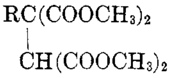
TABLE I

ALKYLATION PRODUCTS OF BIMALONIC ESTER,



$$\begin{array}{l} RC(COOCH_3)_2 \\ | \\ CH(COOCH_3)_2 \end{array}$$

| RX | Yield, % | M.P. (B.p.°/mm.) | Formula | Calcd. | | Found | |
|---|---|---|---|---|---|---|---|
| | | | | C | H | C | H |
| $CH_3I$ | 74 | (142–145/5)[a] | $C_{11}H_{16}O_8$ | 47.8 | 5.84 | 47.8 | 6.14 |
| $C_2H_5I$ | 82 | 54–56 (150/3) | $C_{12}H_{18}O_8$ | 49.6 | 6.25 | 49.5 | 6.42 |
| $n$-$C_4H_9Br$ | 30[c] | 67–70 | $C_{14}H_{22}O_8$ | 52.8 | 6.97 | 52.5 | 7.22 |
| $CH_2{=}CHCH_2Br$ | 89[d] | (151/3)[b] | $C_{13}H_{18}O_8$ | 51.7 | 6.00 | 51.8 | 6.20 |
| $C_6H_5CH_2Cl$ | 79 | 98–100 | $C_{17}H_{20}O_8$ | 57.9 | 5.68 | 58.0 | 5.97 |

[a] $n_D^{22}$ 1.4468. [b] $n_D^{25}$ 1.4589. [c] 50% of bimalonic ester recovered, 11 hr. reaction time. [d] Hydrolysis and decarboxylation using hydrochloric acid gave the known lactone of 4-hydroxy-1,2-pentanedicarboxylic acid, m.p. 66–68°.

*cyclopentanedicarboxylic acid* (VI), crystals from ether-ligroin, m.p. 146–148°.

*Anal.* Calcd. for $C_7H_9BrO_4$: C, 35.5; H, 3.83; N.E., 118.5. Found: C, 35.8; H, 4.02; N.E., 120.

Hydrogenolysis of VI (0.6 g.) by shaking with palladium on barium sulfate in water for 3 hr. consumed 85% of the calculated amount of hydrogen and gave 0.18 g. of 1,2-cyclopentanedicarboxylic acid, m.p. 159–160° alone or mixed with an authentic sample.

*Bromination of C-ethylbimalonic ester.* A solution of 0.23 g. of sodium in 25 ml. of methanol was treated with 2.9 g. of C-ethylbimalonic ester, and then with 1.6 g. of bromine in 16 ml. of methanol, resulting in immediate reaction. Methanol was removed and replaced with ether, and the product was washed with water, and dried. There was obtained 2.88 g. of crude or 1.5 g. of pure methyl 1-bromo-1,1,2,2-butanetetracarboxylate, colorless crystals from dilute methanol, m.p. 106–107°.

*Anal.* Calcd. for $C_{12}H_{17}BrO_8$: C, 39.0; H, 4.64. Found: C, 39.3; H, 4.97.

*Acknowledgment.* The authors thank R. W. Amidon, J. S. Buckley, R. W. Cummings, and H. W. Turner for the analytical results.

MINNEAPOLIS, MINN.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

# Condensed Cyclobutane Aromatic Compounds. XIII. An Attempted Synthesis of 1,2-Diphenylbenzocyclobutene

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*Received January 14, 1960*

The synthesis of 1,3-diphenyl-1,3-dihydroisothianaphthene-2,2-dioxide (IV), starting from *o*-dibenzoylbenzene, is described. Pyrolysis of IV at 250° gives 9-phenyl-9,10-dihydroanthracene (XII), rather than the expected 1,2-diphenylbenzocyclobutene (V). The existence of the intermediary quinodimethane (XV) was demonstrated by a Diels-Alder trapping reaction.

Since the pyrolysis of 1,3-dihydroisothianaphthene-2,2-dioxide (I) yields either benzocyclobutene (II) or 1,2,5,6-dibenzocyclooctadiene (III), depending on the conditions used,[1] the pyrolysis of 1,3-diphenyl-1,3-dihydroisothianaphthene-2,2-dioxide (IV) was investigated as a possible route to 1,2-diphenylbenzocyclobutene (V).

