to 1 atmosphere with nitrogen, sealed, and quickly brought to 25.0° in a constant temperature bath in subdued light. Reaction was induced with a 275-watt sunlamp at 12–18 in. Final concentrations were determined by g.l.c.; two chlorinations were performed for each initial mixture. Most analyses were performed at 55° (70° for mixtures containing V) on column "B"; Perkin–Elmer columns "A" (diisodecyl phthalate) and "R" (polypropylene glycol) are also suitable in most cases. Areas were determined from the product of peak height and retention time (essentially no changes in the latter) and used to solve eq. 10 to give the results shown in Tables II and V.

Competitive Chlorination of Olefins and Cyclohexane.—The appropriate mixture of olefin, cyclohexane, and solvent was placed in a flask equipped as for the yield determinations. After the solution was flushed with nitrogen, chlorine (previously measured out in a graduated cold trap) was swept into the solution with nitrogen in the dark; reaction was initiated with illumination as before; g.l.c. analyses for cyclohexyl chloride and the appropriate polychloroethane were performed on column "A"; areas were determined by planimeter and corrected to molar ratios by calibration factors as before; the calibration factors for areas determined by planimeter and determined from the product of peak height and retention time were determined separately and were almost identical. These values were used to solve eq. 13 to give the results listed in Tables III and VI.

Bromotrichloromethane–Olefin Reactions.—The procedure was essentially identical to that of Huyser[27]; g.l.c. analyses were carried out on Perkin–Elmer column "O" (silicone grease) at 78° for bromotrichloromethane, chloroform, and the solvent which served as an internal standard; areas were determined by planimeter and, after proper calibration, used to solve eq. 14 to give the results listed in Table VIII.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO., STAMFORD, CONN.]

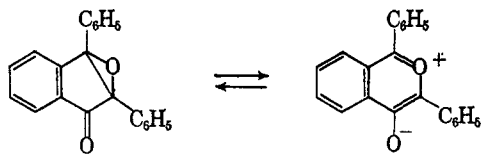
Photochemical and Thermal Valence Tautomerization of 2,3-Diphenylindenone Oxide. II[1]

BY EDWIN F. ULLMAN AND JOHN E. MILKS

RECEIVED APRIL 8, 1964

Heat or ultraviolet light partially converts 2,3-diphenylindenone oxide (I) to an aromatic valence tautomer, the red 1,3-diphenyl-2-benzopyrylium 4-oxide (II). Both the thermal and photochemical processes are reversible. The chemistry of the red species is discussed.

Numerous indenone oxide derivatives have been reported to display unusual photochromic and thermochromic properties.[2] These phenomena have generally been dismissed as evidence for thermal and photochemical decomposition and have not been carefully studied. The existence of these color reactions suggested the possibility of a reversible valence tautomerization of the pyrylium oxide II with the structure I, which is *formally* a canonical form of II. At the outset of this study such a valence tautomerization of a benzenoid system was without precedent, although the photochemical interconversion of *o*-di-*t*-butylbenzene to its "Dewar" bicyclo[2.2.0]hexadiene tautomer has since been reported.[3]



I II

Since 2,3-diphenylindenone oxide (I) was readily accessible and was the only indenone oxide derivative which had been subjected to even a limited study in regard to its color-forming properties, this compound was chosen for the present investigation. The compound was first described by Weitz and Scheffer,[2a] who reported that on strong heating in an inert solvent or on exposure to diffuse daylight it turned red, and that this red coloration faded on cooling or standing in the dark. Rapid cooling of the hot solutions led to a longer lifetime of the red color, but rewarming accelerated the fading process. These data led these authors to conclude that the red species was probably a transient radical-like intermediate which was present in very low concentrations. This conclusion was supported by the observation that after 24–48 hr. a refluxing xylene solution was no longer red and the indenone oxide I could not be recovered.

Reinvestigation of the properties of I confirmed these observations. The red species observed on heating or on ultraviolet irradiation of the solid compound or its solutions proved to be very sensitive to numerous reagents. While fading generally occurred in benzene solution in a few minutes at room temperature, the rate could be greatly reduced by careful exclusion of oxygen, or greatly accelerated by peroxides, halogens, acids, bases, and mercaptans, all of which presumably reacted directly with the red compound.

Intensely colored solutions could be developed by rapid heating up to near 200° or by long irradiation in deoxygenated benzene solutions with filtered (3200–3900 Å.) light from a high pressure mercury arc. The color intensity attained by irradiation proved to be very dependent on wave length. Unfiltered light was less effective in producing the colored species while visible radiation (>4500 Å.) led to rapid and complete decoloration of previously colored solutions. Thus the photostationary state concentrations of the red species appeared to be dependent principally on the ratio of light absorbed by the red compound to that absorbed by the indenone oxide I, and represented steady-state concentrations of either an intermediate in an irreversible rearrangement or a tautomer in true photoequilibrium with I.

Ultraviolet irradiation (2600–3900 Å.) of a benzene solution of the indenone oxide I led to the appearance of a sharp new peak in the infrared at 6.38 μ suggestive of the enolate-like C–O grouping in II together with a weaker peak at 8.03 μ. A simultaneous and

(1) A preliminary report of this work has appeared previously: E. F. Ullman and J. E. Milks, *J. Am. Chem. Soc.*, **84**, 1315 (1962).

