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$$\delta = f\mathcal{F} + r\mathcal{R} = i$$

where i is the intercept of the equation and f and r are the regression coefficients; see ref 18. $\mathcal{F}$ and $\mathcal{R}$ are contributions arising from field and inductive effects taken together and resonance effects, respectively.
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Highly Stereoselective Methanolysis of Diazaoxyphospholenes

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Received May 24, 1977

When the diazaoxyphospholene *cis*-**2** is placed in a neutral absolute methanol solution, it gives both isomerization to *trans*-**2** and ring opening with exclusive formation of only one (**3b**) of the four possible diastereomeric β-phenylhydrazone methylphosphinates **3.** In the same conditions the isomer *trans*-**2** gives the same diastereomer **3b.** The relative configuration of the two chiral centers in **3b** is tentatively assigned. The high stereoselectivity is explained in terms of pentacoordinate phosphorus intermediates, in which steric factors have a considerable influence on their stability.

The discovery of the role played by a small ring containing phosphorus in determining the behavior of the nucleophilic displacement reaction at a phosphoryl center has led to wide research in this field.[1-5] Generally these attacks on phosphorus contained in a five- or four-membered ring are rationalized by assuming the formation of intermediates with pertacoordinated phosphorus.[5,6]

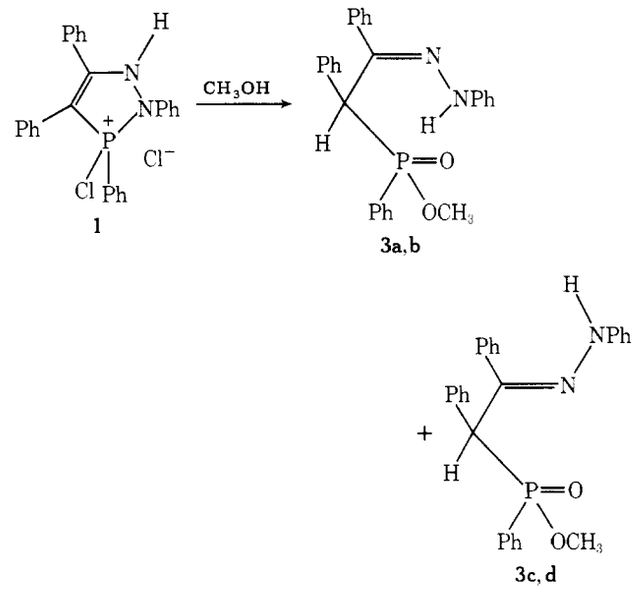
Considerable information is now available[6-8] on the factors which effect the stability of such phosphorane derivatives and control the process of ligand reorganization within them. Two factors turn out to be important in this connection: (a) the preference of electronegative groups for the apical positions and (b) the preference of a small-membered ring for an apical–equatorial situation.[7-10] However, the reaction stereochemistry may also be dependent on the steric interactions as well as on the specific reaction conditions.

In this paper we report a case in which a steric effect is the main factor in highly stereoselective stereochemical results.

Results

In previous communications we reported that the diazaphospholene cycloadduct **1** undergoes exclusive ring opening when treated with neutral absolute methanol,[11] while ring retention was observed when the adduct was treated with water under the same reaction conditions.[12] This unexpected behavior was rationalized[11] on the basis of the relative apicophilicities of hydroxyl and methoxy groups compared to the diaza group. Each one of the four diastereomeric β-phenylhydrazone methyl phosphinates **3** was isolated in pure form.

Configurational assignment about the C=N has been determined by proton NMR spectroscopy. From the data presented in Table I, it should be noted that the methine proton in isomers **3a** and **3b** resonates at lower magnetic fields (deshielded) than that of **3c** and **3d,** suggesting[13] that isomers **3a** and **3b** have the syn configuration defined as that in which the anilino and benzylic groups are on the same side of the C=N bond. Moreover, our NMR data were in good agreement with Karabatsos[14] on the analysis of the anisotropic effects of the benzene ring on the syn and anti methinic hydrogens.



1 **3a,b** **3c,d**

Another NMR correlation which is potentially useful for configurational assignments involves the chemical shift difference in the NH proton resonance of diastereomers **3.** The NH of **3a** and **3b** is strongly intramolecularly bonded as evidenced from the low-resonance value.

