THE JOURNAL OF Organic Chemistry®

Volume 22, Number 11

November 12, 1957

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinone Imides. XLV. Structures of Aromatic Amine Adducts of *p*-Benzoquinonedibenzimide*

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Received June 17, 1957

The adduct of benzene and *p*-benzoquinonedibenzenesulfonimide has been shown to be 2-phenyl-*p*-phenylenedibenzenesulfonamide by an unequivocal synthesis. 2-Piperidino- and 2-morpholino-*p*-phenylenedibenzamide, formed from *p*-benzoquinonedibenzimide and piperidine and morpholine, respectively, were synthesized by another route. Aniline adds 1,6 to *p*-benzoquinonedibenzimide as shown by the preparation of the benzoyl derivative from 4-amino-4′-nitrodiphenylamine. Methylaniline and dimethylaniline add to *p*-benzoquinonedibenzimide with the carbon atom para to the amine function taking part in the reaction and becoming attached in the 2-position.

The reactions of quinone imides with secondary aliphatic, alicyclic, and aliphatic aromatic amines and with primary aliphatic and aromatic amines follow various pathways, depending on the reaction conditions, the nature of the quinonoid system, and the substituent on the imide nitrogen. Thus *p*-benzoquinonedibenzenesulfonimide and morpholine[2] may lead to any or all of several different products, including 2-morpholino- and 2,5-dimorpholinodibenzenesulfonamide and *p*-benzenesulfonamidophenylmorpholine. The addition of aniline follows a comparably complex course resulting mainly in benzenesulfonamide, N,N′-diphenyl-*p*-phenylenediamine, and 2,5-dianilino-*p*-benzoquinonedianil. Methylaniline and dimethylaniline,[3] however, yield only single products, the 2-substituted diamides, in which addition was postulated to involve the carbon atom of the aromatic ring *para* to the amine function.

In the case of 1,4-naphthoquinonedibenzenesulfonimide,[2–4] on the other hand, morpholine, aniline, and methylaniline all add to form single products which were assumed to have the nitrogen of the reagent attached to the 2-carbon atom of the diamide. The structures were assigned merely on the basis of the non-reactivity of dimethylaniline, the addition of *p*-toluidine, and spectroscopic evidence.

Morpholine was found to react with *p*-benzoquinonedicarbethoxyimide and *p*-benzoquinonedicarbobenzoxyimide,[5] piperidine with *o*-benzoquinonedibenzimide and 4-chloro-*o*-benzoquinonedibenzimide,[6] and aniline, morpholine, and piperidine with *p*-benzoquinonedibenzimide[5] to form adducts, which presumably are diamides with the nitrogen atom of the reagent attached in the 2-position. However, no proofs of structure were included in the investigation.

The addition of aniline to 2,3,5,6-tetrachloro-*p*-benzoquinonedibenzenesulfonimide[7] resulted in a product for which the chemical and spectroscopic evidence indicated formula I to be the correct structure.

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* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

[1] An abstract of a thesis submitted by Leslie M. Werbel to the Graduate College of the University of Illinois in partial fulfillment of the degree of Doctor of Philosophy, 1957; Minnesota Mining & Manufacturing Co. Fellow, 1952; Allied Chemical and Dye Corp. Fellow, 1955–56; Dow Chemical Fellow, 1956–57.

(2) R. Adams and K. A. Schowalter, *J. Am. Chem. Soc.*, **74**, 2597 (1952).

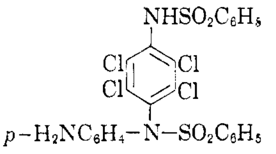
(3) R. Adams, B. H. Braun and S. H. Pomerantz, *J. Am. Chem. Soc.*, **75**, 4642 (1953).

(4) R. Adams and R. A. Wankel, *J. Am. Chem. Soc.*, **73**, 131 (1951).

(5) R. Adams and D. S. Acker, *J. Am. Chem. Soc.*, **74**, 5872 (1952).

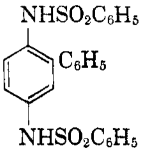
(6) R. Adams and J. W. Way, *J. Am. Chem. Soc.*, **76**, 2763 (1954).

