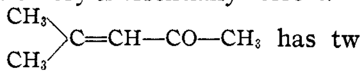
T-effect is partially canceled in benzaldehyde. Thus, C_{phenyl} is different in cinnamaldehyde than in benzaldehyde. The ΣC_i for cinnamaldehyde is 3.21. Therefore, the C_{phenyl} not adjacent to carbonyl is +0.80. Using the group constants summarized in Table II, $E^0_{1/2}$ values may be calculated for other compounds composed of the groups for which C_i values are known. For acetophenone the ΣC_i is 0.54 for the phenyl group plus 1.41 for the carbonyl group minus 0.41 for the methyl group or 1.54. Substituting this value in Equation (16) or consulting Fig. 1, $E^0_{1/2}$ calcd. is −1.044 volt *vs.* S.C.E. Similar calculations were made for the remainder of the compounds in Table I. The excellent agreement between the experimental and calculated $E^0_{1/2}$ values is shown in the fourth column of Table I and may be taken as evidence that the theory is essentially correct.

TABLE II

GROUP CONSTANTS

—CH=CH—	1.000
>C=O	1.41
H—	0.000
CH_3—	−0.41
$Phenyl_1$ adjacent to carbonyl	0.54
$Phenyl_2$ removed from carbonyl by one double bond	0.80

Mesityl oxide,  $(CH_3)_2>C{=}CH{-}CO{-}CH_3$ has two methyl groups on a single carbon atom, thus the inductive effect of each one is partially canceled out by the other. Assuming bond angles of 120°, the vectorial effect of the two methyl groups is simply

$$2(-0.41 \sin 30°) = 2(-0.41 \times 1/2) = -0.41 \quad (20)$$

This is probably too large since the bond angle between the methyl groups is probably somewhat greater than 120° due to electrostatic repulsion between the methyl groups and attraction between the more electronegative oxygen atom and each of the methyl groups. On the basis of this oversimplified picture, the calculated $E^0_{1/2}$ for mesityl oxide is −1.02 volts. The experimental value is −0.96 volt on the basis of Pasternak's[4] data for 48% ethanol. This agreement is undoubtedly within the uncertainty of the experimental value. If the group constants are simply added without considering this cross-conjugation effect, the predicted $E^0_{1/2}$ value is −1.24 volts.

Resonance Energies.—Formaldehyde and acetaldehyde are taken as reference compounds since they are the first members of the aldehyde and methyl ketone series. If a phenyl group is substituted for one of the hydrogen atoms in formaldehyde, benzaldehyde results. The difference between the formaldehyde and benzaldehyde half-wave potentials is 0.227 volt, which corresponds to an energy of 5.2 kcal. Therefore there is 5.2 kcal. resonance energy between the benzene ring and the carbonyl group. Similar calculations for the other compounds give the resonance energies listed in the last column of Table I. The polyene aldehydes, crotylideneacetone, acetophenone, benzalacetone and mesityl oxide are considered to be derivatives of acetaldehyde. The remainder of the compounds in Table I are taken as derivatives of formaldehyde.

These resonance energies were derived from the data for polarographic reductions in 50% dioxane solutions and may not be exact for the gaseous, pure liquid, or solid state of the compound. As noted in the previous paper,[1] different results are obtained for pure aqueous solutions due to the low solubilities of some of the organic compounds.

[4] R. Pasternak, *Helv. chim. Acta*, **31**, 753 (1948).

LOS ANGELES, CALIF. RECEIVED JUNE 9, 1951

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC COMPANY]

Neighboring Group Interaction in the Reduction of 2,2'-Dinitro-4,4'-bis-(trifluoromethyl)-biphenyl

BY SIDNEY D. ROSS AND IRVING KUNTZ

The sodium sulfide reduction of 2,2'-dinitro-4,4'-bis-(trifluoromethyl)-biphenyl proceeds stepwise to yield 2,2'-dinitroso-4,4'-bis-(trifluoromethyl)-biphenyl, 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline-5-oxide and 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline. Catalytic hydrogenation results in a mixture containing 2,2'-diamino-4,4'-bis-(trifluoromethyl)-biphenyl in addition to the above benzo(c)cinnoline and benzo(c)cinnoline oxide. The mechanisms of these reductions are discussed. The deamination reaction on 2,2'-diamino-4,4'-bis-(trifluoromethyl)-biphenyl yields either the benzo(c)cinnoline or a mixture of the benzo(c)cinnoline and 4,4'-bis-(trifluoromethyl)-biphenyl, depending on the reaction conditions.