In contrast the NH of the other forms **3c** and **3d,** incapable of this hydrogen bonding, resonates at higher magnetic field (masked by aromatic protons). Hence, in the diastereomers

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Table I. NMR Spectra of β-Phenylhydrazonephosphinates 3

Compd	Solvent	δ $POCH_3$	J_{POCH_3}	δ PCH	J_{PCH}	δ arom	δ NH
3a	$CDCl_3$	3.70 (d)	10.5	5.03 (d)	20.7	6.70–8.00 (m)	11.05
	C_6D_6	3.05 (d)	10.5	4.88 (d)	20.2	6.40–7.75 (m)	11.64
3b	$CDCl_3$	3.75 (d)	10.5	5.15 (d)	22.2	6.50–7.80 (m)	10.50
	C_6D_6	3.10 (d)	10.5	4.97 (d)	21.7	6.10–7.90 (m)	11.09
3c	$CDCl_3$	3.45 (d)	10.5	4.25 (d)	18.0	6.50–7.70 (m)	*b*
	C_6D_6	3.15 (d)	10.5	4.30 (d)	17.2	6.35–7.80 (m)	*b*
3d	$CDCl_3$	3.49 (d)	10.5	4.32 (d)	21.7	6.30–7.60 (m)	*b*
	C_6D_6	3.25 (d)	10.5	4.40 (d)	21.0	6.25–7.70 (m)	*b*

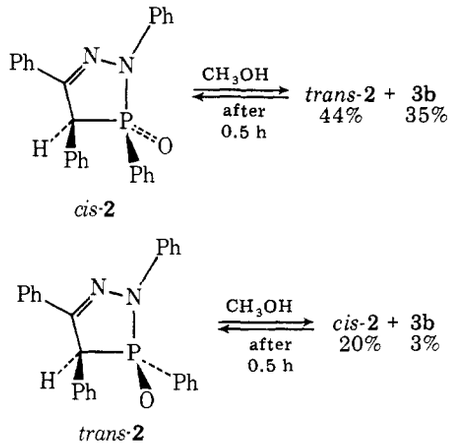
[a] Concentrations of 3–5 mol % phenylhydrazone were used; chemical shifts in parts per million from Me_4Si; *J* values in hertz. [b] Masked by aromatic protons.

Table II.[a] Methanolysis of *trans*- and *cis*-2

Time, h	% trans	% cis	% 3b	% 3a
		trans-2		
0	100	0	0	0
0.5	82	15	3	0
1	74	20	6	0
2	65	26	8	0
4	58	29	13	0
8	49	25	26	0
24	40	20	40	0
96	23	11	66	Traces
		cis-2		
0	0	100	0	0
0.5	43	21	36	0
1	38	19	43	0
2	35	18	45	0
4	27	14	59	0
8	21	10	69	0
24	19	8	70	3
96	18	7	68	7

[a] The ratios (±5%), determined as stated in the text, are the average of four separate reactions.

Scheme I[a]



[a] Only one enantiomer of each compound is shown in Scheme I, although racemic mixtures were used in this study.

3a and **3b** the NH and PO groups interacted and must therefore be on the same side of the C=N bond. The same relationship was confirmed by the infrared spectra (in chloroform solutions) of the isomers **3** (see the Experimental Section).

The UV spectra show the maximum of **3a** and **3b** (ε 18 000) displayed by +47 nm relative to the isomers **3c** and **3d** (ε 11 000). On the assumption that this bathochromic and hyperchromic shift must be the result of a change in configuration about the C=N bond, the isomer which absorbs with greater intensity at a longer wavelength is taken as the syn isomer. The anilino and conjugated aromatic ring are then on the opposite sides of the C=N bond and can attain coplanarity; this is not possible in the other configuration. Examples of analogous assignments are reported[15] in the literature for similar systems.

It is interesting to note that such isomers **3** are not interconvertible in several solvent solutions ($CDCl_3$, CH_2Cl_2, C_6H_6), even after many hours at room temperature under neutral conditions, while interconversion of isomers **3** was observed to occur slowly under acidic conditions.

We now report that when the diazaoxyphospholene *cis*-**2** (3,4-dihydro-2,3,4,5-tetraphenyl-2*H*-1,2,3-diazaphosphole 3-oxide)[16] is placed in a neutral absolute methanol solution at room temperature, after only 0.5 h both isomerization to *trans*-**2** and ring opening with exclusive formation of **3b** are obtained.

