ture, crude, crystalline anhydroactidione. After one recrystallization from aqueous ethanol analytically pure material, m.p. 130–133°, $[\alpha]^{25}\text{D}$ −12.7 (c = 3.7, $CHCl_3$), was obtained in 46% yield. Exhaustive recrystallizations from aqueous acetonitrile afforded a single isomer of anhydroactidione, m.p. 139–141°, $[\alpha]^{25}\text{D}$ −33.2 (c = 1.7, $CHCl_3$), ultraviolet maximum at 240 mμ (log ϵ = 3.94) in ethanol,[10] (*Anal.* Calcd. for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32. Found: C, 68.55; H, 8.29; N, 5.25). This compound, by comparison of melting points and mixture melting points, infrared (potassium bromide disk) and ultraviolet spectra, and optical rotations, proved to be identical with authentic anhydroactidione, prepared by dehydration of Actidione with phosphorus pentoxide,[2] or with an aqueous solution of hydrochloric acid and acetic acid. In both cases repeated recrystallizations from aqueous ethanol were required to yield the pure isomer melting at 139–141°.

For comparison, racemic anhydroactidione was prepared. Hydrogenation of 2,4-dimethylphenol[11] followed by dichromate oxidation[2] yielded *dl*-2,4-dimethylcyclohexanone, b.p. 53–54° (8–9 mm.), $n^{25}\text{D}$ 1.4430, semicarbazone (96% yield) melting at 188–189°.[12] The relationship of this ketone with the alkaline degradation ketone already has been demonstrated.[2] Then essentially following the procedure outlined above, there was obtained racemic anhydroactidione, m.p. 118–120°, ultraviolet maximum at 240 mμ (log ϵ = 3.99), infrared spectrum (chloroform solution) identical with that of enantiomorphic anhydroactidione (Found: C, 68.33; H, 7.97; N, 5.33). The key step, namely, the condensation of an aldehyde (III) with the anion of an α-formyl ketone (V), exemplifies an interesting approach to the α,β-unsaturated ketonic moiety, and will be amplified in a full paper.

The author expresses his warm appreciation to Dr. Coy W. Waller and members of the Chemistry Staff at Mead Johnson, to Professor D. H. R. Barton, and to Professor John W. Huffman for helpful and stimulating discussions.

[10] Woodward's ultraviolet rule (R. B. Woodward, THIS JOURNAL, **64**, 76 (1942)) predicts this value for the α,β-unsaturated ketone embodied in anhydroactidione.

[11] H. E. Ungnade and A. D. McLaren, *ibid.*, **66**, 118 (1944).

[12] D. Capon and co-workers, *Bull. soc. chim.*, 837 (1958).

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RECEIVED NOVEMBER 19, 1960

STUDIES OF HALOGEN ATOMS ABSTRACTION BY METHYL RADICALS[1]

Sir:

Although extensive studies were carried out on reactions involving abstraction of hydrogen by radicals and free atoms, very little is known about those processes in which these reagents abstract other atoms, *e.g.*, halogens. This note reports preliminary data pertinent to reactions of the type $RX + CH_3 \rightarrow R + CH_3X$, where X denotes I, Br or Cl. In determining the relative rate constants (k_2) of those reactions our usual technique[2,3] was applied. A radioactive labelling technique had to be used in studies of the exchange reactions $CH_3I + CH_3$ and $CH_3Br + CH_3$.

The results are summarized in Tables I and II. They show clearly the expected reactivity gradation in the series MeX, EtX, iso-PrX and *t*-BuX, as well as in the series CH_3X, CH_2ClX, $CHCl_2X$ and CCl_3X. They show also that the ratio $k_{2,\text{I}}/k_{2,\text{Br}}$ remains approximately constant ($\sim 9.10^3$ for Me, 1.2×10^3 for $PhCH_2$ and 4.6×10^3 for CH_2Cl). On assumption that the entropy of activation is approximately constant (this seems to be partially justified by the data quoted in Table II) the difference in $E_{2,\text{Br}} - E_{2,\text{I}}$ for any pair RBr and RI is calculated to be about 5–6 kcal./mole, corresponding approximately to $^1/_2\{D(\text{R–Br}) - D(\text{R-I})\}$, *i.e.*, $^1/_2$ of 11–14 kcal./mole. A similar conclusion is arrived at from the data based on the only available example of CCl_3Br and CCl_3Cl.