Sulfone IV, m.p. 200–201°, was obtained by the peracetic acid oxidation of the known sulfide, VI.[2] Methods are described in the literature for each of the preceding synthetic steps, *viz.*, the reduction of *o*-dibenzoylbenzene (VII) to 1,3-diphenylisobenzofuran (VIII);[3] the conversion of VIII to 1,3-diphenylisothianaphthene (IX) by phosphorus pentasulfide;[4] and the reduction of IX to the sulfide, VI. However, since we experienced considerable difficulty in obtaining reproducible results in all three of these reactions, modified preparations of VI and IX were developed, and these are reported in the Experimental section In addition, a new method is reported for the conversion of *o*-dibenzoylbenzene (VII) into furan VIII by the partial reduction of VII with potassium borohydride, followed by treatment of the primary reduction product (X) with acid. The success of this procedure is probably due to the tendency of the intermediary ketoalcohol, X, to exist mostly as the phthalan (XI)[5] in the basic reduction medium. Even so, good yields of VIII could be ob-

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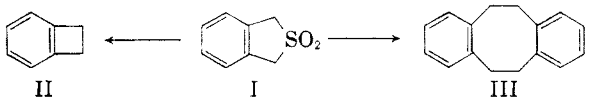
(1) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959), paper VI of this series.

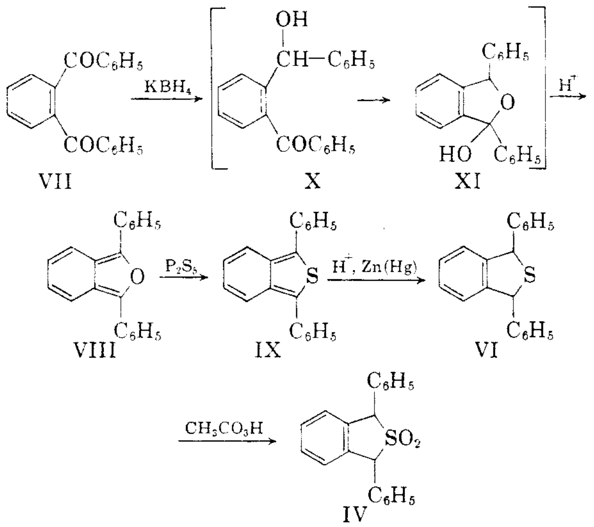
(2) A. Bistrzycki and B. Brenken, *Helv. Chim. Acta*, **5**, 20 (1922). The precursor of VI (compound IX) is described incorrectly in this paper as "*phenylmesothioanthracendihydrid.*" See ref. 4 for the clarification of this point.

(3) R. Adams and M. H. Gold, *J. Am. Chem. Soc.*, **62**, 56 (1940).

(4) C. Dufraisse and D. Daniel, *Bull. soc. chim.*, [5] **4**, 2063 (1937).

(5) A. Guyot and J. Catel, *Compt. rend.*, **140**, 1348 (1905).

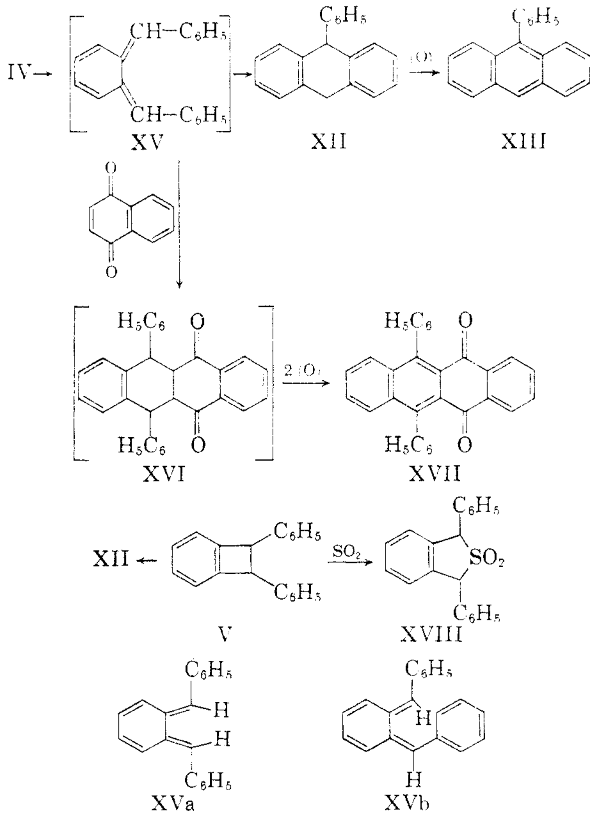




tained only by treating VII alternately with borohydride and mineral acid, thereby avoiding the accumulation of large amounts of the intermediate in the reaction mixture. It may be noted that furan VIII was found to be completely stable under the conditions of the reduction.