(2) (a) E. Weitz and A. Scheffer, *Chem. Ber.*, **54**, 2327 (1921); (b) C. F. H. Allen and J. W. Gates, Jr., *J. Am. Chem. Soc.*, **65**, 1230 (1943); (c) R. DeFazi and A. Banchetti, *Gazz. chim. ital.*, **76**, 283 (1946); (d) A. Banchetti *ibid.*, **76**, 459 (1946); (e) R. DeFazi and S. Carboni, *ibid.*, **78**, 567 (1948); (f) S. Carboni, *ibid.*, **81**, 225 (1951); (g) L. A. Shchukina and E. P. Semkin, *J. Gen. Chem. USSR*, (Eng. trans.), **32**, 476 (1962).

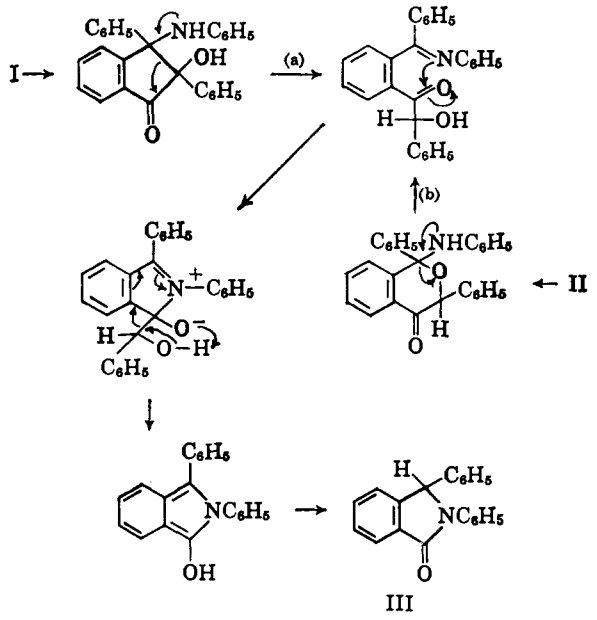
(3) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962).

proportionate decrease in the intensity of the 5.76 μ carbonyl absorption of I amounting to up to about 17% of the original intensity was also observed. On bleaching this solution with visible light a nearly complete restoration of the original spectrum was obtained which provided strong evidence that *the red species was photochemically reconverted to the indenone oxide.*

The ultraviolet spectrum of an irradiated indenone oxide solution in hexane showed a general increase in absorptivity over that observed prior to irradiation, with new maxima 288, 391, 408, 548, and 575 (sh) mμ which were completely destroyed on irradiation with visible light. Similar spectral changes were also observed on heating a mineral oil solution of I, which provided evidence for the identical nature of the thermally and photochemically generated red species. In contrast, the n.m.r. spectrum of I was insignificantly affected by irradiation, a result which suggests that the red species probably does not have radical or triplet character. This conclusion is also supported by the absence of an electron spin resonance signal of irradiated solutions even at very low temperature.

On the assumption that II was the correct structure for the colored species, an attempt was made to trap it by interchange of the ring oxygen with the nitrogen of aniline in analogy to the known conversion of pyrylium salts by amines to the corresponding pyridinium salts.[4] Although the red color was not rapidly discharged by aniline at room temperature, a reaction occurred on heating an aniline solution of the indenone oxide I at 140°. The principal product showed infrared carbonyl absorption at 5.94 μ (mineral oil) and an n.m.r. aliphatic proton peak (singlet) at 4.05 τ ($CDCl_3$) together with a group of peaks corresponding to fourteen aromatic protons. These data were in good accord with structure III, which was verified by independent synthesis.[5] While the formation of this product can formally be accounted for by a direct nucleophilic attack by aniline on I (reaction path a), this mode of attack appears unlikely in view of the considerable hindrance at the 3-position of the 2,3-disubstituted indanones to backside attack.[6] A more plausible explanation requires the intermediacy of the pyrylium oxide II (reaction path b).

More compelling evidence for structure II for the red species was provided by the observation that the substance is rapidly destroyed by reactive dienophiles. Thus, for example, on ultraviolet irradiation of solutions of I in dimethyl acetylenedicarboxylate or norbornadiene no color was generated, and 1:1 adducts IV and



V, respectively, were obtained. The isolation of the same adducts by heating I with these reagents provides conclusive evidence that *the colored products formed by heating and irradiation were identical.*

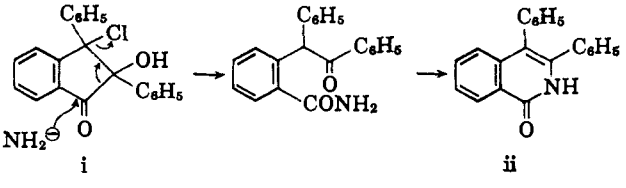
The proposed structure IV for the dimethyl acetylenedicarboxylate adduct was in accord with the spectral evidence. Ester carbonyl peaks appeared in the infrared at 5.75 (sh) and 5.79 μ and absorption at 5.87 μ was consistent with an electronegatively substituted aromatic six-membered ring ketone. While the ultraviolet spectrum was not that expected for a simple tetralone, catalytic hydrogenation of IV yielded a dihydro derivative which displayed a spectrum very similar to that of tetralone. The infrared carbonyl absorption was only slightly modified with peaks at 5.71, 5.76 (sh), and 5.87 μ. The marked changes in the ultraviolet spectrum on reduction of the double bond in IV is not unexpected; similar nonbonded electronic interactions in bridged β,γ-unsaturated ketones have frequently been observed.[7]