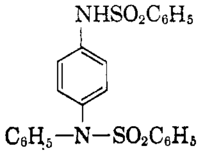
(7) R. Adams and B. H. Braun, *J. Am. Chem. Soc.*, **74**, 5869 (1952).


I

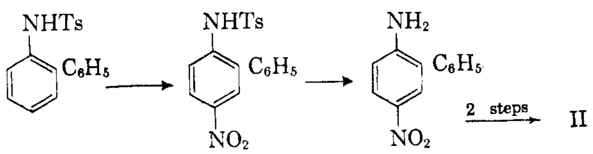
This investigation suggested the desirability of a restudy of the structures of the products obtained from addition not only of the aromatic and alicyclic amines but also of aromatic hydrocarbons in the presence of anhydrous aluminum chloride to *p*-benzoquinone diimides.

The product of addition of benzene to *p*-benzoquinonedibenzenesulfonimide was assumed[8] to have structure II in spite of the fact that lead tetraacetate oxidation of the adduct resulted in degradation with formation of *p*-benzoquinonedibenzenesulfonimide.

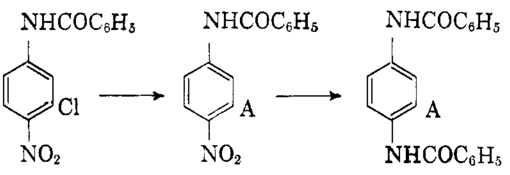

II


III

Structure III for the adduct, which involves 1,6-addition, was not considered as a possibility in the initial paper. Therefore, synthesis by an unequivocal method of structure II was undertaken. 2-*p*-Toluenesulfonamidobiphenyl (IV) was nitrated to 5-nitro-2-*p*-toluenesulfonamidobiphenyl (V). Detosylation with hydrobromic acid and phenol (VI), followed by reduction and benzenesulfonation resulted in a product (II) identical with the adduct of benzene to *p*-benzoquinonedibenzenesulfonimide.

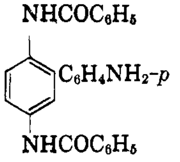

IV V VI

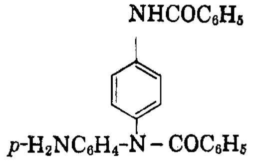
The structures of the adducts of amines to *p*-benzoquinonedibenzimide were next considered. Unequivocal syntheses of 2-morpholino-, 2-piperidino-, and 2-anilino-*p*-phenylenedibenzamide in which the nitrogen atoms of the amines were attached to the 2-positions in the rings were successfully completed. 3-Chloro-4-nitroaniline was benzoylated (VII) and then treated with morpholine, piperidine, and aniline, to replace the chlorine atom and provide the three amine derivatives. Subsequent reduction of the products followed by benzoylation gave the desired diamides (IX.)


VII VIII IX

A = (a) piperidino
(b) morpholino
(c) anilino

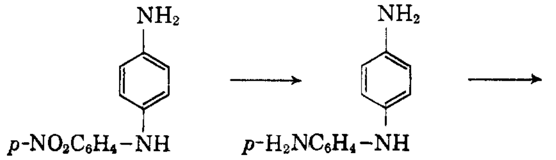
The piperidine and morpholine compounds were identical with the piperidine and morpholine adducts of *p*-benzoquinonedibenzimide, thus establishing the constitutions of the latter. But the aniline compound was different. Therefore, the adduct of aniline to *p*-benzoquinonedibenzimide was assumed to have one of the two structures X or XI.

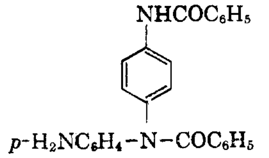

X


XI

Either structure satisfies the infrared spectrum and accounts for the presence of a primary amino group as shown by diazotization and coupling with β-naphthol and preparation of tosyl and benzoyl derivatives.

Structure XI was shown to be the correct one by comparison of its benzoyl derivative (XII) with a compound synthesized by an unequivocal route. *N*-*p*-Nitrophenyl-*p*-phenylenediamine (XIII) was reduced and the resulting triamine (XIV) benzoylated to give compound XII.


XIII XIV


XII

Thus a second example of 1,6-addition to *p*-benzoquinone diimides has been established and for the first time this mode of addition has been conclusively substantiated by chemical evidence.

