(24) We have been unsuccessful in preparing the corresponding *O,O'*-diethyl derivative of DTS^{2-} by treatment of diethyl squarate (**8**) with B_2S_3 [F. M. Dean, J. Goodchild, and A. W. Hill, *J. Chem. Soc. C*, 2192 (1969)] or P_4S_{10}.

(25) F. J. Hollander and D. Coucouvanis, *J. Am. Chem. Soc.*, **96**, 5646 (1974); D. G. Holah and D. Coucouvanis, *ibid.*, **97**, 6917 (1975); D. Coucouvanis, D. G. Holah, and F. J. Hollander, *Inorg. Chem.*, **14**, 2657 (1975); D. Coucouvanis, D. Swenson, N. C. Baenziger, D. G. Holah, A. Kostikas, A. Simopoulos, and V. Petrouleas, *J. Am. Chem. Soc.*, **98**, 5721 (1976).

(26) E. E. Reid, "Organic Chemistry of Bivalent Sulfur", Vol. IV, Chemical Publishing Co., New York, N.Y., 1962, pp 31–33.

(27) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

(28) Since no reaction had occurred after 18 h when **2b** was dissolved in ethanol, a diketene intermediate is not involved. Ring opening could also occur after addition of only one molecule of amine to give a ketene enolate which could go on to the observed product.

(29) A. T. Blomquist and E. A. LaLancette, *J. Am. Chem. Soc.*, **83**, 1387 (1961).

(30) W. Ried and R. Lantzsch, *Chem. Ber.*, **104**, 679 (1971).

(31) E. Müller and A. Huth, *Tetrahedron Lett.*, 1031, 1035, 4359 (1972); *Chem.-Ztg.*, **96**, 585 (1972); J. Hambrecht, H. Straub, and E. Müller, *Chem. Ber.*, **107**, 3962 (1974).

(32) T. L. Cottrell, "The Strengths of Chemical Bonds", 2d ed, Butterworths, London, 1958, pp 270–289, Table 11.5.1.

(33) R. C. DeSelms, C. J. Fox, and R. C. Riordan, *Tetrahedron Lett.*, 781 (1970).

Crystal and Molecular Structure of *trans*-Biphthalyl, $C_{16}H_8O_4$. Reaction of Substituted Phthalic Anhydrides with Trialkyl Phosphites

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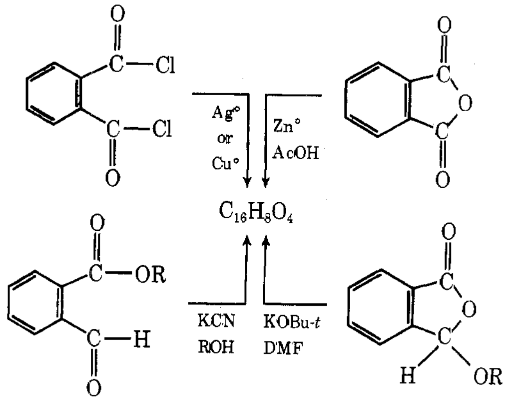
The crystal and molecular structure of *trans*-biphthalyl, the main product of the reaction of phthalic anhydride with triethyl phosphite, has been elucidated by x-ray crystallographic techniques. The yellow substance crystallizes in the monoclinic system, space group $P2_{1/c}$ with four asymmetric units per unit cell. The structure was refined by full-matrix least-squares techniques to a final R factor on F of 3.5% based on 571 observations above background. The molecule is planar, and some of the bond angles formed by the trigonal carbon atoms are significantly larger ($\Delta \sim 12°$) than the normal 120° value. It is suggested that the flexibility inherent in C–C–C, C–C–O, and C–O–C bond angles permits (a) the observed angle expansions which are required to allow for coplanarity of the chromophore O=C–C=C–C=C–C=C–C=O in the crowded molecule; and (b) the observed angle contractions, which are required to establish the five-membered rings. This effect accounts for the existence of octaphenyl-, octachloro-, and octabromo-*trans*-biphthalyl, although there is no assurance that the octahalo compounds have completely planar molecules.

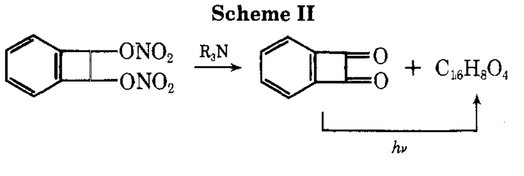
The classical researches on the structure of phthalic anhydride, phthaloyl chloride, phthalaldehydic esters, and 3-alkoxyphthalides (Scheme I) led to a series of yellow and colorless isomers of the formula $C_{16}H_8O_4$, known as "biphthalyls".[2,3] Some of those experiments were later repeated[4] and extended.[5]

Scheme I



Structurally related $C_{16}H_8O_4$ compounds have been recently obtained from benzocyclobutene-1,2-diol dinitrate[6] (Scheme II), and from the photolysis[7–9] of benzocyclobutadienoquinone.[6]

