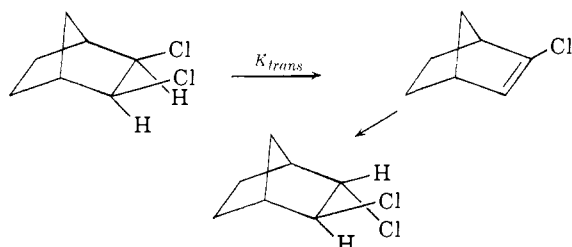


Further evidence for the concerted elimination may be derived from the ρ of the reaction, a low value (< 4) being associated with a *more concerted* elimination. As a corollary to this, one might predict that as the dihedral angle approached 90° from either 0 or 180° , the elimination would approach E1CB and that ρ for the reaction would increase. These predictions are currently being tested.

Using the above predictions, certain results reported in the literature become more meaningful. Cristol and Hoegger⁷ have reported that *cis* is faster than *trans* elimination in the bicycloheptyl system.



Obviously, a coplanar transition state is readily available for *cis* elimination but very difficult for *trans* elimination. Further evidence in support of these predictions is derived from the study of 11,12-dichloro-9,10-ethanoanthracene by Cristol and Hause.⁸ In this system *k-cis/k-trans* is about 8 and again it can be seen that for *cis* elimination a coplanar transition state can occur, whereas such a state is impossible (or nearly so) for *trans* elimination.

(7) S. J. Cristol and E. F. Hoegger, *J. Am. Chem. Soc.*, **79**, 3438 (1957).

(8) S. J. Cristol and N. I. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952).

(9) Alfred P. Sloan Fellow.

(10) Shell Oil Fellow, 1961-1962.

DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY
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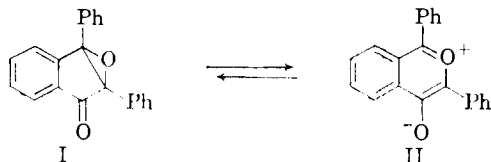
C. H. DEPUY⁹
R. D. THURN¹⁰
GENE F. MORRIS

RECEIVED JANUARY 13, 1962

REVERSIBLE VALENCE TAUTOMERIZATION OF AN AROMATIC SYSTEM

Sir:

While tropones have been observed to undergo light-induced valence tautomerizations,¹ no other aromatic compound has yet been converted to a valence tautomeric form.² We wish to report a remarkably facile equilibrium between the aromatic 1,3-diphenyl-2-benzopyrylium-4-oxide (II) and its valence tautomer, 2,3-diphenylindenone (I).

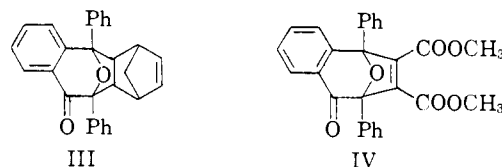


Although the latter compound has long been

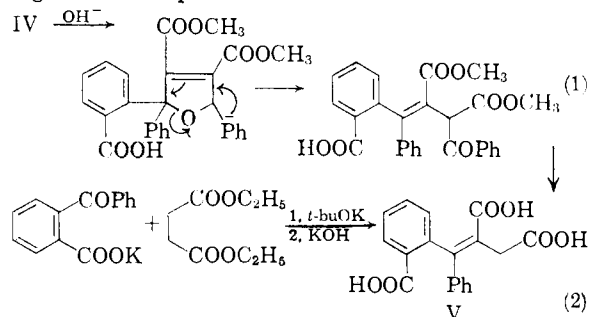
(1) E. J. Forbes, *J. Chem. Soc.*, 3864 (1955); O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **80**, 6685 (1958); **82**, 3642 (1960).