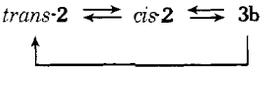
In the same conditions the isomer *trans*-**2** interconverts to *cis*-**2** but with a slower formation of the same diastereomer **3b** (Scheme I). The course of the reaction was followed by ^1H NMR appearance of the new $POCH_3$ and NH peaks and of the characteristic methine absorptions. The course of the reaction can also be conveniently monitored by TLC (silica gel). The different proportions at different times of each reaction are reported in Table II.

This methanolysis reaction can be considered highly *stereoselective* because both isomers **2** give exclusively the ring-opening isomer **3b.** The good stability observed in neutral methanol solution of these β-phenylhydrazone methyl phosphinates excludes the possibility of rapid isomerization of these compounds in the reaction mixture and confirms the "syn" configuration for the isomer **3b.**

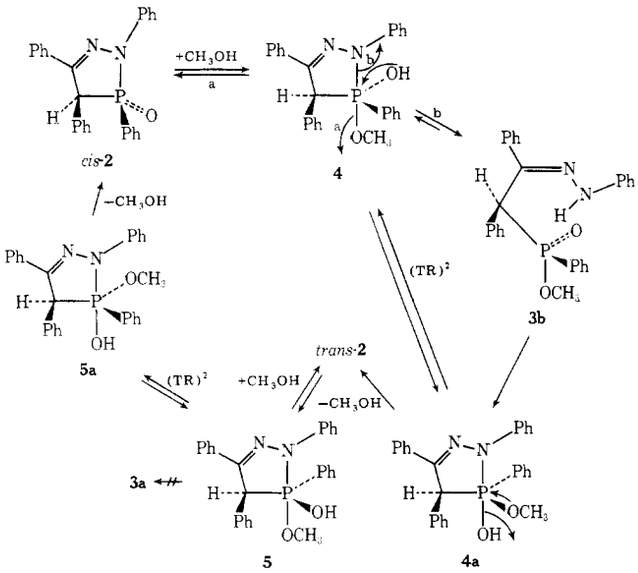
The observation that in the first times of the reaction the methanolysis of the *cis*-**2** isomer gives a larger extent of **3b** than *trans*-**2** could suggest that only the *cis*-**2** isomer undergoes direct ring opening. This could also be evidence of the fact that at first the *trans*-**2** must isomerize to *cis*-**2** and then *cis*-**2** undergoes ring opening.

Moreover, it should be noted that after about 4 days this methanolysis reaction leads to a *trans*-**2**:*cis*-**2**:**3b** ratio of about 20:10:70 in both cases; after 4 days this ratio remains constant if we neglect the increase of isomer **3a** which appears after longer reaction times.

On the other hand, when **3b** is left in a methanol solution, a slow recyclization with formation of both isomers is observed (as well as a slower collateral isomerization to **3a**) and after 4 days a *trans*-**2**:*cis*-**2**:(**3b** + **3a**) ratio of about 20:10:70 is obtained. In this mixture the **3b**:**3a** ratio is about 4:1. Then, if one neglects the slower collateral reaction of isomerization of ring-opening compounds **3**, the methanolysis reaction is simplified to



Scheme II[a]



[a] The TR and $(TR)^3$ processes[18] are neglected in Scheme II because they lead to unfavorable phosphorane intermediates with the NPh group in the equatorial position. However, the same stereochemical conclusions can be deduced if we assume that these intermediates are participating in the process.

Discussion

The large number of relatively stable phosphoranes[6,17] and the theoretical background that now exists on their structure and dynamic stereochemistry[5,8,9] provide an adequate interpretation for our findings. The mechanism we propose for the methanolysis here described (see Scheme II) involves the formation of metastable phosphoranes which presumably are sufficiently long-lived to allow stereomutation or positional interchange at pentacoordinated phosphorus by a Turnstile rotation (TR)[18] or a resultwise equivalent Berry pseudorotation (BPR).[19] However, the latter is less likely to be applied here because of the presence of the five-membered ring.[9]

The transformation of the tetracoordinate phosphorus compound **2** into the pentacoordinate species such as **4** results from an apical attack of methanol at the tetrahedral phosphorus atom.