Scheme II



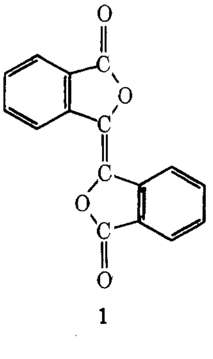
The biphthalyls were initially formulated as the trans and cis isomers, **1** and **2**, of the bis-γ-lactone of *o,o'*-dicarboxybenzoin.[2,3] However, the work of Cava[6] and of Bird[10] suggests that, with one exception,[7,8] the colorless substance designated as *cis*-BP (**2**)[11] is identical with the biisocoumarin (**3**) that was obtained as a by-product of the benzocyclobutadienoquinone synthesis[6] (Scheme II). Thus, the *acid-catalyzed* isomerization

$$\text{yellow } trans\text{-BP } (1) \xrightarrow{H(+)} \text{colorless "}cis\text{-BP } (2)\text{"}\ ^{5}$$

is actually

$$trans\text{-BP } (1) \xrightarrow{H(+)} \text{biisocoumarin } (3)^{10}$$

Scalar molecular models disclose an increasing degree of intramolecular crowding in the series: **3** < **1** ≪ **2**. Nevertheless (and this constitutes the exception mentioned above), Staab[7,8] has reported the isolation of authentic *cis*-BP (**2**, 5%), together with **1** (25%) and **3** (4%) from the photolysis of benzocyclo-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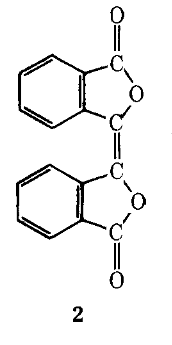
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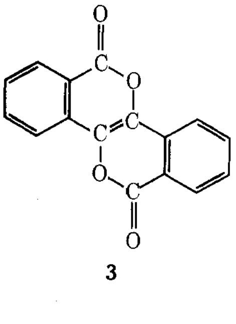
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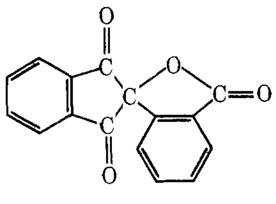
butadienoquinone.[6] The thermal *cis*-**2** → *trans*-**1** isomerization was observed at 200 °C.

In 1959 we reported the deoxygenative coupling of PA[11] to *trans*-BP (**1**), by means of triethyl phosphite.[12,13] Bird and Wong[14] confirmed these results, and made the significant observation that biisocoumarin[6] (**3**) was formed as a by-product in about 25% yield. These authors,[15] as well as Markgraf et al.,[16] have extended the biphthalyl condensation to thiophthalic anhydride.

There is in the literature a fourth related $C_{16}H_8O_4$ isomer, the spirolactone[17] **4**. This substance was obtained by Brown[9]



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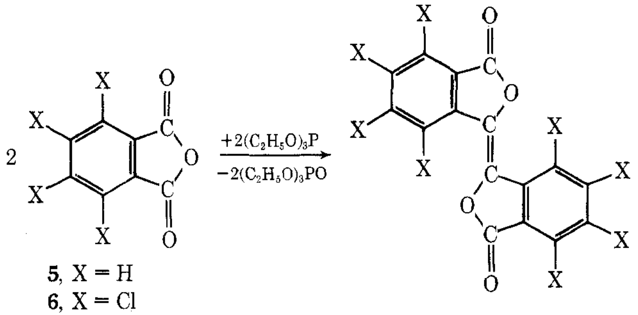
(but not by Staab[7,8]) from the photolysis of benzocyclobutadienoquinone, and has been isomerized into *trans*-BP (**1**), thermally[17] (250–300 °C), and on heating with tertiary amines.[9,17,18]



5, X = H
6, X = Cl
7, X = Br
8, X = C_6H_5

1, X = H
9, X = Cl
10, X = Br
11, X = C_6H_5

The present investigation had three purposes: (1) to study the molecular structure of yellow BP (**1**) by x-ray crystallography; (2) to confirm the BP structure (**9**) previously assigned[13] to the yellow-orange crystals obtained from tetrachloro-PA (**6**) and triethyl phosphite, and to extend the reaction to other hindered PA derivatives, **7** and **8**; (3) to correlate the new and the published data in order to arrive at a rational explanation for the formation of *trans*- and *cis*-BP, and of biisocoumarin, in the various reactions mentioned above.

Experimental Section

Reaction of Phthalic Anhydride with Triethyl Phosphite. A mixture of phthalic anhydride and freshly distilled triethyl phosphite (½ mol ratio) was stirred under argon for 24 h at ca. 190 °C. A third molar equivalent of the phosphite was introduced, and the mixture was stirred for an additional 24-h period. The crystals which separated at 20 °C were collected, and were washed repeatedly with warm benzene; they represented 65% of the expected *trans*-BP (**1**), mp ca. 350 °C (see Table II). The pale-yellow crystals used in the x-ray analysis were obtained after recrystallization from mesitylene.

The mother liquid which remained after filtration of the *trans*-BP (**1**) was distilled under vacuum to remove triethyl phosphate. Unreacted phthalic anhydride was recovered by sublimation, and the residue was submitted to TLC (Table II). A spot attributed to biisocoumarin (**3**) was observed at R_f 0.48; the remaining **1** gave a spot at R_f 0.61, and there was a relatively weak spot at R_f 0.37.

The crystals of **1** obtained from xylene or from mesitylene sublimed at ca. 260 °C during slow heating on a hot stage. In open capillary, sublimation was also detected at ca. 260 °C. The sublimate resublimed at about the same temperature. On relatively rapid heating, the material melted to a clear liquid at 352–354 °C. When a sealed tube containing crystals of *trans*-biphthalyl was immersed in a bath preheated to 370 °C and the sample was kept for 2.5 h at that temperature, a clear melt was produced. This melt resolidified to a material which proved to be identical with the initial **1**, according to ir spectrum (Nujol mull) and TLC behavior.

