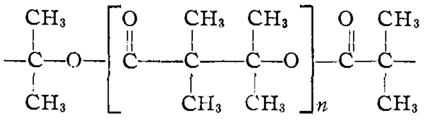
by reduction of tetramethyl-β-propiolactone with $LiAlH_4$.

The results of the reduction of (I) indicate that it consists of an alternating copolymer of the two monomers, having the chemical structure



$$-\overset{CH_3}{\underset{CH_3}{C}}-O-\left[\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-O\right]_n-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-$$

The presence of ester groups is also confirmed by a strong absorption band at 5.80 μ.

Polymerization of mixtures containing acetone and dimethylketene in molar ratios higher than one always leads to the product described above.

Starting from mixtures in which dimethylketene prevails, some homopolymer of this monomer is present in the polymerizate.

When polymerizing mixtures of dimethylketene and acetophenone, an alternating copolymer also is produced which, however, proves to be amorphous on X-ray examination.

It is known that by treating ketenes with ketones in the presence of Friedel-Crafts catalysts, β-lactones are obtained.[1] Some β-lactones, such as β-propiolactone and β-butyrolactone, yield polyesters on heating.[2] We have observed, however, that under the same conditions tetramethyl-β-propiolactone loses quantitatively carbon dioxide. Even in the presence of lithium alkyls, this lactone does not yield a polyester. These results demonstrate that the alternating copolymerization of dimethylketene with acetone does not take place through successive reactions, with formation of a β-lactone as a stable intermediate product.

(1) H. J. Hagemeyer, Jr., *Ind. Eng. Chem.*, **41**, 765 (1949).

(2) T. L. Gresham, J. E. Jansen and F. W. Shaver, THIS JOURNAL, **70**, 998 (1948).

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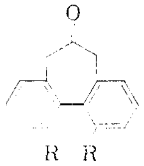
RECEIVED SEPTEMBER 5, 1960

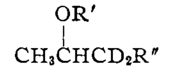
ON THE MAGNITUDE OF POSSIBLE STERIC SECONDARY KINETIC DEUTERIUM ISOTOPE EFFECTS: (+)-(S)-2-PROPANOL-1-d_3

Sir:

It has been suggested[1] that some secondary deuterium isotope effects may to an important degree be accounted for by changes in non-bonded interaction due to differences in vibrational amplitudes of hydrogen and deuterium. A direct and sensitive test of differential non-bonded interaction is available in the partial asymmetric Meerwein–Ponndorf–Verley reduction[2] of Ia which, unlike Ib, has extraordinary optical rotatory power in a region of low absorption.[3] Thus, optical purities of less than 0.01% are still detectable beyond experimental error since (S)-Ia, with $[\alpha]^{27}_{435}$ −1922° (benzene), has α^{27}_{435} −384° (*c* 10, *l* 2). Table I shows rate ratios observed in partial reductions of racemic Ia with carbinols (+)-(S)-AlkCHOHCH₃ at 63° in dioxane, and the corresponding values of $\Delta\Delta F^{\ddagger}$.



I



$$\overset{OR'}{\overset{|}{CH_3CHCD_2R''}}$$

II

Ia, R = CH_3
Ib, R = NO_2

IIa, R′ = CH_2Ph, R″ = OH
IIb, R′ = CH_2Ph, R″ = Bros
IIc, R′ = CH_2Ph, R″ = D
IId, R′ = H, R″ = D

With (+)-(S)-2-propanol-1-d_3 (IId, 2.9 atoms of D) the reducing agent, residual (after 29% reduction) Ia had α^{25}_{435} 0.00 ± 0.01° (*c* 8.84, *l* 2, benzene); it can be shown that k_R/k_S 1.0000 ± 0.0002 and $\Delta\Delta F^{\ddagger}$ not more than ~0.0001 kcal./m. We conclude that differences in non-bonded interaction between CH_3 and CD_3 are not capable of giving rise to secondary kinetic deuterium isotope effects in this and possibly other systems.

