conversion of triphenylamine is considerably slower than that of N-methyldiphenylamine consistent with the much shorter lifetime of the 610 mμ intermediate of triphenylamine. Presumably, the rapid conversion of the intermediate to the ground state competes with its thermal oxidation to carbazole. Diphenylamine itself is also photo-converted to carbazole, but with considerable side reaction.

The formation of intermediate II in the course of the reaction may be understood as a consequence of charge migration from the nitrogen atom into the rings, in the excited state I, followed by bond formation by nucleophilic attack in the polar excited form, to yield II.

Further details of these and related experiments will be published shortly.

Acknowledgment.—This work is supported by a grant from the U. S. Atomic Energy Commission to Brandeis University (AT-30-1-2003).

DEPARTMENT OF CHEMISTRY　　　KARL-HEINZ GRELLMANN
BRANDEIS UNIVERSITY　　　　　　GWENDOLYN M. SHERMAN
WALTHAM, MASSACHUSETTS　　　　HENRY LINSCHITZ

Measurement of an Amine Inversion Rate Using Nuclear Magnetic Resonance

Sir:

In spite of considerable interest in barriers to inversion of amines, it has thus far been possible to measure rates of inversion only for amines possessing NH bonds, where the observed large rates found using microwave spectroscopy have been attributed to tunneling,[1] or in

Fig. 1.—The CH$_2$ and CH$_3$ peaks in the n.m.r. spectrum of 0.35 M dibenzylmethyl ammonium chloride at pH 2.0.

ethyleneimines where it is suggested that the rates, observed using n.m.r. spectroscopy, are unusually slow due to steric restriction.[2,3]

We wish to report a new method of employing n.m.r. spectroscopy to measure these rates, which is applicable over a wide range of values including the rates of typical tertiary amines.

When a benzyl group is bonded to an amine having two dissimilar groups attached as well, it is expected that the CH$_2$ hydrogens will experience different chemical shifts due to the asymmetric environment, which should be similar to that produced by an asymmetric carbon.[4,5] Inversion of the amine then results in interchange of the chemical shifts. If this occurs rapidly enough, the expected AB quartet of the CH$_2$ will coalesce

(1) W. Gordy, W. V. Smith and R. F. Trambarillo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953.
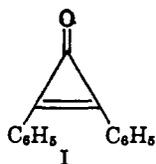
(2) A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5203 (1958).

(3) J. F. Kincaid and F. C. Henriques, Jr., *ibid.*, **62**, 1474 (1940).

(4) G. M. Whitesides, F. Kaplan, K. Nagarajan and J. D. Roberts, *Proc. Natl. Acad. Sci.*, **48**, 1112 (1962).

(5) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962).

to a singlet. Observation of this phenomenon with change of temperature would enable measurement of the rate, but only if the rate could be slowed to 50 sec.$^{-1}$ or slower. This has thus far been impossible in the case of any amine tried at the lowest temperature attainable. Therefore, another method of reducing the rate was devised. Dibenzylmethylamine was dissolved in concentrated hydrochloric acid and the n.m.r. spectrum observed. In addition to splitting of the CH$_2$ and CH$_3$ peaks due to coupling with the NH, the CH$_2$ peak showed the effects of non-equivalence of the protons, since inversion cannot occur in the ammonium salt. It was found necessary to use low concentrations of the salt since the chemical shift between the CH$_2$ hydrogens was a function of the concentration and was a maximum at low concentration. Because of the high conductivity of these samples, it was found necessary to use the arrangement of pulse equipment suggested by Meiboom[6] for eliminating noise produced by modulation of leakage. Decreasing the acid concentration resulted in coalescence of the methyl doublet because of NH exchange of the salt with free amine. The rate of this process was measured using the method of Meiboom.[7] At 0.35 M salt concentration and 25° with 2 N HCl present, a pseudo first-order rate constant of 5 sec.$^{-1}$ was found. Using a pK_a of 7.5 $\pm$ 0.1, which was obtained spectroscopically, a second-order rate constant for the proton transfer of 6 $\pm$ 3 $\times$ 10^8 l./mole sec. was obtained. On going to still weaker acid, the NH exchange becomes faster and the methyl peak becomes a singlet; however, the CH$_2$ hydrogens were found to be still not equivalent (Fig. 1). This demonstrates that the salt can lose its proton to give the amine and be reprotonated without inversion. On raising the pH to 2.5, the doublet was observed to coalesce. Since the inversion can occur only during the time spent as amine, and the rate of interconversion of amine and salt is rapid