Crystal Data. *trans*-Biphthalyl, $C_{16}H_8O_4$: monoclinic; $P2_{1/c}$; a = 10.196 (6), b = 3.778 (3), c = 15.090 (8) Å, cos β = −0.1228 (2); ($\lambda_{\mathrm{CuK}\alpha}$ = 1.5418 Å at 21 °C); Z = 2 (half a molecule per asymmetric unit); d_{calcd} = 1.52 g cm^{-3}, d_{meas} (by flotation in benzene–diiodomethane) = 1.50 (1) g cm^{-3}; μ(Cu Kα) = 9.38 cm^{-1}.

Data Collection and Structure Refinement. Precession and Weissenberg photographs of the ($hk0$), (hkl), ($0kl$), ($1kl$), and ($h0l$) zones showed systematic absences ($h0l$) for l odd and ($0k0$) for k odd implying space group $C_{2h}{}^5 = P2_{1/c}$. The cell dimensions were determined by a least-squares fit of the observed 2θ angles for 26 reflections centered automatically on a four-circle diffractometer.

Intensity data were collected from a light yellow crystal of rectangular prismatic habit and dimensions 0.3 × 0.1 × 0.05 mm. The crystal was mounted on a glass fiber and oriented along b^* (the prism axis). Data were obtained on a computer-controlled Picker four-circle diffractometer[19] using nickel-filtered Cu Kα radiation. Two independent sets of data (hkl and $\bar{h}kl$) were collected for 2θ (Cu Kα) < 55°. The 1337 observations gave 571 independent reflections with $F_o{}^2 > 3\sigma_{\mathrm{count}}(F_o{}^2)$ with $\sigma(F_o{}^2)$ being based on Poisson counting statistics. The intensities of two standard reflections were measured periodically, and there was no evidence of crystal deterioration. Data were collected by θ–2θ step scans using a fixed scan width $\Delta 2\theta$ = 2.00° and a step size $\delta 2\theta$ of 0.02°. The center of the scan range was set at the Bragg angle calculated for 1.5418 Å. Background was measured as the average of the first and last ten points of the scan. The take-off angle was 3.0° and pulse height–pulse shape discrimination system was used.

Structure factors were derived in the usual way; no absorption correction was necessary. Normalized structure factors (E's) were used in a multiple solution direct methods technique as described by Germain, Main, and Woolfson[20] to determine phases from which an E map revealed the coordinates of all nonhydrogen atoms. The structure was refined by full-matrix least squares, minimizing the function $\Sigma w\Delta^2$ with $\Delta = |F_o| - |F_c|$ with weights $w = 4F_o{}^2/\sigma^2(F_o)^2$ and $\sigma^2(F_o{}^2) = \sigma_{\mathrm{count}}{}^2(I) + (0.03F^2)^2$. All hydrogen atom positions were located by difference Fourier synthesis following isotropic refinement. The atomic scattering factors for all nonhydrogen atoms were taken from a standard source,[21] while that for hydrogen atoms was the best spherically averaged value of Stewart et al.[22]

The final least-squares cycles included anisotropic thermal parameters for the nonhydrogen atoms and individual isotropic thermal parameters on the hydrogen atoms. The final values of $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = \{[w||F_o| - |F_c||^2]/\Sigma wF_o{}^2\}^{1/2}$ were 0.035 and 0.043, respectively,[23] and the error in an observation of unit weight was 2.34. The maximum density in a final difference electron density synthesis was 0.15 electrons Å^{-3}, approximately 25% of the height of a hydrogen atom. The final parameters are presented in Table III.[24]

Reaction of Tetrasubstituted Phthalic Anhydrides with Triethyl Phosphite. Tetrachloro-PA (**6**) or tetrabromo-PA (**7**) was mixed with 10 molar equiv of triethyl phosphite and the mixture was stirred, under N_2, for 5 min at 155 °C. The mixture was cooled, and the yellow crystals were filtered off and washed repeatedly with warm benzene, for octachloro-BP (**9**), or with warm toluene for octabromo-BP (**10**). A mixture of tetraphenyl-PA (**8**) and triethyl phosphite (10 molar equiv) was stirred for 48 h at 180 °C, and the crystals of octaphenyl-BP (**11**) were washed with warm benzene. Additional data are furnished in Table II.

Anal. Calcd for $C_{16}O_4Br_8$: C, 21.5; Br, 71.4. Found: C, 21.3; Br, 71.2. Calcd for $C_{64}H_{40}O_4$: C, 88.0; H, 4.6. Found: C, 88.0; H, 4.7.

The octahalo-BP undergo extensive decomposition on prolonged heating with trialkyl phosphites.

Reaction of Biphthalyls with Concentrated Sulfuric Acid. *trans*-BP (**1**) was mixed with concentrated H_2SO_4, and the mixture was stirred for 2 h at 140 °C, cooled to 20 °C, and poured into ice. The colorless crystals of crude biisocoumarin (**3**) (ca. 50%) were purified as described;[10] cf. Table II. The same procedure was applied to the octachloro- and octabromo-BP (**9** and **10**) but in those cases no pure new compound could be isolated.

Results and Discussion

Molecular Structure of *trans*-BP (1). The structure and numbering system for the atoms in an individual molecule, whose two halves are related by the center of symmetry, are shown in Figure 1. The 50% probability vibrational ellipsoids

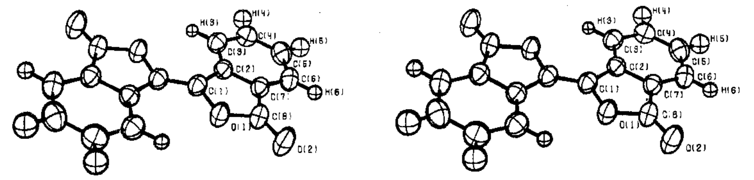


Figure 1. Stereoscopic drawing of an isolated molecule of *trans*-biphthalyl (1), $C_{16}H_8O_4$. The 50% probability ellipsoids are shown (hydrogen atoms are isotropic).