The adducts of methylaniline and dimethylaniline with *p*-benzoquinonedibenzimide were assumed to have structures similar to those postulated for

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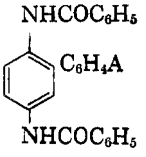
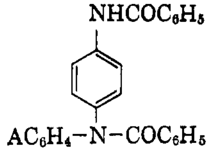
[8] R. Adams and K. R. Eiler, *J. Am. Chem. Soc.*, **73**, 1149 (1951).

the analogous *p*-benzoquinonedibenzenesulfonimide adducts, as indicated by type formula XV. If, however, 1,6-addition had occurred the structures would be those shown by type formula XVI. The analogy in structure of the monomethylaniline and dimethylaniline adducts was determined in the dibenzenesulfonamide series by conversion of the former to the latter by methylation with methyl iodide in dimethylformamide.[3] Similar results now have been obtained in the dibenzamide series by effecting methylation with formaldehyde and formic acid. The selection of type formula XV for the adducts was indicated by active hydrogen determinations on the dimethylaniline adducts of the dibenzenesulfonimide and dibenzimide. Both compounds possess two active hydrogens whereas only one should have been found if type structure XVI were correct.



XV



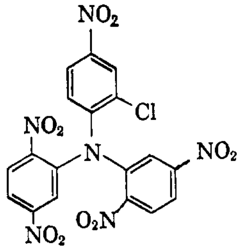
XVI

A = (a) p-$N(CH_3)_2$
(b) p-$NHCH_2$

The dimethylaniline adduct of *p*-benzoquinonedibenzimide showed a wide melting range and a mixture was suspected. However, a similar melting point was observed for the same product when prepared by methylation of the sharp-melting monomethylaniline adduct. The wide melting point is apparently a function of the crystallinity of the material.

The yields of the adducts of methylaniline and dimethylaniline to *p*-benzoquinonedibenzenesulfonimide and *p*-benzoquinonedibenzimide were excellent and only single entities were obtained. In contrast, aniline added to give mixtures from which the chief products were sometimes difficult to isolate in pure form. On the other hand, all the amines added to 1,4-naphthoquinonedibenzenesulfonimide in good yield through the nitrogen function and hence no reaction occurred with dimethylaniline.

In attempting to prepare 2-chloro-1,4-dinitrobenzene from 2-chloro-4-nitroaniline by means of oxidation with peroxytrifluoroacetic acid,[9] an interesting red crystalline by-product was obtained which appears to be a triphenylamine derivative (XVII) formed by condensation of one mole of 2-chloro-4-nitroaniline with two moles of the product, 2-chloro-1,4-dinitrobenzene.



XVII

EXPERIMENTAL

All melting points are corrected.

5-Nitro-2-p-toluenesulfonamidobiphenyl (V). A mixture of 2.5 g. of 2-*p*-toluenesulfonamidobiphenyl,[10] 25 ml. of water, and 25 ml. of yellow fuming nitric acid was warmed on a steam bath for 13 hr. On cooling, a deep orange solid mass resulted. This was powdered, filtered, and recrystallized from acetic acid to yield 1.5 g. (53%) of product, m.p. 170–172° (lit.[10] m.p. 169°).

2-Amino-5-nitrobiphenyl (VI). A mixture of 1 g. of 5-nitro-2-*p*-toluenesulfonamidobiphenyl, 2 g. of phenol, and 15 ml. of commercial 48% hydrobromic acid[11] was heated under reflux for 1.5 hr. After cooling and pouring into 100 ml. of water the solution was made basic with 15% aqueous sodium hydroxide. The yellow precipitate which formed was filtered and recrystallized from ethanol, yielding 0.32 g. (56%) of yellow crystals, m.p. 124.0–125.5°.

Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 67.07; H, 4.70; N, 13.01.

2,5-Dibenzenesulfonamidobiphenyl (II). In a 100 ml. three-neck round bottom flask equipped with stirrer, dropping funnel, and reflux condenser was placed a solution of 1 g. of 2-amino-5-nitrobiphenyl in 20 ml. of absolute methanol, and approximately 0.5 g. of a water slurry of Raney nickel. The stirrer was started and a solution of 0.3 g. of 100% hydrazine hydrate in 8 ml. of methanol was added dropwise. Gas evolution occurred. After the addition was complete the mixture was heated under reflux on the steam bath for 45 min. The catalyst was removed by filtration, and the pale purple filtrate evaporated to dryness. The resulting dark purple liquid was dissolved in 25 ml. of pyridine and 3.3 g. of benzenesulfonyl chloride added. After the heat generated had dissipated, the solution was poured into iced hydrochloric acid. The resultant pink solid was filtered and dried to yield 1.87 g. of crude diamide, m.p. 189–191° (86.4% based on nitro amine). It was purified by three crystallizations from ethanol; white crystals, m.p. 202–203°.

