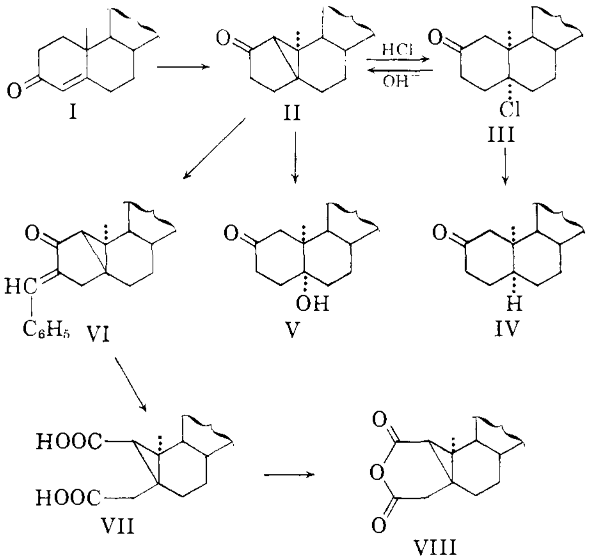
a peak at 307.5 mμ ([M] +11,700°), a +29,000°! This spectrum bears a strong resemblance to those of dihydrolumisantonin (peak +8,000° at 310 mμ and trough at 275 mμ, a +22,000°) and dihydrolumi-1-dehydro-4-methyltestosterone acetate (peak +8,400° at 315 mμ and trough at 280° mμ, a +22,600°).[12]



Brief treatment of II with hydrochloric acid in acetic acid afforded (95%) a chloro ketone (III), m.p. 155–156°, $[\alpha]^{25}\mathrm{D}$ +53°. This substance was reconverted to lumicholestenone in nearly quantitative yield by refluxing (10 min.) ethanolic potassium hydroxide. The infrared spectrum of III has a carbonyl band at 1711 cm.$^{-1}$ (cyclohexanone). The n.m.r. spectrum shows the 19-Me at only 0.08τ lower field than that of cholestan-3-one and thus indicates that the chlorine atom is positioned at least one atom removed from C-10.[13] The assignment of configuration at C-5 is supported by the weak negative Cotton effect (a, −3000°) in the rotatory dispersion curve as well as by the facile interconversion of II and III which suggests a near linear disposition of the chlorine atom and two carbon atoms involved.

Reduction of III with sodium–ammonia afforded a mixture of 10-epicholestan-2-one (IV), m.p. 99–100°, $[\alpha]^{25}\mathrm{D}$ +50° and an alcohol which was converted readily to IV by mild oxidation. Support for formulation IV came from the infrared spectrum (carbonyl absorption at 1712 cm.$^{-1}$) and the rotatory dispersion curve which was nearly superimposable on that of the chloro ketone (III).

When II was heated under reflux in aqueous acetic acid it furnished 5α-hydroxy-10-epicholestan-2-one (V), m.p. 166–167°, $[\alpha]^{25}\mathrm{D}$ +61°. Infrared absorption at 3530 and 1709 cm.$^{-1}$ suggested that ring-opening had followed the same course as in the II → III conversion. Proton resonance of the 19-Me group was observed at 0.02τ lower than in cholestan-3-one.

Treatment of either II or III with benzaldehyde and potassium hydroxide (methanol) afforded the same benzylidene derivative (VI), m.p. 196–197°. Ozonation of VI and then treatment with hydrogen peroxide gave dicarboxylic acid VII, m.p. 198–201°, $[\alpha]^{25}\mathrm{D}$ +68°. The anhydride (VIII) was prepared from VII by reaction with acetic anhydride, m.p. 144–146°, $[\alpha]^{26}\mathrm{D}$ +106°. The positions in the infrared of the anhydride bands at 1787 and 1738 cm.$^{-1}$ are as might be expected for a glutaric anhydride (1802 and 1761 cm.$^{-1}$) fused to a cyclopropane ring.

Several interesting transformation products of the diacid (VII), including members of the 10-epi-A-norcholestane series, were prepared. These will be described later in the complete paper.