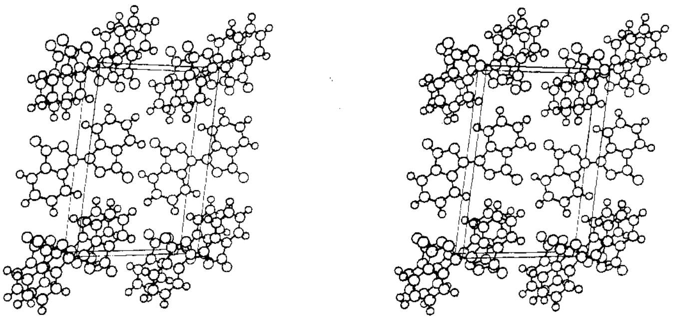
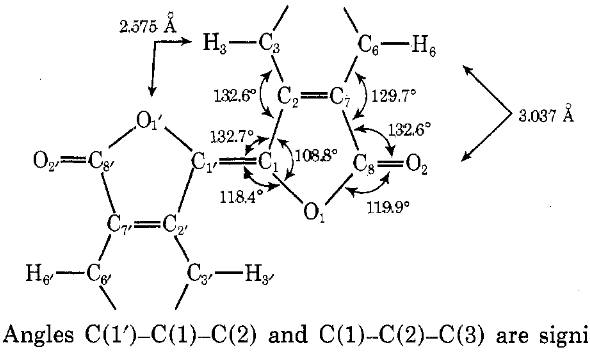


Figure 2. Stereoscopic drawing showing the contents of the unit cell with all molecules, $C_{16}H_8O_4$, completed ($Z = 2$). In addition, there are two complete molecules no parts of which lie within the unit cell; these appear at the far upper left and near lower right hand corners, and are included to show the packing arrangement. The asymmetric unit consists of half a molecule (or $C_8H_4O_2$), and there are four asymmetric units per unit cell. The view is approximately along *b*, and *c* is vertical.

are also displayed in Figure 1. The packing of the molecules in the crystal is depicted in Figure 2. The interatomic distances, bond angles, and their standard deviations are summarized in Table I and were calculated from the positional parameters given in Table III[24] and the correlation matrix. Some significant least-squares planes are presented in Table IV.[24]

The data confirm the structure and the configuration assigned to the main product of the reaction of phthalic anhydride with triethyl phosphite.[12,13] The molecule of *trans*-BP (1) is perfectly planar, as shown in Table IV.[24] The bond distances are unexceptional, and the most interesting features of the molecule reside in the bond angles which are emphasized in the partial formula.



Angles C(1′)–C(1)–C(2) and C(1)–C(2)–C(3) are significantly larger than the trigonal 120° value. Angle O(1)–C(1)–C(2) is smaller than 120°. The net effect of these bond angle deformations is to move H(3) away from O(1′). The nonbonded distance H(3)–O(1′) is 2.575 Å, while the estimated[25] van der Waals radii for H and O are about 1.1 and 1.40 Å, respectively. There is enough available space in the planar molecule to accommodate at least a hydrogen atom on the aromatic C(3) position.

A second set of expanded bond angles included O(2)–C(8)–C(7) and C(8)–C(7)–C(6), and this effect increases the separation between H(6) and O(2); cf. the nonbonded distance H(6)–O(2).

Table I. Bond Distances (Å) and Angles (Deg)

Distances		Angles	
	A. In Five-Membered Ring		
C(1)–C(1′)[a]	1.329 (4)	C(1′)[a]–C(1)–C(2)	132.7 (3)
C(1)–C(2)	1.452 (3)	C(1′)–C(1)–O(1)	118.4 (3)
C(2)–C(7)	1.388 (3)	C(1)–C(2)–C(3)	132.6 (2)
C(7)–C(8)	1.460 (3)	C(1)–C(2)–C(7)	106.7 (2)
C(8)–O(1)	1.395 (3)	C(2)–C(7)–C(8)	108.4 (2)
O(1)–C(1)	1.397 (3)	C(7)–C(8)–O(1)	107.4 (2)
O(2)–C(8)	1.196 (3)	C(8)–O(1)–C(1)	108.6 (2)
		O(1)–C(1)–C(2)	108.8 (2)
		O(2)–C(8)–C(7)	132.6 (2)
		O(2)–C(8)–O(1)	119.9 (2)
		C(8)–C(7)–C(6)	129.7 (2)
	B. In Six Membered Ring[b]		
C–C	1.386 (6)	C–C–C	120.0 (22)
C–H	0.99 (3)	H–C–C	120.0 (80)

[a] Atom C(1′) is related to C(1) by the center of symmetry. [b] These are average quantities. The estimated standard deviation in parentheses is the larger of an individual deviation or the standard deviation as calculated on the assumption of equivalence.

Table II. Properties of *trans*-Biphthalyl, Biisocoumarin, and Some Octasubstituted Biphthalyls

Compd	Subst X	Mp, °C	Ir bands,[a] cm^{-1} C=O	R_f[b]	Yield,[c] %
		Biphthalyls			
1	H	352–354[d]	1780	0.61	65
9	Cl	375–377[e]	1780 1730		44
10	Br	408–409[f]	1780 1730		40
11	C_6H_5	407–409[g]	1780	0.79	45
		Biisocoumarin[h]			
3	H	330–334[i]	1720[j]	0.48	

[a] Nujol mulls. [b] On unactivated silica gel plates, using toluene (1) or toluene–ethyl acetate, 19:1 (11). No suitable solvent was found for 9 or 10. [c] Based on the corresponding phthalic anhydride. [d] From xylene or mesitylene. The crystals sublime at ca. 260 °C; the melting point was obtained on rapid heating, in open or sealed capillaries. [e] From *o*-dichlorobenzene. [f] Before and after repeated washings with warm toluene. [g] Before and after repeated washings with warm benzene. [h] Prepared as described in ref 10. [i] From toluene. [j] A sharp band at 1175 cm^{-1} is useful for characterization purposes.

