

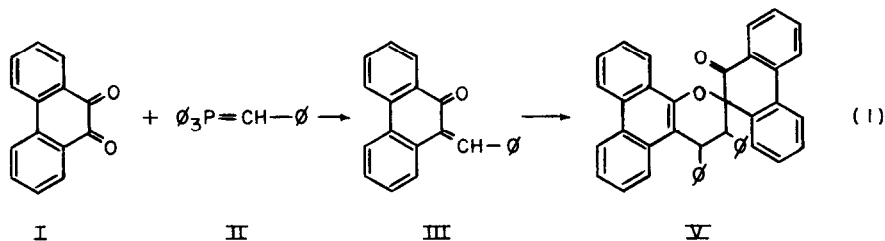
REACTIONS OF QUINONES WITH YLIDES

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Reactions of ylides with aldehydes and ketones have received enormous attention within the past fourteen years (1). Surprisingly benzoquinones have not been studied successfully other than the report (2) that 9,10-phenanthrenequinone (I) reacts with benzylidenetriphenylphosphorane (II) to give 10-benzylidene-9-phenanthrone (III, Equation 1, white, mp 146-147°). It has been found presently that the product previously given as III (2) is a

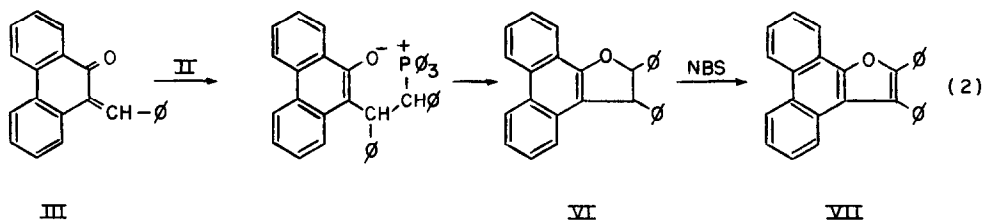


dihydrofuran, that reactions of I with phosphorus ylides may give 10-alkylidene-9-phenanthrones (o-quinomethanes), phenanthro[1]cyclobutenes, 9,10-phenanthroquinodimethanes and phenanthro[1]dihydrofurans, and that 1,4-naphthoquinone (IV) behaves as an effective carbonyl reagent with ylides to yield 4-alkylidene-1-naphthones (p-quinomethanes). Versatile preparative methods for o-quinomethanes are of value because study of the aromatic properties and the chemistry of these highly reactive intermediates and the structures of their dimers can be expedited (3). Phenanthro[1]cyclobutenes are of interest with respect to their structural relationships with 9,10-phenanthroquinodimethanes and for synthesis of phenanthro[1]cyclobutadiene intermediates (4). The behavior of IV with ylides is of importance in that transformations of typical quinones are allowable which cannot be

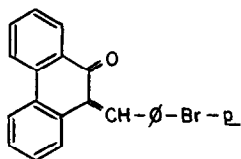
accomplished effectively by organo-metallic reagents (5).

Slow addition of II to excess I in dimethyl sulfoxide at 25°, hydrolysis, and chromatography on alumina yields III (>> 15%), an instable white solid whose melting point is time dependent. The structure of III (6) is established by its carbonyl absorption at 5.98μ, its ultraviolet absorption, and its nmr signals at τ 2.92 (aryl H, multiplet, area 13) and 3.17 (vinyl H, singlet, area 1). III undergoes rapid conversion to a colorless dimer when heated whose structure is assigned as V (mp 250°) on the basis of precedent (3); the structure is consistent however with its absorption and its nmr spectra.

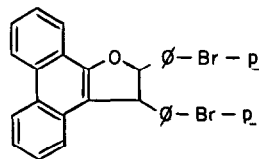
I (2 equivalents) when added to II at 25° or under conditions previously described (2) gives 2,3-diphenylphenanthro[1]dihydrofuran (VI, white, mp 245-247°, 86-46%). VI corresponds exactly to that given previously as III. The structure of VI is assigned from its molecular weight, its infrared absorption (2,7) at 6.14 (C=C), 6.23 (aryl C=C) and 9.78μ (C=C-O), its nmr absorption at τ 2.67 (aryl H, multiplet, area 18), 4.19 (benzyl H, doublet, area 1) and 4.33 (-O-CH-, doublet, area 1), and its conversion by N-bromosuccinimide (Equation 2) to 2,3-diphenylphenanthro[1]furan (VII, white, mp 194°, 81%). The principal spectral features of VII are its absorption at 9.1μ (vinyl ether) and its nmr signals at τ 2.5 (multiplet, 18H).



Reaction of I with *p*-bromobenzylidene triphenylphosphorane is similar to that with II because, depending on the stoichiometry and the order of addition, 10-(*p*-bromobenzylidene)-9-phenanthrone (VIII, white) and 2,3-di-(*p*-bromophenyl)phenanthro[1]dihydrofuran (IX, white, mp 152°) are obtained. The dihydrofurans apparently arise (Equation 2) by Michael addition of the arylalkylidene phosphoranes to the 10-arylalkylidene-9-phenanthrones followed by O-alkylation with expulsion of triphenylphosphine. Formation of dihydrofurans from α,β-unsaturated ketones is a new reaction of phosphoranes.