$$k_{\text{interchange}} = k_{\text{inversion}} \cdot [\text{amine}]/[\text{salt}] + [\text{amine}]$$

The measured pK_a permitted calculation of this fraction as a function of pH. The rate constant for interchange at pH 3.5 was found to be 21 sec.$^{-1}$ using equations derived by Alexander[8] to prepare a computer program which calulates line shape for the A–B system, including the effects of coupling between the protons, and natural line width. Taking account of the fraction of unprotonated amine, we obtained a rate constant for the inversion of 2 $\pm$ 1 $\times$ 10^5 sec.$^{-1}$.

(6) S. Meiboom, personal communication.

(7) A. Lowonstein and S. Meiboom, *J. Chem. Phys.*, **27**, 1067 (1957).

(8) S. Alexander, *ibid.*, **37**, 966 (1962).

DEPARTMENT OF CHEMISTRY　　　　MARTIN SAUNDERS
YALE UNIVERSITY　　　　　　　　　FUKIKO YAMADA
NEW HAVEN, CONNECTICUT

Diphenylquinocyclopropene

Sir:

Although the synthesis of the stable, basic diphenylcyclopropenone (I) in 1958[1] has been accompanied by preparation of several other cyclopropenium aromatic compounds,[2] attempts to isolate stable substances containing the methylenecyclopropene system (II) appear to have been unsuccessful.[3] We wish to report the

(1) R. Breslow, R. Haynie and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959); M. Volpin, Yu. Koreshkov and D. Kursanov, *Izv. Akad. Nauk SSSR*, 560 (1959).

(2) R. Breslow, H. Höver and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962), and references cited therein; D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960).

(3) E.g., R. Breslow and M. Battiste, *ibid.*, **82**, 3626 (1960); H. Prinzbach and W. Rosswog, *Angew. Chem.*, **73**, 543 (1961).

synthesis of a new type of basic quinomethane, the *diphenylquinocyclopropene system*, which as a benzologue of diphenylcyclopropenone contains the elements of the elusive methylenecyclopropene grouping.

Wittig condensation of benzylidenetriphenylphosphorane with 4-benzyloxybenzaldehyde gave a 4-benzyloxystilbene, m.p. 168–169°, λ_{max}^{MeOH} 304, 318 (332) mμ, log ϵ 4.49, 4.47 (*Anal.* Found: C, 88.05, H, 6.63), converted by way of the dibromide[4] to 4-benzyloxytolane, m.p. 119–120°, λ_{max}^{MeOH} 289, 296, 307 mμ, log ϵ 4.49, 4.40, 4.41 (*Anal.* Found: C, 88.33; H, 5.72). Addition of phenylchlorocarbene to the latter according to the procedure of Breslow and Chang[5] led to the 1-(p-benzyloxyphenyl)-2,3-diphenylcyclopropenium ion III, analyzed as the perchlorate, expl. 248–250°, λ_{max}^{MeCN} 275, 329, 342 mμ, log ϵ 4.20, 4.64, 4.67 (*Anal.* Found: C, 70.97; H, 4.64).[6] Pyrolysis of the crude, unstable bromide of cation III at 180° was attended by debenzylation[7] to give the phenolic cyclopropenium bromide IV, dec. 280–282°, $\lambda_{max}^{CH_3CN\,(H^+)}$ 272, 341 mμ, log ϵ 4.54, 4.70 (*Anal.* Found: C, 68.92; H, 4.55; Br, 21.79).