The five-membered rings have bond angles which are close to those of the regular pentagon (108°).

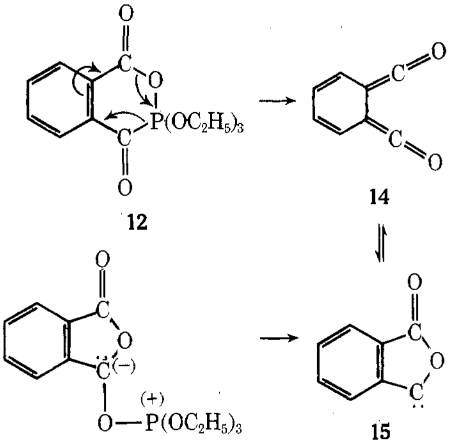
It appears that the flexibility inherent in C–C–C, C–C–O, and C–O–C bond systems permit the bond angle expansions which are required to allow for the coplanarity of the chromophore O=C–C=C–C=C–C=C–C=O in the relatively crowded *trans*-BP (1). This angle flexibility permits also the contractions which are required to establish the five-membered rings in the shape of a regular pentagon.

There are no unusual intermolecular distances in the crystals of *trans*-BP (1); however, the packing shows an interesting feature (cf. Figure 2). Pairs of molecules (at the upper and lower edges of the figure) are perfectly stacked, but other pairs (in the middle of the figure) are not stacked with respect to each other or in relation to the stacked pairs. This relatively inefficient packing may account for the sublimation that is observed at about 260 °C. We speculate that there could be another phase transition above this temperature leading to a more efficient packing which would account for the observed melting point of 352–354 °C. However, the postulated second phase transition was not detected in the present investigation.

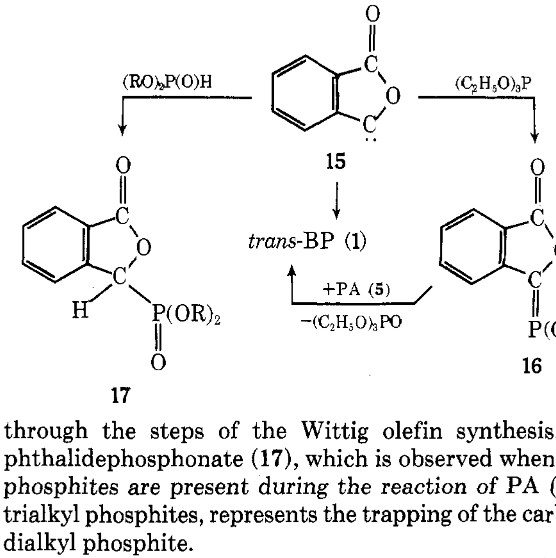
Reaction of Tetrasubstituted Phthalic Anhydrides with Triethyl Phosphite. The data in Table II support the conclusion that the yellow-orange substance isolated from the reaction of tetraphenyl-PA (8) is also the *trans*-BP derivative, 11. The estimated[25] half-width of the benzene ring is 1.85 Å; and with a van der Waals radius of 1.40 Å for the divalent oxygen, it is evident that a planar octaphenyl derivative 11 analogous to 1 requires even greater bond angle deformations than those observed in 1. Yet the similarities of the C=O stretching bands of 11 and 1, as well as the color of the two substances, suggest similar molecular structures.

The steric problem may be comparable or worse for the octachloro-*trans*-BP (9) (Cl radius[25] ~1.80 Å), and much worse for the octabromo-*trans*-BP (10) (Br radius ~1.95 Å). The Nujol mulls of the analytical samples of both yellow octahalo derivatives exhibited two carbonyl bands. Repeated recrystallizations of the chloro compound, 9, did not alter the spectrum. The bromo compound, 10, could not be recrystallized. Neither halogen derivative could be analyzed by TLC for lack of solubility. It is possible, but unlikely, that the 1730-cm^{-1} peak is due to contamination of the crystals with the corresponding octahalobiisocoumarin (analogous to 3). The latter compounds, however, could not be made from the reaction of concentrated sulfuric acid with the octahalo-BP (9 and 10). If the two C=O bands in the spectra of 9 and 10 result, indeed, from the pure compounds, the phenomenon may indicate that these very crowed molecules are not entirely planar. In the planar *trans*-BP (1) the two carbonyl groups are aligned in opposite directions, and the symmetric vibration mode does not result in a change in dipole moment; consequently, one expects only a single carbonyl band, due to the asymmetric mode, despite the fact that extensive vibrational coupling is taking place, of the type that is responsible for the well-known doublet in symmetrical anhydrides.[26] This restriction need not apply if the molecule is not entirely planar. All efforts to obtain single crystals of 9 or 10 suitable for x-ray analysis have failed.