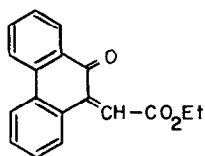


VIII

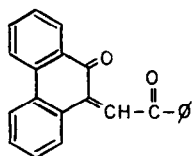


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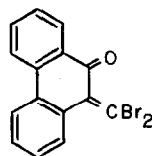
I is converted by one equivalent of carboethoxymethylenetriphenylphosphorane, α -benzoylmethylenetriphenylphosphorane or diethyl phenacylphosphonate anion, dibromomethylenetriphenylphosphorane and fluorenylidetriphenylphosphorane (8) to X (yellow, mp 158° ; >C=O at 5.79 and 5.87μ), XI (yellow, mp 222° ; >C=O at 5.99 - 6.00μ , doublet), XII (yellow, mp 135° , >C=O at 5.96μ) and XIII (red, mp 205° , >C=O at 6.01μ). XX-XIII exhibit ultra-violet and nmr properties which agree with the structures proposed. Since the \underline{o} -quinomethanes X-XIII do not dimerize as readily as do III and VIII, electronegative or/and bulky substituents at the 11-position in these derivatives retard such processes.



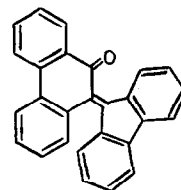
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XI

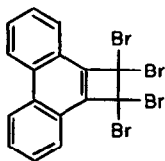
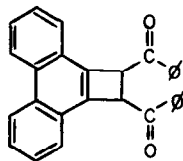


XII



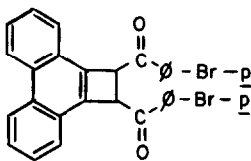
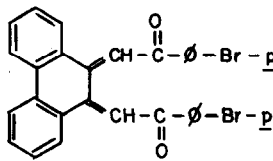
XIII

I or its subsequent \underline{o} -quinomethanes will react with appropriate ylides to give substituted phenanthro[1]cyclobutenes advantageously. Dibromomethylenetriphenylphosphorane affords 1,1,2,2-tetrabromophenanthro[1]cyclobutene (XIV, white, mp 165 - 167°) in reaction with I or with XII. Excess α -benzoylmethylenetriphenylphosphorane or diethyl phenacylphosphonate anion (8) react effectively ($> 65\%$) with I to give 1,2-dibenzoylphenanthro[1]cyclobutene (XIV, white, mp 232°). The structure of XIV is confirmed from its single carbonyl peak at 6.0μ , its nmr signals at τ 2.04 and 5.04 for 18 aryl and 2 benzyl protons, and its

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ultraviolet absorption at 256 (ϵ 64,500), 275 (ϵ 49,100) and 324 $m\mu$ (ϵ 29,500). Reactions of the ylides thus occur with the intermediate XI at the carbonyl group at C-9 rather than at C-12 or by Michael addition as found with III and VIII. XIV then probably results from intramolecular cyclization of the crowded intermediate quinodimethane.

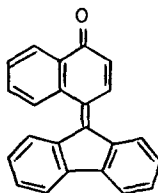
I and α -*p*-bromobenzoylmethylenetriphenylphosphorane yield 1,2-di(*p*-bromobenzoyl)phenanthro[1]cyclobutene (XVI, white, mp 275 $^{\circ}$) and 9,10-phenanthroquinodi-(α -*p*-bromobenzoyl)methane (XVII, yellow, mp 255 $^{\circ}$). XVI is a phenanthro[1]cyclobutene because of its

XVIXVII

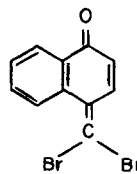
color and the similarity of its infrared and ultraviolet spectra to that of XV. XVII is the only quinodimethane isolated in this study. Its structure is indicated by its yellow color, its strong infrared absorption for carbonyl and olefin groups at 6.0 (singlet) and 11.58 μ , its ultraviolet maxima at 253 (ϵ 69,000), 261 (ϵ 72,500), 284 (ϵ 41,000), 308 (ϵ 31,000) and 360 $m\mu$ (ϵ 10,000), and its conversion to XVI upon heating.

1,4-Naphthoquinone (IV) reacts with fluorenylidetriphenylphosphorane and with dibromomethylenetriphenylphosphorane in benzene at 25 $^{\circ}$ giving 4-(9-fluorenylidene)-1-naphthone (XVIII, red, $>C=O$ at 5.85 μ) and 4-dibromomethylene-1-naphthone (XIX, yellow, $>C=O$ at 5.83 μ). The *p*-quinomethanes are readily isolable products which may be prepared efficiently. The structures of XVIII and XIX are assignable from their analyses, spectral properties

and on the basis of their origins.



XVIII



XIX

Acknowledgment: This research was supported by the National Science Foundation and by the Petroleum Research Fund.

References

1. A. W. Johnson, Ylid Chemistry, Academic Press, New York, N. Y. (1966).
2. J. Parrick, Can. J. Chem., 42, 190(1964).
3. P. D. Gardner and H. Sarrafizadeh R., J. Am. Chem. Soc., 25, 641 (1960).
4. M. P. Cava and D. Mangold, Tetrahedron Letters, 1751 (1964); M. P. Cava and B. Y. Hwang, ibid., 2297 (1965).
5. H. M. Crawford and M. McDonald, J. Am. Chem. Soc., 71, 2681 (1949).
6. All new compounds reported have proper analyses and molecular weights. Products given without melting points decompose on heating.
7. The weak infrared absorption at 6.14μ was previously (2) misassigned as that for carbonyl.
8. For literature concerning preparation of these reagents, see reference 1.