Another set of phosphoranes enantiomeric with structure **4** is generated by attack at a different enantiotopic face of the phosphorus tetrahedron. However, as a rule,[6,9] five-membered rings are unable, for reasons of strain, to occupy the diequatorial position of the trigonal bipyramid and, therefore, only conformers with apical–equatorial rings are considered to participate in the permutational process. This preference in our heterocyclic system is strongly supported by the results[20] of an x-ray analysis of a *cis*-**2** parent compound (where there is a benzyl in C_5) which indicates that the C–P–N ring angle is 90°. This provides a considerable driving force for the formation of a trigonal-bipyramidal phosphorane intermediate such as **4** by the addition of a nucleophile to the phosphorus involving relatively small additional bond angle deformations.

On the other hand, since more electronegative atoms tend to prefer the apical positions,[8,9] the pentacoordinated structures with apical nitrogen may be favored over those with apical ring carbon; thus, we propose that the favored attack of the methanol is at the face opposite the P–N bond with formation of **4** which leads to **4a** after a $(TR)^2$ process.[18] Since there is an intramolecular overcrowding in trigonal-bipyramidal structures,[21] the steric factors will have a considerable influence on the stability of such phosphoranes. One consequence of this structural feature is that **4a** may be favored over **4** because it will avoid the steric interaction of P-phenyl with C_4-phenyl.

Apical departure (requirement of microscopic reversibility[2,22,23]) of the hydroxyl group from **4a** will yield the *trans*-**2.** Another possibility for the form **4** is to return to tetracoordination by apical cleavage of the P–N bond with formation of **3b** with inversion of the P chirality. Compound **3b** is expected to be thermodynamically more stable than **2** because ring strain is the main factor of instability in tetracoordinate phosphorus[21] (while the corresponding cyclic phosphoranes gain in stability). When methanol attacks the *trans*-**2** the hypothetical phosphorane **5,** which can also isomerize to **5a** by a $(TR)^2$, is obtained.

The form **5** should be more stable than **4** and **5a,** having less steric interference between the two phenyl groups. This gain in stability of **5** relative to **4** should reduce considerably the formation of **3a** via the ring opening of **5.** This is in agreement with the fact that **3b** appears exclusively also when pure *trans*-**2** is used in the methanolysis reaction, and in this case the slower formation of **3b** may be evidence that at first *trans*-**2** interconverts to *cis*-**2** which subsequently undergoes ring opening.

The data on recyclization are consistent with the proposed mechanism which involves in recyclization of **3b** the same hypothetical intermediate **4** (involved in ring opening). However, from our findings, we cannot exclude the possibility of formation of the intermediate **4a** in recyclization. This would represent an "irregular isomerization" [7] of **4** and **4a.** It is evident also that isomerization of **2** can proceed by this irregular process. That is

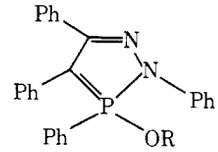
$$cis\text{-}\mathbf{2} \leftrightarrows \mathbf{4} \rightleftarrows \mathbf{3b} \rightarrow \mathbf{4a} \rightarrow trans\text{-}\mathbf{2}$$

However, the small amounts of **3b** in the first times of reduction suggest that this "irregular process" should not be the only process of isomerization of **2.** Both the **4** → *trans*-**2** and **5a** → *cis*-**2** conversions may be explained on the basis of a nucleophilic attack by hydroxyl (after its apical departure) at the methoxy carbon with C–O bond cleavage.

An analogous mechanism has been observed in phospholanium and phosphorinanium salts.[24] The rupture of the P–OH bond and the formation of the new C–O bond may be synchronous. Since there is more back-donation of electrons from the equatorial position than from the apical position toward the central phosphorus,[8] the equatorial methoxy carbon is activated to undergo the nucleophilic attack by the apical hydroxy.

