cal Society (Grant 488-C) and to the National Science Foundation (G-14289) for financial support.

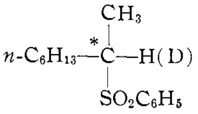
KEDZIE CHEMICAL LABORATORY JAMES L. CORBIN
MICHIGAN STATE UNIVERSITY HAROLD HART
EAST LANSING, MICHIGAN CHARLES R. WAGNER

RECEIVED MARCH 15, 1962

CONFIGURATIONAL STABILITY OF CARBANIONS STABILIZED BY *d*-ORBITALS[1]

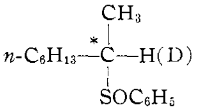
Sir:

In an earlier investigation, the stereochemical course of base-catalyzed hydrogen–deuterium exchange of sulfone I was studied through determination of k_e/k_α, in which k_e was the rate constant for exchange and k_α for racemization. Values of this ratio varied between a high of about 2000 with *tert*-butyl alcohol as solvent to a low of 10 with dimethyl sulfoxide.[2]



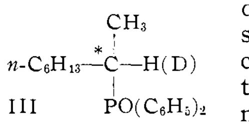
$n\text{-}C_6H_{13}-\overset{*}{C}(CH_3)(SO_2C_6H_5)-H(D)$

I



$n\text{-}C_6H_{13}-\overset{*}{C}(CH_3)(SOC_6H_5)-H(D)$

II



$n\text{-}C_6H_{13}-\overset{*}{C}(CH_3)(PO(C_6H_5)_2)-H(D)$

III

We have now prepared by conventional reactions both diastereomers of sulfoxide II[3] and phosphine oxide III[3] in optically pure states, and have determined approximate values of the ratio of k_e/k_α for the three substances in a number of different solvents (see Table I). Since the configuration at sulfur of IIa and IIb was unaltered during the exchange at carbon, k_α for these compounds actually is associated with the rate at which the systems approached epimeric equilibrium. This was measured by oxidizing each sample to sulfone I, whose rotation and deuterium content were measured by methods previously reported.[2b] With phosphine oxide, the polarimetric rates were measured in a conventional manner, and the deuterium content measured through use of the infrared bands at 10.98 and 14.29 μ present in the deuterated and absent in the undeuterated compounds.

TABLE I

STERIC COURSE OF HYDROGEN–DEUTERIUM EXCHANGE

Compound			Base			
Nat.	Concn. N	Solvent	Nature	Concn. N	T, °C.	k_e/k_α
IIa-h	0.17	$(CH_3)_3COD$[a]	$(CH_3)_3COK$	0.78	60	2
IIa-d	0.17	$(CH_3)_3COH$	$(CH_3)_3COK$	0.79	60	3
IIb-h	0.17	$(CH_3)_3COD$[a]	$(CH_3)_3COK$	0.78	60	3
III-h	0.20	$(CH_3)_3COD$[a]	$(CH_3)_3COK$	0.34	100	3
III-d	0.20	$(CH_3)_3COH$	$(CH_3)_3COK$	0.34	100	3
IIa-d	0.17	$(CH_3)_2SO$[b]	CH_3OK	0.23	60	1
III-d	0.20	$(CH_3)_2SO$[b]	CH_3OK	0.21	75	1
III-h	0.20	$DOCH_2CH_2OD$[a]	$DOCH_2CH_2OK$	0.28	175	1
III-d	0.21	$HOCH_2CH_2OH$	$HOCH_2CH_2OK$	0.29	175	1
III-d	0.21	CH_3OH	CH_3OK	0.30	175	1

[a] 99% deuterated (ref. 1b). [b] 1.2 *M* in methanol.

Comparison of the steric courses of the exchange reactions of sulfoxides II and phosphine oxide III with that of 2-phenylbutane indicates that the d-orbital containing functional groups exercise even less stereochemical control over the course of the exchange reaction than does a phenyl group.[4] Indeed, the data suggest that what stereospecificity is observed with the sulfoxide and phosphine oxide systems is associated with asymmetric solvation rather than with carbanion asymmetry. This conclusion is in striking contrast to that drawn for sulfone system I, which provided high though differing retention for exchange in all solvents.

Two different hypotheses could account for the difference in behavior of carbanions derived from sulfone I and oxides II and III. (1) Non-stabilized carbanions probably have sp^3 hybridization similar to amines. Carbanions stabilized by d-orbitals might have a tendency to rehybridize to sp^2-p since p-d overlap might be more favorable than sp^3-d overlap. However, many investigators have concluded that d-orbital stabilization of carbanions does not have rigid geometric requirements, although different geometries provide different stabilities.[5] Superimposed on overlap effects are electrostatic effects. In the most favorable conformations, repulsion between the negative charge on carbon and the partial charges on oxygen attached to sulfur or phosphorus would be less for sp^3 than for sp^2-p hybridization at carbon. Thus the overlap and electrostatic effects might oppose one another and a continuous spectrum of configurations at carbon ranging from trigonal to tetrahedral can be envisioned. Possibly no configurational stability is associated with trigonal carbon, whereas

---

[1] We are pleased to acknowledge financial support of the research reported here by the National Science Foundation.