TABLE I

RELATIVE RATE CONSTANTS FOR REACTIONS $RX + CH_3 \rightarrow R + CH_3X$ (k_2) EXPRESSED AS RATIO k_2/k_1, WHERE k_1 REFERS TO THE REACTION $CH_3 + PhCH_3 \rightarrow CH_4 + PhCH_2$ (k_1); ALL DATA AT 65°

R	1	Br	Cl	H[a]
CH_3	45	$\sim 5.10^{-3}$	.....	4×1.10^{-4}[b]
C_2H_5	180	......	.....	6×0.011
s-C_3H_7	870	......	.....	2×0.16
t-C_4H_9	1680	......	.....	1.85
$PhCH_2$	7560	6.5	.....	3×0.33
CH_2Cl	6400	1.4	.....	......
$CHCl_2$	....	131	.....	......
CCl_3	....	7400	4×1.1	......
CF_3	20,000		.....	......

[a] Extrapolated from results reported by Steacie (see Steacie's "Atomic and Free Radical Reactions"). [b] Using recent data by Dainton, Ivin and Wilkinson, *Trans. Faraday Soc.*, **55**, 929 (1959), a value of 4×5.10^{-5} is obtained.

TABLE II

$$RI + Me \rightarrow R + MeI \; .\,.\,.\,. \; k_2$$
$$Ph{\cdot}CH_3 + Me \rightarrow Ph{\cdot}CH_2 + MeH \; .\,.\,. \; k_1$$

R	$E_2 - E_1$, kcal./mole	A_2/A_1
CH_3	-1.8 ± 1.5	3
C_2H_5	-1.9 ± 1.0	10
s-C_3H_7	-2.9 ± 1.0	11

This "simple" relation does not hold when RX is compared with RH. As shown by the data in the last column of Table I, the H abstraction is relatively much faster than expected on the basis of the high values of $D(\text{R-H})$'s. Whereas $D(\text{R-H}) - D(\text{R-Br})$ is 30–35 kcal./mole, the calculated $E_{2,\text{Br}} - E_{2,\text{H}}$ are less than 2 or 3 kcal./mole if the assumption of a constant frequency factor is valid. It seems that $A_{\text{Br}}/A_{\text{H}}$ or $A_{\text{I}}/A_{\text{H}}$ are $\sim$10–30 (see Table II) which would make the $E_{2,\text{Br}} - E_{2,\text{H}}$ even smaller.

This striking observation may be accounted for in this way: The activation energy of the abstraction can be represented by a sum of two terms, the energy required to stretch the C–X bond to its length in the transition state and the repulsion energy required to bring the radical to the stretched

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[1] This investigation was supported by the National Science Foundation.

[2] M. Levy and M. Szwarc, THIS JOURNAL, **77**, 1949 (1955).

[3] R. P. Buckley and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A240**, 396 (1957).

C–X bond. The first term decreases along the series R–H, R-Cl, R-Br, R-I as expected on the basis of decreasing D(R-X). On the other hand, the second term seems to be negligible for X—H (no repulsion between p electron of a radical and a positive H), but it probably is considerable for X = halogen. This accounts for the reported facts. Moreover, presence of electron withdrawing groups should decrease this repulsion and increase, therefore, the reactivity. For example, although $D(CH_3\text{-}I)$ is approximately equal to $D(CF_3\text{-}I)$,[4] the reactivity of CF_3I is greatly larger than that of CH_3I, pointing to the change in the repulsion energy. The same is found when reactivities of $PhCH_2Br$ and CCl_3Br are compared, since again $D(PhCH_2\text{-}Br) \sim D(CCl_3\text{-}Br)$.[4] The effect of repulsion energy in determining the rate of halogen abstraction reactions seems therefore to be indisputable.