The relatively strong apicophilicity of the diaza group[8,11] may be a further factor which favors this nucleophilic attack at carbon. In competition with this S_N2 attack at carbon the formation of an ylide form such as **6a** is possible, which may also be considered as an alternative route for stereomutation of **2.**

Indeed we have noted that deuterium exchange occurs when *cis*-**2** is dissolved in CH_3OD, but this exchange is slower than



6a, R = CH_3
b, R = H

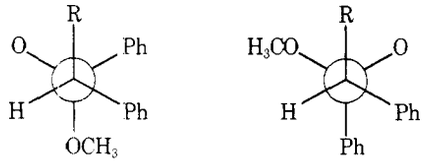
isomerization. Moreover, the formation of **6** is favored by its possible "aromatic character".[25]

However, an exclusive mechanism via ylide for stereomutation of **2** would require the involvement of pentacoordinate species in order to understand the other results. Similar ste-

reoselective results in trichlorosilane reduction of this heterocyclic system were explained[26] on the basis of pentacoordinate intermediates.

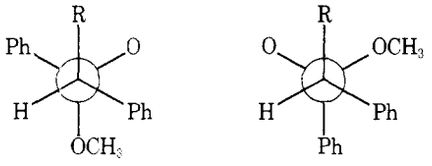
From the proposed mechanism, the relative configuration of the two chiral centers in **3b** should be the one reported in Scheme II (*dl*-erythro form). The favored formation of an intramolecular hydrogen bonding between NH and P=O groups[27] in the isomer **3b** may favor the "gauche" rotamers with respect to the "anti" rotamer. On the other hand, in the isomer **3a** (*dl*-threo form) the same hydrogen bonding will favor only one of the "gauche" forms and the "anti" form.

An examination of these assumed predominant conformations reveals that there is a larger *cis*-Ph character in **3a** than in **3b**, as the Newman projections show. This is supported



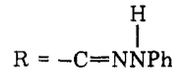
"gauche" "gauche"

3b, *dl*-erythro form



"anti" "gauche"

3a, *dl*-threo form



by the NMR data reported in Table I. The methine proton is more shielded and has a smaller value for coupling constant J_{PCH} in **3a** than in **3b**. An equal behavior is observed for the methoxy group of those isomers. This configurational assignment of **3b** would confirm the proposed mechanism.

In conclusion, we think that our results clearly indicate that, because of the greater crowding in trigonal-bipyramidal phosphoranes, steric factors play a large part in determining the stereochemistry of nucleophilic attack on phosphorus and emphasize the fine balance between pseudorotation and product formation in phosphorane intermediates.

Experimental Section

All reactions were carried out with rigorous exclusion of oxygen under a nitrogen atmosphere. Methanol was freshly dried with magnesium. **1** was prepared by the previously[12] described method. Melting points were determined on a Kofler hot-stage and are uncorrected.

The IR spectra were determined on a Perkin-Elmer spectrometer Model 257 and the UV spectra on a Perkin-Elmer Model 402. The NMR spectra were recorded on a Jeol *JMMC 60 HC* spectrometer. ^1H NMR chemical shifts are expressed in parts per million from internal Me_4Si. The microanalyses were performed on mixtures of the isomers as well as on pure isomers. The results obtained were practically identical.

Reaction of 1 with Methanol. Separation of β-Phenylhydrazone Phosphinates 3. A slight excess of dry methanol (1 mL) was added to 9.2 g (0.02 mol) of **1** in 70 mL of dry methylene chloride. An exothermic reaction and evolution of CH_3Cl were observed. The mixture was stirred for 20 min at 20 °C and then titrated with 20% sodium hydroxide to pH 7. This solution was extracted with 5 × 100 mL of CH_2Cl_2. The combined organic layers were dried over sodium sulfate and evaporated to give a crude solid which after crystallization from CH_2Cl_2–hexane gave 5.70 g (65%) of **3**. Only small amounts (~10%) of **2** were obtained. The NMR spectrum ($CDCl_3$) of the crude product showed (**3a** + **3b**) and (**3c** + **3d**) in 30:70 ratio.

Separation of small amounts of the diastereomers was accomplished by chromatography on a silica gel column [elution with benzene–ether (8:2) mixture]. The isomer **3a** (R_f 0.55) had mp 126–128 °C; UV max ($CHCl_3$) 340 nm (ε 18 000); IR ($CHCl_3$) 3240 (NH), 1235 cm^{-1} (P=O). **3b** (R_f 0.48) had mp 157–159 °C; UV max ($CHCl_3$) 340 nm (ε 18 000); IR ($CHCl_3$) 3240 (NH), 1240 cm^{-1} (P=O). **3c** (R_f 0.16) had mp 154–156 °C; UV max ($CHCl_3$) 293 nm (ε 11 000); IR ($CHCl_3$) 3330 (NH), 1260 cm^{-1} (P=O). **3d** (R_f 0.10) had mp 119–121 °C; UV max ($CHCl_3$) 293 nm (ε 11 000); IR ($CHCl_3$) 3330 (NH), 1260 cm^{-1} (P=O).