[2] (a) D. J. Cram, W. D. Nielsen and B. Rickborn, *J. Am. Chem. Soc.*, **82**, 6415 (1960); (b) D. J. Cram, D. A. Scott and W. D. Nielsen, *ibid.*, **83**, 3696 (1961).

[3] Carbon, hydrogen, sulfur and phosphorus analyses deviated from theory by a maximum of 0.28%. Deuterated IIa, IIb and III contained 97–98% deuterium in the position indicated (combustion analysis and falling drop method by J. Nemeth). Isomer IIa had m.p. 20.5–21.5°, $[\alpha]^{25}_{546}$ −192 ± 3° (*c* 2, 95% ethanol), and isomer IIb was an oil which was separated from IIa by chromatography on silica gel, $[\alpha]^{25}_{546}$ +166 ± 3° (*c* 2, 95% ethanol). These isomers possessed the same configuration at carbon, but differed at sulfur. Compound III possessed m.p. 94–96°, $[\alpha]^{26}_{546}$ −14.7° (*c* 6, carbon tetrachloride). All three compounds were prepared from optically pure 2-octyl tosylate.

[4] In *tert*-butyl alcohol, $k_e/k_\alpha > 10$ for the exchange of 2-phenylbutane-2-*d* [ref. 1a and D. J. Cram, C. A. Kingsbury and B. Rickborn, *J. Am. Chem. Soc.*, **83**, 3688 (1961)].

[5] (a) W. E. Doering and L. K. Levy, *ibid.*, **77**, 511 (1955); (b) H. E. Zimmerman and B. S. Thyagarajan, *ibid.*, **82**, 2505 (1960); (c) R. Breslow and E. Mohacsi, *ibid.*, **83**, 4100 (1961); (d) S. Oae, W. Tagaki and A. Ohno, *ibid.*, **83**, 5037 (1961).

tetrahedral carbon might maintain degrees of configurational stability due to electrostatic inhibition of inversion. Electrostatic effects in the anion of sulfone I should be much greater than in the anions of either sulfoxide II or phosphine oxide III, and therefore the sulfone anion might exhibit configurational stability and the oxide anions lack of stability, as has been observed.

(2) When free from constrictions due to ring systems, carbanions stabilized by d-orbitals might provide better p-d overlap when trigonally hybridized. Several conditions would have to be fulfilled before stereospecificity for exchange reactions involving such species was observed. (a) The rotomer that gave the best p-d overlap would have to be asymmetric. (b) The rotomer would have to be formed and consumed through a *transition state that involved only one particular conformation.*[6] (c) The carbanion would have to undergo proton capture faster than the carbanion equilibrated (by rotation) with its enantiomer. These conditions might come closer to fulfillment with the sulfone than with the oxide anions. The d-orbitals of the sulfone group are more stabilizing than those of the oxide groups, and might impose more severe geometric requirements with respect to conformation than do the d-orbitals of the two oxides. Attempts are being made to test these notions in other systems that involve d-orbital-stabilizing groups.

(6) Application of the principle of microscopic reversibility indicates that if a carbanion is formed by loss of a proton from a particular side of the molecule, the same side will be involved when the proton is recaptured.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
AT LOS ANGELES, LOS
ANGELES 24, CALIF.
D. J. CRAM
RICHARD D. PARTOS
STANLEY H. PINE
HERB JÄGER

RECEIVED FEBRUARY 5, 1962

THE MOLECULAR CONFIGURATION OF 2,4,6-TRIPHENYLTROPONE-IRON TRICARBONYL

Sir:

The recent syntheses of several cycloheptatrienone (tropone) complexes by Hübel and coworkers[1-4] have stimulated discussion about their molecular geometry and the type of bonding between the metal orbitals and the π-orbitals of the organic ring system. On the basis of simple molecular-orbital theory and the presumed similarity of these compounds to the cyclopentadienone–metal complexes, Brown[5] suggested a planar tropone ring with the iron bonding equally to all three double bonds of the ring. Hübel and co-workers[6] later found that one of the double bonds could be hydrogenated and this together with the existence of isomers for each tropone complex led them to postulate interaction of the iron atom with only two of the three double bonds.[4]