Treatment of the adduct IV with hot alcoholic potassium hydroxide gave benzoic acid plus a $C_{18}H_{14}O_6$ tricarboxylic acid VI which had an ultraviolet spectrum similar to that of *o*-carboxycinnamic acid. The n.m.r. spectrum of VI displayed a singlet at 6.77 (CH_2), a multiplet at 2.06–2.95 (9 ArH), and two very broad bands centered at 0.0 and 6.7 τ (3H) attributable to rapidly exchanging carboxylic acid protons. These data suggested structure VI for this product, a structure which might readily arise from IV by the sequence shown. This structure, and hence the structure for the adduct IV, was confirmed by a Stobbe condensation of *o*-benzoylbenzoic acid (VII) with diethyl succinate followed by hydrolysis to give a product that was identical with the degradation product VI.[8,9]

(4) F. Brody and P. R. Ruby in "Pyridine and Its Derivatives," E. Klingsberg, Ed., Part I, Interscience Publishers, Inc., New York, N. Y., 1960, p. 210.

(5) H. Meyer, *Monatsh.*, **28**, 1211 (1907).

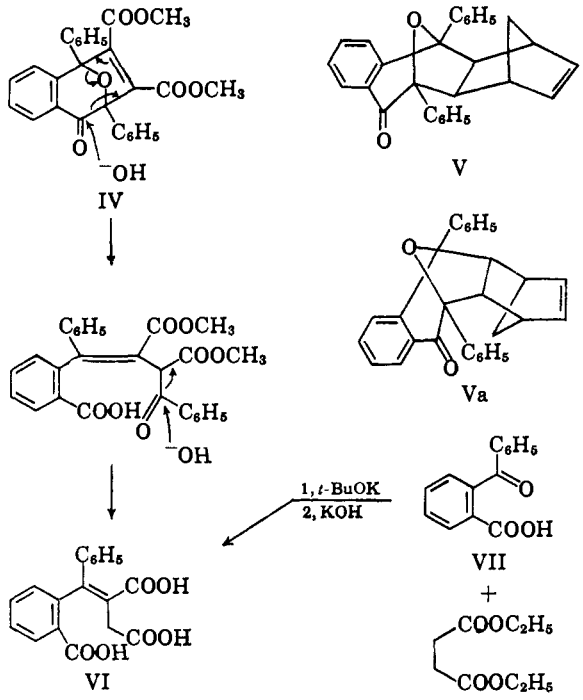
(6) While the 3-position in substituted 2,3-diphenylindanones is reactive in solvolytic reactions (A. Banchetti, *Gazz. chim. ital.*, **81**, 419 (1951), and references 2a, b, and e), it is exceptionally inert toward S_N2 attack. Thus, for example, i is readily converted to the corresponding diol with water, but it reacts slowly, if at all, with ammonia, and with sodamide the isoquinolone ii is formed by attack at the carbonyl rather than the chlorine-bearing carbon: E. F. Ullman and R. Lopresti, unpublished observation.



(7) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

(8) The use of a salt of an o-ketobenzoic acid in the Stobbe condensation to prevent phthalide formation has been described previously: E. F. Ullman, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1956. The fact that this reaction proceeds despite the strong electrostatic repulsion of the carboxylate grouping on the attacking anion emphasizes the extraordinary driving force of this reaction: W. S. Johnson, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 1.

(9) The geometry given for VI is expected from the structure of IV. The same geometry is predicted from a consideration of the eliminative

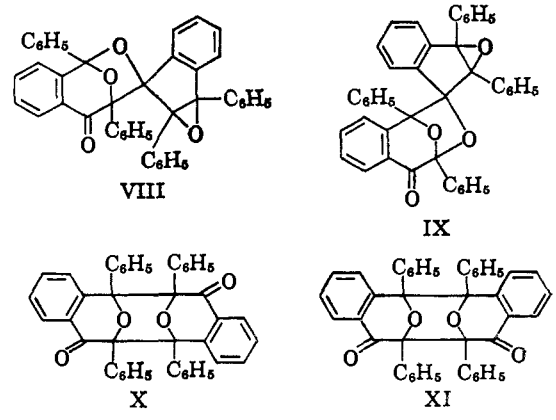


A degradation of the norbornadiene adduct V was not carried out, and the structure is assigned principally from the spectral data and by analogy with IV. Thus its ketonic infrared absorption at 5.89 μ and ultraviolet spectrum were very similar to those of dihydro IV and the n.m.r. spectrum was consistent with a 5,6-disubstituted norbornene (see Experimental). Several attempts to dehydrate V with acid to the corresponding benzotropone were unsuccessful. The compound was unaffected by hot boron trifluoride etherate and gave intractable tars with boron trichloride in chloroform.[10]

The formation of only one stereoisomer of V is expected. Norbornadiene normally forms *exo* Diels–Alder addition products,[11] two of which, V and Va, are possible in this case. However, models show that the bridge methylene in Va is severely hindered by the fused aromatic ring and accordingly it is improbable that this isomer would be formed.