(2) The only report of such an isomerization, E. C. Taylor, W. W. Paudler and I. Kuntz, Jr., *ibid.*, **83**, 2967 (1961), was subsequently found to be incorrect, E. C. Taylor, R. O. Kan and W. W. Paudler, *ibid.*, **83**, 4484 (1961).

known to be thermochromic,³ the exact nature of this phenomenon has not been investigated. In agreement with the earlier observations, solutions of I were found to become red on heating to 80 – 100° , and to fade on standing at room temperature. In addition, it was found that the disappearance of the red color (λ_{max} $538 \text{ m}\mu$ in CH_3CN) was greatly accelerated by the addition of a variety of reagents including mineral acids, alkalis, bromine or oxygen. Significantly, the red color was destroyed instantaneously with bicyclo[2.2.1]-heptadiene or dimethyl acetylenedicarboxylate, reagents known to be highly reactive toward dipolar ions.⁴ Indeed, after heating at 135 – 145° for four hours, solutions of I in these reagents were converted in good yields to the 1:1-adducts, III, m.p. 214 – 215° , and IV, m.p. 170 – 171° , respectively.⁵



The structures of these compounds were supported both by the shifts of the infrared carbonyl peaks (Nujol mulls) of III (5.89μ) and dihydro-IV (5.87μ) from that of I (5.78μ), and by the close similarity of the ultraviolet spectra of III and dihydro-IV to that of tetralone. Compelling evidence for structure IV ultimately was obtained by treatment of IV with hot alcoholic alkali which led to the isolation of a $\text{C}_{13}\text{H}_{14}\text{O}_6$ tricarboxylic acid and benzoic acid. The new compound had a n.m.r. spectrum which showed a 9:2 ratio of aromatic (multiplet, 2.06 – 2.95τ) to aliphatic (singlet, 6.77τ) protons and an ultraviolet spectrum generally similar to that of *o*-carboxycinnamic acid. These data were in accord with the structure V expected upon consideration of the probable degradative sequence 1. Proof of structure V was



obtained by comparison with an authentic sample synthesized by an application of the Stobbe condensation in which diethyl succinate is condensed directly with potassium *o*-benzoylbenzoate⁶ (sequence 2).

(3) E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

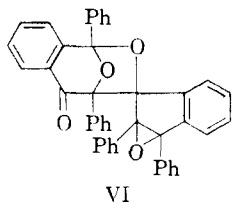
(4) R. Huisgen, R. Grashey, P. Lauer and H. Leitermann, *Angew. Chem.*, **72**, 416 (1960); R. Huisgen, H. Stangl, H. J. Sturm and H. Wagenhofer, *ibid.*, **73**, 170 (1961).

(5) All new compounds described herein have satisfactory carbon and hydrogen analyses.

(6) Use of the free salt rather than the ester of an *o*-ketobenzoic acid to prevent phthalide formation in the Stobbe condensation has been successfully employed previously, E. F. Ullman, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1956.

With the structures of IV and, by analogy, III thus established, there was little doubt that the colored species produced on heating of I must be the pyrylium oxide II, and indeed the appearance of a strong new band in the infrared of the colored species at 6.37μ (benzene) attributable to an enolate grouping provided strong support for this conclusion. On the other hand, the decolorization reaction could not necessarily be assumed to lead to the regeneration of I, since an irreversible conversion of II to other colorless products could also produce apparent thermochromic behavior. Clarification of this point was provided by the recovery of unchanged I after heating in benzene at 150° under conditions which led to its complete disappearance *via* II when bicyclo[2,2,1]heptadiene was used as solvent. Hence, the rate of disappearance of I is lower than the rate of its conversion to II, and therefore the pyrylium oxide II must be reconverted to its valence tautomer I.

In addition to recovered starting material, a dimer was also isolated after heating I in benzene. The new compound reacted readily with a 0.5 *N* solution of hydrochloric acid in moist acetonitrile at 25° to give a monohydrated derivative, $C_{42}H_{30}O_5$. Like I, the dimer was also thermochromic, the same colored species arising as shown by the reaction of the dimer with excess dimethyl acetylenedicarboxylate at 190 – 200° to give two equivalents (82% yield) of the adduct IV which had previously been isolated from the reaction with I itself. Based on its acid lability, a single infrared carbonyl peak at 5.86μ , and an ultraviolet spectrum which was very similar to that of III in both peak positions and extinction coefficients, the dimer is tentatively assigned structure VI.



VI

Additional evidence concerning the structure and stereochemistry of this product, and a further elaboration of the chemistry of I and related compounds will be presented in a future publication.

