

Effect of a Polyelectrolyte on the Over-all Rate.—The effect of polydiallyldimethylammonium nitrate (PDDANO₃) on k_T (see eq. 4) is shown in Fig. 5. No attempt was made to separate the four individual rate constants. The over-all rate increases with increasing polyelectrolyte concentration until the normality of the PDDA⁺ is equal to the normality of AcPO₄⁻ + HPO₄⁻. Further increase in [PDDA⁺] leads to a decrease in rate and a cloudiness in the solution, the cloudiness disappearing when the polyelectrolyte normality becomes twice that of the bivalent anions. These data suggest that the polyquaternary cation is a more effective catalyst than tetramethylammonium cation, and that association on a one-to-one charge basis takes place. The decrease in rate in the presence of larger amounts of polyelectrolyte may be ascribed tentatively to further complexing and resultant shielding of the AcPO₄⁻ by the PDDA⁺.

Preliminary experiments were carried out on a heterogeneous system using a quaternary ammonium type anion exchange resin (Amberlite IR-400) as the added ionic species. After an initial rapid decrease, the acetyl phosphate concentration in the solution phase decreased according to first-order kinetics as in the homogeneous systems. The first-order over-all glycinolysis rate constant appeared to be increased by the resin far more than was the first-order over-all hydrolysis rate constant.

Acknowledgment.—We are indebted to Professor Arthur C. Wahl of Washington University for several helpful discussions during the course of this work and to Professor Myron Bender of Illinois Institute of Technology and Dr. Henry E. Berkheimer of Harvard University for a critical reading of the manuscript.
St. Louis, Mo.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

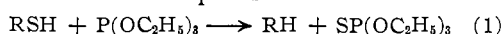
Some Extensions of the Reaction of Trivalent Phosphorus Derivatives with Alkoxy and Thiyl Radicals; a New Synthesis of Thioesters¹

BY CHEVES WALLING, OTTOKAR H. BASEDOW AND EMMANUEL S. SAVAS

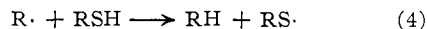
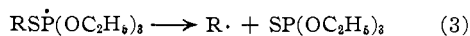
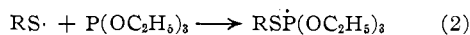
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A number of new reactions have been investigated. Evidence for a transient tetravalent phosphoranyl radical is given by the formation of small amounts of toluene in the reaction of benzyl diethyl phosphite with mercaptans. Thiophenol reacts sluggishly with trialkyl phosphites and inhibits the reaction of other mercaptans. The major reaction is a non-radical alkylation of the thiophenol. The reaction of di-*t*-butyl peroxide with triphenylphosphine has been reinvestigated and found to follow the same path as the reaction with phosphites. No *t*-butyl ether is produced. Alkyl disulfides, trialkyl phosphites and CO react to give good yields of thioesters *via* a radical chain. Some *n*-valeraldehyde is produced in the same way when the disulfide is replaced by *n*-butyl mercaptan.

Recent work in this Laboratory² has provided evidence that the facile reaction between trialkyl phosphites and mercaptans



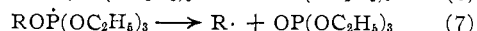
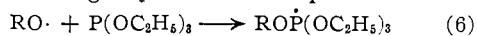
first described by Hoffmann and co-workers³ is a radical chain process with the chain-carrying steps



We also have found that, when mercaptan is replaced by disulfide, an alternate chain occurs with (4) replaced by



Further, alkoxy radicals (*e.g.*, from di-*t*-butyl peroxide) attack trialkyl phosphites in an analogous manner, although by a non-chain process.



This paper reports some extensions of these reactions which both give further support to the mechanisms proposed earlier and show the possibility of involving additional species in the radical chains.

Reaction of Benzyl Diethyl Phosphite with *n*-Butyl Mercaptan.—The formulation given above

(1) Support of a portion of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) C. Walling and R. Rabinowitz, *THIS JOURNAL*, **81**, 1243 (1959).

