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The Acid-catalyzed Cleavage of 2,6-Di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexadien-1-one in the Hydroxylic Solvent. The Solvolysis of a Protonated Dienone[*1]

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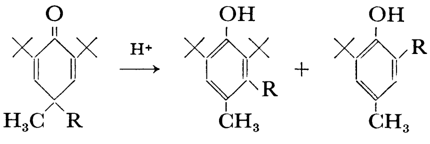
In acetic acid, aqueous methanol, and phenol solvents, 2,6-di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexadien-1-one (I) did not undergo a typical dienone-phenol rearrangement in the presence of sulfuric or perchloric acid, but yielded the solvolysis products, *viz.*, 1-phenylethyl acetate, 1-phenylethyl methyl ether, and 1-phenylethyl phenyl ether, in the respective solvents, along with 2,6-di-*t*-butyl-4-methylphenol (II). The reactions carried out with the optically-active dienone (Ia) yielded solvolysis products which were predominantly racemized, but accompanied by a net inversion of the configuration. The polarimetric rate constant of racemization, measured in acetic acid containing sulfuric acid at 25°C, is in agreement with the spectrophotometric rate constants for the decrease in the dienone Ia and for the increase in the phenol II, essentially within the limits of experimental error. These stereochemical results can be accomodated by a typical S_N1 mechanism, in which the dienone I, protonated on the carbonyl-oxygen, acts as a substrate, and the phenol II, as a leaving group.

Transformations of *p*-cyclohexadienones to phenols in the presence of acidic catalysts have been known for many years; recently Miller and Margulies[1] have observed some interesting 1,2- or 1,3-allyl migration rearrangements of 2,6-di-*t*-butyl cyclohexadienones (III), accompanied by the loss of the *t*-butyl group.

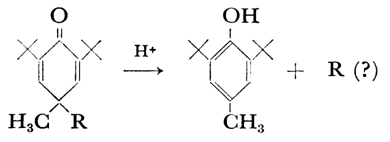


(III) R=Allyl

They have also observed the loss of a migrating group R, *e.g*, crotyl and isopropyl, under the conditions of such a dienone-phenol rearrangement:

[*1] Presented at the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1969; Preprints, III, p. 1643.

[1] B. Miller and H. Margulies, *Tetrahedron Lett.*, **1965**, 1727; *J. Amer. Chem. Soc.*, **87**,5106 (1965).



R=Crotyl and Isopropyl (II)

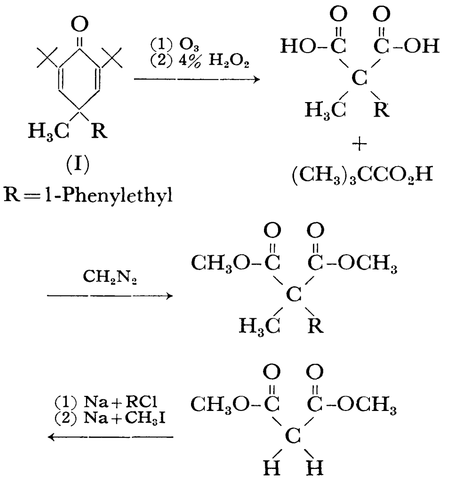
However, little study has been made of the fate of the eliminated group.

We have now prepared 2,6-di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexadien-1-one (I) in connection with our study of the solvolysis mechanism of 1-phenylethyl halide, and have confirmed, in the course of its structural assignment, that this dienone I loses its 1-phenylethyl group in acidic hydroxylic solvents and gives 2,6-di-*t*-butyl-4-methylphenol (II) in a fashion similar to the above-mentioned case for the crotyl and isopropyl dienone (III).[1]

In this paper, we will report on the results of our examinations of the fate of the 1-phenylethyl group so eliminated and of its stereochemical course. Our results show that the 1-phenylethyl group is converted into a racemized solvolysis product, with a net inversion of configuration, and that this transformation of the dienone I into the phenol II and a 1-phenylethyl derivative may be considered to be a typical S_N1 reaction of the protonated dienone I, containing the phenol II as a leaving group.

Results and Discussion

Preparation of 2,6-Di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexadien-1-one (I). This dienone I was synthesized from 1-phenylethyl halide and potassium 2,6-di-*t*-butyl-4-methylphenoxide according to the method of Kornblum and Seltzer.[2] For example, the reaction of 1-phenylethyl bromide and potassium 2,6-di-*t*-butyl-4-methylphenoxide, prepared *in situ* from potassium and the phenol II, was carried out in a *t*-butanol-tetraethylene glycol dimethyl ether solvent (1.7 : 1.0 by vol.) for 20 min at 20°C; the dienone I, bp 113—118°C/0.21—0.24 mmHg, was thus obtained in an 87% yield. The structure of I was deduced from its elemental composition and from the IR, UV, and NMR spectra (see Experimental section). This assignment was confirmed by the ozonolysis of I, which is shown in the following scheme (see also Experimental section):



(I)
R=1-Phenylethyl

The optically active S-(+)-2,6-di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexadien-1-one (Ia) was prepared from R-(+)-1-phenylethyl chloride and potassium 2,6-di-*t*-butyl-4-methylphenoxide in a fashion similar to that used in the reaction with a

TABLE 1. PREPARATION OF OPTICALLY ACTIVE 2,6-DI-*t*-BUTYL-4-METHYL-4-(1-PHENYLETHYL)-CYCLOHEXADIEN-1-ONE (Ia)

t-BuOK M	DBC[a] M	R-(+)-RCl[b] M	R-(+)-RCl[b] α_D[c]	Solvent *t*-BuOH: TGDM[e]	Temp. °C	Time hr	S-(+)-Dienone Ia Yield[f]	$[\alpha]_D$[g]	Max. $[\alpha]_D$[h]
0.505	0.474	0.474	+26.26°[d]	1:1 vol.	20	13.5	78.0%	+18.6°	+88.5°
0.436	0.415	0.442	+16.15°	1:2.6 vol.	25	8.5	68.8%	+11.2°	+86.6°
0.236	0.225	0.241	+16.15°	1:2.6 vol.	25	9.5	52.7%	+10.63°	+82.5°
0.164	0.156	0.167	+16.15°	1:2.6 vol.	25	9.5	52.5%	+11.1°	+86.0°

a) DBC=2,6-Di-*t*-butyl-4-methylphenol.
b) RCl=1-Phenylethyl chloride.
c) Neat, 1 dm, at 13.5°C.
d) Measured at 23.0°C.
e) TGDM=Tetraethylene glycol dimethyl ether.
f) Based on DBC.
g) *c* 16.4—27.1, benzene, at 19—21°C.
h) The maximum rotation of R-(+)-1-phenylethyl chloride was taken to be 125° (1 dm, neat; H.M.R. Hoffmann and E.D. Hughes, *J. Chem Soc.*, **1964**, 1244).