Anal. Calcd. for $C_{24}H_{20}N_2O_4S_2$: C, 62.05; H, 4.34; N, 6.03. Found: C, 62.29; H, 4.27; N, 6.02.

N-Benzoyl-3-chloro-4-nitroaniline (VII). To a solution of 5.3 g. of 3-chloro-4-nitroaniline[12] in pyridine was added 4.9 g. of benzoyl chloride. The mixture was warmed for 3 hr. on the steam bath, cooled, and poured into iced hydrochloric acid. The resultant precipitate weighed 7.85 g. (91.3%). Crystallization from ethanol yielded yellow needles, m.p. 163–164°.

Anal. Calcd. for $C_{13}H_9ClN_2O_3$: C, 56.43; H, 3.28; N, 10.13. Found: C, 56.74; H, 3.36; N, 10.00.

N-Benzoyl-3-anilino-4-nitroaniline (VIIIc). In a 50 ml. side-arm flask fitted with a reflux condenser and nitrogen inlet tube was placed 1.9 g. of *N*-benzoyl-4-chloro-4-nitroaniline and 25 ml. of aniline that had been distilled over zinc dust. The mixture was heated at 185° for 3 hr. under a nitrogen atmosphere, cooled, and poured into 100 ml. of water and steam-distilled to remove excess aniline. Upon cooling a black-orange solid remained in the container.

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(9) W. D. Emmons, *J. Am. Chem. Soc.*, **76**, 3470 (1954).

(10) F. Bell, *J. Chem. Soc.*, 2773 (1928).

(11) H. R. Snyder and R. E. Heckert, *J. Am. Chem. Soc.*, **74**, 2006 (1952).

(12) H. H. Hodgson and A. Kershaw, *J. Chem. Soc.*, 2919 (1929).

This was filtered and treated with 25 ml. of ethanol, resulting in 1.2 g. of orange solid, m.p. 216.5–218° (52.4%). The melting point was unchanged by recrystallization from ethanol.

Anal. Calcd. for $C_{19}H_{15}N_3O_3$: C, 68.46; H, 4.54; N, 12.61. Found: C, 68.51; H, 4.28; N, 12.61.

2-Anilino-p-phenylenedibenzamide (IX). To a solution of 0.4 g. of *N*-benzoyl-3-anilino-4-nitroaniline in approximately 75 ml. of methanol was added a small scoop of Raney nickel, followed by 0.4 ml. of 100% hydrazine hydrate. An exothermic reaction occurred and bleaching of the original color was noted. The mixture was heated on the steam bath for 1 hr., the catalyst removed by filtration, and the filtrate evaporated to dryness. The resultant brown gum was taken up in pyridine and treated with 0.2 ml. of benzoyl chloride. The solution was heated for 1 hr. on the steam bath, cooled, and poured into a slurry of ice and hydrochloric acid. The precipitated violet solid weighed 0.3 g. (32.4%). It was purified by recrystallization from dilute ethanol; white crystals, m.p. 248–249°.

Anal. Calcd. for $C_{26}H_{21}N_3O_2$: C, 76.64; H, 5.20; N, 10.31. Found: C, 76.52; H, 5.21; N, 10.45.

N-Benzoyl-3-morpholino-4-nitroaniline (VIIIb). A mixture of 0.7 g. of *N*-benzoyl-3-chloro-4-nitroaniline and 2 ml. of morpholine was heated under reflux for 1.5 hr., cooled and poured into ice and water. The oil which formed solidified upon standing to yield 0.83 g. (quant.) of bright yellow solid. Recrystallization from dilute ethanol afforded yellow crystals, m.p. 150–151.5°.

Anal. Calcd. for $C_{17}H_{17}N_3O_4$: C, 62.37; H, 5.24; N, 12.84. Found: C, 62.59; H, 5.57; N, 12.85.