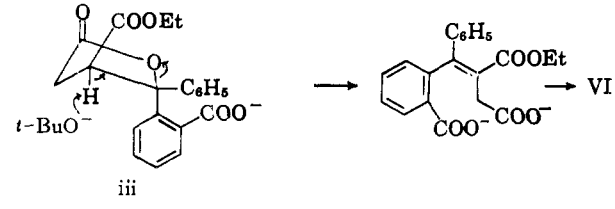
While the foregoing data demonstrate the existence of both a light- and heat-induced reaction of the indenone oxide I to its red isomer II, the reverse reaction has only been shown to occur photochemically. The fact that fading of the red species occurs spontaneously in the dark is not evidence that it is reconverted to I, for this could be due entirely to decomposition. That decomposition is indeed a very important factor under normal atmospheric conditions is seen by the observation that complete fading does not occur at room temperature in carefully deoxygenated solvents.[12] A test of the reversibility of the thermal coloration process was made by subjecting the indenone oxide I in an inert medium to conditions at least as forcing as those required to convert it essentially completely to the red isomer as estimated by the extent of trapping in the presence of a dienophile. Thus on heating I for 7 hr. at 135° in norbornadiene no more I could be detected, while in contrast, a benzene solution of I heated at 150° for the same period led to an estimated 10% of unchanged starting material. Similarly, heating of I in dimethyl acetylenedicarboxylate at 175° for 10 min. led to the isolation of the pure adduct in 70% yield which was not significantly increased in longer heating, while after 24 min. at the same temperature using diethyl succinate as solvent 18% of the indenone oxide was recovered unchanged. The fraction of II used up in the presence of a trapping agent exceeded in each case the fraction used up in its absence, and hence *the untrapped pyrylium oxide II must be thermally reconverted back to the indenone oxide I.*

The unrecovered indenone oxide I from the pyrolysis experiments proved to have been converted to a mixture made up predominantly of two dimers. Each compound displayed a single infrared carbonyl peak at 5.86 μ which was suggestive of structures similar to the adducts IV and V. The incorporation in the dimer structures of two substantially intact pyrylium oxide or indenone oxide nuclei was suggested by the observation that these compounds were strongly thermochromic and that, on heating, 2 moles of the red pyrylium oxide II was generated. This was shown by trapping experiments in which nearly 2 equivalents of the adduct IV was formed on heating the major dimer in the presence of dimethyl acetylenedicarboxylate. These data suggest that the dimers may arise either by addition of the carbonyl of I to the pyrylium oxide II to give VIII or IX, or by direct dimerization of II to give X or XI. Any of these structures might undergo thermal cleavage to their components and all are consistent with the infrared spectra.



An indication that the dimer structures were two of the possible stereoisomers of VIII or IX was obtained

ring opening of the intermediate Stobbe lactone iii (arrows) where electrostatic repulsion of the partially charged ester substituent by the carboxylate anion would favor a transition state leading to a *trans* orientation of these two groups; *cf.* H. E. Zimmerman and L. Ahramjian, *J. Am. Chem. Soc.*, **81**, 2086 (1959).

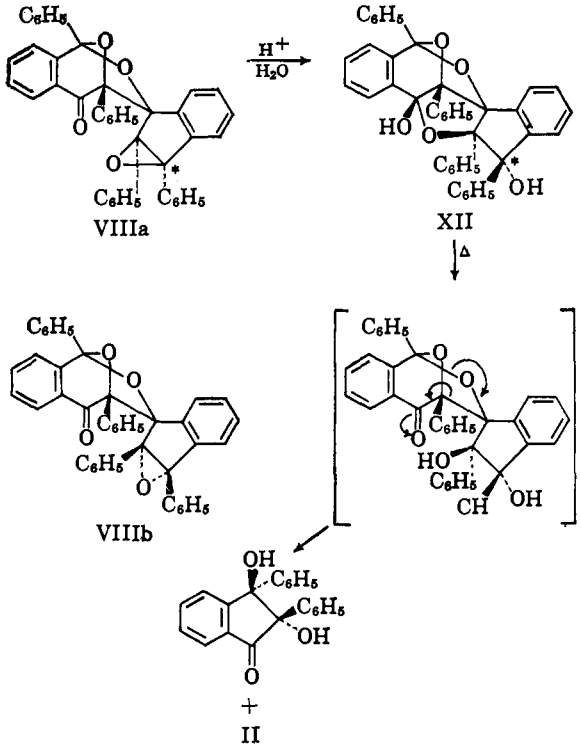


(10) It is noteworthy that another bridged ether which might have been expected to dehydrate to a tropone has been reported to be resistant to acid dehydration: A. W. Fort, *ibid.*, **84**, 4979 (1962). Presumably recyclization of the intermediate hydroxyolefin resulting from cleavage of a single C–O bond is so much more rapid than cleavage of the second C–O bond that no net reaction ensues.

(11) J. K. Stille and D. A. Frey, *ibid.*, **81**, 4273 (1959).