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[2] N. Kornblum and R. Seltzer, *ibid.*, **83**, 3668 (1961).

TABLE 2. ACID-CATALYZED CLEAVAGE OF 2,6-DI-*t*-BUTYL-4-METHYL-4-(1-PHENYLETHYL)-CYCLOHEXADIEN-1-ONE IN HYDROXYLIC SOLVENTS

Solvent	Acid M	Dienone M	Temp. °C	Time hr	Product	Yield %
CH_3CO_2H[a]	H_2SO_4, 3.94×10^{-3}	5.00×10^{-1}	25	20	DBC[b]	90.9
					ROAc[c]	92.2
					Styrene	0.0
MeOH-H_2O (85.9:14.1 by vol.)	$HClO_4$, 2.16	9.65×10^{-2}	25	6	DBC	94.8
					ROMe	80.0
					ROH	7.6
$ClCH_2CH_2Cl$	CF_3CO_2H, 5.82×10^{-2}	3.23×10^{-2}	25	22	DBC	77.4
					CF_3CO_2R	61.9
					Styrene	1.4
					Others[d]	14
PhOH	—	1.95×10^{-1}	75	1.5	DBC	91.5
					ROPh	12.2
					p-R-PhOH	48.6
					o-R-PhOH	30.0

a) Containing 1.5×10^{-3} wt% of water.
b) DBC=2,6-Di-*t*-butyl-4-methylphenol.
c) R=1-Phenylethyl.
d) Substituted phenols.

racemic 1-phenylethyl bromide. The results are summarized in Table 1.

The maximum rotation for the optically active dienone, Ia, was calculated from the rotation of the dienone obtained from R-(+)-1-phenylethyl chloride and potassium 2,6-di-*t*-butyl-4-methylphenoxide. The initial concentrations of the chloride and of the phenoxide were varied over the range from 0.1 to 0.5M. Despite such a wide range of variation in the initial concentration, the calculated values for the maximum rotation of the dienone I seem to be little affected (see Table 1). This indicates that the racemization of 1-phenylethyl chloride during this S_N2 reaction, if any, is slight. Considering this, we took the highest value among those cited in Table 1, *i.e.*, +88.5°, as the maximum rotation of the optically active dienone I with the S-configuration.

Products of the Acidic Cleavage of 2,6-Di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexadien-1-one (I) in Hydroxylic Solvents. The acidic cleavage of the dienone I was carried out in wet acetic acid (containing *ca.* 1.5×10^{-3} wt% of water), aqueous methanol (14.1 vol% of water), 1,2-dichloroethane, and phenol. Sulfuric acid (*ca.* 10^{-3}M), perchloric acid (*ca.* 2M), and trifluoroacetic acid (*ca.* 10^{-2}M) were used as the acid catalyst in acetic acid, aqueous methanol, and 1,2-dichloroethane solvents respectively. In the case of the phenol solvent, no acid catalyst was added. The results are summarized in Table 2.

For each reaction, the substitution products and the phenol II were obtained in fairly good yields; in acetic acid, 1-phenylethyl acetate was obtained in a 92% yield and no elimination product was isolated from the products; in aqueous methanol, 1-phenylethyl methyl ether and 1-phenylethyl alcohol were obtained in 80 and 8% yields respectively; in phenol, 1-phenylethyl phenyl ether, *p*-1-phenylethylphenol, and *o*-1-phenylethylphenol were obtained in 12, 49, and 30% yields respectively; even in 1,2-dichloroethane containing a catalytic amount of trifluoroacetic acid, 1-phenylethyl trifluoroacetate was obtained in a 62% yield.

Rates of the Acid-catalyzed Cleavage of 2,6-Di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexadien-1-one (I). The rates of the cleavage of the dienone I were followed spectrophotometrically; the change in the optical density at 249 mμ (or 352 mμ for the reaction in aqueous methanol) was followed with the reaction mixture placed in an absorption cell. The decrease in the optical density corresponding to the dienone I obeyed good first-order kinetics. The results for wet acetic acid,[3] aqueous methanol (15.1 vol% of water), and 1,2-dichloroethane solvents are summarized in Table 6 (see Experimental section).

In Fig. 1 the logarithm of the first-order rate constant is plotted against the logarithmic concentration of perchloric acid (or trifluoroacetic acid). From the graphical presentation in Fig. 1, the ability of cleavage for these acidic media is seemingly in the sequence: perchloric acid in wet

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[3] The water arose from the 70% perchloric acid used as the catalyst.

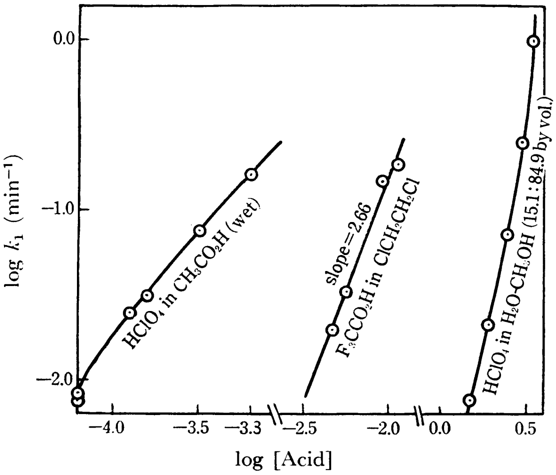

Fig. 1. Rates of acid-catalyzed cleavage of dienone I in various solvents at 25.0°C.