Mechanisms of the Biphthalyl Condensation and Related Reactions. We suggested the possible intervention of the bisketene (14)[12] and the related carbene (15)[12,13] in the formation of *trans*-BP (1) from PA (5) and triethyl phosphite. These hypothetical intermediates may arise via a cyclic oxyphosphorane[12,27] (12), or via a dipolar 1:1 adduct[13] (13), which represent the attack by the phosphite at the carbon or at the oxygen of the carbonyl function of PA (5), respectively. The reactions of trivalent phosphorus compounds with carbonyl functions can give rise to a variety of products[28] which may be pictured as arising from the two types of 1:1 adducts, X_3P^+-C-O$^-$ and X_3P^+-O-C$^-$. Apparently, these adducts can be subject to relative rapid equilibration, rearrangements, eliminations, and additions of other reagents, including a second molecule of the carbonyl compound.[28] In the biphthalyl condensation, which occurs at relatively high temperature, there are no compelling reasons to exclude either of these modes of attacks by the phosphite on PA (5) as the source of the carbene (15).

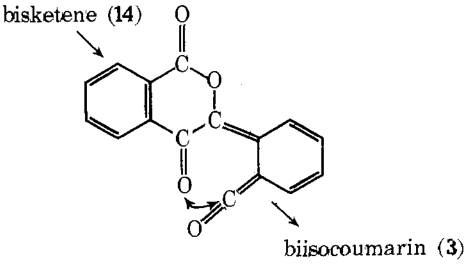


The *trans*-BP (1) may arise by direct dimerization of the carbene (15),[12,13] or via the phosphite ylide (16)[29] which represents the trapping of the carbene (15) by the phosphite. From the ylide (16) and PA (5), *trans*-BP (1) is formed through the steps of the Wittig olefin synthesis.[29] The phthalidephosphonate (17), which is observed when dialkyl phosphites are present during the reaction of PA (5) with trialkyl phosphites, represents the trapping of the carbene by dialkyl phosphite.



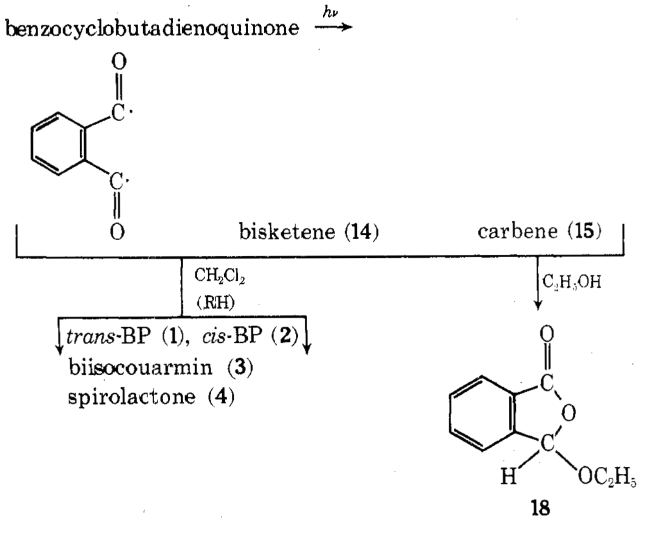
The biisocoumarin (3) recently detected by Bird[14] among the by-products of the biphthalyl condensation may result from a dimerization of the bisketene (14, Scheme III).

Scheme III

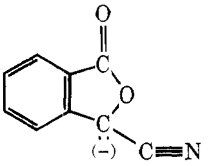


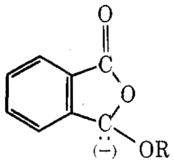
In support of the bisketene (14) ⇌ carbene (15) hypothesis, one can mention the results of the photolysis[7–9] of the quinone[6] as has been pointed out by Stabb[7,8] and by Brown[9] (Scheme IV). The dimerization of the carbene (15) to *trans*- and *cis*-BP (1 and 2), and of the ketene (14) to biisocoumarin (3), as well as the carbene insertion on the quinone to give the spirolactone (4), are reasonable. The trapping of the carbene by ethanol to give the 3-alkoxyphthalide[7,8] (18, Scheme IV) provides an analogy for the similar trapping by dialkyl phosphite.

Scheme IV

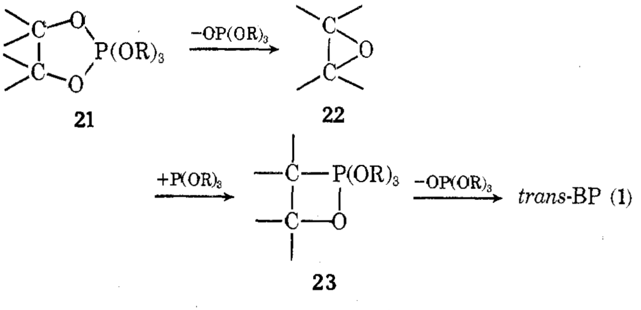


The carbene (**15**) is a likely intermediate in the early work[2,3] with phthaloyl chloride (Scheme I). Moreover, the formation of *trans*-BP (**1**) and/or biisocoumarin (**3**) from phthalaldehydic esters[2,3] or from 3-alkoxyphthalides[5] (Scheme I) suggest also a carbenoid mechanism (via **19** and **20**).


19

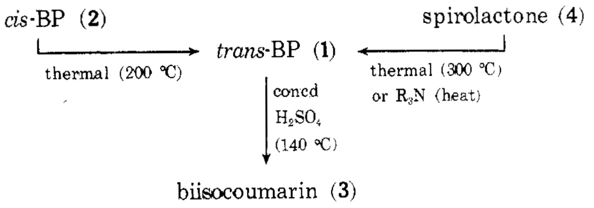

20

The formation of *trans*-BP (**1**) from the phosphite ylide (**16**) via the Wittig reaction[29] seems more reasonable than the simple carbene dimerization, and has been favored by several authors.[10,14–16,30] Phosphite ylides are known[31,32] and there is precedent for the formation of certain phthalylidene derivatives from phosphine ylides and phthalic anhydride.[33] However, neither the phosphite ylide (**16**), nor the carbene (**15**) are *mandatory* intermediates in the biphthalyl condensation. There is a reasonable pathway in which the dipolar ion (**13**) adds to PA (**5**) carbonyl to yield the 1,3,2-dioxaphospholane (**21**).[34] Subsequent steps have precedent, in other related reactions of cyclic oxyphosphoranes.[27–29] as was recognized by Markgraf.[16] The 1,2-oxaphosphetane (**23**)[35] depicted in this pathway is the intermediate in the Wittig olefin synthesis.