The phenol IV reacted with bromine in acetonitrile to form a crystalline 1:1 adduct (*Anal.* Found: Br, 45.46) having an infrared spectrum nearly identical with that of the phenol; iodometric titration showed one mole of "free" bromine and suggested a cyclopropenium tribromide structure. In contrast, the phenol IV underwent strikingly facile *substitution* with N-bromosuccinimide in cold acetonitrile to give the nearly insoluble bromide of a dibromo derivative, dec. 278–280°, $\lambda_{max}^{MeCN\,(H^+)}$ 249, 273, 328, 342 mμ, log ϵ 4.42, 4.22, 4.53, 4.55 (*Anal.* Found: C, 49.28; H, 2.40; Br, 44.84; "free" Br, 0). Structure V, assigned to this bromide on mechanistic grounds, was confirmed by comparison of the 60-Mc. proton magnetic resonance spectra of the phenols IV and V (taken in trifluoroacetic acid). As seen from Fig. 1, both compounds exhibited the characteristic low field signal near $\delta = 8.8$ representing the six protons *ortho* to the cyclopropenium ring,[8] but the spectrum of the substitution product V lacked the two-proton doublet near $\delta = 7.6$ ($J = 9$ c.p.s.) clearly arising from the protons *ortho* to the phenolic hydroxyl in IV.

Addition of a tertiary amine to dilute acetonitrile solutions of the phenolic cyclopropenium bromides (IV, V) effected their immediate and complete conversion to the corresponding orange quinocyclopropenes (VI, VII); strong acid regenerated the cyclopropenium systems. Attempts to isolate the unsubstituted diphenylquinocyclopropene VI ($\lambda_{max}^{CH_3CN}$ 387 mμ, log ϵ 4.8) as a pure, crystalline substance were unsuccessful. In the case of the dibrominated system, however, recrystallization of the sparingly soluble product from
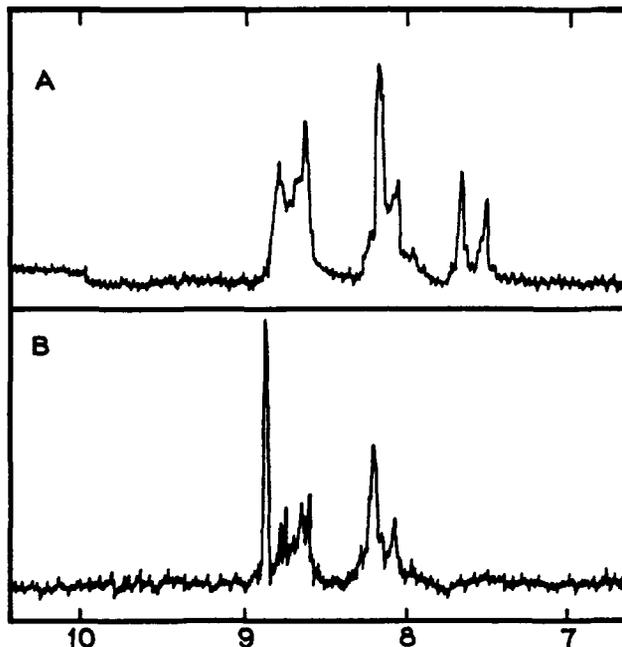
(4) L. I. Smith and M. M. Falkof, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons. Inc., New York, N. Y., 1955 p. 350.

(5) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

(6) The ultraviolet spectra observed for compounds III, IV and V closely resembled each other and were in excellent accord with that reported by Breslow (ref. 5) for the 1-anisyl-2,3-diphenylcyclopropenyl cation.

(7) The same conversion to phenol IV occurred on debenzylation of crude III bromide with dry hydrogen bromide in acetic acid at 40°; yields were comparable.

(8) The characteristic proton magnetic resonance spectra of arylcyclopropenium salts are discussed in ref. 2, pp. 3171–3173. We are indebted to Mr. V. Canady for the measurements illustrated in Fig. 1 of this communication.