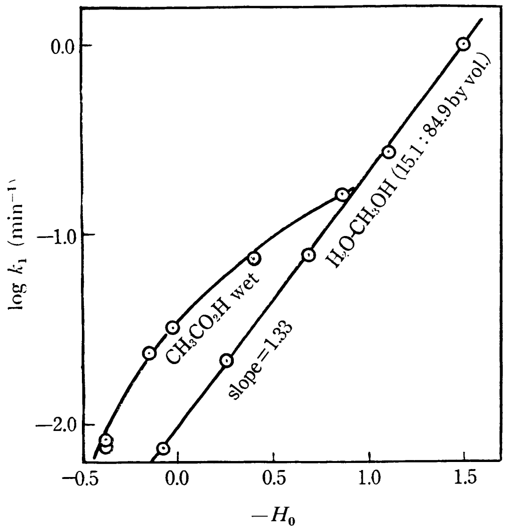

Fig. 2. Rates of cleavage of dienone I in the presence of perchloric acid at 25°C.

acetic acid (containing about 10^{-4} wt% of water)$>$ trifluoroacetic acid in 1,2-dichloroethane$>$perchloric acid in aqueous methanol (15.1 vol% H_2O).

However, as is shown in Fig. 2, when the logarithm of the rate constant is plotted against the acidity function, H_0, of the acidic medium, the curve for the acetic acid solvent is not far over the line for the aqueous methanolic solvent. Consequently, the medium composed of perchloric acid and acetic acid is not so efficient as it seems in Fig. 1. In this connection, if the H_0 of these media is a measure of the ability of proton donation to the dienone I, the gap between the two in Fig. 2 may be attributed to the difference in the solvent effect on the intrinsic cleavage rate of the protonated dienone I.

The $-H_0$ value for 1,2-dichloroethane containing about 10^{-2}M trifluoroacetic acid is estimated to be -3.3—-4.0 by extrapolation from the date (see Table 7) on the medium with higher concentrations of trifluoroacetic acid. These H_0 values are too small to be plotted in Fig. 2. However, it is obvious that 1,2-dichloroethane containing trifluoroacetic acid is the most effective medium among the media shown in Figs. 1 and 2 for the cleavage of the protonated dienone I. In other words, the solvent effect for the cleavage of the protonated dienone I is in the sequence: 1,2-dichloroethane$>$acetic acid$>$aqueous methanol.

In Figs. 1 and 2, the plots of $\log k$ are linear against neither $\log$[Acid] nor $-H_0$, except in the cases of aqueous methanol in Fig. 2 and of 1,2-dichloroethane in Fig. 1. Even in these cases, the linear plots have a slope different from 1. Consequently, for these acid-catalyzed reactions the Hammett-Zucker hypothesis,[4] which discusses the details of the mechanism on the basis of the proportionality of $\log k$ to H_0 or to log [Acid], seems to be invalid. This discrepancy can probably be ascribed to the deviation of the dienone I from a group of normal Hammett bases.[5]

The Steric Course of the Acid-catalyzed Cleavage of Optically Active 2,6-Di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexadien-1-one (Ia). The optically active dienone Ia was subjected to acid-catalyzed cleavage in wet acetic acid (10^{-3}—10^{-4} wt% H_2O) containing perchloric acid or sulfuric acid, in aqueous methanol (13 vol% H_2O) containing perchloric acid and in phenol. The results are summarized in Table 3.

On the basis of the absolute configuration and of the maximum rotation for the relevant solvolysis products (see Table 3, Footnote i), it is confirmed that the cleavage of the dienone Ia gives predominantly racemized solvolysis products, with some net inversion of the configuration in wet acetic acid and also in phenol; in aqueous methanol, the cleavage affords the methyl ether with a predominant inversion of configuration. These are the stereochemical characteristics of an S_N1 type reaction.

As is shown in Table 4, one of the solvolysis products, 1-phenylethyl acetate, was found to racemize about 10% in the presence of acid under the same reaction conditions as those of the cleavage reaction. Therefore, in the calculation of the extent of racemization (or inversion) for 1-phenylethyl acetate, we made a correction for the racemization of the acetate during the course of the acidic cleavage. The rotation of 1-phenylethyl methyl ether was not affected in aqueous methanol, even at higher perchloric acid concentrations than in the

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[4] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, **61**, 2791 (1939).

[5] This problem is now being examined in these laboratories.

TABLE 3. ACID-CATALYZED CLEAVAGE OF OPTICALLY ACTIVE 2,6-DI-*t*-BUTYL-4-METHYL-4-(1-PHENYLETHYL)-CYCLOHEXADIEN-1-ONE AT 25°C

Solvent	Acid M	Dienone		Time hr	RY[c]	Yield	α_D[d]	α_D[h]	Net steric course[i]
		M	$[\alpha]_D$[d]						
CH_3CO_2H ($10^{-3}-10^{-4}$ wt% H_2O)	$HClO_4$ 1.38×10^{-4}	0.148	+10.88°	5	ROAc	51%	+0.935°[e]	+1.02°	6.4% inv.
	$HClO_4$ 6.90×10^{-4}	0.148	+10.88°	1	ROAc	45%	+0.72°[e]	+0.79°	5.0% inv.
	H_2SO_4 3.94×10^{-3}	0.500	+18.6°	20	ROAc	92.2%	+2.63°[f]	+3.04°	11.2% inv.
	H_2SO_4 4.26×10^{-3}	0.156	+11.2°	6	ROAc	69%	+1.52°[e]	+1.76°	10.5% inv.
H_2O-MeOH (13:87 by vol.)	$HClO_4$ 2.24	0.182	+10.28°	3.5	ROMe	71.5%	+8.02°[f]	—	57% inv.
PhOH[a]	—	0.195	+11.2°	1.5	ROPh	12.2%	−1.33°[f]	—	13.5% inv.
					p-RPhOH	48.6%	−0.344°[g]	—	15.9% inv.
					o-RPhOH	30.0%	+0.65°[f]	—	10.2% inv.

a) The reaction was conducted at 75°C
b) Benzene, *c* 15—17, at 20—21°C.
c) R=1-Phenylethyl.
d) Measured at 19—21°C.
e) α_D for 1 dm, calculated from the value for the neat liquid composed of ROAc and 2,6-di-*t*-butyl-4-methylphenol (*ca.* 2:3 by wt.).
f) α_D for 1 dm, measured with a neat sample.
g) $[\alpha]_D$, *c* 68.3, benzene.
h) Corrected for the racemization of ROAc during the course of the reaction.
i) The rotations of the optically pure materials are taken to be 88.5° for the titled S-(+)-dienone (see text), 129° for R-(+)-ROAc (determined in these laboratories), 120° for R-(+)-ROMe (K. Mislow, *J. Amer. Chem. Soc.*, **73**, 4043 (1951)), 46.6° for S-(+)-ROPh (K. Okamoto *et al.*, This Bulletin, **39**, 299 (1966)), 10.26° for S-(+)-*p*-RPhOH (K. Okamoto *et al.*, *loc. cit.*), and 27.85° for R-(+)-*o*-RPhOH (K. Okamoto *et al.*, *loc. cit.*).

