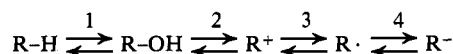


Electrochemical Determinations of pK_a 's. Triphenylmethanes and Cycloheptatriene

Sir:

Recently we reported¹ a new method for determining pK_a 's of hydrocarbons, and applied this to a determination of the pK_a of triphenylcyclopropene. The essential point was that the thermodynamics of direct conversion of a hydrocarbon to its conjugate base could also be determined from the thermodynamics of indirect conversion, through the sequence



Step 1 is the only step for which data are not easily obtained. We assume that the difference in heat of formation of a hydrocarbon and its related alcohol is constant, at least for closely similar compounds. For step 2, the commonly available thermodynamic parameter is the pK_{R^+} . For steps 3 and 4, the $E_{1/2}$'s for successive addition of two electrons can be determined by a variety of electrochemical techniques, of which cyclic voltammetry is particularly convenient in obtaining reversible potentials with very reactive species.

Recently Volz and Lotsch² have reported $E_{1/2}$'s for the one-electron reduction of a series of substituted triphenylmethyl cations. For eight of their cations, pK_{R^+} 's had also been determined by Deno,³ and these are listed in Table I. In order to apply our method we also require $E_{1/2}$ for the second reduction, of radical to carbanion, but in the series listed in Table I this is likely to be almost constant. The substituents listed will interact most strongly with the carbonium ion, not the radical, so the substituent effect on the potential for two-electron reduction of cation to anion should be found almost entirely in the first wave. We have confirmed this by the finding that under the conditions previously described¹ the potential for reduction of radical to anion is constant at -0.41 V *vs. sce*, within 0.03 V, for triphenylmethyl, 4-methoxytriphenylmethyl, and 4,4'-dimethoxytriphenylmethyl.

Given the constancy, in this series, of energy changes for steps 1 and 3, we can calculate the pK_a 's shown in Table I. The method uses a standard compound, unsubstituted triphenylmethyl, to fix the scale; thus all pK_{R^+} 's are referred to the pK_{R^+} of -6.63 for triphenylmethyl cation,³ while pK_a 's are relative to a value of 33^4 for triphenylmethane. A typical calculation is that for the tris-*p*-methoxyphenyl system: the cation is 7.45 pK units more stable than trityl; the first electron adds at 0.47 V more negative potential than in trityl; the second electron is assumed to go in at the same potential as in trityl (as we have shown in two related cases); therefore the substituents increase the cation-anion energy gap by $0.47 \times 23 = 10.81$ kcal/mol or 7.83 pK units; thus the anion is 0.4 pK unit less stable than trityl, so its pK_a is 33.4 .

All the pK_a 's are calculated to be almost the same, starting from cations whose pK_{R^+} 's range over 17 units. This is strong support for the validity of this new method of determining pK_a 's, since these substituents should not

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Table I. Triphenylmethyl Cations and Anions

4,4',4'' substituents	pK_{R^+} ^a	$E_{1/2}$ (first electron) ^b	Calcd pK_a
None	-6.63	+0.27	33.00
Trichloro	-7.74	+0.38	32.3
Monomethoxy	-3.40	+0.07	33.1
Trimethoxy	+0.82	-0.20	33.4
Tris(dimethylamino)	+9.36	-0.79	34.7
Trimethyl	-3.56	+0.05	33.6
Triisopropyl	(-6.51)	+0.07	(36.2)
Tri- <i>t</i> -butyl	(-6.5)	+0.13	(35.2)

^a Reference 3. ^b Reference 2.

perturb the energy of the carbanion much. The variations in pK_a 's may reflect real substituent effects in the carbanions (*e.g.*, in the trichloro derivative), or they may result from errors in our assumptions or in the experimental pK_{R^+} 's or reduction potentials.

We have also applied our technique to tropylium. By cyclic voltammetry, using the system described previously,¹ we find the first $E_{1/2}$ at -0.17 V *vs. sce* (lit.² -0.17 V by dc polarography) and the second wave with $E_{1/2} -0.91$ V. Combining this with the two potentials for triphenylmethyl, and the pK_{R^+} 's for the two systems, indicates that the pK_a for tropylium anion is 36, three units above triphenylmethyl anion. Dauben had also estimated⁵ $pK_a = 36$ from equilibration experiments.

These results confirm the validity of our method of determining pK_a 's, and point to wide-ranging applications of the technique. They also support our previous observation, by this method, that the lower limit pK_a for triphenylcyclopropenyl anion is 51. This remarkably high pK_a was of course inaccessible by any other technique.⁶

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(6) Advice by Professor W. Reinmuth and financial support by the National Institutes of Health are gratefully acknowledged.