We wish to thank Dr. John Meyer for his help in counting the radioactive samples.

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(4) A. H. Sehon and M. Szwarc, *Proc. Roy. Soc.* (*London*), **A209**, 110 (1951).

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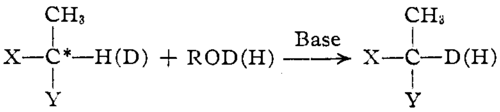
Received November 4, 1960

EFFECT OF STRUCTURE OF CARBANION-STABILIZING SUBSTITUENTS ON STEREOCHEMICAL COURSE OF HYDROGEN-DEUTERIUM EXCHANGE REACTIONS AT SATURATED CARBON

Sir:

Base-catalyzed hydrogen–deuterium exchange reactions at benzyl carbon of optically pure 2-phenylbutane and 1-phenylmethoxyethane previously were reported to occur with high retention of configuration in *tert*-butyl alcohol, and with complete racemization in dimethyl sulfoxide.[1] We have now found that the steric course of the reaction varies widely with the structure of the carbanion-stabilizing group attached to the seat of substitution. The steric course in each case was established through comparison of the amount of racemization and exchange that had occurred after a short reaction period. The types of systems examined, the experimental conditions, and the results are recorded in Table I.



$$X\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle Y}{C^*}}\text{—}H(D) + ROD(H) \xrightarrow{\text{Base}} X\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle Y}{C}}\text{—}D(H)$$

Clearly 2-octyl phenyl sulfone undergoes electrophilic substitution[2] with high retention of configuration (85 to >97%) irrespective of the dissociating power of the solvent, the concentration of proton or deuteron donors, or the nature of the cation of the basic catalyst (runs 1–7). In contrast, the steric course of reaction of 2-phenylbutane and 1-phenylmethoxyethane depends markedly on these factors (runs 8, 9 and ref. 1). A third type of behavior is exhibited by 2-methyl-3-phenylpropionitrile, N,N-diethyl-2-phenylpropionamide and *tert*-butyl 2-phenylpropionate. In these systems, substitution occurs with complete racemization, irrespective of solvent character.

Although a detailed explanation requires further work, general patterns are visible in these results. In the first type of system exemplified by the sulfone, the carbanion formed as intermediate is probably asymmetric, and the stereospecificity of the reaction is not entirely dependent on maintaining an asymmetric solvent envelope. The carbanion might exist either as a d-orbital stabilized sp^3 hybrid with exchange occurring faster than inversion, or as a rehybridized but still asymmetric species in which carbon is "doubly bonded" to sulfur by p–d orbital overlap. In the latter case, formation and disposal of the carbanion might occur preferentially from the same side due to steric and (or) dipole–dipole interactions. Under such circumstances substitution could occur with retention of configuration.