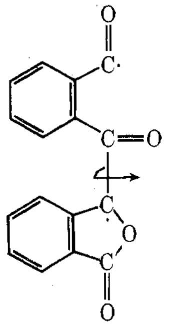


In view of the intramolecular crowding revealed by the x-ray analysis of the unsubstituted *trans*-BP (**1**), one may raise the question of prohibitive steric hindrance in the various intermediates discussed above, the 1,2-oxaphosphetane (**23**), 1,3,2-dioxaphospholane (**21**), and epoxide[36] (**22**). In that case, the direct carbene dimerization could still provide a plausible mechanism for the biphthalyl condensation.

Several isomerizations of the various $C_{16}H_8O_4$ structures discussed above have been discussed:



The homolytic acyl–oxygen bond cleavage required in the cis → trans isomerization[6,7] could be facilitated by resonance stabilization in species **24**. A similar effect in species **25** would account for the thermal spirolactone *trans*-BP rearrangement;[9,17] this picture is analogous to that suggested[9] for the amine catalysis of that reaction.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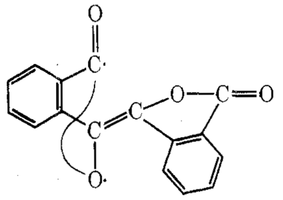
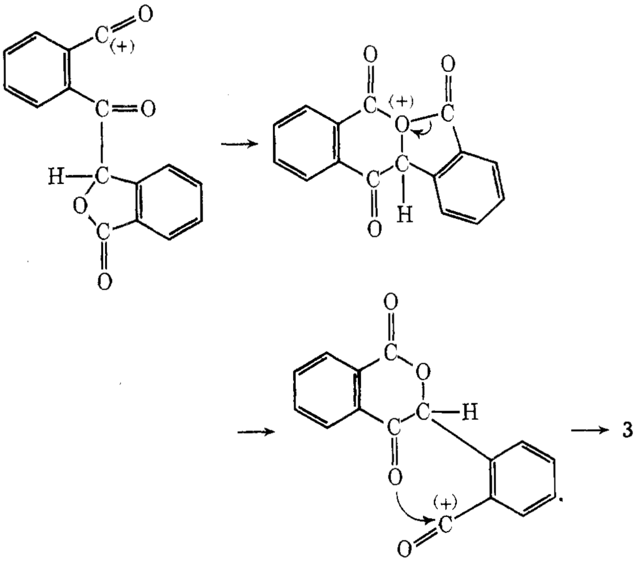

25

We have found that *trans*-BP (**1**) and octachloro-BP (**9**) are recovered unchanged after heating to 370 and 175 °C, respectively, and have verified the acid-catalyzed *trans*-BP (**1**) → biisocoumarin (**3**) isomerization,[10] which could simply be an acylium cation mediated rearrangement, Scheme V.

Scheme V



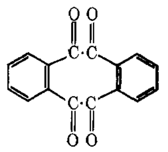
Registry No.—**1**, 19357-64-3; **3**, 7433-92-3; **5**, 85-44-9; **6**, 117-08-8; **7**, 632-79-1; **8**, 4741-53-1; **9**, 60260-50-6; **10**, 60260-51-7; **11**, 60260-52-8; triethyl phosphate, 122-52-1.

Supplementary Material Available. Positional and thermal parameters (Table III) and equations of best least-squares planes (Table IV) (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) State University of New York at Stony Brook. Research supported by Grant GM 20672 from the National Institute of General Medical Sciences, and Grant MPS73-04944 from the National Science Foundation; (b) Brookhaven National Laboratory; (c) address correspondence to this author at the Department of Chemistry, Windham College, Putney, Vt.

(2) "Diphthalyl, $C_{16}H_8O_4$" was first mentioned by E. Ador, *Justus Liebigs Ann. Chem.*, **164**, 229 (1872), who formulated it as a bis-1,2-diketone. The



bis-γ-lactone alternative was proposed by C. Graebe, *Ber.*, **15**, 1673 (1882); J. Wislicenus, *ibid.*, **17**, 2178 (1884); C. Graebe and H. Guye, *ibid.*, **17**, 2851 (1884); and C. Graebe and H. Schmalgigaug, *Justus Liebigs Ann. Chem.*, **228**, 126 (1885). Graebe's "yellow" crystals had mp 334–335 °C (from phenol), while Wiscilenus' "colorless" crystals had mp 320 °C (from acetic acid). A later sample of "yellow" crystals by P. Karrer, W. Werli, E. Biedermann, and M. dalla Vedov,, *Helv. Chim. Acta*, **11**, 233 (1928), had mp 335 °C (from benzene).