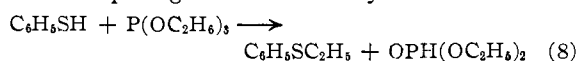
implies the formation of a tetravalent phosphoranyl radical as a transient intermediate formed in reactions 2 or 6. If the four bonds are actually equivalent, it is possible that an alkyl group from the original phosphite rather than the attacking radical will be split off in the subsequent decomposition, reactions 3 or 7. The reactions of benzyl diethyl phosphite present a favorable case, because of the high resonance stabilization of any benzyl radical produced. When benzyl diethyl phosphite was treated with *n*-butyl mercaptan at 60°, approximately 3% of toluene was detected among the products indicating some benzyl radical formation. The balance of the reaction yielded the normal products, *n*-butane and trialkyl phosphorothionate, indicating that cleavage of a C-S bond is the preferred process.⁴ Nevertheless, the experiment certainly provides evidence for the existence of the postulated phosphoranyl radical, and higher yields of the "abnormal" cleavage might be expected in other systems.

Reaction of Thiophenol with Triethyl Phosphite.—The reaction sequence 2-4 where R = phenyl (or other aryl group) if successful should provide a novel method of generating phenyl (or other aryl)

(3) F. W. Hoffmann, R. J. Ess, T. C. Simmons and R. S. Hanzel, *ibid.*, **78**, 6414 (1956).

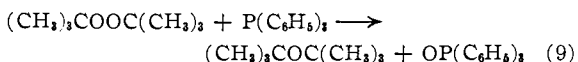
(4) Bond dissociation energies for C-S bonds are in general lower than those for corresponding C-O bonds; *cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 49.

radicals. *A priori* the large transfer constants of thiophenol in polymerization reactions⁵ suggests that step 4 should occur with great ease, but the small resonance energy of the phenyl radical and the possibility of additional strengthening of the C₆H₅-S bond due to overlap between the π -electron system and the unshared electron pairs of sulfur might strongly retard the phosphoranyl radical dissociation (3). Results with thiophenol-triethyl phosphite are consistent with these expectations. At 60–70° in the presence of azobisisobutyronitrile (AIBN) or strong ultraviolet light no reaction occurs. Further, addition of 20% thiophenol to a *n*-butyl mercaptan-triethyl phosphite system strongly inhibits the AIBN initiated reaction, indicating the preferential formation of benzenethiyl radicals. At 145° in the presence of di-*t*-butyl peroxide a slow reaction does take place between thiophenol and triethyl phosphite, and 10–15% triethyl phosphorothionate and benzene could be isolated from the products. However, the major products proved to be diethyl phosphite and phenyl ethyl sulfide. That these are the result of a competing non-radical alkylation

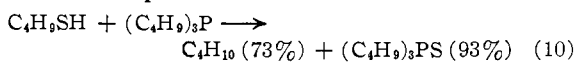


was demonstrated by heating together thiophenol and the phosphite in the absence of peroxide. Both phenyl ethyl sulfide and diethyl phosphite were obtained in good yield, but neither benzene nor the phosphorothionate could be detected.⁶

Reactions with *t*-Phosphines.—Radical reactions analogous to those of trialkyl phosphites might be anticipated with trisubstituted phosphines. However Horner and Jurgeleit⁷ have reported that the reaction of di-*t*-butyl peroxide and triphenylphosphine takes a different course



We find that *n*-butyl mercaptan reacts readily with tri-*n*-butylphosphine at 60° in the presence of AIBN as expected



We also have reinvestigated Horner's reaction with results shown in Table I. Much the same mixture of products is obtained as in the reaction with triethyl phosphite, and we have been unable to detect any trace of *t*-butyl ether in spite of the fact that authentic *t*-butyl ether is well resolved from the other reaction products in our gas chromatographic analysis. No *t*-butyl ether was detected in a similar experiment at 114° run for 92 hours (Horner's conditions), but considerable unreacted peroxide remained. We accordingly conclude that formulation 9 is erroneous, and

(5) R. A. Gregg, D. M. Alderman and F. R. Mayo, *THIS JOURNAL*, **70**, 3740 (1948).