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The Total Synthesis of Logenin

Sir:

The naturally occurring iridoid glucoside logenin is a key intermediate on the biosynthetic pathway to the *Corynanthe*, *Aspidosperma*, *Iboga*,¹⁻³ and *Ipecacuanha*⁴ alkaloids. Its structure and stereochemistry was recently established as **1**⁵⁻⁸ and confirmed by X-ray analysis.⁹

We now wish to describe a total synthesis whose key step allowed the construction of the methyl tetrahydro-

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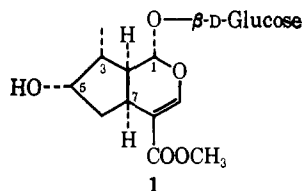
(5) S. Brechbühler, C. J. Coscia, P. Loew, C. v. Szczepanski, and D. Arigoni, *ibid.*, 136 (1968).

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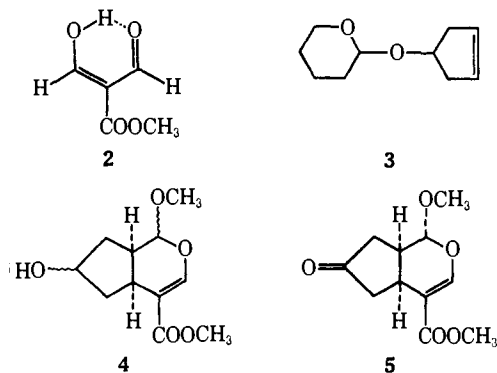
(7) A. R. Battersby, E. S. Hall, and R. Southgate, *J. Chem. Soc., C*, 721 (1969).

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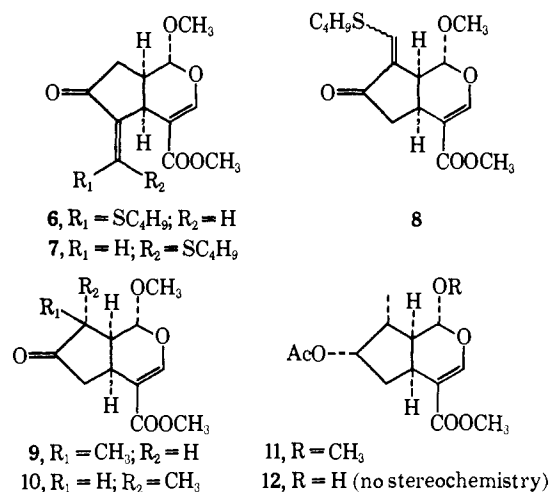


coumalate moiety characteristic of iridoids in a single photochemical operation.¹⁰ Methyl 3,3-dimethoxypropionate prepared from trimethyl orthoformate and ketene¹¹ when condensed with methyl formate in the presence of sodium¹² gave the liquid 2-formylmalonaldehydic acid methyl ester (**2**); nmr (CCl₄) δ 14.6 (1 H, exchanged with D₂O), 8.95 (2 H, s), and 3.74 (3 H, s); uv (95% EtOH) 274, 244 m μ (ϵ 8640; 8020); (EtOH, NaOH) 278, 241 m μ (ϵ 12,800; 14,900). Ultraviolet irradiation with a high-pressure Hanovia mercury lamp (450-W) of a 10% solution of the β -tricarboxyl compound **2** in olefin **3**, available from 3-cyclopentenol^{13,14} and dihydropyran, followed by treatment of a methanol solution of the crude photoproducts with Amberlite IR-120 cation-exchange resin afforded the liquid hydroxyacetals **4** (45%). Oxidation with Collins' reagent¹⁵ gave a 3:1 mixture of ketones, probably differing only in the configuration of the acetal carbon atom, from which the major isomer **5**, mp 90–91°, could be isolated by crystallization (45% from **4**). Its stereochemistry is based on the presumption that acetalization under equilibrating conditions yields the most stable diastereomer with *cis*-fused rings¹⁶ and axially oriented methoxy group (anomeric effect).¹⁷ Inspection of molecular models reveals the sterically less crowded epimer to have the C₁- α -OCH₃ configuration.