Experiments designed to give information regarding the nature of the excited state involved in the photoisomerization of Δ^4-cholesten-3-one are not yet complete. It is important to note, however, that the process differs from the isomerization of homoannular dienones in that it must begin with the breaking (concerted to some extent with other changes) of a *sigma* bond. This formalism is characteristic of ground state reactions having an ionic origin and thereby suggests that the excited state giving rise to II is polar.

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[12] D. Arigoni, H. Bosshard, H. Bruderer, G. Büchi, O. Jeger and L. J. Krebaum, *Helv. Chim. Acta*, **40**, 1732 (1957). Values given here were estimated from the published curve.

[13] L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, pp. 53–54.

KINETICS OF DISSOCIATION OF ORGANIC DIMERIC DI-ANIONS INTO MONOMERIC RADICAL-IONS[1]

Sir:

In electron transfer initiation of anionic polymerization[2] the monomer M is converted into radical-ions, M$^-$. Dimerization of M$^-$ yields di-anions, *e.g.*, $2\mathrm{CXY{=}CH_2}^- \rightarrow {}^-\mathrm{CXYCH_2CH_2CXY}^-$, whereas their reaction with the monomer yields dimeric radical-ions, *i.e.*, $\mathrm{CXY{=}CH_2}^- + \mathrm{CH_2CXY} \rightarrow {}^-\mathrm{CXYCH_2CH_2CXY}\cdot$. Studies of the kinetics of these reversible processes are currently being pursued in our Laboratory, and some methods for determining the rate constants of dissociation of $^-\mathrm{M{\cdot}M}^-$ into 2M$^-$ are reported in this note.

Di-anions of 1,1-diphenylethylene do not undergo any polymerization on monomer addition as the bulkiness of phenyl groups introduces too large a steric strain. Hence, the rate constant of the dissociation

$$^{-}\mathrm{C(Ph)_2CH_2CH_2C(Ph)_2}^{-} \xrightarrow{k_d} 2\mathrm{CH_2{=}C(Ph)_2}^{-}$$

was determined[3] by studying the exchange between the di-anions and the radioactive monomer in tetrahydrofuran solution. Thus, k_d was found[3] to be 8×10^{-7} sec.$^{-1}$ at 30°, the respective E_d being about 10 kcal./mole.

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[1] This investigation was supported by the National Science Foundation through Grant No. G14393.

[2] (a) M. Szwarc, M. Levy and R. Milkovitch, *J. Am. Chem. Soc.*, **78**, 2656 (1956). (b) M. Szwarc, *Nature*, **178**, 1168 (1956); *Makromol. Chemie*, **35**, 132 (1960).

[3] G. Spach, H. Monteiro, M. Levy and M. Szwarc, *Trans. Faraday Soc.*, in press.

A different approach was necessary to study the dissociation of the α-methylstyrene dimer

$$^{-}C(CH_3)(Ph)CH_2CH_2C(CH_3)(Ph)^{-} \xrightarrow{k'_d} 2CH_2{=}C(CH_3)(Ph)^{-}$$

since this species undergoes further polymerization on addition of the monomer. The exchange between the deuterated dimer $^{-}C(CD_3)(Ph)CD_2CD_2C(CD_3)(Ph)^{-}$ and the hydrogenated one which occurs as a result of the dissociation, was investigated and the rate of formation of the resulting mixed dimer was determined.

The deuterated α-methylstyrene, synthesized from CD_3COCD_3 of 90% isotopic purity, was used for preparing the tetrahydrofuran solution of the deuterated dimer. Equivalent amounts of hydrogenated and deuterated di-anions, which did not contain any free monomer, were mixed and the mixture divided into 3 ampoules. The contents of the first one was immediately "killed" by adding a few drops of acidified tetrahydrofuran. The second ampoule was left for 2 days and the third for 10 days before their contents were "killed." After evaporating the solvent the respective residues were analyzed by low ionizing voltage mass spectrograph, using 8 v. electron accelerating potential, which gives essentially the parent ions only. The results are listed in Table I. The hydrogenated dimer showed masses 238 and 239, the latter resulting from the naturally present C^{13}. The main component of the deuterated dimer was 248 (C^{13} yielding 249), and, because of the lack of isotopic purity, the masses 247, 246, 245, 244, and 243 also appeared, of course in decreasing proportion. The component 243, *i.e.*, the mixed dimer, formed only 0.2% of the deuterated material, and on addition of the hydrogenated dimer its proportion fell to 0.1%. As a result of the dissociation the proportion of the 243 component increased by 0.3% after 2 days and by 1.5% after 10 days (see Table I). If f_H, f_D, and f_{HD} denote the fractions of the hydrogenated, deuterated, and mixed dimers, respectively, then

$$df_{HD}/dt = k'_d\text{-}\{2(f_H + {}^1/_2 f_{HD})(f_D + {}^1/_2 f_{HD}) - f_{HD}\}$$