TABLE I

Alk	k_R/k_S[a]	$\Delta\Delta F^{\ddagger}$, kcal./m.
CH_3[b]	1.00	0.00
C_2H_5	1.29	.17
n-C_3H_7	1.31	.18
i-C_4H_9	1.58	.31
n-C_6H_{13}	1.59	.31
neo-C_5H_{11}[c]	1.87	.42
i-C_3H_7	1.92	.44
t-C_4H_9	2.91	.72

[a] Unreduced Ia always (−) at 435 mμ. [b] Standard group. [c] Resolved *via* brucine salt of acid phthalate. Carbinol has $[\alpha]^{27}D$ +24.8° (neat), acid phthalate $[\alpha]^{25}D$ +77.4° (chf.).

IId was prepared as follows. The (−)-methyl ester of (+)-(S)-lactic acid was converted ($PhCH_2Br/Ag_2O$) to methyl O-benzyl lactate (b.p. 89–91° (1 mm.), $n^{25}D$ 1.4918, $\alpha^{26}D$ −78.4° (*l* 1, neat); found: C, 68.03; H, 7.25) which was reduced ($LiAlD_4$) to IIa (b.p. 106° (2 mm.), $n^{25}D$ 1.5106, $\alpha^{27}D$ + 28.6° (*l* 1, neat); found at. % excess D (= 100D/(D+H)): 14.09, 14.15). Reduction of the brosylate (IIb, m.p. 59–60°, $[\alpha]^{26}D$ −4.2° (*c* 2.3, benzene); found at. % excess D: 11.70, 11.52) with $LiAlD_4$ to IIc (b.p. 79°(16 mm), $n^{25}D$ 1.4829, $\alpha^{26}D$ +1.2°, α^{26}_{365} +3.7° (*l* 1, neat); found at. % excess D: 20.65, 20.50) followed by catalytic (5% Pd/C) hydrogenolysis in toluene–HCl, afforded IId (b.p. 82–82.5°, $n^{25}D$ 1.3737, $\alpha^{25}D$ + 0.27°, α^{25}_{365} + 0.98° (*l* 1, neat); found at. % excess D: 36.00, 36.22), purified *via* the acid phthalate (m.p. 79–81.5°, $[\alpha]^{27}D$ + 0.2° $[\alpha]^{27}_{365}$ + 1.2° (*c* 4, chf.); found at. % excess D: 24.30, 24.21).

The optical activity of IIc, IId and the acid phthalate of IId is in line with that observed[4] for citric acid-2-d_2. If deuterium is less polarizable than hydrogen, the (+)-sign of (S)-IId is in accord with the atomic asymmetry rule,[5] provided that the

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(1) L. S. Bartell, *Tetrahedron Letters*, No. 6, 13 (1960).

(2) K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

(3) K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg and C. Djerassi, THIS JOURNAL, **82**, 4740 (1960).

(4) C. Martius and G. Schorre, *Ann.*, **570**, 140 (1950).

(5) J. H. Brewster, THIS JOURNAL, **81**, 5475 (1959); *Tetrahedron Letters*, No. 20, 23 (1959); private communication.

rule is applicable in situations where only second-order effects are operative.

(6) Support by the Alfred P. Sloan Foundation is gratefully acknowledged.

(7) Trubek Fellow, 1958–1959; N.S.F. Cooperative Fellow, 1959–1960.

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RECEIVED AUGUST 15, 1960

PERFLUOROALKYLATION OF AROMATIC COMPOUNDS

Sir:

While trifluoromethyl-substituted aromatic compounds are well known,[1,2,3,4,5] and certain perfluoroethyl- and perfluoropropyl-substituted benzenes have been obtained by much more lengthy syntheses,[3,4,5] no procedure has been available for the direct introduction of perfluoroalkyl groups into aromatic nuclei. It is thus of particular importance to report a very general new reaction for the perfluoroalkylation of aromatic compounds, based upon free-radical substitution of aromatic hydrogen, which appears to be limited in scope only by the stability of the aromatic compound under the rather strenuous reaction conditions.