When the pyrolysis of sulfone IV was carried out in diethyl phthalate at 250°, neither 1,2-diphenylbenzocyclobutene (V) nor a dimer of this substance was obtained. There was isolated instead, in 94% yield, 9-phenyl-9,10-dihydroanthracene (XII), the constitution of which was confirmed by dehydrogenation to 9-phenylanthracene with the mild reagent, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.[6] The thermal decomposition of sulfone IV therefore follows a course analogous to that of 1,1,3-triphenyl-1,3-dihydroisothianaphthene-2,2-dioxide (XIV)[7,8] which similarly yields anthracene derivatives by intramolecular rearrangement of the primary pyrolysis product.[9] The great ease with which the expected pyrolysis intermediate XV rearranges to 9-phenyl-9,10-dihydroanthracene is demonstrated by an experiment in which sulfone IV was pyrolyzed at 250° in the presence of an excess of 1,4-naphthoquinone. Diels-Alder addition of the intermediary quinomethane XV to 1,4-naphthoquinone did indeed occur, as shown by the isolation in 42% yield of 6,11-diphenyl-5,12-naphthacenequinone (XVII).[10] However, a significant portion of intermediate XV failed to react with the naphthoquinone, as evidenced by the isolation in 20% yield of the aromatized rearrangement product, 9-phenylanthracene (XIII).

During the course of this work a successful synthesis of 1,2-diphenylbenzocyclobutene (V) was reported.[11] The diphenyl derivative was found to be remarkably reactive; on heating, it rearranged to 9-phenyl-9,10-dihydroanthracene (XII), probably *via* the transient intermediate XV. In addition, it reacted with sulfur dioxide under surprisingly mild conditions to yield a sulfone (XVIII), m.p. 232.5–234° dec.; this sulfone differs from our sulfone IV which has a melting point of 200–201° dec.,[12] yet it gives the same pyrolysis product, hydrocarbon XII. The two sulfones, IV and XVIII, are apparently related as *cis-trans* isomers. Sulfone IV and its precursor, sulfide VI, are probably *trans* isomers, since VI is derived from the isothianaphthene IX by a metal and acid reduction, a process which may favor the formation of the thermodynamically stable *trans* product. Furthermore, the sulfone derived from 1,2-diphenylbenzocyclobutene and sulfur dioxide, *i.e.*



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[6] E. A. Braude, A. G. Brook, and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954). We are indebted to Dr. P. M. G. Bavin for a sample of this quinone.

[7] H. Staudinger and F. Pfenninger, *Ber.*, 49, 1941 (1916).

[8] H. Kloosterziel and H. J. Backer, *Rev. trav. chim.*, **71**, 1235 (1952).

[9] For a more complete discussion of this case, see ref. 1.

[10] C. Dufraisse and P. Compagnon, *Compt. rend.*, **207**, 585 (1938)

[11] F. R. Jensen and W. E. Coleman, *J. Am. Chem. Soc.*, **80**, 6149 (1958).

[12] In addition, the melting point of sulfone IV is depressed (185–193°) upon admixture with sulfone XVIII, and the infrared spectra of the two sulfones differ in the 8–15 μ range. We are indebted to Dr. F. R. Jensen for a comparison sample of authentic sulfone XVIII.

sulfone XVIII, might be expected to be the *cis* isomer, since sulfur dioxide probably adds in a concerted manner to quinodimethane XV, or at least takes part in a transition state approaching structure XV. It is to be noted that, of the various *cis* and *trans* isomers which can be drawn for XV, only isomer XVa, which would give a *cis*-sulfone when treated with sulfur dioxide, fulfills the steric requirements for full resonance stabilization as a coplanar structure. Indeed, mild thermal isomerization of XVa would lead to structure XVb which would have not only *less* orbital overlap stabilization, but a more favorable conformation for subsequent intramolecular ring closure to form XII.