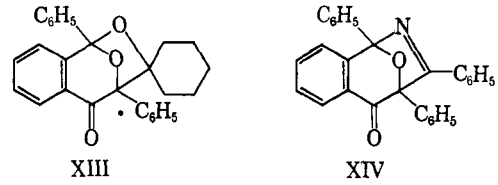
(12) E. F. Ullman and W. A. Henderson, in press.

from the ultraviolet spectra which were both very similar to those of dihydro IV and V, but which displayed extinction coefficients consistent with only one tetralone chromophore per molecule. A definite choice between these alternatives in the case of the principal dimer was provided by the observation that the compound was readily converted by hydrochloric acid in moist acetonitrile to a monohydrate XII which displayed no carbonyl band in the infrared and only benzenoid ultraviolet absorption. Like its precursor, the monohy-



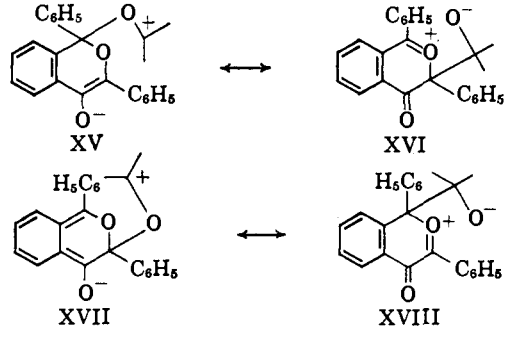
drate was thermochromic, but on heating with dimethyl acetylenedicarboxylate less than 1 equivalent of the adduct IV was formed suggesting that only one indenone oxide or pyrylium oxide nucleus remained intact and that the carbonyl of this moiety was masked most probably by a hemiketal linkage. Consideration of the possible hydrolysis routes of each of the possible dimeric structures VIII-XI leads to the conclusion that only VIII could lead to a monohydrate showing the observed properties. Thus, only in the monohydrate XII derived from VIII or in an epimer of XII differing in configuration at the starred atom does the stereochemistry permit hemiketal formation. Moreover, only two of the four possible stereoisomers of VIII, namely, VIIIa and VIIIb, are suitably arranged to provide the required stereochemistry in XII. Of these VIIIa is strongly favored, since epoxide ring hydrolysis can proceed in this isomer at the least hindered and electronically favored benzhydryl position (VIIIa, starred atom) and still lead to an appropriate configuration of the hydroxyl group engaged in hemiketal formation.

While an unambiguous structural assignment to the second dimer is not possible with the present data, the above-described ultraviolet spectra suggest that this compound is also derived by addition of the carbonyl group of I to II and hence has structure VIII or IX. A choice between these alternatives is possible from the observation that the symmetrical "dipolarophiles," cyclohexanone and benzonitrile, each added to II in high yield (>80%) to give *single* adducts to which we assign structures XIII and XIV, respectively, by analogy to the structure of the predominant dimer VIIIa.



The absence of isomeric adducts analogous to IX arising by the opposite mode of addition strongly suggests that a similar selectivity should be operative in the formation of the dimers, and that the minor dimer is therefore a stereoisomer of VIII. Moreover, of the possible stereoisomers, only VIIIa and VIIIb are relatively uncrowded and hence structure VIIIb can probably be assigned to this product.

The observed direction of addition of ketones to the pyrylium oxide II implies that the transition state XV ⟷ XVI would be favored over XVII ⟷ XVIII. This is in accord with the expectations that XV would be favored over XVII where distribution of negative charge onto oxygen requires interruption of benzenoid



resonance, and XVI would be favored over XVIII where the positive charge can be effectively distributed to only one aromatic ring. The same prediction also arises from molecular orbital calculations. Thus using the Hückel approximation,[13] we find XV favored over XVII by 0.260 and XVI favored over XVIII by 0.158β

Of some interest is the observation that the dimers VIIIa and VIIIb, the dimer hydrate XII, and the adducts XIII and XIV are all found to dissociate partially into their components near 200° with formation of a deep red color. Rapid cooling of hot solutions of these compounds led to the retention of the color which was shown to be due to the presence of the pyrylium oxide II by its sensitivity to visible light. The photochemically bleached solutions showed the characteristic photochromism of the indenone oxide I which provided additional support for the reversible character of the photochemical process I ⇄ II. The failure of the acetylenic ester and norbornadiene adducts IV and V to undergo similar dissociation at high temperature probably reflects the higher reactivities of these dienophiles coupled with a mass action effect resulting from the ability of these compounds to react with a second mole

(13) The heteroatom parameters used were those given by A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 135.

of the pyrylium oxide II. Thus dihydro IV, which is formally an adduct of dimethyl maleate and the pyrylium oxide II, becomes colored, but only above 250°, and fades very rapidly on cooling in keeping with the intermediate reactivity of this dienophile and its capacity to add only 1 mole of II.

Experimental[14,15]

Reactions of 2,3-Diphenylindenone Oxide (I). Aniline.—A solution of 1.5 g. (5.0 mmoles) of the indenone oxide I in 50 ml. of aniline was heated at 138–142° for 6 hr. under a nitrogen atmosphere. The solvent was removed *in vacuo* and the residue crystallized from ethanol to give 0.80 g. (56%) of crude product, m.p. 192–198°. A second recrystallization gave analytically pure 2,3-diphenylphthalimidine (III), m.p. 192–194°. The product gave no melting point depression on admixture with an authentic sample.[5]

Bicyclo[2.2.1]heptadiene. A.—A solution of 1.0 g. (3.4 mmoles) of the indenone oxide I in 50 ml. of freshly distilled bicyclo[2.2.1]heptadiene contained in a water-cooled quartz reaction vessel was irradiated with light from a 100-watt medium pressure mercury arc for 5 hr. Evaporation of the excess reagent *in vacuo* and trituration of the residue with 25 ml. of hot ethanol gave 0.83 g. (63%) of the adduct V, m.p. 203–207°. Recrystallization of the product from ethanol gave analytically pure material, m.p. 215–216°.

In later experiments the yield was increased to over 90% by irradiation with 3200–3900 Å. light from a B-H6 source equipped with suitable filters.

