure or, if unsymmetrical, it rearranges to its enantiomer faster than it reverts to the ketone. The symmetrical ion may be described approximately by the three canonical structures IIIa, b, c,[5] or by either of the mesomeric formulations IVa or IVb (shown as partial structures).



IIIa IIIb IIIc



IVa



IVb

TABLE II

Time, hr.	% Molecules with— No D	% Molecules with— One or more D	% Racemized
12	75	25	26
24	48	52	52
36	29	71	69
48	13	87	88

These results reveal the existence of homoenolate anions and bring into consideration the general concept of homoenolization. This concept may be extendable to transformations of biological interest, to sulfur and phosphorus compounds (*e.g.*, sulfones, phosphine oxides), to polyfunction molecules, *etc.*, and work along these lines is in progress.

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[4] An equivalent statement is that the fraction of molecules not racemized corresponds to the fraction that contains no deuterium.

[5] If the ion can have an unsymmetrical structure then IIIa and IIIb could differ slightly in geometry, in which case the resonance arrows would be replaced by equilibrium arrows.

[6] This work was supported in part by the Petroleum Research Fund' administered by the American Chemical Society, and in part by the Alfred P. Sloan Foundation. The results were presented at the 142nd Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1962.

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RECEIVED OCTOBER 15, 1962

INHERENTLY DISSYMMETRIC CHROMOPHORES: THE ABSOLUTE CONFIGURATION OF (−)-*trans*-CYCLOÖCTENE

Sir:

It is recognized that the contribution to a transition moment associated with the oscillation of charge between 2p orbitals positioned on two separate atomic centers can be either electric dipole allowed-magnetic dipole forbidden, or magnetic dipole allowed-electric dipole forbidden, depending on whether the orbitals are directed parallel or perpendicular to each other, as indicated in I and II, respectively. Any conformation in which the orbitals are mutually disposed at some intermediate relative angle γ (*e.g.*, III) may be viewed as a superposition of I and II. In such circumstances the transition moment can be both electric and magnetic dipole allowed, and the relevant electric and magnetic transition moment contributions are directed collinearly. More specifically, for an angle of twist γ, situation I contributes to the extent cos γ and situation II to the extent sin γ, so that the contribution to the rotational strength associated with situation III will be proportional to sin γ cos γ or to sin 2γ. Evaluation of the relevant matrix elements indicates that a (+)-sign is to be associated with the chirality indicated by III.[1] Hence any transition involving such a conformation of orbitals may be viewed as arising from an inherently dissymmetric chromophore whose transitions are perforce optically active. Such a situation would arise in the case of an olefin containing a twisted ethylenic bond and would manifest itself experimentally by a marked increase in the magnitude of the optical activity (relative to that of comparable but unstrained olefins) as measured in the visible and near ultraviolet.

In light of the above discussion, the molecule (−)-*trans*-cycloöctene[2] ($[\alpha]^{29}_{\text{D}}$ −411° or molecular

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[1] R. Deen, Dissertation, Leiden, 1961.

[2] A. C. Cope, C. R. Ganellin and H. W. Johnson, Jr., *J. Am. Chem. Soc.*, **84**, 3191 (1962).