Fig. 1.—Proton magnetic resonance spectra, taken at 60 Mc. with trifluoroacetic acid as solvent and tetramethylsilane (int.) as standard, of (A) 1-(p-hydroxyphenyl)-2,3-diphenylcyclopropenium bromide, IV, and (B) its dibromo substitution product, V. Units (δ) are p.p.m. downfield from tetramethylsilane.

acetonitrile gave orange needles of analytically pure dibromodiphenylquinocyclopropene VII, dec. >230°, $\lambda_{max}^{CH_3CN}$ 278, 393 mμ, log ϵ 4.41, 4.76 (*Anal.* Found: C, 57.33; H, 2.91; Br, 36.44, 36.59; Br (as bromide), 0). Compound VII was stable to light and to prolonged heating at 140° in the solid state, but was rapidly destroyed by hydroxylic solvents. The proton magnetic resonance spectrum of VII in trifluoroacetic acid was identical with that of the cyclopropenium bromide V in the same solvent.
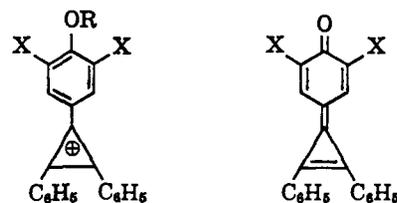
III, R = CH$_2$C$_6$H$_5$, X = H
IV, R = H, X = H
V, R = H, X = Br

VI, X = H
VII, X = Br

SCF molecular orbital calculations[9] for the π-system of VI suggest appreciable covalent character of the cyclopropene ring, consistent with the pronounced peak at 5.47 μ (C=C)[5] in the paraffin oil or KBr disk spectrum of the dibromo derivative VII. The calculations suggest further that the π-electron system of VI should be more basic than that of the "parent" cyclopropenone I. A preliminary comparison of the basicity of the quinocyclopropene VII with that of appropriate Hammett indicators in the inert solvent o-dichlorobenzene shows it to possess a base strength comparable to that of p-chloroaniline, pK_a 3.8. The quinocyclopropene system evidently is much more basic than the "parent" ketone I, which is reported to be only half-protonated in 12 N hydrochloric acid.[10] Moreover, we find compound VII to be approximately 2 pK_a units more basic than

(9) Calculations were carried out in collaboration with Prof. R. Daudel and O. Chalvet, Centre de Mécanique Ondulatorie Appliquée, Paris (to be published), for whose hospitality and advice the author is greatly indebted.

(10) R. Breslow and R. Peterson, *J. Am. Chem. Soc.*, **82**, 4426 (1960).

the closely related 4-diphenylmethylene-2,5-cyclo-hexadienone, which lacks the potential cyclopropenium core of VII. Further evidence bearing on these and related points will be described subsequently.

ORGANIC CHEMICAL RESEARCH SECTION   ANDREW S. KENDE
LEDERLE LABORATORIES DIVISION
AMERICAN CYANAMID COMPANY
PEARL RIVER, NEW YORK
RECEIVED APRIL 12, 1963

Nucleophilic Reactions of Trivalent Phosphorus Compounds: A New Synthesis of Epoxides

Sir:

Continuing our investigation on the nucleophilic behavior of trivalent phosphorus compounds, we wish to describe the reaction of phosphorous triamides, $(R_2N)_3P$, (I) with aldehydes.

The addition of Ia (R = CH_3), to two moles of benzaldehyde yielded, after 70 hr. at room temperature, a slurry of white crystals in a pale yellow liquid. Analysis of the crystals (m.p. 118–119°; mol. wt. 266 ± 2%; C, 57.8; H, 8.8; P, 11.3) indicated the composition of a 1:1 adduct of benzaldehyde and Ia. Hydrogen n.m.r. [multiplets in the aromatic region (δ 7.14 to 7.55 p.p.m.; area 5.3), a doublet (δ 3.88; J = 17.9 c.p.s.; area 1.0) and a set of three doublets of equal areas (δ 2.77, J = 9.3; δ 2.33, J = 0.7 and δ 2.24 p.p.m., J = 8.5 c.p.s., total area 18.0)] indicated structure IIa for the adduct