Anal. Calcd. for $C_{28}H_{22}O_2$: C, 86.12; H, 5.68. Found: C, 86.49; H, 5.78.

The adduct displayed spectral maxima consistent with the presence of a tetralone chromophore: $\lambda_{max}^{C_6H_{12}}$ 248 mμ (ε 11,600), 288 (1900), 298 (2020), 337 sh (116), 349 (150), 365 (144), and 379 sh (74), and λ_{max} 5.89 μ (C=O). The n.m.r. spectrum was consistent with a 2,3-disubstituted norbornene grouping, τ_{CDCl_3} 1.85–3.00 (14 aromatic-H), 3.92 (2 olefinic-H), 7.27 (3 *t*-H), 7.46 (1 *t*-H), 8.26 (1 *sec*-H, doublet), and 9.25 (1-*sec*-H, doublet). The extraordinarily high-field position of the latter methylene proton peak is in accord with the position expected from the effect of the anisotropy of the two phenyl groups in V. Models suggest that a much greater shift would be expected if Va were the correct structure.[16]

B.—A solution of 3.0 g. (10 mmoles) of the indenone oxide in 45 ml. of bicyclo[2.2.1]heptadiene was heated at 135° for 7 hr. in a glass-lined bomb. The residue obtained after evaporation of the solvent *in vacuo* was extracted with several portions of hot ethanol. Concentration and cooling of the extracts gave 2.3 g. (59%) of the adduct V, m.p. 211–214°.

Dimethyl Acetylenedicarboxylate. A.—A solution of 0.107 g. (0.36 mmole) of the indenone oxide in 1.0 ml. of dimethyl acetylenedicarboxylate was heated at 175° for 10 min. The residue obtained on evaporation of the excess reagent *in vacuo* crystallized from methanol to give 0.110 g. (70%) of the adduct IV, m.p. 168–170°. Recrystallization increased the melting point to 169–171°. The compound showed absorption maxima at $\lambda_{max}^{CH_3CN}$ 230 (sh) mμ (ε 17,850), 300 sh (1870), 360 sh (160), 368 (282), and 385 sh (180), and $\lambda_{max}^{CHCl_3}$ 5.75 (sh) μ, 5.79 ($COOCH_3$), and 5.87 (C=O).

Anal. Calcd. for $C_{27}H_{20}O_6$: C, 73.63; H, 4.58. Found: C, 73.46; H, 4.51.

B.—A product identical with that obtained above was obtained by irradiation instead of heating the reaction mixture.

Cyclohexanone.—A solution of 1.00 g. (3.36 mmoles) of the indenone oxide I in 11 ml. of cyclohexanone was heated under nitrogen at 145–150° for 16 hr. Removal of the solvent *in vacuo* and trituration of the residue with ethanol gave 1.11 g. (83%) of a yellow solid, m.p. 185–190° (red coloration). Recrystallization from ethyl acetate gave colorless XIII, m.p. 196–197° (red coloration). The compound displayed spectral maxima at $\lambda_{max}^{CH_3CN}$ 255 mμ (ε 10,400), 263 sh (8600), 293 (1950), 301 (1740), 332 sh (112), 344 (153), 358 (149), and 372 sh (76), and $\lambda_{max}^{CHCl_3}$ 5.88 μ (C=O).

Anal. Calcd. for $C_{27}H_{24}O_2$: C, 81.79; H, 6.10. Found: C, 81.52; H, 5.90.

Benzonitrile.—The preceding procedure was repeated using 0.924 g. (3.08 mmoles) of the indenone oxide in benzonitrile. One recrystallization of the crude product (1.00 g., 80% yield, after trituration with ethanol) from acetonitrile gave 0.827 g. (70%) of the pale yellow XIV, m.p. 148–151.5° (red coloration). The compound showed absorption maxima at $\lambda_{max}^{CH_3CN}$ 247 (sh) mμ (ε 17,200), 259, (18,000), 358 sh (196), 370 (204), and 380 sh (130), and $\lambda_{max}^{CHCl_3}$ 5.87 μ, 5.90 (C=O), and 6.20 (C=N).

Anal. Calcd. for $C_{28}H_{19}O_2N$: C, 83.77; H, 4.77; N, 3.49. Found: C, 83.95; H, 4.71; N, 3.63.

Hydrogenation of the Dimethyl Acetylenedicarboxylate Adduct IV.—A solution of 2.0 g. (4.55 mmoles) of the adduct in 45 ml. of ethyl acetate was stirred with 0.2 g. of prereduced platinum oxide under a hydrogen atmosphere for 8.5 hr. At the end of this period 4.78 mmoles of hydrogen had been absorbed. The residue obtained after filtration and evaporation of the solution *in vacuo* was extracted with 5 ml. of hot methanol and then recrystallized from methanol to give 0.8 g. (40%) of dihydro IV, m.p. 165–166° (reversibly turns red above ~250°). The compound displayed absorption maxima at $\lambda_{max}^{CH_3CN}$ 204 mμ (ε 58,400), 252 (16,200), 290 (2640), 300 sh (2020), 335 (168), 348 (155), and 364 (84), and $\lambda_{max}^{CHCl_3}$ 5.70 μ, 5.76 ($COOCH_3$), and 5.86 (C=O).

Anal. Calcd. for $C_{27}H_{22}O_6$: C, 73.29; H, 5.01. Found: C, 73.18; H, 5.12.