(6) Several examples of alkylation by trialkyl phosphites are known, *e.g.*, of mono- and dialkyl phosphates and phosphonic acids; C. Walling, F. W. Stacey, S. E. Jamison and E. S. Huyser, *ibid.*, **80**, 4546 (1958).

(7) L. Horner and W. Jurgeleit, *Ann.*, **591**, 139 (1955). However, evidence for a radical chain reaction of triphenylphosphine and bromoform proceeding through a phosphoranyl radical has been given by F. Ramirez and N. McKelvie, *THIS JOURNAL*, **79**, 5829 (1957).

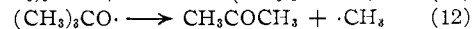
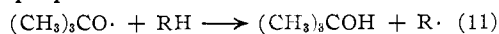
Horner's product probably was a mixture of peroxide, *t*-butyl alcohol, octanes and octenes which are very difficult to separate by distillation, or to distinguish from the ether by chemical properties. The unreacted peroxide found in the 114° experiment also indicates that the peroxide is disappearing only *via* its thermal dissociation, and no faster direct reaction with triphenylphosphine is taking place.

TABLE I

REACTION OF DI-*t*-BUTYL PEROXIDE WITH TRIPHENYLPHOSPHINE AND WITH TRIETHYL PHOSPHITE

| Products, in moles/mole peroxide | Triphenylphosphine | Triethyl phosphite |
|----------------------------------|--------------------|--------------------|
| Isobutane | 0.27 | 0.36 |
| Isobutylene | .12 | 0.42 |
| Neopentane | .01 | ... |
| Isopentane | .007 | 0.007 |
| Isopentene (?) | .009 | .009 |
| Acetone | 1.21 | .74 |
| <i>t</i> -Butyl alcohol | 0.32 | .30 |
| Isooctane | .025 | .078 |
| Octenes | .007 | .006 |
| Tetramethylbutane | .02 | .066 |
| Triphenylphosphine oxide | .98 | ... |
| Triethyl phosphate | ... | ~1.0 |

The considerable amounts of acetone and *t*-butyl alcohol reported in Table I presumably arise because of the 1:1 mole ratio of peroxide to phosphorus derivative employed. The stoichiometry of the reaction requires a 1:2 ratio, and the alkoxy radicals produced after the phosphorus derivative has been exhausted undergo hydrogen abstraction and disproportionation reactions.



In our earlier experiments using a 1:4 mole ratio no appreciable acetone or *t*-butyl alcohol was detected.² The neopentane and isopentane plus isopentene found in the present reaction presumably arise from reactions of methyl radicals with *t*-butyl radicals and with isobutylene, respectively.

Reactions with Carbon Monoxide.—The ability of alkyl radicals to react with CO was first clearly shown in the copolymerization of CO and ethylene,⁸ and subsequently has been demonstrated in a number of other reactions.⁹ Accordingly, it seemed possible that, in the presence of CO, the reaction between disulfides and trialkyl phosphites might be modified to yield thioesters by replacing step 5 by the sequence



The success of this expectation is shown in Table II. Under a high pressure of CO, yields of butyl thiovalerate from butyl disulfide are almost quantitative, and they are significant even at 1 atmosphere pressure. Reaction mixtures were analyzed by gas chromatography, and no significant peaks other than butyl sulfide, butyl thio-

(8) M. M. Brubaker, D. D. Coffman and H. H. Hoehn, *THIS JOURNAL*, **74**, 1509 (1942).