(3) For a review of the early literature, see Beilstein, "Handbuch der Organischen Chemie", 4th ed, J. Springer, Berlin: (a) **19**, 176 (1910); (b) **I**, 688 (1919); (c) **II**, 192 (1929).
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(9) R. F. C. Brown and R. K. Solly, *Tetrahedron Lett.*, 169 (1966).
(10) C. W. Bird and D. Y. Wong, *Tetrahedron*, **31**, 31 (1975).
(11) BP = biphthalyl; PA = phthalic anhydride.
(12) F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Org. Chem.*, **24**, 1838 (1959). The yellow BP, mp 352–354 °C (xylene), was erroneously drawn in the cis configuration; cf., however, the correct trans configuration in ref 13.
(13) F. Ramirez, H. Yamanaka, and O. H. Basedow, *J. Am. Chem. Soc.*, **83**, 173 (1961).
(14) C. W. Bird and D. Y. Wong, *Organomet. Chem. Synth.*, **1**, 421 (1972).
(15) C. W. Bird and D. Y. Wong, *Chem. Commun.*, 932 (1969).
(16) J. H. Markgraf, C. I. Heller, and Noyes L. Avery, III, *J. Org. Chem.*, **35**, 1588 (1970).
(17) M. Pailer, H. Woerther and A. Meller, *Monatsh. Chem.*, **92**, 1037 (1961).
(18) In view of the relatively low melting point of the yellow product, 334 °C, vs. that of pure *trans*-BP (**1**), it is possible that some biisocoumarin (**3**) was also formed in the pyrolysis of spirolactone **4**.
(19) Unpublished results.
(20) G. Germain, P. Main, and M. M. Woofson, *Acta Crystallogr., Sect. B*, **26**, 274 (1970); *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
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(22) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(23) These values were 0.117 and 0.176 before addition of hydrogen atoms and anisotropic refinement.
(24) See paragraph at end of paper regarding supplementary material.
(25) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960.
(26) L. J. Bellamy, "Advances in Infrared Group Frequencies", Methuen, London, 1968, p 128.
(27) F. Ramirez, *Acc. Chem. Res.*, **1**, 168 (1968).
(28) For a recent review see F. Ramirez, *Synthesis*, 90 (1974).
(29) IUPAC Conference on Phosphorus Compounds, Heidelberg, Germany, May 1963; F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); cf. p 367.
(30) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry", Academic Press, New York, N.Y., 1965, p 185.
(31) (a) F. Ramirez, O. P. Madan, and C. P. Smith, *Tetrahedron Lett.*, 201 (1965); (b) *J. Org. Chem.*, **30**, 2284 (1965).
(32) F. Ramirez, A. S. Gulati, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 6283 (1967).
(33) P. A. Chopard, R. F. Hudson, and R. J. G. Searle, *Tetrahedron Lett.*, 2357 (1965).
(34) F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3041 (1961).
(35) A direct conversion of **21** into **23** by attack of $(RO)_3P$ on the carbon of **21** and elimination of $(RO)_3PO$ is conceivable.
(36) In principle the carbene **15** could be trapped by PA (**5**) to give the epoxide **22** directly.

Notes

On the Catalytic Role of the Carboxyl Group in the Hydrolysis of *o*-Carboxybenzyl Bromide

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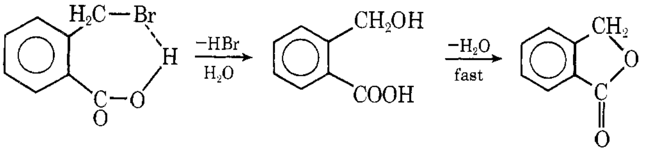
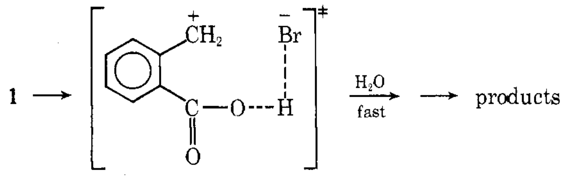
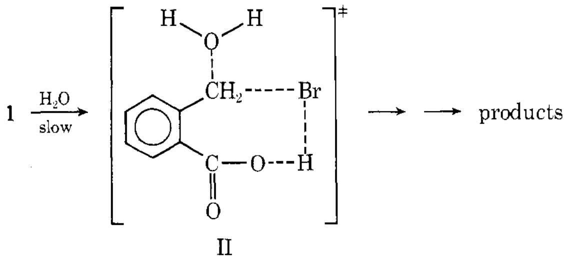
Of the isomeric carboxybenzyl bromides, *o*-carboxybenzyl bromide (1) is known to undergo solvolytic reactions many times more rapidly than *p*-carboxybenzyl bromide (2).[1] This difference—the ortho isomer (1) reacts some 84–87 times as fast as the para isomer (2)—reverses the usual order of reactivity among isomers of this type. Although differences are rarely this dramatic, the para isomer is nearly always more reactive.[2] The greater reactivity of 1 is attributed to internal participation by the un-ionized carboxyl group.[3] Such participation is not possible for **2** because of unfavorable molecular geometry. Manifestly the equation above does not show how the solvent acts.



Solvolyses of benzyl halides have been studied extensively.[4] The findings cannot be interpreted in terms of simple SN1 or simple SN2 mechanisms. It has been suggested that the mechanisms of benzyl halide solvolysis be interpreted as SN2 (1) and SN2 (2); in the former, bond ionization plays the predominant role, while the latter is more like the conventional SN2 type, nucleophilic attack being more important.[5] Two possible transition states can be postulated for the particular reaction now being discussed:



I



II

If the reaction proceeds through the transition state I, sufficient stretching of the reactive bond must occur to produce an ion-pair-like species. The subsequent nucleophilic attack on the ion is expected to be very fast. In this case, the carboxyl group can be said to act as an electrophilic catalyst. Reactions proceeding through this state should be little affected by nucleophiles but appreciably sensitive to the ionic strength or dielectric constant of the solvent medium. If the reaction goes through the transition state II, less bond stretching is required. The reactive bond is stretched only enough to in-