IIa
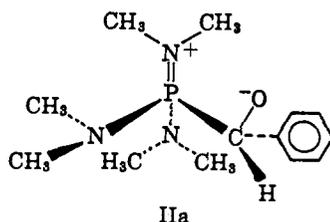
The mother liquor of the crystals contained hexamethylphosphoramide, $[(CH_3)_2N]_3PO$, III ($\delta_{P_{11}}$ −23.4 p.p.m.), and two isomeric structures identified as *trans*- and *cis*-stilbene oxide, δ (H, oxirane) 3.78 and 4.23 p.p.m., respectively.

The following reactions of benzaldehyde with I are indicated

$C_6H_5CHO + [(CH_3)_2N]_3P \longrightarrow$ IIa   (1:1 adduct)

$+ III$

IV (X:H), *cis* and *trans*
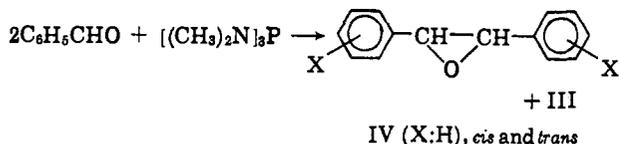
The reaction of I with aldehydes subsequently was found to be of a general nature. Aromatic aldehydes with electronegative substituents, especially in the *ortho* position, yield, in a highly exothermic and practically instantaneous reaction, predominantly epoxides. Electron releasing substituents on the benzene ring favor the formation of adducts, generally in a slow but noticeably exothermic reaction.

The H^1 and P^{31} n.m.r. characteristics of some adducts (II) are [X: ring substituent, δ_H (benzylic), J, δ_H (dimethylamino) p.p.m. (3 pairs), J (c.p.s.), $\delta_{P_{11}}$ (H_3PO_4) p.p.m.]: *p*-F, *3.89*, 17.5, *2.71*, 8.98, *2.29*, 0.8, *2.20*, 8.2, *−30.1;* 3,4-$(CH_3O)_2$, —, —,[1] *2.68*, 8.8, *2.31*, 0.8, *2.24*, 8.2, *−29.7;* *m*-CH_3O, —, —,[1] *2.70*, 8.72, *2.29*, 0.9, *2.21*, 8.4, *−29.8;* *o*-CH_3O, *4.82*, 18.1, *2.76*, 8.92, *2.35*, 0.7, *2.23*, 8.42, *−30.3;* 3,4-CH_2O_2, *3.89*, 18.3, *2.75*, 9.28, *2.32*, 0.8, *2.30*, 8.60, *−30.7*.

(1) One or both peaks are covered by the methoxyl frequencies.

The following examples are illustrative of the scope of the epoxide forming reaction (IV, X: ring substituent, δ (oxirane) *cis*, δ (oxirane) *trans*, yield % (total), *trans/cis* ratio): *o*-Cl, *4.49*, *3.99* (m.p. 72–74°), 90, 1.38; *p*-Cl, *4.17*, *3.65* (m.p. 123–125°),[2] 40, 4.0; *m*-Br, *4.07*, *3.56* (m.p. 84–86°), 53, 2.6; *o*-Br, *4.54*, *4.05*, 95, 1.45; *o*-F, *4.53*, *4.20*, 96, 1.54; 3,4-Cl_2 *4.14*, *3.63*, 93, 1.50; 2,6-Cl_2 *5.26*, *4.67*, 36, 8; *m*-O_2N, *4.58*, *4.08* (m.p. 156–158°), 80, 2.8; *p*-NC, *4.46*, *3.92*, 95, 1.33; *p*-OCH, *4.48*,*3.96*,80,1.1[3]; α-naphthaldehyde,*4.95*,*4.40*,87,1.13.