TABLE 4. RACEMIZATION OF 1-PHENYLETHYL ACETATE AND OF 1-PHENYLETHYL METHYL ETHER IN THE PRESENCE OF STRONG ACIDS IN HYDROXYLIC SOLVENTS AT 25°C

Substrate		Acid M	Solvent	Time hr	Substrate recovered	
M	α_D				α_D	Racemization %
ROAc 0.152	+67.4°[a]	$HClO_4$ 6.90×10^{-4}	HOAc[c]	1	+61.02°[a]	9.4
ROAc 0.152	+67.4°[a]	$HClO_4$ 1.38×10^{-4}	HOAc[c]	5.2	+61.12°[a]	9.4
ROAc 0.589	+6.23°[b]	H_2SO_4 3.68×10^{-3}	HOAc[c]	24	+ 5.38°[b]	13.6
ROMe 0.564	−7.17°[a]	$HClO_4$ 1.81	H_2O-MeOH (12.3:87.7 by vol.)	3.2	− 7.18°	0.0

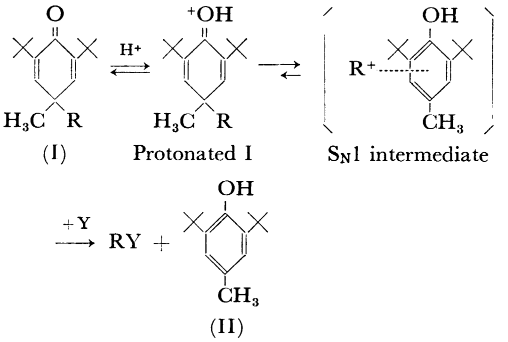
a) 1 dm, neat, at 20°C for ROAc and at 15°C for ROMe.
b) $[\alpha]_D^{23}$ *c* 9.6, HOAc.
c) Containing 10^{-3} wt% of water.
d) Containing 10^{-4} wt% of water.

case of 1-phenylethyl acetate.

Mechanism of the Acid-catalyzed Cleavage of 2,6-Di-*t*-butyl-4-(1-phenylethyl)-4-methylcyclohexadien-1-one (I). Polarimetric rate measurements were carried out with an acetic acid solution of the dienone Ia (0.500M) at 25°C, using 3.94×10^{-3}M sulfuric acid as the acid catalyst. For purposes of comparison, the spectrophotometric rate measurements were conducted by the use of the same reaction mixture as that used for the polarimetric run; the decrease in the dienone I and the increase in the phenol II were followed at the characteristic bands of 249 and 284 mμ respectively.

The polarimetric rate constant, k_P, the rate constant for the decrease in the dienone I, k_D, and the rate constant for the increase in the phenol II, k_{DBC}, were graphically calculated; as is illustrated in Figs. 3,4, and 5, the observed values for the three *k*'s are all essentially the same within the limits of experimental error.

All the results, *i.e.*, steric and kinetic, are most readily accomodated by an S_N1 solvolysis mechanism of the protonated dienone I; this is illustrated by the following scheme:



(I) Protonated I S_N1 intermediate

(II)

The protonation of a dienone with a structure similar to that of the dienone I has been confirmed in the case of 2,6-di-*t*-butyl-4-dichloromethyl-4-methylcyclohexadien-1-one by the use of the spectrophotometric method.[6]

Since the k_P is equal to k_D or to k_{DBC}, the rate for the return of the S_N1 intermediate to the protonated dienone would be negligibly small as compared with rate for the attack of the solvent nucleophile, Y, on the S_N1 intermediate.

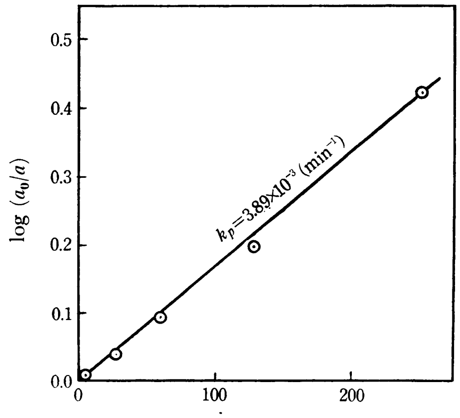


Fig. 3. Polarimetric rate constant for the conversion of optically active dienone Ia in wet acetic acid at 25°C.
[Dienone]$_0$=0.500M
[H_2SO_4]=3.94×10^{-3}M

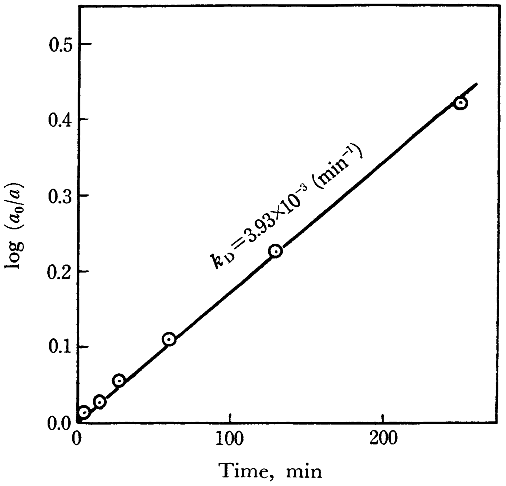


Fig. 4. Rate of decrease of the dienone I in wet acetic acid at 25.0°C.
[Dienone]$_0$=0.500M
[H_2SO_4]=3.94×10^{-3}M