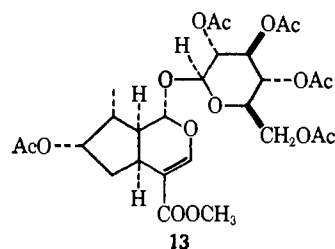


The ketone **5** was converted to a mixture of hydroxymethylene ketones (75%) and without separation to the butylthiomethylene derivatives.¹⁸ Chromatography afforded the useless isomers **6** (11%) and **7** (8%) both with nmr absorptions at δ 3.8 caused by the C₇ proton and an

inseparable stereoisomeric mixture of the desired butylthiomethylene derivatives **8** (58%). Desulfurization¹⁸ of the sulfides **8** with Raney nickel gave a mixture of epimeric ketones, mp 75–85° (92%), containing mostly **9** which with sodium methoxide was converted to the more stable epimer **10**, mp 90–92° (90%). Infrared,



mass, and nmr spectra of the ketone **10** were indistinguishable from those of optically active 1-O-methyldehydrologanin aglucone, mp 118–120°,¹⁹ prepared independently from natural loganin using a different method by Battersby.⁷ Reduction of the racemic ketone **10** with sodium borohydride followed by consecutive treatments of the resulting alcohol with methanesulfonyl chloride and with tetraethylammonium acetate^{7,16} yielded the racemic acetate **11**, mp 63–64° (71% from **10**). Hydrolysis to an anomeric mixture of racemic loganol 5-acetate (**12**), gum (51%) [uv (EtOH) 235 m μ ; (EtOH–NaOH) 274 m μ], was accomplished in aqueous acetic acid containing perchloric acid. Condensation of the racemic aglucone **12** with 2,3,4,6-tetra-O-acetyl- β -D-glucose in dichloroethane at room temperature in the presence of boron trifluoride,²⁰ followed by thin layer chromatography and crystallization, gave, presently in low yield, optically active loganin pentaacetate (**13**), mp 137–139°, $[\alpha]^{25}_D -77^\circ$ (CHCl₃) pure and mixed with authentic material, $[\alpha]^{25}_D -78^\circ$ (CHCl₃). Identity was confirmed by comparison of ir spectra and chromatographic behavior. Loganin pentaacetate (**13**) has previously been transformed to loganin (**1**).⁷



(10) This method is an extension of that pioneered by de Mayo for the synthesis of δ -diketones through photochemical cycloaddition of enolized β -diketones to olefins: B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. de Mayo, *J. Org. Chem.*, **34**, 794 (1969), and earlier papers cited.

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(16) G. Büchi and R. E. Manning, *Tetrahedron*, **18**, 1049 (1962).

(17) R. U. Lemieux in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1964, p 733.

(18) Procedure of R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

(19) We wish to express our sincere thanks to Professor D. Arigoni for a sample of loganin pentaacetate and an unpublished efficient procedure for its conversion to 1-O,5-O-diacytloganin.

(20) Method of M. Kuhn and A. v. Wartburg, *Helv. Chim. Acta*, **51**, 1631 (1968). We are much indebted to Dr. von Wartburg for a generous supply of tetraacetylglucose.

Acknowledgment. This work was supported by the National Institutes of Health and Hoffmann-La Roche, Inc.

(21) National Institutes of Health Predoctoral Fellow, 1966–1969.
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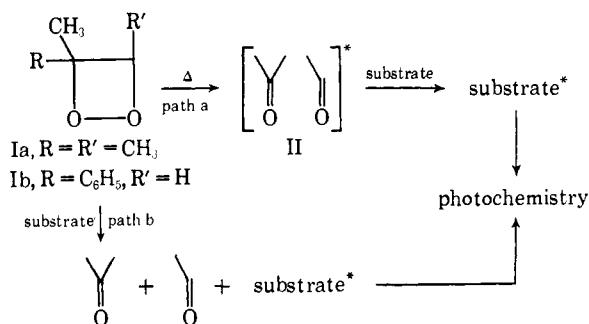
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Utilization of Chemically Generated Excited States

Sir:

We have shown recently that it is possible to effect "photochemistry without light"¹ by using chemically produced electronically excited states. We now report that this method can lead to quantum yields in the useful range, that the excited states formed appear identical with those arrived at by means of photon absorption, and that triplet states are involved in all the cases studied with the additional implication of triplet-energy transfer in the dioxetane-driven dimerization of acenaphthylene (III).

Energy Sources. In most reactions studied, trimethyl-1,2-dioxetane (Ia)^{1,2} was used as the energy source. By working at -5° , omitting the solvent, and



distilling the product *in vacuo*, dioxetane Ia has been obtained as a pure liquid³ (**Caution: potential explosive**). Dioxetane Ib has also been prepared, but appears to give lower yields of photoproducts than Ia.