Alkaline Hydrolysis of the Dimethyl Acetylenedicarboxylate Adduct IV.—A solution of 1.0 g. of potassium hydroxide and 0.8 g. (1.8 mmoles) of the adduct IV in 100 ml. of methanol was concentrated on a steam bath to ~50 ml., diluted with 50 ml. of water, and again concentrated to ~50 ml. The resulting solution was treated with 4.0 g. of potassium hydroxide, refluxed overnight, and then acidified with concentrated hydrochloric acid. Evaporation of this solution to dryness *in vacuo* left 0.5 g. of a residue which on extraction with 30 ml. each of water and chloroform melted at 170–171° dec. Several recrystallizations from water gave 0.2 g. (34%) of 2-carboxymethyl-3-phenyl-*o*-carboxycinnamic acid (VI), m.p. 190–191° dec. The compound displayed absorption maxima at $\lambda_{max}^{0.1NHCl}$ 265 (sh) mμ (ε 8450), $\lambda_{max}^{0.1NNaOH}$ 230 (sh) mμ (ε 14,600) and 263 (10,650), and λ_{max} 5.87 μ (COOH) and 6.14 (C = C). The n.m.r. spectrum showed peaks at τ_{CHCl_3} 2.06–2.95 (9 aromatic-H), 6.77 (2 aliphatic-H, singlet), and ~0 and ~6.7 (3 COOH, very broad).

Anal. Calcd. for $C_{18}H_{14}O_6$: C, 66.25; H, 4.32; neut. equiv., 109. Found: C, 66.10; H, 4.23; neut. equiv. (phenolphthalein end point), 123.

Evaporation of the above chloroform extracts and repeated recrystallization of the residue from water gave a small quantity of pure benzoic acid.

2-Carboxymethyl-3-phenyl-*o*-carboxycinnamic Acid (VI).—To a solution of 4.3 g. (110 mmoles) of potassium metal in 90 ml. of dry *t*-butyl alcohol was added under nitrogen 13.0 g. (75 mmoles) of diethyl succinate and 12.2 g. (54 mmoles) of *o*-benzoylbenzoic acid, and the mixture was refluxed for 3 hr. Although the initially formed precipitate of potassium *o*-benzoylbenzoate had not completely dissolved at the end of this period, the mixture was cooled, diluted with 50 ml. of water, and filtered. After concentration of the filtrate to about 50 ml. *in vacuo* and extraction with ether to remove unreacted diethyl succinate, the mixture was treated with 6 g. of potassium hydroxide and allowed to stand for 2 hr. at room temperature followed by 1 hr. on a steam bath. Acidification of the reaction mixture with hydrochloric acid and evaporation to dryness *in vacuo* gave a residue which was extracted with 50 ml. of chloroform and 40 ml. of hot water. On cooling, the aqueous extract deposited 2.0 g. (11%) of the crude acid, m.p. 163–165°. Two recrystallizations from water gave a pure sample, m.p. 190–192° dec., undepressed on admixture with the alkaline hydrolysis product of IV. The two samples were spectrally indistinguishable.

2,3-Diphenylindenone Oxide Dimers (VIIIa and VIIIb).—A solution of 10 g. (33.5 mmoles) of 2,3-diphenylindenone oxide (I) in 45 ml. of benzene was heated in a glass-lined bomb at 150° for 7 hr. The deep red solution obtained on cooling overnight faded rapidly on exposure to the air. The solvent was removed *in vacuo* and the residue crystallized from 25 ml. of acetone to give 4.7 g. (47%) of product, m.p. 200–202° (red coloration). Recrystallization from a 1:1 mixture of ethanol–acetonitrile gave an analytical sample of VIIIa, m.p. 203–204° (red coloration). The compound displayed absorption maxima at $\lambda_{max}^{CH_3CN}$ 257 mμ (ε

(14) Melting points reported for all compounds which were thermochromic at or below their melting point were variable and dependent on the rate of heating and state of subdivision of the compound. This was particularly pronounced in the case of the dimer hydrate XII.

(15) Infrared spectra of mineral oil suspensions are reported unless otherwise specified.

(16) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

10,400), 295 (1850), 305 sh (1550), 328 sh (119), 343 (143), 358 (137), and 375 (66), and λ_{max} 5.86 μ (C=O).

Anal. Calcd. for $C_{42}H_{28}O_4$: C, 84.54; H, 4.73; mol. wt., 596.6. Found: C, 84.47; H, 4.58; mol. wt. (thermal osmometer), 574.

On standing, the mother liquors deposited an additional 1.9 g. of solid which was extracted with 80 ml. of a hot 1:1 mixture of ethanol-acetonitrile and then recrystallized by dissolution in acetonitrile and addition of water to the hot solution. On cooling, 0.32 g. of VIIIb was collected, m.p. 235° (red coloration). An additional 0.10 g. (total yield 4.2%), m.p. 233° (red coloration), was isolated by dilution of the hot extracts with water followed by cooling. A second recrystallization of the combined product from acetonitrile-water gave 0.38 g., m.p. 238° (red coloration). The compound displayed absorption maxima at $\lambda_{max}^{CH_3CN}$ 245 (sh) mμ (ϵ 9300), 292 (1730), 300 sh (1550), 332 sh (80), 343 (104), 355 (100), and 372 sh (50), and λ_{max} 5.80 μ (C=O).