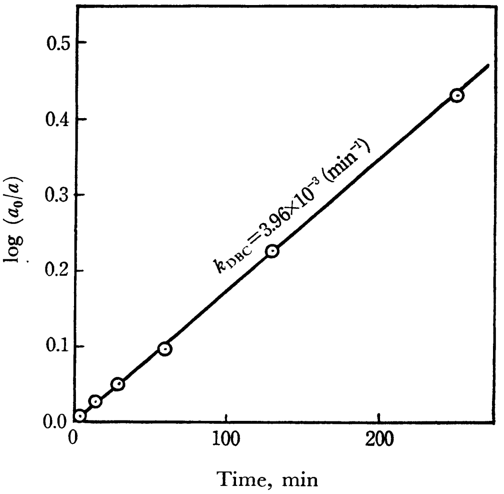


Fig. 5. Rate of increase of the phenol II in wet acetic acid at 25.0°C.
[Dienone]$_0$=0.500M
[H_2SO_4]=3.94×10^{-3}M

In view of the existence of carbonium ion-aromatic hydrocarbon charge-transfer complexes in various solvents,[7] the S_N1 intermediate would be close to a charge-transfer complex between the 1-phenylethyl cation and the phenol II.

This reaction of the protonated dienone I is considered to be an example of the S_N1 reaction of the "missing-charge" type;[8] a phenol molecule,

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6) H. Budzikiewicz, *Tetrahedron Lett.*, **1960**, 12.

7) a) M. Feldman and S. Winstein, *J. Amer. Chem. Soc.*, **83**, 3338 (1961); b) H. J. Dauben, Jr., and J. D. Wilson, *Chem. Commun.*, **1968**, 1629.

8) E. D. Hughes and D. J. Whittingham, *J. Chem. Soc.*, **1960**, 806.

TABLE 5. PREPARATION OF 2,6-DI-*t*-BUTYL-4-METHYL-4-(1-PHENYLETHYL)CYCLOHEXADIEN-1-ONE (I)

Substrate	Reagent		Solvent	Temp.	Time	Dienone I
RBr[a)] 0.50 M	DBC[b)] 0.455 M	*t*-BuOK 0.455 N	*t*-BuOH:TGDM[c)] 26:15[d)]	20°C	20 min	87%
RCl 0.54 M	DBC 0.54 M	*t*-BuOK 0.54 N	*t*-BuOH:TGDM 32:35	30°C	6 hr	79%
RCl 0.57 M	DBC 0.57 M	*t*-BuOK 0.59 N	*t*-BuOH:DGM[e)] 28:20	60°C	3 hr	59% [g)]
RBr 0.035 M	KDBC[f)] 0.039 N		CH_3CN	82°C	17.5 hr	79% [h)]

a) R=1-Phenylethyl.
b) DBC=2,6-di-*t*-butyl-4-methylphenol.
c) TGDM=tetraethylene glycol dimethyl ether.
d) m*l*:m*l*
e) DGM=diethylenglycol dimethyl ether.
f) KDBC=potassium 2,6-di-*t*-butyl-4-methylphenoxide.
g) Unchanged RCl (23%) was recovered.
h) Styrene (11%)was obtained.

II, acts as a leaving group of the charged substrate, *i.e.*, the protonated dienone I. The observed solvent effect (*vide supra*) for the cleavage of the protonated dienone is consistent with that observed for such S_N1 reactions of the "missing-charge" type as the solvolyses of *t*-butyldimethylsulfonium ion[9)] and of cyclohexylmercuric perchlorate.[10)]

Experimental[11)]

2,6-Di-*t*-butyl-4-methyl-4-(1-phenylethyl)-cyclohexadien-1-one (I). The dienones, racemic and optically active, were prepared under various conditions, according to the method of Kornblum and Seltzer.[2)] The results are tabulated in Tables 1 and 5. The details of a representative run will now be described.

To a mixture of a *t*-butanol solution (22.4 m*l*) of potassium *t*-butoxide (0.87N), tetraethylene glycol dimethyl ether (15 m*l*), *t*-butanol (4 m*l*), and 2,6-di-*t*-butyl-4-methylphenol (II) (4.41 g, 0.02 mol), 1-phenylethyl bromide (3.0 m*l*, 0.022 mol) was added in one portion at 20°C. The titration analysis of an aliquot showed that the reaction was 87.5% complete within 20 min. After the mixture had stood overnight at room temperature, benzene (50 m*l*) was added; the benzene solution was then washed with water and condensed to leave an oily material (8.47 g), which was chromatographed over alumina (146 g, 200—300 mesh). The dienone I (5.25 g and 0.37 g; total yield 86.7%) was eluted successively by *n*-hexane (400 m*l*) and benzene (80 m*l*).

Found: C, 85.43; H, 10.07%; mol. wt, 322.0 (cryoscopic, benzene). Calcd for $C_{23}H_{32}O$: C, 85.13; H, 9.94%; mol. wt, 324.5.

The IR spectrum for the dienone I shows a doublet carbonyl absorption at 1640 and 1655 cm^{-1}, corresponding to a conjugated dienone; the UV maximum appears at 249 mμ (ε=10650, methanol), showing a cross structure for the conjugated dienone I. In the NMR spectrum (60 MHz) of the dienone I, five phenyl protons appear as a multiplet centered at τ 2.9; two vinyl protons, as a quartet showing an AB pattern (ν_A τ 3.55, ν_B τ 3.73, J_{AB}=3 Hz); a methine proton, as a quartet centered at τ 7.16 (J=7.5 Hz); 18 *t*-butyl protons, as two singlets (nine for each) at τ 8.78 and 8.87; three protons on a methyl group, attached to a quaternary carbon, as a singlet at τ 8.89. Three methyl protons of the 1-phenylethyl group appear in the range of τ 8.7—9.0, but they could not be well characterized because of the overlapping of the other methyl proton signals. The magnetic non-equivalence for two vinyl protons and for the protons of two *t*-butyl groups may be attributed to the asymmetric structure of the 1-phenylethyl group.