Table I

	Starting material[a]					Base						
Run	X	Y	L[b]	Concn., *M*	Solvent	Type	Concn., *M*	Temp., °C.	Time, hr.	% Rac.	% Exch.[e]	Net steric course
1	$C_6H_5SO_2$	$n\text{-}C_6H_{13}$	H[c]	0.4	$(CH_3)_3COD$[d]	$(CH_3)_3COK$	0.396	25	0.05	4.5	62	93% Ret.
2	$C_6H_5SO_2$	$n\text{-}C_6H_{13}$	D[f]	.4	$(CH_3)_3COH$	$(CH_3)_3COK$	.224	25	0.70	8.0	96	92% Ret.
3	$C_6H_5SO_2$	$n\text{-}C_6H_{13}$	D[f]	.4	$(CH_3)_3COH$	$(CH_3)_4N^+OH^-$	.048	25	0.80	6	40	85% Ret.
4	$C_6H_5SO_2$	$n\text{-}C_6H_{13}$	D[f]	.4	$HOCH_2CH_2OH$	$HOCH_2CH_2OK$	.5	75	165	2.2	69	97% Ret.
5	$C_6H_5SO_2$	$n\text{-}C_6H_{13}$	H[c]	.4	$DOCH_2CH_2OD$[g]	$DOCH_2CH_2OK$	.5	100	2.25	4.5	53	91% Ret.
6	$C_6H_5SO_2$	$n\text{-}C_6H_{13}$	D[f]	.4	CH_3OH	CH_3OK	.5	100	7.0	48	100	High Ret.
7	$C_6H_5SO_2$	$n\text{-}C_6H_{13}$	D[f]	.4	$(CH_3)_2SO\text{–}CH_3OH$[h]	CH_3OK	.200	25	1.0	9.8	98	90% Ret.
8	C_6H_5	C_2H_5	D[i]	.19	$(HOCH_2CH_2O)_2H$	$(HOCH_2CH_2O)_2K$	.36	260	140	20	13	51% Inv.[j]
9	C_6H_5	OCH_3	D[k]	.12	$(HOCH_2CH_2O)_2H$	$(HOCH_2CH_2O)_2K$	.40	260	420	6.6	4	Rac. or inv.
10	$C_6H_5CH_2$	CN	H[l]	.14	$(CH_3)_3COD$[d]	$(CH_3)_3COK$	.013	25	1.3	20	19	100% Rac.
11	$C_6H_5CH_2$	CN	H[l]	.23	$DOCH_2CH_2OD$[g]	$DOCH_2CH_2ONa$	.14	84	19	52	52	100% Rac.
12	C_6H_5	$CON(C_2H_5)_2$	H[m]	.12	$(CH_3)_3COD$	$(CH_3)_3COK$	.17	70	1.5	54	51	~100% Rac.
13	C_6H_5	$CO_2C(CH_3)_3$	H[n]	.15	$(CH_3)_3COD$	$(CH_3)_3COK$	.0051	25	0.25	25	23	~100% Rac.

[a] Optically pure unless otherwise specified. [b] Leaving group, H or D. [c] M.p., 47.5–48.0° $[\alpha]^{26}_{546}$ −13.3° (C, 5.37, $CHCl_3$). [d] Analyzed by combustion and falling drop method to be 99% O-D. [e] Analyzed by combustion and falling drop method. [f] M.p. 47.5–48.0°, $[\alpha]^{31}_{546}$ −14.0 (C, 5.06, $CHCl_3$), 97% C–D by combustion and falling drop method. [g] Analyzed by combustion and falling drop method to be 99% $(O\text{–}D)_2$. [h] 92% $(CH_3)_2SO$, 8% CH_3OH by weight. [i] 87% optically pure 81% α-D, by infrared analysis (see ref. 1). [j] Corrected for lack of optical purity and incomplete deuteration of starting material. [k] 97% α-D, by combustion and falling drop method. [l] $\alpha^{22}D$ +37.4° (*l*, 1 dm., neat), almost optically pure. [m] $\alpha^{25}D$ 118.1° (*l*, 1 dm., neat). [n] $\alpha^{25}D$ +35.6° (*l*, 1 dm., neat).

The second type of system, exemplified by 2-phenylbutane, probably forms a carbanion which is essentially flat, due to delocalization of charge

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(1) D. J. Cram, C. A. Kingsbury and B. Rickborn, This Journal, **81**, 5835 (1959).

(2) Hydrogen or deuterium are only two of a number of possible leaving groups in this general reaction [see D. J. Cram, A. Langemann, J. Allinger and K. R. Kopecky, *ibid.*, **81**, 5740 (1959)] and subsequent papers of the series.