2-Morpholino-p-phenylenedibenzamide (IXb). To a solution of 0.25 g. of *N*-benzoyl-3-morpholino-4-nitroaniline in 15 ml. of methanol was added a small amount of Raney nickel and sufficient 100% hydrazine hydrate (about 1 ml.) to bleach the color. Evolution of heat caused the methanol to boil. The mixture was heated on the steam bath for 25 min., filtered, and evaporated to dryness. The gummy residue was taken up in pyridine and 0.3 ml. of benzoyl chloride added. After heating on the steam bath for 1.5 hr. the mixture was poured into ice and hydrochloric acid. The pinkish solid that resulted weighed 0.2 g. (65.3%). Recrystallization from dilute ethanol gave white crystals, m.p. 213.5–214.5°.

Anal. Calcd. for $C_{24}H_{23}N_3O_3$: C, 71.80; H, 5.77; N, 10.47. Found: C, 72.08; H, 5.90; N, 10.27.

N-Benzoyl-3-piperidino-4-nitroaniline (VIIIa). This material was prepared analogously to the morpholine compound. Yellow crystals were obtained in yield of 78.5% and were purified by recrystallization from a mixture of benzene and cyclohexane, m.p. 117.5–118.5°.

Anal. Calcd. for $C_{18}H_{19}N_3O_3$: C, 66.45, H, 5.89; N, 12.92. Found: C, 66.56; H, 5.91; N, 12.79.

2-Piperidino-p-phenylenedibenzamide (IXa). This material was prepared analogously to the morpholine compound. A quantitative yield of white, feathery solid, m.p. 180–181°, resulted. It was purified by recrystallization from dilute ethanol.

Anal. Calcd. for $C_{25}H_{25}N_3O_2$: C, 75.16; H, 6.31; N, 10.52. Found: C, 75.11; H, 6.37; N, 10.55.

p-Toluenesulfonamide of adduct of aniline and p-benzoquinonedibenzimide: N-benzoyl-4-benzamido-4′-p-toluenesulfonamidodiphenylamine. A solution of 0.1 g. of the adduct of aniline and *p*-benzoquinonedibenzimide in pyridine was treated with 55 mg. of *p*-toluenesulfonyl chloride and heated on the steam bath for 3 hr., cooled, and poured into ice and hydrochloric acid. The white solid weighed 0.15 g. (quant.). Purification was effected by recrystallization from ethanol; white plates, m.p. 260.5–262.5°.

Anal. Calcd. for $C_{33}H_{27}N_3O_4S$: C, 70.57; H, 4.85; N, 7.48. Found: C, 70.20; H, 5.05; N, 7.40.

Addition of benzene to p-benzoquinonedibenzenesulfonimide. Attempted duplication of the preparation of the benzene adduct of *p*-benzoquinonedibenzenesulfonimide according to the original directions[8] disclosed that the reaction did not always proceed with the facility indicated. A crude brown-green solid which was obviously a mixture was sometimes obtained from the reaction. It could not be purified by crystallization so was subjected to chromatographic separation on a column of aluminum oxide. The solid was suspended on top of the column. Elution with 2:1 ethyl acetate–acetone produced 2-phenyl-*p*-phenylenedibenzenesulfonamide, followed by *p*-phenylenedibenzenesulfonamide and 2-chloro-*p*-phenylenedibenzenesulfonamide. Melting points of mixtures of these materials, after recrystallization respectively from ethanol, glacial acetic acid, and benzene, with authentic samples showed no depression.

Addition of aniline to p-benzoquinonedibenzimide. Repetition of this preparation according to the original directions[5] indicated that the reaction was not always a simple one. Although a good yield of amorphous solid was formed, only 8.5% of pure adduct could be isolated by the recommended purification techniques.

Addition of methylaniline to p-benzoquinonedibenzimide; 2-(p-methylaminophenyl)-p-phenylenedibenzamide (XV). A solution of 2 g. of *p*-benzoquinonedibenzimide in 20 ml. of chloroform was treated with 0.69 g. of redistilled methylaniline in 20 ml. of chloroform. The mixture was allowed to stand for 24 hr. and then poured into approximately 300 ml. of petroleum ether (b.p. 80–100°). The product precipitated as a grey solid (quant.). Recrystallization from dilute ethanol afforded white plates, m.p. 209.5–211.5°.