In all the four isomers of **3**, strong bonds in the infrared region (KBr) were caused by the P=O stretching vibrations (1210 and 1260 cm^{-1}), by the $POCH_3$ stretchings (1020 and 1110 cm^{-1}), and the PPh stretching (1440 cm^{-1}). Strong bonds were found also at 1600 and 1500 cm^{-1}.

The NMR data ($CDCl_3$ and C_6D_6) are reported in Table I. Anal. Calcd for $C_{27}H_{25}N_2O_2P$: C, 73.62; H, 5.67; N, 6.36. Found: C, 73.86; H, 5.64; N, 6.20.

Methanolysis of *cis*-2. A solution of pure *cis*-**2** (1.22 g) in dry methanol (420 mL) was kept at room temperature under nitrogen in a flask sealed with a serum cap. At appropriate intervals of time (until no further appreciable changes were noted) aliquots (40 mL) were removed from the flask by using a hypodermic syringe, in order to prevent contact of the reaction solution with moisture. The solvent was stripped off and the residue was dissolved into $CDCl_3$.

NMR analysis of these samples showed the presence of *trans*-**2** and the exclusive formation of the ring-opening isomer **3b**. After 4 days a mixture was obtained in which the *trans*-**2**:*cis*-**2**:**3b** ratio was ca. 20:10:70 (obtained by integration of the methoxy and methinic NMR absorptions). The composition of the samples is reported in Table II. No changes were observed after 4 days if we neglected the slow increase of isomer **3b** which appeared after longer reaction times.

A separate but identical reaction was allowed to proceed for 4 days and the whole resulting mixture was chromatographed using benzene–ether as eluent yielding the following: first fraction **3a**, mp 126–128 °C (5%); second fraction **3b**, map 157–159 °C (65%); third fraction *trans*-**2**, mp 202–204 °C (17%); fourth fraction *cis*-**2**, mp 174–177 °C (10%). Identification of the products was based on comparison of their spectroscopic data with those of pure isomers obtained from **1**.

Methanolysis of *trans*-2. The same procedure as above was followed using 1.22 g of pure *trans*-**2** in 420 mL of dry methanol. Interconversion of isomer **2** was observed but in the first times of the reaction the percent of **3** was smaller than the one given by *cis*-**2**.

After 4 days a product ratio which was almost identical with that obtained with the cis isomer was observed. The reaction was repeated several times with each isomer and the ratios at different intervals of time reported in Table II are the average of four separate reactions.

Sometimes these ratios may vary for separate reactions and this variability appears to be caused by traces of water in the used methanol. In fact, when the methanol was freshly dried with magnesium, when care was taken to clean and dry the apparatus thoroughly, and when the methanolysis flask was sealed with a serum cap, then the yield of **3b** after 96 h was ~70%. When 1 equiv of water was deliberately added, the yield of **3b** fell to 11%.

When pure isomer *cis*-**2** (0.66 g) was dissolved in CH_3OD (21 mL), a detectable exchange of methine protons and isomer crossover without exchange was observed. The percent exchange was followed by integration of the area in the methine region relative to the area of aromatic protons. After 24 h ~30% exchange in the products was observed.

Recyclization of 3b in Methanol Solution. A solution of pure **3b** (0.66 g) in dry methanol (210 mL) was kept at room temperature under nitrogen in a flask sealed with a serum cap. Aliquots (40 mL) were removed at appropriate intervals of time, the solvent was stripped off, and the residue was dissolved into $CDCl_3$.

NMR analysis of these samples showed the presence of **2** (cis and trans) and of **3a**.

After 4 days a *trans*-**2**:*cis*-**2**:**3b**:**3a** ratio of 16:8:61:15 was obtained. After 8 days this ratio became 17:8:53:22. After 10 days **3c** and **3d** were detectable in appreciable extent. No recyclization was obtained when pure **3c** (or **3d**) was dissolved in dry methanol under the same conditions of **3b**.