Since $df_{HD}/dt = (0.15 \times 10^{-2})(1.7)$/day (the factor 1.7 arises from the lack of isotopic purity), k'_d is calculated to be 0.6×10^{-7} sec.$^{-1}$ at 25°, *i.e.*, this constant is ~one-tenth as large as k_d of dissociation of the dimeric dianion of 1,1-diphenylethylene.[3]

TABLE I

PERCENTAGE OF THE VARIOUS ISOTOPIC COMPONENTS IN THE INVESTIGATED MATERIAL

m/e	H-dimer	D-dimer	Mixture $t = 0$	Mixture $t = 2$ days	Mixture $t = 10$ days
236	0.3	...	0.1	0.1	0.1
237	0.9	...	0.3	0.3	0.4
238	81.8	...	39.4	39.4	38.4
239	15.4	...	8.0	7.9	7.7
240	1.5	...	0.7	0.7	0.8
241	0.1	...	...	0.1	0.1
242	...	0.1	...	0.2	0.6
243	...	0.2	0.1	0.4	1.6
244	...	0.5	0.2	0.5	0.5
245	...	2.5	1.2	1.2	1.2
246	...	11.6	5.7	5.7	5.5
247	...	33.0	16.9	16.7	16.5
248	...	42.7	22.6	22.2	22.0
249	...	8.6	4.4	4.2	4.2
250	...	0.8	0.4	0.4	0.4

Total % of H dimer in the mixture at $t = 0$, 48.1%
Total % of D dimer in the mixture at $t = 0$, 51.5%

The mass-spectrographic analyses were carried out in The Research Laboratories of Texaco, Inc., Beacon, New York, and our special thanks go to Mr. F. M. Roberts, Mr. J. H. Shiveley, and Mr. R. H. Kicha for their most valuable help in this investigation.

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HOMOLYTIC DECARBOXYLATION: A NOVEL TECHNIQUE FOR GENERATING FREE ARYL RADICALS IN SOLUTION

Sir:

A method has been discovered for effecting the one-step homolytic decarboxylation of aromatic acids in the liquid phase. This reaction provides a new source of free aryl radicals in solution and has a number of features which are of considerable theoretical interest. When conducted in the presence of aromatic solvents, it constitutes a novel synthesis of biaryls.

In general, homolytic decarboxylation may be accomplished by treating a well-stirred solution of the aromatic acid in an appropriate solvent with oxygen and di-*t*-butyl peroxide at temperatures high enough to cause rapid thermolysis of the latter component. The reaction is catalyzed strongly by cobaltous naphthenate and is best performed by employing slow addition of the peroxide in conjunction with continuous removal of low-boiling products. Table I summarizes some typical results. Complete conversion of the starting acid was not achieved in any of these experiments; hence they probably do not serve to define optimum synthetic conditions. For example, benzoic acid was recovered in yields of 20 and 64% in the tabulated runs giving 36 and 3%, respectively, of dichlorobiphenyls.

Evidence has been obtained for the presence of other products derived from benzoic acid (methyl benzoate, toluic acids, biphenylcarboxylic acids, dichloroterphenyls); however, the complexity of the product mixtures has so far precluded the obtention of satisfactory material balances. Although carbon dioxide was detected in the effluent gases, no attempts were made to measure it quantitatively, since stoichiometric correspondence between the amount formed and the amount of starting material which had reacted was not expected.

Carbon dioxide also could result from the oxidation of methyl radicals[1] and from the homolytic

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(1) A. R. Blake and K. O. Kutschke, *Can. J. Chem.*, **39**, 278 (1961).