Ia reacts also with saturated and heterocyclic aldehyde and yields preferentially adducts (aldehyde, $\delta_{P_{11}}$ (p.p.m.): propionaldehyde, *−31.8;* 1,2,3,6-tetrahydrobenzaldehyde, *−31.6;* 2-furaldehyde, *−28.2;* 2-thiophenecarboxaldehyde, *−28.4*. The reaction of I with chloral takes a different course and yields the dichlorovinyloxyphosphonium compound, $Cl_2C{=}CH{-}O{-}\overset{+}{P}[N(CH_3)_2]_3Cl^-$ (δ_{CH_3} 2.94, J_{PH} = 10.36; $\delta_{HC=}$ *8.47* p.p.m., J_{PH} = 4.1 c.p.s.; $\delta_{P_{11}}$ −34.8 p.p.m.).

The following mechanism is suggested for the transformations

IV
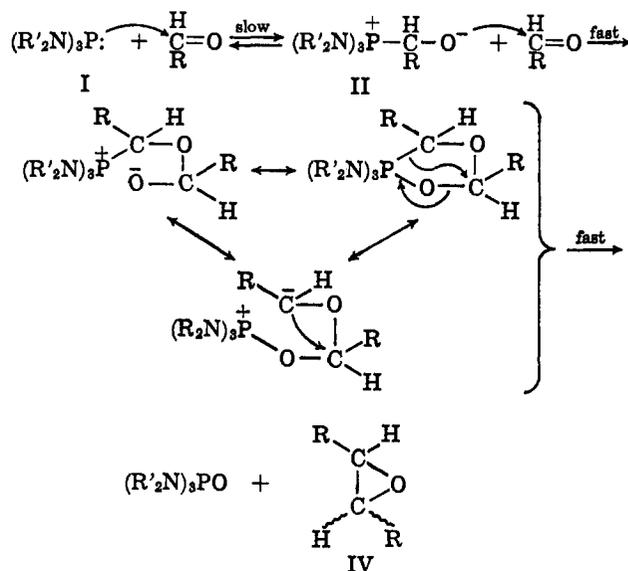
When the carbonyl group is relatively a poor acceptor of nucleophile I, the 1:1 adducts are preferentially obtained.[4] When R is an electronegative substituent and when I is *added slowly* to the aldehyde, IV is the major product.

The collapse of the postulated 2:1 adduct intermediate can be compared with the second step of the Wittig reaction: in both cases a carbon–phosphorus and a carbon–oxygen bond cleavage results in the formation of a phosphorus–oxygen and a carbon–carbon bond (π bond in the second case). An even closer analogy of the intramolecular S_N2 decay of the 2:1 adduct can be found in the recent work of Denney,[5] Wadsworth[6] and McEwen.[7,8]

(2) Reported m.p. 123–124° (R. E. Lutz and R. S. Murphey, *J. Am. Chem. Soc.*, **71**, 478 (1949)).

(3) The aldehydic hydrogen frequencies of IV, *p*-OCH, are at 9.88 p.p.m. for the *cis* and at 10.05 p.p.m. for the *trans* isomer.

(4) The solvation of the aldehyde by I probably explains the formation of II when no excess aldehyde is employed. The postulated mechanism is intended to apply to non-solvated aldehydes only.

(5) D. B. Denney, J. J. Vill and M. J. Boskin, *J. Am. Chem. Soc.*, **84**, 3944 (1962).

(6) W. S. Wadsworth and W. D. Emmons, *ibid.*, **83**, 1733 (1961).

(7) W. E. McEwen, *et al.*, *ibid.*, **84**, 676, 677 (1962).

(8) Referee I suggested an alternate mechanism, consisting of a nucleophilic attack by phosphorus on carbonyl oxygen followed by an attack on carbonyl carbon by the resultant 1:1 adduct (which is not identical with the isolated betaine) and concluded by displacement on carbon by oxide [*cf.* Ramirez and co-workers, *ibid.*, **84**, 1317 (1962), and references therein]. The data presented above do not exclude a similar interpretation.