(9) For a summary of recent references *cf.* C. Walling and E. S. Savas, *ibid.*, **82**, 1738 (1960).

valerate, triethyl phosphorothionate and unreacted triethyl phosphite were detected. Since yields of thioester depend upon the successful competition of sequence (13-14) with (5), and accordingly upon the CO/disulfide ratio, high yields are favored either by high CO pressure or a low disulfide concentration. Thus a significant increase in yield at 1 atmosphere CO pressure was obtained by slowly adding the disulfide to phosphite over a 24-hour reaction period.

We have also investigated the analogous reaction

$$\text{RSH} + \text{CO} + \text{P}(\text{OC}_2\text{H}_5)_3 \longrightarrow \text{RCHO} + \text{SP}(\text{OC}_2\text{H}_5)_3 \quad (15)$$

even though it appears intrinsically less attractive because of the very high rate of reaction 4 compared with 5. When *n*-butyl mercaptan was treated with triethyl phosphite at 50° in the presence of AIBN under a pressure of 184 atmospheres of CO the major products were butane and phosphorothionate. However a small amount (estimated at 1-2% by gas chromatographic analysis) of *n*-valeraldehyde was detected and identified as its 2,4-dinitrophenylhydrazone. The

TABLE II

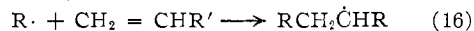
REACTION OF *n*-BUTYL DISULFIDE WITH TRIETHYL PHOSPHITE IN THE PRESENCE OF CO

| T, °C. | P _{CO} , atm. | Initiator | Products, % | |
|---------|------------------------|-------------------|-----------------|---------|
| | | | Thioester | Sulfide |
| 120-144 | 325 | DTBP ^a | 99 | 1 |
| 120 | 7-12 | DTBP ^a | 47 | 53 |
| 50 | 1 | U.v. | 18 | 82 |
| 50 | 1 | U.v. | 36 ^b | 64 |
| 50 | 1 | U.v. | 13 ^c | 87 |

^a Di-*t*-butyl peroxide. ^b Slow addition of disulfide during reaction. ^c Isobutyl disulfide used in this experiment.

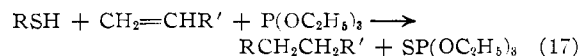
possibility that additional aldehyde was formed but disappeared by some sort of radical reaction with phosphite was eliminated by heating *n*-butyraldehyde and triethyl phosphite in the presence of AIBN. Both starting materials were recovered unchanged.

Reactions with Olefins.—In the presence of olefins, the alkyl radicals produced in reactions 3 and 7 might be expected to add to the olefin



leading to additional products, and preliminary experiments indicate that this is actually the case. When di-*t*-butyl peroxide, triethyl phosphite and 1-hexene were allowed to react together at 140°, the hexene was consumed as well as the other reactants, and a considerable amount of material boiling above triethyl phosphite was obtained containing at least six unidentified components.

In the presence of olefins, the mercaptan-phosphite reaction could lead to alkylation of the olefin if reaction 16 occurs, *e.g.*



Preliminary experiments with cyclohexene, 1-hexene and styrene, however, gave chiefly mercaptan addition to the olefin, indicating that



is rapid compared with reaction 2. Both of these

reactions are being investigated further and results will be reported later.

Experimental

Reagents were in general commercial materials. Where such treatment was applicable, they were dried and redistilled before use.

Benzyl diethyl phosphite was prepared by transesterification of 2 moles triethyl phosphite and 1 mole benzyl alcohol as described by Hoffmann, Ess and Usinger¹⁰; b.p. 144.5-146° (20 mm.), *n*_D²⁰ 1.4885.

***t*-Butyl ether** was prepared from Ag₂CO₃ and *t*-butyl chloride in ether¹¹; b.p. 100-105°, *n*_D²⁰ 1.3936 (lit.¹¹ *n*_D²⁰ 1.3949). Gas chromatographic analysis showed it to be homogeneous except for a small amount of *t*-butyl chloride.

Tributylphosphine sulfide was prepared by slowly adding 0.32 g. of sulfur to 2.5 g. of the phosphine, refluxing for an hour and distilling at 0.1 mm.