Ozonolysis of the Dienone I. A solution of the dienone I (2.32 g) in a mixture of acetic acid (150 m*l*) and ethyl acetate (90 m*l*) was treated with ozonized oxygen at 0°C. A stream of ozonized oxygen (1.6 mmol of ozone/*l*) was passed into the solution at a rate of 80 m*l*/min. The amount of unchanged ozone was determined every 20 or 30 min by collecting it in a potassium iodide trap and titrating the liberated iodine. After an uptake of 30 mmol of ozone in 7 hr, the mixture was treated with a mixture of 30% hydrogen peroxide (6 m*l*) and water (40 m*l*). After it had stood overnight and ether (500 m*l*) had subsequently been added, the resulting mixture was washed with 5% aqueous sodium chloride (6×50 m*l*), condensed to 100 m*l*, and washed with additional 5% aqueous sodium chloride (8×25 m*l*). From the alkaline extracts of the organic layer, an acidic oily material (1.869 g) was recovered by the usual working-up. The oil was distilled *in vacuo* to give a mixture of acetic acid and tri-

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9) C. G. Swain, L. E. Kaiser and T. E. C. Knee, *J. Amer. Chem. Soc.*, **80**, 4092 (1958).

10) F. R. Jensen and R. J. Ouellette, *ibid.*, **83**, 4478 (1961).

11) The melting points are uncorrected. Rotations were measured with a Zeiss-Winkel "Kreis-Polarimeter 0.01°." The infrared spectra and ultraviolet spectra were obtained on Shimadzu spectrometers models IR-27 and UV-50M. The gas-liquid chromatograms were obtained with a Shimadzu model GC2B apparatus. The microanalyses were performed by the Microanalysis Center, Kyoto University.

methylacetic acid (bp *ca.* 50°C/5 mmHg, 0.810 g), leaving a residual oil (the acid equivalent: 150±10, 1.059 g). The residual oil (1.000 g) was dissolved in ether (6 m*l*), and treated with diazomethane (11.4 mmol) in ether (24 m*l*). After the usual working-up, the methylated products were distillated *in vacuo* to afford a fraction with bp of 77—91°C/0.3 mmHg. This fraction was analyzed on a 2 m×4 mm copper tubing packed with high vacuum silicone grease on Celite under the following conditions: column temperature, 175°C; hydrogen flow rate, 70 m*l*/min. The fraction contained component with the retention time of 5.1 min (26%) and dimethyl α-methyl-α-(α-phenylethyl)malonate (68%; retention time, 14.6 min). After several injections, the dimethyl ester was collected as eluted (51% of recovery; 102 mg; the IR spectrum was identical with that of the authentic sample).

Preparation of the Authentic Dimethyl α-Methyl-α-(α-phenylethyl)-malonate. To a solution of sodium (1.13 g, 49.1 mmol) in a mixture of methanol (8 m*l*) and diglyme (15 m*l*), we added dimethyl α-(α-phenylethyl)-malonate (9.03 g, 40.3 mmol), which had been prepared according to the method of Snyder and Brewster.[12] To the cooled mixture, methyl iodide (9.17 g, 64.6 mmol) was added drop by drop; after 1.5 hr, the mixture was diluted with benzene (100 m*l*), washed with 10% aqueous sodium chloride, and condensed to give a viscous oil. The vacuum distillation of the oil gave a fraction with a bp of 102—116°C/0.3 mmHg (7.1 g); this fraction was a mixture of dimethyl α-(α-phenylethyl)-malonate (27%) and dimethyl α-methyl-α-(α-phenylethyl)-malonate (73%). The composition analysis was performed by means of GLC under the abovementioned conditions; the retention time for dimethyl α-(α-phenylethyl)-malonate was 10.9 min. The pure dimethyl α-methyl-α-(α-phenylethyl)-malonate was collected as eluted by GLC.

Prepration of 1-Phenylethyl Trifluoroacetate. A mixture of trifluoroacetic anhydride (1.00 m*l*), 1-phenylethyl alcohol (0.50 m*l*, 4.17 mmol), and a drop of pyridine was kept at 0°C overnight. After the evaporation of the low-boiling materials *in vacuo*, distillation gave 1-phenylethyl trifluoroacetate; bp 63.0—63.2°C/5 mmHg; 0.80 g, 88% yield; IR: 1700 (C=O) and 1220 (C–O–C) cm^{-1}.

Product Analysis for the Cleavage Reaction of the Racemic (I) and Optically Active (Ia) Dienones. The results are summarized in Tables 2 and 3. The details of the experimental procedure for representative runs, which were carried out in various solvents, will be described below.

The Acidic Cleavage Reaction of the Optically Active Dienone Ia in Acetic Acid (Product Analysis and Rate Measurements). To a solution of the dienone Ia (1.6226 g, 5.00 mmol, $[\alpha]^{19}_{\rm D}$ +18.6°, benzene, *c* 16.4) in acetic acid (3 m*l*), a solution of sulfuric acid *ca.* 9×10^{-3}M) in acetic acid was added to make 10 m*l* of a reaction mixture (3.94×10^{-3}M sulfuric acid). After a specified length of time at 25.0°C, an aliquot (1 m*l*) was withdrawn and neutralized with a solution (0.10 m*l*) of sodium acetate (0.10N) in acetic acid. From the neutralized aliquot (1.10 m*l*), an aliquot of 0.100 m*l* was then withdrawn and diluted to 34 times its volume with methanol; the optical density at 249 mμ (the dienone Ia) and 284 mμ (the phenol II) was measured using an absorption cell 10 mm thick. The rest of the neutralized acetic acid solution was used for the rotation measurements employing a tube 1 dm long. Six aliquots (1 m*l* for each) were withdrawn from the reaction mixture in a period of 4 hr. The results of the graphical calculation of the respective rate constants are illustrated in Figs. 3, 4, and 5.