Acknowledgements. We wish to thank the Italian CNR for financial support.

Registry No.—**1** (charged form), 51849-77-5; **1** (uncharged forms), 64057-38-1; *cis*-**2**, 64057-39-2; *trans*-**2**, 64057-40-5; **3a**, 64090-79-5; **3b**, 64090-78-4; (*z*)-*dl*-*erythro*-**3**, 64129-88-0; (*Z*)-*dl*-*threo*-**3**, 64090-77-3.

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Kinetic Study of the *N*-Bromosuccinimide Bromination of Some 4-Substituted 3-Cyanotoluenes

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Received April 2, 1976

Twelve 4-substituted 3-cyanotoluenes (**3**-X) were prepared from 4-substituted 3-aminotoluenes, 4-amino-3-nitrotoluene, or *m*-tolunitrile (**3**-H). The relative rates of NBS bromination of **3**-X vs. **3**-H were determined in benzene at 80 °C. These relative rates, k/k_0, increased in the following substituent order: $NO_2 < CN < Ac < F < Cl < Br < I < H < Ph < CH_3 < N{=}NPh < OCH_3$. The substituent effects were discussed in terms of polar transition state and bond dissociation energy arguments. A linear dependence on σ^+ was found with $\rho = -1.13 \pm 0.12$. Several withdrawing substituents were believed to provide "extra" resonance in this free-radical reaction.

Substituent influences on the homolytic process have been studied in a wide variety of reactions. In spite of this, the effects, both stabilizing and destabilizing, of substituents on free-radical sites are not nearly as well understood as the corresponding substituent influences on positive and negative sites in a molecule. Linear free-energy studies of the Hammett type have proven to be a major tool used to help elucidate organic reaction mechanisms of both the heterolytic and homolytic types. One of the systems that has yielded much valuable information about free-radical substituent effects is the H atom abstraction reactions of substituted toluenes. Most common free radicals have been reacted with substituted toluenes. Russell[1] and Pryor[2] list nearly 20 different free radicals that have been studied in this reaction including: H·, Ph·, CH_3·, *t*-BuO·, Cl·, Br·, etc. Because of this wealth of information available on the benzyl free radical, it was chosen as the substrate in this study.

Many H atom abstraction reactions are known to be dependent on σ or σ^+. The usual explanation of this is illustrated by eq 1, where Y–H represents a substituted toluene, ·Z the abstracting radical, and Y· a benzyl radical. The susceptibility of the transition state to polar influences is represented by **2b** and **2c**, where **2b** is important when Z is electronegative and **2c** is important when Z is electropositive. This explanation had become so well accepted that if polar effects were possible they were expected to overshadow the free radical influences.

Recently, a paradigm shift[3] from this polar transition state explanation to a bond dissociation energy (E) explanation was attempted by Zavitsas.[4] Pryor[5] and Henderson[6] have successfully defended the polar transition state explanation by finding several reactions that have positive ρ values consistent with contributions of **2c** above but inconsistent with Zavitsas' explanation. It is also very difficult experimentally to determine accurate bond dissociation energies for benzyl C–H bonds whose only difference is a meta or para substituent.

$$\underset{\mathbf{1}}{Y\text{–}H} + \cdot Z \rightarrow [\underset{\mathbf{2a}}{\dot{Y}H\dot{Z}} \leftrightarrow \underset{\mathbf{2b}}{Y^+\dot{H}Z^-} \leftrightarrow \underset{\mathbf{2c}}{Y^-\dot{H}Z^+}]^{\ddagger} \rightarrow Y\cdot + H\text{–}Z \quad (1)$$

Most attempts to study free-radical influences in H atom abstraction reactions have been to decrease the electronegativity of Z in eq 1 so that the polar effects will become less important. This has been successfully accomplished by using ·Z = ·CH_3,[7] ·Ph,[8] or ·H;[2] and sure enough ρ was found to be near zero in each case. The approach used in this work is to diminish the polar effects by a substrate change (addition of a *m*-CN group) instead of a change in Z. The strongly electron-withdrawing cyano substituent should increase the potential energy of the benzyl cationic contributor **2b**, and consequently the free-radical contributor **2a** should be relatively more important. This is another way of saying the polar effects should not be as important in this free radical reaction.

0022-3263/78/1943-0220$01.00/0