Anal. Calcd. for $C_{42}H_{28}O_4$: C, 84.54; H, 4.73; mol. wt., 596.6. Found: C, 84.56; H, 5.42; mol. wt. (thermal osmometer), 619.

By evaporation of the original mother liquors, dissolution of the residue in alcohol, and fractional precipitation with water, 0.1 g. of 2,3-diphenylindenone oxide could be isolated from the more soluble fraction. The mother liquors were shown spectrally to contain about 10% of the original weight of the starting material.

In a second run using conditions similar to those used in the formation of the dimethyl acetylenedicarboxylate adduct IV, a solution of 0.14 g. (0.47 mmoles) of the indenone oxide in 125 ml. of freshly distilled diethyl succinate was rapidly heated under nitrogen up to 175° and maintained at this temperature for 24 min. After cooling and allowing to stand for 65 hr., the resulting red solution was evaporated *in vacuo* and the residue crystallized from methanol to give 0.055 g. of crude dimer. The mother liquors yielded a total of 0.025 g. (18%) of unchanged 2,3-diphenylindenone oxide.

Acid Hydrolysis of Dimer VIIIa.—To a solution of 1.05 g. (1.76 mmoles) of the dimer in 20 ml. of benzene was added 60 ml. of acetonitrile followed by 3.0 ml. of concentrated hydrochloric acid. After stirring for 1 hr. at room temperature, the mixture was poured into water and the organic solvents were removed *in vacuo*. The aqueous solution was decanted from the gummy precipitate and the latter washed, dried, and recrystallized by dissolving in 5 ml. of ethanol at room temperature and then cooling. The product 0.750 g., after trituration with three ~4-ml. portions of acetonitrile weighed 0.159 g., m.p. 230–232° (red coloration).[14] The combined extracts were concentrated to ~7 ml., added to an equal volume of ethanol, and diluted with water to the cloud point to give 0.450 g., m.p. 200–220° (red coloration). Dissolution of this product in a little alcohol at room temperture followed by cooling gave an additional 0.441 g. (total yield of XII, 55%), m.p. 220–222° (red coloration),[14] which was spectrally indistinguishable from the higher melting product. If the product was heated at any stage during the work-up, purification became more difficult and lower yields were obtained. The product showed only benzenoid absorption in the ultraviolet and no carbonyl absorption in the infrared: λ_{max} 2.82 μ (OH).

Anal. Calcd. for $C_{42}H_{30}O_5$: C, 82.08; H, 4.89. Found: C, 81.93; H, 5.21.

Reaction of Dimer VIIIa with Dimethyl Acetylenedicarboxylate.—A mixture of 0.211 g. (0.354 mmole) of the dimer in 0.5 ml. (4.1 mmoles) of dimethyl acetylenedicarboxylate was heated under nitrogen for 20 min. in a bath maintained at 190–200°. The excess reagent was removed under reduced pressure at 100° and the resulting residue triturated with methyl alcohol to give 0.250 g. (0.581 mmole, 82%) of the adduct IV, m.p. 169–171°.

Reaction of Dimer Hydrate XII with Dimethyl Acetylenedicarboxylate.—The preceding procedure was repeated using 0.197 g. (0.32 mmole) of the hydrate XII. The crude product crystallized from methanol to give 0.100 g. (0.228 mmole, 71%) of IV, m.p. 165–169°. No other product was isolated.

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH 13, PENNSYLVANIA]

General Base Catalyzed Ethanolysis of Ethyl Trifluoroacetate

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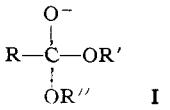
General base catalyzed ethanolysis of ethyl trifluoroacetate has been found. This finding is inconsistent with a concerted mechanism. The numerical value of the catalytic constant is consistent with a mechanism involving the base-assisted formation of an anionic tetrahedral intermediate but is not consistent with the alternative mechanism which involves the specific base–general acid catalyzed formation of a neutral tetrahedral intermediate.

Introduction

In substitution reactions on the carbonyl carbon of carboxylic esters of the type RCO_2R' no reaction intermediate definitely lying on the reaction path has ever been detected by kinetic means, or by the observation of a transient intermediate during the course of the reaction.[1] A tetrahedral intermediate, I, has been observed from the reaction of RCO_2R' with $M^+OR''^-$ in



I

dibutyl ether as detected by the disappearance of $\nu_{C=O}$ in the infrared.[4,5] The acyl part of RCO_2R' must contain strongly electron-withdrawing groups for this reaction to take place and the solvent must have a very low dielectric constant in order to favor I over $M^+OR''^-$. The tetrahedral intermediate formation has been observed for a number of R'' groups,[5] including ethyl, *n*-butyl, isopropyl, and *t*-butyl. It is at least reassuring when postulating tetrahedral reaction intermediates that such intermediates can be observed under special conditions.

Further evidence[6–11] of tetrahedral intermediate formation comes from concurrent hydrolysis and O^{18} exchange into the ester when hydrolysis is carried out in H_2O^{18}. The partitioning of the intermediate as measured by the ratio of the rates of hydrolysis and O^{18} exchange into the ester is equal to $2k_2/k_{-1}$ in the scheme

(1) However, Bruice and Fedor have kinetically demonstrated the necessity for an intermediate in the reaction of hydroxylamine with a thiol acetate,[2] and Hand and Jencks have similarly demonstrated the necessity for an intermediate in the reaction of amines with imido esters.[3]

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