Anal. Calcd. for $C_{27}H_{23}N_3O_2$: C, 76.94; H, 5.50; N, 9.97. Found: C, 76.95; H, 5.43; N, 9.84.

Addition of dimethylaniline to p-benzoquinonedibenzimide; 2-(p-dimethylaminophenyl)-p-phenylenedibenzamide (XV). The reaction was conducted in a manner exactly analogous to the monomethylaniline addition. A quantitative conversion resulted. The product was purified by recrystallization from ethanol, m.p. 230°.

Anal. Calcd. for $C_{28}H_{25}N_3O_2$: C, 77.22; H, 5.79; N, 9.65. Found: C, 77.26; H, 5.83; N, 9.83.

The pure dimethylaniline adduct recrystallized from ethanol melted mainly at 230° but a small portion always remained unmelted up to about 244° (capillary). Similar results were obtained when the material was crystallized from benzene-cyclohexane. However, the melting point on a micro hot stage was sharp, m.p. 226.5–228.5°.

Conversion of monomethylaniline adduct to the dimethylaniline adduct. A solution of 0.5 g. of monomethylaniline adduct in 15 ml. of 90% formic acid and 140 mg. of 35% formaldehyde was heated on the steam bath for 8 hr. After cooling and pouring onto ice it was made basic with 15% aqueous sodium hydroxide. The resulting solid weighed 0.49 g. Recrystallization from dilute ethanol gave white crystals, m.p. 230.5° (except for a small amount which did not melt until 243°).

Anal. Calcd. for $C_{28}H_{25}N_3O_2$: C, 77.22; H, 5.79; N, 9.65. Found: C, 77.45; H, 6.07; N, 9.33.

N,N′,N″-Tribenzoyl-4,4′-diaminodiphenylamine (XII). *A.* To 0.2 g. of the adduct of aniline and *p*-benzoquinonedibenzimide in pyridine was added 0.1 ml. of benzoyl chloride. The mixture was warmed on the steam bath for 1 hr., cooled, and poured into ice and hydrochloric acid. The white solid, weighing 0.24 g. (95%), was recrystallized from ethanol; white plates, m.p. 310–312°.

Anal. Calcd. for $C_{33}H_{25}N_3O_3$: C, 77.48; H, 4.93; N, 8.21. Found: C, 77.54; H, 5.09; N, 8.07.

B. A solution of 0.2 g. of 4-amino-4′-nitrodiphenylamine in methanol was treated with a pinch of Raney nickel and approximately 0.1 ml. of 100% hydrazine hydrate. After the vigorous bubbling had subsided the suspension was warmed on the steam both for 1 hr. and filtered, yielding a violet solution which darkened quickly. The solution was evaporated rapidly to dryness. The crystalline solid which resulted was taken up in pyridine and heated under reflux for 4 hr. with 0.3 ml. of benzoyl chloride. The solution was then cooled and poured onto a mixture of ice and hydrochloric acid. The resulting solid was formed in quantitative yield. Recrystallization from ethanol gave white plates, m.p. 309–311°.

Anal. Calcd. for $C_{33}H_{25}N_3O_3$: C, 77.48; H, 4.93; N, 8.21. Found: C, 77.46; H, 5.01; N, 8.13.

The melting point of a mixture of this material with that prepared in *A* by the benzoylation of the aniline adduct was not depressed.

Peroxytrifluoroacetic acid oxidation of 2-chloro-4-nitroaniline. Into a 200-ml. three-neck round bottom flask equipped with stirrer, reflux condenser, and dropping funnel was placed 65 ml. of trifluoroacetic acid. The liquid was heated to boiling (71°), and 5 g. of 2-chloro-4-nitroaniline was dissolved in the hot acid. To the refluxing solution was added 17.3 ml. of 30% hydrogen peroxide dropwise during a 30 min. period. The color of the solution bleached at first and then became deep red. The solution was heated under reflux for 1 hr. after the addition was complete, cooled to room temperature, and poured into ice water. The orange solid removed by filtration weighed 4.0 g. One gram of this material when extracted with petroleum ether (b.p. 80–100°) gave 0.17 g. of deep red insoluble material. The ether soluble material melted at 57–59° and was undoubtedly the desired 2-chloro-1,4-dinitrobenzene. The red insoluble material was recrystallized from benzene, m.p. 280–281°.