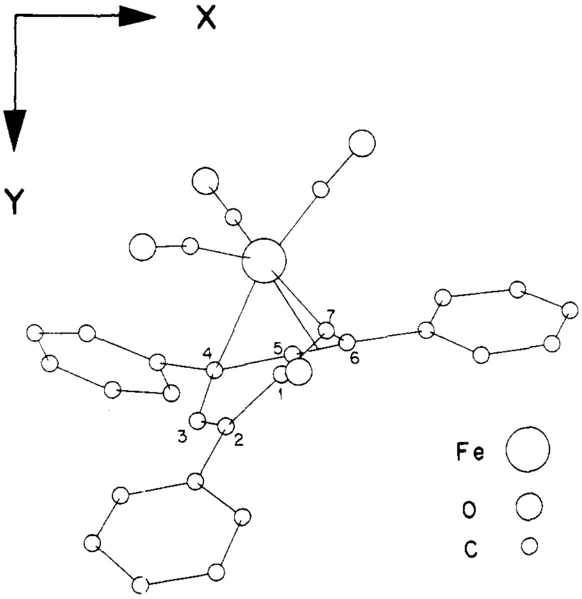


Fig. 1.—[001] Molecular projection of $[C_6H_3(C_6H_5)_3CO]$-$Fe(CO)_3$: bond distances for the tropone ring are 1.45 and 1.49 Å. for C_4–C_5 and C_6–C_7, respectively; 1.38 Å. for C_5–C_6, 1.34 Å. for the normal double bond C_2–C_3, 1.44 Å. (av.) for the other three bonds, and 1.26 Å. for C_1–O (all with e.s.d. ± 0.02 Å.). Fe–C distances are 2.17, 2.00, 2.09, and 2.13 Å. to carbon atoms $C_4 \ldots C_7$, respectively; iron distances to the midpoints of C_4–C_5, C_5–C_6 and C_6–C_7 are 1.96, 1.93 and 1.98 Å., respectively. Other non-bonding iron–tropone distances are $Fe \ldots C_1 = 2.97$ Å., $Fe \ldots C_2 = 3.46$ Å., and $Fe \ldots C_3 = 3.12$ Å. Fe–C (carbonyl) = 1.73 Å. (av.), C–O = 1.18 Å. (av.) (all with e.s.d. ± 0.02 Å). C–C bond lengths in phenyl rings range from 1.31 to 1.51 Å. (e.s.d. ± 0.03) with average length 1.40 Å.). Bond angles are (C_6H_5)–C_4–C_5 = 118.2°, (C_6H_5)–C_4–C_3 = 112.2°, C_3–C_4–C_5 = 122.4°, C_4–C_5–C_6 = 124.3°, C_5–C_6–C_7 = 116.2°, (C_6H_5)–C_6–C_5 = 126.0°, (C_6H_5)–C_6–C_7 = 117.5°, C_6–C_7–C_1 = 129.5°, C_7–C_1–C_2 = 125.0°, C_1–C_2–C_3 = 121.8°, (C_6H_5)–C_2–C_1 = 117.3°, (C_6H_5)–C_2–C_3 = 119.9°, C_2–C_3–C_4 = 127.7° (all with e.s.d. $\pm$ 1.6°). The dihedral angle between the two planes in the tropone ring is 139°.

To resolve this conflict we have carried out an X-ray structural analysis of one isomer of a substituted tropone, 2,4,6-triphenylcycloheptatrienone-iron tricarbonyl, $[C_6H_3(C_6H_5)_3CO]Fe(CO)_3$. The dark red crystals[3] are orthorhombic with lattice parameters a = 19.53 Å., b = 7.62 Å., and c = 15.03 Å. Systematic absences show $P2_12_12_1$ as the probable space group. For four molecules per unit cell the calculated density is 1.41 g./cc. in agreement with the density, 1.41 g./cc., measured by the flotation method.

X-Ray intensity data obtained with MoKα radiation by the usual equi-inclination Weissenberg techniques were estimated visually. A three dimensional structural analysis of the data including isotropic least squares refinement[7] and error analysis[8] has yielded the molecular configuration

---

(1) W. Hübel, E. H. Braye, A. Clauss, E. Weiss, V. Krüerke, D. A. Brown, G. D. S. King, and C. Hoogzand, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959).

(2) W. Hübel and E. H. Braye, *ibid.*, **10**, 250 (1959).

(3) W. Hübel and E. Weiss, *Chem. and Ind.*, 703 (1959).

(4) E. H. Braye, C. Hoogzand, W. Hübel, V. Krüerke, R. Merényi, and E. Weiss, "Advances in the Chemistry of the Coordination Compounds," edited by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, pp. 190–198.

(5) D. A. Brown, *J. Inorg. Nucl. Chem.*, **13**, 212 (1960).

(6) W. Hübel, private communication, 1960.

(7) W. R. Busing and H. A. Levy, "A Crystallographic Least Squares Refinement Program for the IBM 704," ORXLS, 1959.

(8) W. R. Busing and H. A. Levy, "A Crystallographic Function and Error Program for the IBM 704," ORXFE, 1959.