The course of the reaction is indicated by the equation

$$\mathrm{ArH} + 2\mathrm{R_fI} \xrightarrow{250^\circ} \mathrm{R_f\text{-}Ar} + \mathrm{R_fH} + \mathrm{I_2}$$

with yields of 60 to 65% commonly being attained; disubstitution also occurs, the corresponding yield rising as high as 25% when no excess of aromatic compound is present. A wide variety of aromatic hydrocarbons and their derivatives have been perfluoroalkylated successfully, examples being benzene, toluene, naphthalene, halobenzenes, perfluoroalkylbenzenes, benzonitrile, phthalic anhydride, even fully formed dyes.

The perfluoroheptylation of benzene provides an illustration of the general procedure. Perfluoroheptyl iodide was prepared by the method of Brice and Simons[6]; it had b.p. 138.5° and $n^{25}\mathrm{D}$ 1.3274.

Anal. Calcd. for $C_7F_{15}I$; C, 16.95; F, 57.46. Found: C, 17.1; F, 58.1.

Into a 43 ml. Aminco stainless steel autoclave was placed 26.0 g. (0.052 mole) of n-$C_7F_{15}I$ and 2.1 g. (0.027 mole) of benzene. The autoclave was sealed, a 3000 p.s.i.-nickel rupture disk being employed, and the contents were heated for 15 hours at 250°, then chilled to 0°. The autoclave was opened cautiously and rinsed out with 50 ml. of cyclo-$C_6F_{12}O$[7] (b.p. 55°), the free iodine remaining undissolved. The solution was fractionally distilled through a 10-cm. Podbielniak "Heli-pak" column. There was obtained 7.2 g. (62%) of n-$C_7F_{15}C_6H_5$, b.p. 200°, $n^{25}\mathrm{D}$ 1.3576, and 2.8 g. (26%) of (n-$C_7F_{15})_2C_6H_4$, b.p. 270°, m.p. 88° (after recryst. from cyclo-$C_6F_{12}O$).

Anal. Calcd. for $C_{13}H_5F_{15}$: C, 34.99; F, 63.88. Found: C, 35.0; F, 64.0. Calcd. for $C_{20}H_4F_{30}$: C, 29.50; F, 70.00. Found: C, 29.5; F, 69.9.

When twice as much benzene was used, disubstitution was reduced to 8% but the yield of monosubstituted product was not improved substantially.

The infrared spectra of such compounds are unusually difficult to interpret, owing to the exceedingly strong bands contributed by the perfluoroalkyl groups in the "fingerprint region" which ordinarily is highly characteristic for aromatic derivatives. Retention of the benzenoid structure is confirmed by ultraviolet spectroscopy, electrophilic bromination and nitration, and especially by proton and fluorine nuclear spin resonance spectroscopy.

I am particularly indebted to B. W. Nippoldt and P. B. Olson for elementary analyses, and to Dr. W. E. Keiser and Dr. John McBrady for infrared spectroscopy.

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ST. PAUL 19, MINN.

GEORGE V. D. TIERS

RECEIVED SEPTEMBER 12, 1960

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(1) J. H. Simons, ed., "Fluorine Chemistry," Academic Press, New York, N. Y., Vol. I, 1950. pp. 494–498 and 506–513; Vol. II, 1954, pp. 220–223.

(2) R. N. Haszeldine and A. G. Sharpe, "Fluorine and its Compounds," Methuen and Co., Ltd., London, 1951, pp. 116–126.

(3) E. T. McBee and O. R. Pierce, *Ind. Eng. Chem.*, **39**, 397, 399 (1947).

(4) E. T. McBee, C. W. Roberts and A. F. Meiners, THIS JOURNAL, **79**, 335 (1957).

(5) W. R. Hasek W. C. Smith and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

(6) T. J. Brice and J. H. Simons, U. S. Patent 2,614,131 (1952).

(7) T. J. Brice and R. I. Coon, THIS JOURNAL, **75**, 2921 (1953).