After 24 hr at 25°C, an aliquot of 1.50 m*l* was pipetted out from the reaction mixture and added to ether (30 m*l*). The resulting ethereal solution was washed with 10% aqueous sodium bicarbonate (5 m*l*) and 10% aqueous sodium chloride (2×10 m*l*) and then evaporated to give an oily material (0.265 g) which was composed of 1-phenylethyl acetate (92.2% yield, based on the dienone Ia) and the phenol II (90.9% yield, based on the dienone Ia). The analysis was performed on a 2 m×4 mm copper tubing column packed with 20% Apiezon grease L on Neosorb N under the following conditions: column temperature, 122°C for 1-phenylethyl acetate and 169°C for the phenol II; hydrogen flow rate, 80 m*l*/min; retention times: 1-phenylethyl acetate, 10.3 min (122°C); the phenol II, 14.9 min (169°C).

The rest of the reaction mixture was chromatographed over alumina. The phenol II (124.9 mg, 84.6% yield, based on the dienone Ia) and 1-phenylethyl acetate (86 mg, the IR spectrum was identical with that of the authentic sample) were eluted with *n*-hexane (150 m*l*) and with benzene (45 m*l*) respectively. The latter was distilled *in vacuo* to give a purified, optically active sample (74.3 mg); this sample was then diluted with racemic 1-phenylethyl acetate (87.3 mg) to give $\alpha_{\rm D}$+1.21° (1 dm, neat, at 22°C). The rotation of the original sample was calculated to be $\alpha_{\rm D}$+2.63° (1 dm, neat, at 22°C).

The Acidic Cleavage Reaction of the Optically Active Dienone Ia in Phenol. A mixture of the dienone Ia (3.9765 g, 12.25 mmol, $[\alpha]^{19}_{\rm D}$ +18.6°, benzene, *c* 16.4) and phenol (57.0 g) was kept at 75°C for 1.5 hr. After the addition of ether (100 m*l*) the ethereal solution was washed with 10% aqueous sodium hydroxide (5×50 m*l*) and 10% aqueous sodium chloride (3×100 m*l*), and then concentrated to give an oily material (4.356 g). The oil was then subjected to chromatography on silica gel (100 g). The phenol II (2.460 g, 91.2% based on the dienone Ia) was eluted with *n*-hexane-benzene (15:1 by vol., 50 m*l*); 1-phenylethyl phenyl ether (containing a hydroxylic compound), with *n*-hexane-benzene (15:1 by vol., 500 m*l*); *o*-1-phenylethylphenol (743 mg, 30.0% yield), with benzene (600 m*l*), and finally *p*-1-phenylethylphenol (812 mg), with benzene-ether (4 : 1 by vol., 150 m*l*).

From the alkaline extracts additional amounts of *p*-1-phenylethylphenol (369 mg; the total yield was 48.6%) were recovered by the usual working-up and by subsequent distillation *in vacuo* (bp 120°C/4 mmHg, bath temp.).

1-Phenylethyl phenyl ether was rechromatographed over alumina with *n*-hexane as an eluent to give a pure sample (272 mg, 12.2% yield) and a hydroxylic compound (43.5 mg). The latter was not identified.

Each compound so isolated gave a sole spot in TLC on silica gel and exhibited the same IR spectrum as the corresponding authentic sample;[13] the isolated com-

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12) H. R. Snyder and J. H. Brewster, *J. Amer. Chem. Soc.*, **71**, 291 (1949).

13) For the authentic samples, see K. Okamoto, M. Hayashi, K. Komatsu and H. Shingu, This Bulletin, **40**, 624 (1967).

Table 6. Rates of acid-catalyzed cleavage of the dienone I in various solvents at 25.0°C

Solvent-Acid	Dienone M	Acid M	k_1 min^{-1}	$-H_0$	H_2O
Wet acetic acid-Perchloric acid	2.59×10^{-2}	6.25×10^{-4}	1.64×10^{-1}	0.86	1.49×10^{-3} M
	2.59×10^{-2}	3.13×10^{-4}	7.50×10^{-2}	0.39	7.46×10^{-4} M
	2.77×10^{-2}	3.14×10^{-4}	7.51×10^{-2}	0.39	7.46×10^{-4} M
	2.77×10^{-2}	1.57×10^{-4}	3.19×10^{-2}	−0.03	3.98×10^{-4} M
	2.59×10^{-2}	1.25×10^{-4}	2.30×10^{-2}	−0.14	2.98×10^{-4} M
	2.59×10^{-2}	6.25×10^{-5}	7.27×10^{-3}	−0.37	1.49×10^{-4} M
	2.77×10^{-2}	6.27×10^{-5}	8.50×10^{-3}	−0.37	1.49×10^{-4} M
Aqueous methanol-Perchloric acid	1.02×10^{-4}	3.44	1.02	1.50	15.1 vol%
	1.02×10^{-4}	2.94	2.69×10^{-1}	1.10	14.3 vol%
	1.02×10^{-4}	2.94	2.47×10^{-1}	—	15.6 vol%
			(2.54×10^{-1})[a]	(1.09)[a]	(15.1 vol%)
	1.02×10^{-4}	2.45	7.55×10^{-2}	0.73	13.4 vol%
	1.02×10^{-4}	2.45	6.82×10^{-2}	—	16.0 vol%
			(7.06×10^{-2})[a]	(0.69)[a]	(15.1 vol%)
	1.02×10^{-4}	1.96	2.16×10^{-2}	0.37	12.5 vol%
	1.02×10^{-4}	1.96	2.23×10^{-2}	—	16.5 vol%
			(2.20×10^{-2})[a]	(0.26)[a]	(15.1 vol%)
	7.64×10^{-5}	1.47	1.32×10^{-2}	0.14	6.5 vol%
	1.02×10^{-4}	1.47	5.32×10^{-3}	—	17.0 vol%
			(6.70×10^{-3})[a]	(−0.08)[a]	(15.1 vol%)
1,2-Dichloroethane-Trifluoroacetic acid	9.18×10^{-5}	1.12×10^{-2}	1.88×10^{-1}	(−3.3)[a]	
	7.83×10^{-5}	9.22×10^{-3}	1.48×10^{-1}		
	9.13×10^{-5}	5.60×10^{-3}	3.36×10^{-2}		
	7.83×10^{-5}	4.61×10^{-3}	1.94×10^{-2}		
	7.83×10^{-5}	2.31×10^{-3}	3.47×10^{-3}		
	7.83×10^{-5}	2.31×10^{-3}	3.34×10^{-3}		
	7.83×10^{-5}	1.15×10^{-3}	8.89×10^{-4}		
	7.83×10^{-5}	5.75×10^{-4}	3.06×10^{-4}	(−5.9)[a]	

a) Extrapolated or interpolated values.

pounds were redistilled *in vacuo* and then the optical rotation was measured: 1-phenylethyl phenyl ether, 235 mg, bp 100°C/0.05 mmHg (bath temp.), α_D^{20} $-1.33\pm0.08°$ (1 dm, neat); *p*-1-phenylethylphenol, 731 mg, bp 150°C/0.05 mmHg (bath temp.), $[\alpha]_D^{19}$ $-0.344°$ (benzene, *c* 68.3); *o*-1-phenylethylphenol, bp 140°C/0.05 mmHg (bath temp.), α_D^{19} $+0.65\pm0.04°$ (1 dm, neat).