Reaction of Benzyl Diethyl Phosphite and *n*-Butyl Mercaptan.—No reaction occurred when 4.6 g. (0.02 mole) of benzyl diethyl phosphite and 1.8 g. (0.02 mole) of *n*-butyl mercaptan were heated together at 60° for 1 hour. Addition of 33 mg. of AIBN gave a rapid evolution of butane, and the reaction was complete in 1 hour. Gas chromatographic analysis showed a small peak identified as toluene by retention time, and calibration with known mixtures indicated an amount corresponding to a 3% yield.

Reactions with Thiophenol.—Triethyl phosphite and a slight excess of thiophenol, irradiated for 10 hours at 70° with a Hanovia ultraviolet lamp or heated 25 hours with 3 mole % AIBN at 60° gave only starting materials. A mixture of 10 mmole of *n*-butyl mercaptan, 0.2 mmole of thiophenol, 8.5 mmole of triethyl phosphite, 0.05 mmole of AIBN and 10 mmole of bromobenzene (as an internal standard for gas chromatographic analysis) showed approximately 10% conversion to triethyl phosphorothionate in 40 min. at 60°. In a similar mixture without the thiophenol complete reaction occurred in the same time.

Thiophenol (55 g., 0.5 mole) and triethyl phosphite (166 g., 1.0 mole) were refluxed together 20 hours under N₂ and the reaction mixture fractionated through a Podbielniak column at 29 mm. to give ethanol (12.5 g.) and unreacted triethyl phosphite (90.0 g.). The material boiling above triethyl phosphite contained three components which could not be resolved entirely by fractional distillation. These were purified further by gas chromatography and characterized as diethyl phosphite (47.5 g., b.p. 90-91° (29 mm.), *n*_D²⁰ 1.4094, retention time identical with authentic material (*Anal.* C, 36.50; H, 8.01; P, 22. Calcd. for C₄H₁₁PO₃: C, 36.78; H, 8.03; P, 22.43); phenyl ethyl sulfide (48.0 g.), b.p. 103.0-103.5° (30 mm.), *n*_D²⁰ 1.5632. The material had the correct analysis for C, H and S, and on oxidation with peracetic acid gave phenyl ethyl sulfone, m.p. 42°. The third component (13.5 g.) gave an analysis, C, 44.79; H, 9.03; P, 17.82; S, 0.0, corresponding to no simple formula and probably was a mixture of unidentified substances. The molar ratio of diethyl phosphite and phenyl ethyl sulfide is close to 1:1 and corresponds to a 70% yield of alkylation product. Gas chromatographic analysis of a similar reaction mixture on a Craig polyester succinate column at 168° showed no peak for triethyl phosphorothionate.

When 22.0 g. of thiophenol (0.2 mole), 33.2 g. of triethyl phosphite (0.2 mole) and 1.46 g. of di-*t*-butyl peroxide (0.01 mole) were heated 100 hours under nitrogen in a sealed tube, these products were identified by retention time in gas chromatography using Craig polyester succinate and silicone columns at 165-185°: ethanol, benzene, triethyl phosphite, diethyl phosphite, thiophenol, triethyl phosphite, triethyl phosphorothionate, phenyl ethyl sulfide and a higher boiling unidentified compound. Phenyl ethyl sulfide was the major product and was separated by gas chromatography and identified by oxidation to sulfone, m.p. 42°. Relative yields of phenyl ethyl sulfide and phosphorothionate were 85:15. Benzene was identified in a similar reaction mixture by distilling off the low boiling fraction in a spinning band column and separating by gas chromatography. From 0.1 mole of reagents 0.6 g. (8%) of benzene was obtained, m.p. 5-6°, infrared spectra identical with authentic benzene.

(10) F. W. Hoffmann, R. J. Ess and R. P. Usinger, *THIS JOURNAL*, **78**, 5817 (1956).