Energy transfer from the dioxetane appears to involve path a (and exciplex II²) since fluorescent acceptors do not increase the rate of the decomposition of Ia² and since considerable light emission is seen in the absence of substrates, especially in the gas phase (emission at *ca.* 435 $m\mu$).⁴ This point warrants further examination, however.⁵

Acenaphthylene (III). In the photochemical dimerization of acenaphthylene it has been reported that the singlet state of III, in addition to undergoing intersystem crossing, yields the pure *cis* dimer (V) of acenaphthylene⁶

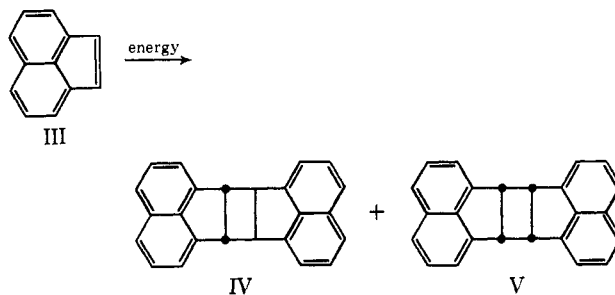
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(3) $\nu_{\text{max}}^{\text{C=O}}$ 1393, 1380, 1156, 1069, 884 cm^{-1} ; nmr (CCl₄) τ 4.78 (quartet, $J = 6.5$ Hz, 1 H), 8.47 (singlet, 3 H), 8.53 (singlet, 3 H), 8.65 (doublet, $J = 6.5$ Hz, 3 H); mol wt 100 (freezing point depression of C₆H₆). *Anal.* Calcd for C₈H₁₀O₂: C, 58.80; H, 9.87. Found: C, 58.49; H, 10.35 (full purification not achieved because of the explosive nature of Ia; traces of acetone seen in the ir and nmr spectra).

(4) A value of 430–440 $m\mu$ has been reported for the decomposition of Ia in benzene.²

(5) Rate acceleration has been found in a related case (M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969)).



or yields the *cis*-dimer V contaminated with only a trace of the *trans*-dimer IV.⁷ The triplet state leads to a ratio of *cis* to *trans* dimers that is solvent dependent,⁶ but in methanol values of 0.44 to 0.58 were found for low-energy sensitizers.⁸

When a benzene solution of Ia (1.8 *M*) and III (0.7 *M*) is heated to 100° for 10 min, then cooled, crystals of dimers IV and V separate. This ready synthesis of IV and V illustrates the usefulness of the new procedure. The dimerization in benzene (Table I) is largely quenched

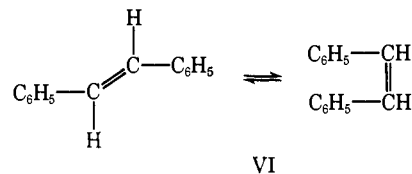
Table I. The Dimerization of Acenaphthylene^a

Solvent	Ia, <i>M</i>	III, <i>M</i>	Temp, $^\circ\text{C}$	Ratio, ^b V:IV	Total yield of IV + V, wt %	Total quantum yield (10 ²) ^c
Benzene	1.8	0.7	95–100	0.30	8	2–
Benzene ^d	1.8	0.7	95–100	0.30	7	1+
Benzene ^e	1.8	0.7	95–100	0.4	0.2	0.04
Methanol	1.3	0.6	40	0.7	2	0.4

^a All solutions degassed, except where noted. ^b Determined by ultraviolet spectra of the products separated on a tlc plate (silica gel developed with cyclohexane at 40°). ^c Mol of dimer/mol of Ia. ^d Solution saturated with oxygen. ^e 0.16 *M* in cyclooctatetraene.

by cyclooctatetraene;⁶ the small amounts of *cis* and *trans* dimers still formed remain in the ratio of about 0.3–0.4, however. Both results, as well as the *cis/trans* ratio in the absence of quenchers, when compared with the photochemical counterparts,^{6–8} show that the triplet state of III is largely responsible for the dimerization.

Stilbene (VI). Data for the chemically sensitized isomerization of stilbene are given in Table II. The



yields of *cis* isomer are somewhat solvent dependent and they are improved by higher temperatures (a similar effect has been noted for the photochemical isomerization⁹); high stilbene concentrations and low dioxetane concentrations also increase the yield. Oxygen was not found to be an efficient quencher, nor was it found to influence the corresponding photochemical

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