## EXPERIMENTAL[13]

*1,3-Diphenylisobenzofuran* (VIII). A solution of 2.86 g. (0.01 mole) of *o*-dibenzoylbenzene[3] in 60 ml. of refluxing ethanol was treated with 2 ml. of a 6% aqueous potassium borohydride solution. Reduction was allowed to proceed for exactly 1 min. and was then stopped by the addition of excess (1–2 ml.) of 5*N* sulfuric acid in ethanol. The reaction mixture was stirred rapidly under reflux for 10 min. and was then made basic by the addition of 5*N* alcoholic potassium hydroxide solution. (The product itself, which is canary-yellow in acid and orange-yellow in base, was used as an internal indicator.) After stirring and refluxing the basic solution for 10 min., a second 2-ml. portion of borohydride solution was added, reduction was again allowed for 1 min. and was then stopped, as before, with acid. The entire cycle was repeated five times *in toto*. After the final reduction step, the reaction mixture was treated with 60 ml. of aqueous 1.5*N* sulfuric acid, heated on the steam bath for 15 min., cooled, and filtered with suction. The crude product (bright yellow flakes) was dried and leached with 100 ml. of warm petroleum ether (b.p. 55–60°) to give 2.1 g. (78%) of the product, 1,3-diphenylisobenzofuran, m.p. 130–131° (reported[3] m.p. 126°), which was obtained in three crops.

*1,3-Diphenylisothianaphthene* (IX). In a 250-ml., one-neck, round-bottom flask provided with a 1-inch magnetic stirring bar and two dozen 6-mm. glass beads were placed 150 ml. of carbon disulfide and 2 g. of phosphorus pentasulfide. The phosphorus pentasulfide was finely dispersed in the carbon disulfide by 1 hr.'s rapid stirring with the glass beads. 1,3-Diphenylisobenzofuran (1.0 g., 3.7 mmoles) was then added, and stirring was continued for 12 hr. at room temperature, in the dark, and under dry nitrogen. Another 2-g. portion of phosphorus pentasulfide was added, and stirring was resumed for a second 12-hr. period. The product was isolated by Dufraisse's method[4]: thus, the reaction mixture was filtered with suction, the filtrate was evaporated to dryness *in vacuo;* the residue was extracted with two 100-ml. portions of benzene, and the extract was refluxed for 4 hr. with 100 ml. of 10% aqueous sodium hydroxide solution in order to remove inorganic sulfides. The resulting clear benzene layer was separated, dried over sodium sulfate, treated with a solution of 500 mg. of maleic anhydride in 5 ml. of benzene to remove unchanged starting material, allowed to stand for 30 sec., and finally was washed thoroughly with three 50-ml. portions of 5% aqueous sodium hydroxide solution. The organic layer was again dried over sodium sulfate and was then evaporated to dryness *in vacuo.* Recrystallization of the residue from ethanol gave 0.64 g. (60%) of the product, 1,3-diphenylisothianaphthene, bright yellow needles, m.p. 119–120° (reported[4] m.p. 118–119°).

*1,3-Diphenyl-1,3-dihydroisothianaphthene* (VI). To a rapidly stirred solution of 100 mg. (0.35 mmole) of 1,3-diphenylisothianaphthene in 20 ml. of warm glacial acetic acid was added 15 g. of amalgamated zinc dust.[14] The resulting suspension was stirred rapidly for 5 min. at 80–85°; 5 ml. of concd. hydrochloric acid was then added all at once, and reduction was allowed to proceed for 1 to 1.5 min. The almost colorless reaction mixture was quickly filtered with suction, and the filtrate was diluted with hot water until a persistent cloudiness was observed. The filtrate was cooled to 15° to give 65 mg. (64.5%) of 1,3-diphenyl-1,3-dihydroisothianaphthene. Recrystallization from ethanol-water gave long white needles, m.p. 107–108° (reported[2] m.p. 106.5–107.5°, 29% yield).