The Acidic Cleavage Reaction of the Racemic Dienone I in 86% Aqueous Methanol. In a 10-m*l* volumetric flask we placed the dienone I (313 mg, 0.965 mmol) and a solution (7.7 m*l*) of perchloric acid in aqueous methanol ($[HClO_4]=2.80$N, $[H_2O]=18.8$ vol%); then some methanol was added to bring the volume of the reaction mixture to 10 m*l*. After standing for 6 hr at 25.0°C, the mixture was poured into 50 m*l* of benzene; the benzene solution was then washed successively with 10% aqueous sodium chloride (3×20 m*l*), 10% aqueous sodium hydroxide (2×20 m*l*), and 10% aqueous sodium chloride (2×20 m*l*). The dried benzene layer was concentrated to about 3 m*l* and made to a 5-m*l* solution in a 5-m*l* volumetric flask by adding some benzene. The composition of the products was determined by GLC using the same column as that employed in the analysis for 1-phenylethyl acetate (at 122°C and the hydrogen flow rate 48.4 m*l*/min): 1-phenylethyl methyl ether, 6.85 min (retention time)(80.0% yield, based on the dienone I); 1-phenylethyl alcohol, 9.1 min (7.6% yield); the phenol II, 22.8 min (at 165°C)(94.8% yield).

The Acidic Cleavage Reaction of the Racemic Dienone I in the Presence of Trifluoroacetic Acid in 1,2-Dichloroethane. The dienone I (574 mg, 1.615 mmol) and a 0.1455M solution (20 m*l*) of trifluoroacetic acid in 1,2-dichloroethane were placed in a 50-m*l* volumetric flask; some 1,2-dichloroethane was then added to bring the volume of the reaction mixture to 50 m*l*. After 22 hr of standing at 25.0°C, a portion of the reaction mixture was subjected to GLC on the Apiezon column described above under the following conditions: column temperature, 140°C; the hydrogen flow rate, 44.3 m*l*/min; retention time for 1-phenylethyl trifluoroacetate, 2.25 min (61.9% yield, based on the dienone I). An aliquot, withdrawn from the reaction mixture, was titrated with 0.1N aqueous sodium hydroxide, and the amount of trifluoroacetic acid consumed was calculated to be 60.2% of the dienone I. Another aliquot was subjected to UV spectroscopy; it was confirmed that the amount of styrene (λ_{max} 248 mμ, $\varepsilon=1.101\times10^4$) produced during the reaction was less than

1.4% of the dienone I.

The rest of the reaction mixture (46 m*l*) was concentrated and distilled *in vacuo* to give 1-phenylethyl trifluoroacetate (101 mg, bp 80°C/2 mmHg (bath temp.); the IR spectrum was identical with that of the authentic sample). The residual oil (485 mg) was subjected to chromatography on alumina (20 g). The phenol II (385 mg, 77.4% yield) was eluted with *n*-hexane (150 m*l*), and some phenolic materials (72 mg) were eluted with benzene and with ethanol. The phenolic materials were characterized by IR analysis.

Racemization of 1-Phenylethyl Acetate and of 1-Phenylethyl Methyl Ether in the Acidic Media. Optically active samples of 1-phenylethyl acetate and of 1-phenylethyl methyl ether were dissolved in the acidic solvents indicated in Table 4. After a specified length of time, the ester or the ether was recovered, purified by distillation *in vacuo*, and subjected to rotation measurements. In the case of the acetic-acid solvent containing sulfuric acid, the solution of 1-phenylethyl acetate was placed in a 1-dm tube; the change in the rotation was followed polarimetrically. The results are summarized in Table 4.

Kinetic Procedure. The rate measurement for the optically active dienone Ia was performed as has been described above. The results are illustrated in Figs. 3,4, and 5. The rate measurement for the racemic dienone I was carried out spectrophotometrically. A glass-stoppered 1-cm quartz cell was placed in a cell-compartment with circulating water thermostated at 25.0°C. Appropriate amounts of a temperature-equilibrated dienone solution was mixed with a temperature-equilibrated acid solution in the cell; the absorbance was followed at a specified wavelength. The first-order rate constants were calculated graphically. The results are summarized in Table 6.

The Measurement of the Acidity Function. The acidity function for each acidic medium measured according to the method of Braude and Stern.[14] For the mixtures of perchloric acid and aqueous methanol, of perchloric acid and acetic acid, and of trifluoroacetic acid and methanol, *o*-nitroaniline (indicator constant, -0.29[15]) was used as the Hammett base; for the mixture of trifluoroacetic acid and 1,2-dichloroethane, *p*-nitroaniline (indicator constant, $+0.99$[15]) was so employed. The absorbance of *o*-nitroaniline decreased in acetic acid in the course of the measurements; the value of absorbance at time zero was extrapolated from the observed data. The results are illustrated in Table 6, while the H_0 values for trifluoroacetic acid in 1,2-dichloroethane are tabulated in Table 7.

TABLE 7. ACIDITY FUNCTION FOR TRIFLUOROACETIC ACID IN 1,2-DICHLOROETHANE AT 25°C

CF_3CO_2H M	0.432	0.259	0.155	0.109	0.076
H_0	0.107	0.592	0.810	0.964	1.119

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[14] E. A. Braude and E. S. Stern, *J. Chem. Soc.*, **1948**, 1976.

[15] M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).