Anal. Calcd. for $C_{18}H_9ClN_6O_{10}$: C, 42.83; H, 1.80; N, 16.65. Found: C, 42.88; H, 1.82; N, 16.26.

Acknowledgment. The authors are indebted to Mr. J. Nemeth, Mrs. M. Stingl, and Miss C. Higham for the microanalyses and to Mr. J. Brader for the infrared spectral determinations.

URBANA, ILL.

[COMMUNICATION NO. 1785 FROM THE KODAK RESEARCH LABORATORIES, EASTMAN KODAK CO.]

Infrared Absorption and Structure of Certain Derivatives of Cyclopropane*

C. F. H. ALLEN, T. J. DAVIS, W. J. HUMPHLETT, AND D. W. STEWART

Received March 12, 1957

The infrared absorptions of twenty derivatives of cyclopropane, mostly with carbonyl or other functional groups adjacent to the ring, have been obtained. Neither the 2.3μ nor the 9.8μ region, previously suggested for characterizing the C_3 ring, affords a clear indication of either the presence or absence of this group.

The infrared spectrum of unsubstituted cyclopropane has been studied in detail and most of the fundamental modes of vibration have been identified.[1–3] In studying the spectra of cyclopropane derivatives which were mostly hydrocarbons, a number of workers[4–6] have reported that a characteristic absorption near 9.8μ (1000–1020 cm.$^{-1}$) is invariably present. Another strong absorption near 11.6μ (866 cm.$^{-1}$) found in some derivatives does not occur consistently.[5] These absorption bands are also found in cyclopropane itself and have been assigned to a ring deformation and to a CH_2 wagging vibration.[3]

In more recent work,[7–9] questions have been raised as to the reliability and usefulness of these bands at longer wave lengths. While Wiberley and Bunce[7] confirmed the 9.8μ band in nine nonhydrocarbon cyclopropyl derivatives, they concluded that absorptions in this region were too common to provide a clear identification of the ring structure and suggested the use of C—H stretching bands at 3.23 and 3.32μ for CH_2 groups in the cyclopropyl system. Two additional ketones containing the cyclopropyl ring also showed[8] this pair of bands, whereas Cole[9] reported only a single band between 3.28 and 3.31μ (3024–3058 cm.$^{-1}$) in isocholestane and two other natural products. No such band was reported for 3-carene, where each of the carbons of the three-membered ring has at least one substituent. In work with dicyclopropyl ketone, -carbinol, and -methane,[10] the two C—H bands were again noted near 3.3μ (3030 cm.$^{-1}$) and 3.23μ (3100 cm.$^{-1}$), as well as several strong bands in the 9.6–10μ region.

In a recent summary of spectral-structure correlations for cyclopropane derivatives,[11] fourteen references are cited to support the use of a band between 9.8 and 10.0μ (1000–1020 cm.$^{-1}$) as indicating a cyclopropyl ring. The presence of a band in this position in the spectra of substances of unknown structure has also been interpreted as sup-

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[*] This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

(1) G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Co., Inc., New York, 1945, pp. 352–353.

(2) A. W. Baker and R. C. Lord, *J. Chem. Phys.*, **23**, 1636 (1955).

(3) Hs. H. Günthard, R. C. Lord, and T. K. McCubbin, Jr., *J. Chem. Phys.*, **25**, 768 (1956).

(4) J. D. Bartleson, R. E. Burk, and H. P. Lankelma, *J. Am. Chem. Soc.*, **68**, 2513 (1946).

(5) J. M. Derfer, E. E. Pickett, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 2482 (1949).

(6) V. A. Slabey, *J. Am. Chem. Soc.*, **74**, 4928 (1952).

(7) S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

(8) F. J. Piehl and W. G. Brown, *J. Am. Chem. Soc.*, **75**, 5023 (1953).

(9) A. R. H. Cole, *J. Chem. Soc.*, 3807 (1954).

(10) H. Hart and O. E. Curtis, Jr., *J. Am. Chem. Soc.*, **78**, 112 (1956).

(11) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen and Co., Ltd., London, 1954, pp. 27–28.