*1,3-Diphenyl-1,3-dihydroisothianaphthene-2,2-dioxide* (IV). A solution of 2.0 g. (7.0 mmoles) of 1,3-diphenyl-1,3-dihydroisothianaphthene in 50 ml. of glacial acetic acid was added dropwise over a period of 30 min. to 20 ml. of commercial (Becco) 40% peracetic acid kept at 25°. The reaction mixture was allowed to stand at room temperature for 2 days and was then treated with 50 ml. of water to give 1.86 g. of small white needles. Concentration of the mother liquor gave a second crop (260 mg.). Recrystallization of the product from methylene chloride–petroleum ether (b.p. 35–55°) gave a total yield of 2.01 g. (90%) of 1,3-diphenyl-1,3-dihydroisothianaphthene-2,2-dioxide, obtained as fine white needles, m.p. 200–201° dec.

*Anal.* Calcd. for $C_{20}H_{16}O_2S$: C, 74.97; H, 5.03; S, 10.01. Found: C, 74.70; H, 4.96; S, 9.91.

*Pyrolysis of 1,3-diphenyl-1,3-dihydroisothianaphthene-2,2-dioxide.* A solution of 160 mg. (0.5 mmole) of dioxide IV in 100 ml. of diethyl phthalate was heated in an oil bath at 250° under a slow stream of nitrogen. The nitrogen–sulfur dioxide gas mixture from the reaction vessel was bubbled through an aqueous solution containing an equivalent amount (0.5 mmole) of iodine (prepared from 5 ml. of 0.03*M* potassium iodate, 1 ml. of saturated potassium iodide solution, and 10 drops of 6*N* hydrochloric acid). When the iodine solution had been decolorized (heating time, 45 min.), the reaction mixture was poured into 200 ml. of 5% alcoholic potassium hydroxide. The resulting soap slurry was allowed to stand in a water bath at 50° for 12 hr. It was then evaporated almost to dryness *in vacuo*, dissolved in 200 ml. of water, and extracted with four 50-ml. portions of petroleum ether (b.p. 30–60°). The combined organic extracts were dried over sodium sulfate and evaporated to dryness *in vacuo* to give 150 mg. of crude product. Chromatography on Grade I neutral alumina (Woelm) with 1:4 ether-benzene, followed by recrystallization from ethanol, gave 120 mg. (94%) of pure 9-phenyl-9,10-dihydroanthracene (XII), m.p. 86–87° (reported[15] m.p. 87–88°). The dihydro compound was characterized further by conversion into 9-phenylanthracene (XIII): thus, a solution of 11.5 mg. (0.045 mmole) of 9-phenyl-9,10-dihydroanthracene in 2 ml. of benzene was mixed with a solution of approximately 35 mg. (0.15 mmole) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[6] in 6 ml. of benzene and warmed in a water bath (75°) for 1.5 hr. The reaction mixture was evaporated to dryness under an air jet, and the residue was triturated with 1 ml. of petroleum ether (b.p. 30–60°) and then extracted twice with the same solvent. Chromatography of the extract

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(13) Melting points are corrected. The analysis of IV was carried out by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(14) The amalgamated zinc dust was prepared by shaking 50 g. of zinc dust with 100 ml. of 1.5% aqueous ammonium chloride solution for 15 min., adding 150 ml. of saturated aqueous mercuric chloride solution, shaking for another 15-min. period, and then washing by decanting with four 100-ml. portions of distilled water. The amalgam was allowed to stand for 24 hr. under the last wash water and was filtered with suction just before use.

(15) W. Schlenk and E. Bergmann, *Ann.*, **463**, 161 (1928).

on Grade I neutral alumina (Woelm) with 1:4 ether-benzene gave 6.8 mg. (59%) of 9-phenylanthracene, m.p. 154–156° (reported[15] m.p. 152°), identical by mixed melting point and ultraviolet analysis ($\lambda_{\max}^{C_2H_5OH}$ 255 m$\mu$, log $\epsilon$ = 5.16)[16] with an authentic sample of XII prepared from anthrone and phenylmagnesium bromide.[17]