(11) J. L. E. Erickson and W. H. Ashton, *ibid.*, **63**, 1769 (1941).

Reaction of Tri-*n*-butylphosphine with *n*-Butyl Mercaptan.—The phosphine (20 mmole), mercaptan (20 mmole), diphenyl ether (20 mmole as internal standard) and AIBN (0.1 mmole) were heated for 140 min. at 60° under N₂ in an erlenmeyer flask connected through a condenser and bubble counter to a cold trap. *n*-Butane (0.8 g., 73%) collected in the trap, and gas chromatographic analysis showed 93% reaction of the phosphine and 92% conversion to phosphine sulfide. The tributylphosphine sulfide was identified by comparison of its retention time with known material.

Reaction of Triphenylphosphine with Di-*t*-butyl Peroxide.—The phosphine (20.5 g., 78 mmole) and peroxide (11.0 g., 75 mmole) were heated 95 hours at 130° in a sealed tube. The tube was cooled to -78°, opened, and products separated by first distilling materials boiling below 50°, fraction I, 1.9 g., into a cold trap, transferring the remainder to a distilling flask, and removing materials volatile under reduced pressure; fraction II, 8.2 g., up to the temperature where decomposition of triphenylphosphine oxide became detectable. Triphenylphosphine oxide, 21.4 g., remained as a residue in the flask. Fractions I and II were analyzed by gas chromatography at 25 and 86°, respectively, using phthalate ester and silicone columns in series, with results summarized in Table I. The reaction of the peroxide with triethyl phosphite was carried out in the same manner using 10 mmole of reagents. Material boiling below 80° (0.46 g.) was analyzed separately from the higher boiling fraction using the same techniques as above.

The absence of *t*-butyl ether in the triphenylphosphine experiments (and in a number of similar runs at 130°) was demonstrated by gas chromatography using a 10-ft. Craig polyester succinate column at 120°. This substrate was found to give good separation of authentic ether from the other reaction products and from di-*t*-butyl peroxide. A reaction run for 92 hours at 114° contained much unreacted peroxide, together with the same spectrum of products formed at 130°.

Reactions with CO.—Reactions under pressure were carried out in a glass-lined hydrogenation bomb⁹ using 10.0 ml. (52 mmole) of *n*-butyl disulfide, 10.0 ml. (58 mmole) of triethyl phosphite and 80 mg. (0.55 mmole) of di-*t*-butyl peroxide, and heating for 11-16 hours. Gas chromatographic analysis (silicone column, 150°) showed small amounts of low-boiling material (probably butane from the peroxide), triethyl phosphite and *n*-butyl sulfide, but chiefly triethyl phosphorothionate and *n*-butyl thiovalerate. The latter material (which is not reported in the literature) was isolated from the 325-atm. run using a 1-in. diam. silicone column, b.p. 219° (uncor.), *n*_D²⁰ 1.4608. *Anal.* C, 61.63; H, 10.42; S, 18.15. Calcd. for C₈H₁₈OS: C, 62.02; H, 10.41; S, 18.39. It showed a carbonyl peak in its infrared spectrum, gave a positive hydroxamic acid test, and a strong odor of mercap-

tan on hydrolysis. Subsequent runs were analyzed by comparison of the sulfide and thioester peaks.

Photochemical reactions were run in a small flask illuminated by a General Electric RS sunlamp and cooled by a stream of air, and using 10.0 ml. each of disulfide and phosphite. The flask was flushed well with CO before illumination, which was continued for 21-24 hours. In one experiment, the phosphite alone was placed in the flask, and the disulfide added dropwise over 24 hours. *n*-Butyl mercaptan (0.191 mole), triethyl phosphite (0.232 mole), and AIBN (0.0003 mole) were heated for 15 hours at 50° under 184 atm. CO pressure. Gas chromatographic analysis showed a peak corresponding to 1-2% *n*-valeraldehyde. The reaction mixture was distilled giving a forerun of 1 ml., b.p. 30-44° (100 mm.). This fraction showed a strong carbonyl peak in the infrared and gave a positive fuchsin test and precipitate with 2,4-dinitrophenylhydrazine. Two recrystallizations gave the 2,4-dinitrophenylhydrazone of *n*-valeraldehyde, m.p. 104.8-105.7°.