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EDWIN P. ULLMAN

J. E. MILKS

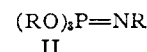
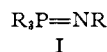
RECEIVED MARCH 3, 1962

PHOSPHORAMIDATE ANIONS: THE PREPARATION OF CARBODIIMIDES, KETENIMINES AND ISOTHIOCYANATES

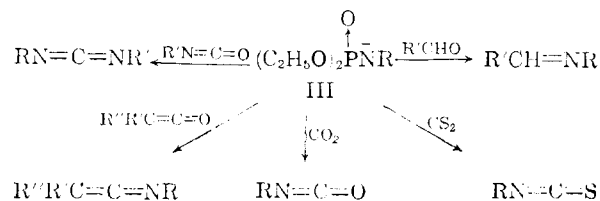
Sir:

The investigation of the utility of dialkyl phosphonate carbanions in olefin synthesis¹ prompted examination of their nitrogen analogs in comparable reactions. We have found the behavior of dialkyl phosphoramidate anions (III) toward carbonyl compounds to be similar to phosphinimines² (I) and phosphorimidates³ (II). The

(1) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).



anion (III), prepared by reaction of sodium hydride with the phosphoramidate in dimethoxyethane, reacts smoothly with isocyanates, ketones, carbon dioxide, carbon disulfide and aldehydes to form, respectively, carbodiimides, ketenimines, isocyanates, isothiocyanates, and imines. Since (in contrast to I and II) the phosphoramidates are readily available,⁴ this synthesis is the basis of convenient laboratory procedures for preparation of unsaturated nitrogen compounds.



The addition of phenyl isocyanate to III (R = C_6H_{11}) in 1,2-dimethoxyethane gave, at room temperature, a precipitate of sodium diethyl phosphate and after distillation of the mother liquor, a 60% yield of N-phenyl-N'-cyclohexyl carbodiimide,⁵ b.p. 116–120 (0.35 mm.). Its infrared spectrum showed characteristic carbodiimide absorption at 2150 cm.^{-1} .⁶ Conversion to N-phenyl-N'-cyclohexyl urea⁷ was accomplished by stirring with dilute HCl.

Treatment of III (R = C_6H_{11}) with phenylethylketene gave a 58% yield of phenylethylketene-cyclohexylimine (R = C_6H_{11} , R' = C_2H_5 , R'' = C_6H_5), b.p. 122–124° (0.5 mm.) (*Anal. Calcd.* for $C_{18}H_{21}N$: C, 84.53; H, 9.25; N, 6.17. Found: C, 84.36; H, 9.28; N, 5.95). The ketenimine structure was confirmed by its strong absorption at 2000 cm.^{-1} .⁸ Treatment with dilute HCl gave N-cyclohexyl- α -phenylbutyramide. The structure of the amide was confirmed by comparing it to an authentic sample prepared from α -phenylbutyryl chloride and cyclohexylamine.

Passage of CO_2 through a solution of I (R = C_6H_{11}) gave two products, cyclohexyl isocyanate (24%), b.p. 70–71° (15 mm.) and dicyclohexylcarbodiimide (53%), b.p. 100–102° (0.75 mm.). The isocyanate is undoubtedly a precursor of the carbodiimide. Addition of carbon disulfide to III (R = $n\text{-C}_4\text{H}_9$) gave *n*-butyl isothiocyanate (75%), b.p. 169–170°. Finally, the treatment of III (R = CH_3O) with benzaldehyde produced *o*-methylbenzaldoxime⁹ (82%), b.p. 90° (15 mm.). The structures of these materials were verified by

(2) H. Staudinger and E. Hauser, *Helvetica Chimica Acta.*, **4**, 861 (1921).

(3) M. I. Kabachnik and V. A. Gelyarov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.*, 790 (1956).

(4) Dialkyl phosphoramidates may be prepared by treating a dialkyl phosphorochloridate with a primary amine or more conveniently by treating a dialkyl phosphite with a primary amine and carbon tetrachloride (F. R. Atherton, H. T. Openshaw, and A. R. Todd, *J. Chem. Soc.*, 660 (1945)).

(5) H. G. Khorana, *J. Chem. Soc.*, 2081 (1952).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 267.

(7) A. Skita and H. Rolfe, *Chem. Ber.*, **53**, 1248 (1920).

(8) M. S. Newman, T. Fukunaga and T. Miwa, *J. Am. Chem. Soc.*, **82**, 873 (1960).

(9) K. V. Auwers and B. Ottens, *Chem. Ber.*, **57**, 447 (1924).