*6,11-Diphenyl-5,12-naphthacenequinone* (XVII) *and 9-phenylanthracene* (XIII). Sulfone IV (160 mg., 0.5 mmole) and 395 mg. (2.5 mmoles) of 1,4-naphthoquinone were mixed together in a test tube (0.8 × 5 cm.). The upper part of the test tube was then melted and drawn out into a fine capillary, which was left open. The tube was immersed up to its tip in a hot oil bath (250°) for 15 min., then cooled and wiped dry. Both the tube and its contents were ground to a fine powder in a mortar and extracted with two 20-ml. portions of 1:4 ether-benzene. The extracts were combined and evaporated to dryness *in vacuo*. The residue was taken up in 10 ml. of 1:4 ether-benzene and chromatographed with the same solvent on Grade I neutral alumina (Woelm). The first fraction (blue-fluorescent) to leave the column consisted of 26 mg. (20%) of 9-phenylanthracene, m.p. 150–153°, identical in mixed melting point with an authentic sample prepared from anthrone.[17] The second fraction (yellow) consisted of 86 mg. (42%) of 6,11-diphenyl-5,12-naphthacenequinone, m.p. 287–288°, identical in melting point and infrared spectrum with an authentic sample prepared from 1,3-diphenylisobenzofuran and 1,4-naphthoquinone.[10]

*Acknowledgment.* We wish to thank the Research Corporation for a grant supporting a part of this work.

COLUMBUS 10, OHIO

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(16) E. Clar and D. G. Stewart, *J. Am. Chem. Soc.*, **74**, 6237 (1952).

(17) J. W. Cook, *J. Chem. Soc.*, 2170 (1926).

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, DIAMOND ALKALI COMPANY]

# The Addition-Chlorination of Aniline

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The benzene ring of aniline has not undergone chlorination by addition in the past because the electron-releasing amine group enables substitution to take place too readily. The use of two electron-withdrawing acyl groups attached to the amine group in aniline did not enable addition-chlorination to take place. Instead, monodeacetylation took place, followed by substitution-chlorination of the acetanilide to 2,4-dichloroacetanilide. The use of non-cleavable electron-withdrawing groups permitted addition-chlorination to take place readily. Thus, phenyl isocyanate and *N*-phenylimidocarbonyl chloride were chlorinated by addition in good yields. Hydrolysis of the addition products suggests that the major stable product from any attempted addition-chlorination of aniline would be 2,4,6-trichloroaniline.

In our previous paper on the addition-chlorination of phenol,[1] we demonstrated that the combination of the phenolic oxygen atom with groups exerting a negative inductive effect permits addition-chlorination of the benzene ring to take place readily. Thus, phenyl trichloroacetate was addition-chlorinated in near quantitative yields.

Aniline, like phenol, contains a strong electron-releasing atom, and readily undergoes substitution chlorination, even in the absence of catalysts. It was the purpose of this work to add chlorine to the benzene ring of an aniline derivative, and to determine the nature of the product of the addition-chlorination of aniline. The direct addition-chlorination of aniline was not attempted because of its ease of substitution, and because the expected product is a *gem*-chloroamine, II, an unstable structure which would not be identifiable.

It is known that the single acetylation of aniline diminishes the *ortho-para*-orienting power of the acetylated group, but does not reduce it sufficiently for *meta* orientation of an incoming group to take place. In another instance, it is known that the single acylation of nitrogen, as in aceto-*p*-toluidide, is not sufficient to reduce the orienting power of the acylamine group below that of the methyl group. However, double acylation is sufficient to enable the methyl group to take control.[2]

In view of the above information, it seemed likely that a doubly acylated amine group would be less *ortho-para* directing than the singly acylated group. It was expected that the deactivation of the nucleus would reduce the rate of the substitution chlorination reaction and permit addition-chlorination to take place more readily. Attempts were made to addition-chlorinate diacetanilide and $\alpha,\alpha,\alpha$-trifluorodiacetanilide. It was hoped that the presence of the halogens on the acetyl group would also tend to reduce the *ortho-para* orientation by virtue of their added inductive effect in this system. The diacetanilide, together with carbon tetrachloride and the theoretical amount of chlorine for addition, was sealed in a borosilicate glass tube and exposed to ultraviolet irradiation. Some activation is needed for the reaction to take place; there is no reaction in the dark. With both starting materials, the same product, 2,4-dichloroacetanilide, was isolated in fair yields. It was assumed that this product was formed predominantly *via* the reaction scheme shown below, involving cleavage of an acyl group

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(1) I. Rosen and J. P. Stallings, *J. Org. Chem.*, **24**, 1523 (1959).

(2) O. L. Brady, W. G. E. Quick, and W. F. Welling, *J. Chem. Soc.*, **127**,2264 (1925).