Reaction with Olefins.—Di-*t*-butyl peroxide (5 mmole), triethyl phosphite (10 mmole), 1-hexene (10 mmole) and bromobenzene (10 mmole as internal standard) were heated 20 hours at 140° in a sealed tube. Gas chromatography indicated consumption of almost all of the olefin as well as the other reagents. The experiment was repeated with 10 times the quantities of reagents, but no bromobenzene. The tube was chilled, opened, and 1.9 g. of gaseous products collected in a cold trap. The 29.7 g. of liquid residue was fractionated using a spinning-band column and the individual fractions analyzed by gas chromatography. Low boiling fractions had similar compositions to those obtained in the absence of olefin, and middle fractions were largely triethyl phosphite. Some 5 g. of higher boiling material also was found containing at least six unidentified components, presumably hydrocarbons resulting from radical addition to 1-hexene.

Several triethyl phosphite-*n*-butyl mercaptan reactions were carried out in the presence of cyclohexene, 1-hexene and styrene, but the major new products identified were the sulfides arising from mercaptan addition to the olefin. In a typical experiment, 0.1-mole quantities of *n*-butyl mercaptan, triethyl phosphite and cyclohexene were heated under N₂ for 24 hours at 60° in the presence of 0.001 mole of AIBN. Fractional distillation and gas chromatography showed 5.70 g. of unreacted cyclohexene, 2.35 g. of unreacted phosphite, 14.35 g. of triethyl phosphorothionate and 3.10 g. of butyl cyclohexyl sulfide, b.p. 100-108° (10 mm.), lit.¹² 101-103° (10 mm.). *Anal.* C, 69.53; H, 11.57; S, 18.82. Calcd. for C₁₀H₂₀S: C, 69.70; H, 11.70; S, 18.60.

(12) W. E. Bacon and W. M. LeSuer, *THIS JOURNAL*, **76**, 670 (1954).

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH]

Nuclear Magnetic Resonance Spectra of Indoles

By LOUIS A. COHEN, JOHN W. DALY, HERMANN KNY AND BERNHARD WITKOP

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Examination of the n.m.r. spectra of a series of indole derivatives has revealed the feasibility of using this technique to determine the extent of substitution at the α - and β -positions of the indole nucleus. The existence of measurable indolenine tautomerism in the ground state of indoles or of ring-chain tautomerism in tryptamines is excluded by these spectra. Previous structural assignments to 2-aminoindolenine and 2-bromo-LSD are confirmed by n.m.r. The spectrum of quebrachamine suggests the absence of N-methyl and α -hydrogen functions.

The application of nuclear magnetic resonance spectroscopy (n.m.r.) to the elucidation of organic structural features has been demonstrated repeatedly in recent years. Indeed, n.m.r. is fast becoming a unique tool for providing particular information on the structures of complex synthetic materials and natural products.¹

(1) Cf. S. Goodwin, J. N. Shoolery and L. F. Johnson, *Proc. Chem. Soc.*, 306 (1958); H. Conroy, P. R. Brook, M. H. Rout and N. Silverman, *THIS JOURNAL*, **80**, 5178 (1958); J. N. Shoolery and M. T. Rogers, *ibid.*, **80**, 5121 (1958).

In connection with several aspects of indole chemistry under investigation in this Laboratory, the n.m.r. spectra of a number of synthetic and natural indoles have been examined and certain correlations of chemical shift with structure have been derived.

Experimental

Spectra were determined at the Instrument Division Laboratories of Varian Associates, Palo Alto, Calif., on a 4300-C high resolution spectrometer at 60 megacycles per second. Compounds were studied in concentrations of 0.1 to 0.5 *M*