In a series of excellent papers Winstein, *et al.*,[1] have thoroughly dealt with the role of neighboring groups in replacement reactions. On low temperature catalytic hydrogenation of 2,2'-dinitro-4,4'-bis-(trifluoromethyl)-biphenyl, I, we obtained products which indicated a comparable interaction of either the 2,2'-nitro groups or of reduction products derived therefrom. To elucidate the nature of this interaction, we have studied both the catalytic and chemical reduction of I.

With tin and hydrochloric acid, I, prepared by modification of the procedure of Bradsher and Bond,[2] is smoothly reduced to 2,2'-diamino-4,4'-bis-(trifluoromethyl)-biphenyl (II). With sodium sulfide and alkali the major products formed are 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline (III), 3,8-bis(trifluoromethyl)-benzo(c)cinnoline-5-oxide (IV) and 3,8-bis-(trifluoromethyl)-benzo(c)cinno-

[1] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948). This paper presents a general theory of neighboring groups and reactivity and contains extensive references to the detailed work in this field.

[2] C. K. Bradsher and J. B. Bond, *ibid.*, **71**, 2659 (1949).

line-5,6-dioxide (V).[3] Benzo(c)cinnoline oxides have been prepared previously by reduction with sodium sulfide,[4a,b,c] but there are no reported preparations of either a benzo(c)cinnoline or a benzo(c)cinnoline dioxide with this reagent.[5] By varying the amount of sodium sulfide used, it is possible to obtain either III, IV or V as the predominant product. Our results are summarized in Table I.

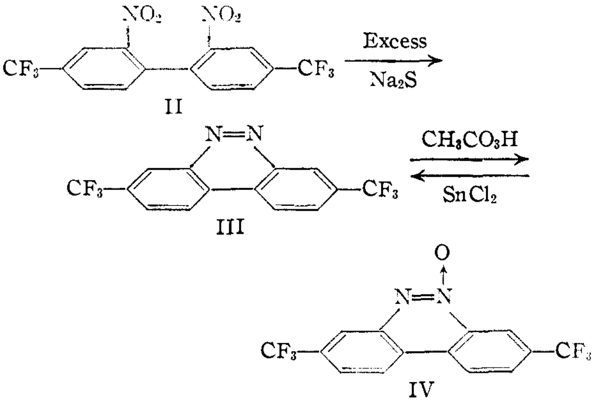
TABLE I

REDUCTION OF 2,2'-DINITRO-4,4'-BIS-(TRIFLUOROMETHYL)-BIPHENYL WITH SODIUM SULFIDE

Moles Na_2S / Mole nitro group	Moles NaOH / Liter of reaction mixture	Reaction time, hr.	Yield, % V	IV	III	I
0.25	0.073	3	43.6	31.1		
1.0	.28	2		21[a]	68[a]	
3.0	.22	22			95	2.4

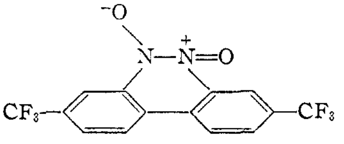
[a] On the basis of analytical data.

As is apparent from Table I, reduction of I with excess sodium sulfide constitutes a satisfactory preparative method for III. The oxide, IV, is best prepared by oxidation of III with peracetic acid in chloroform and can, in turn, be reduced to III with stannous chloride. The relative insolubility of the dioxide, V, makes its separation from IV facile, and it can be obtained readily by reduction of I with small amounts of sodium sulfide.



The structures of III and IV are indicated by their analyses, the interconversions described above and by comparison of their ultraviolet spectra with the published spectra of benzo(c)cinnoline and benzo(c)cinnoline oxide[6a] (Figs. 1 and 2) and azobenzene and azoxybenzene.[6b] The structure of the dioxide, V, deserves special comment. Its absorption spectrum (Fig. 3) and analyses indicate that it has a structure comparable to benzo(c)cinnoline dioxide.[5a] The fact that 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline-5,6-dioxide(V) is the first isolable reduction product from I and the fact that it is a colorless solid which dissolves to give colored solutions suggest that it would be more appropriate to name it 2,2'-dinitroso-4,4'-bis-(trifluoromethyl)-biphenyl.

In the case of this particular dinitroso compound, the two nitrogen atoms are within ready bond forming distance, and *intramolecular* nitroso dimer formation is facile.[7] This dinitroso compound is extensively stabilized by resonance, and it is possible to write more than thirty contributing structures including those for the *intramolecular* nitroso dimer of the type



The significance of the dinitroso compound, V, as a key intermediate which determines the course of any further reduction will be elaborated later in the discussion.

Low pressure hydrogenation of I results in a mixture containing II, III, IV and a high melting solid, to which we have not assigned a structure. III and IV were obtained jointly as mixed crystals which crystallized from ethanol with constant melting point. This mixture was separated by fractional elution from aluminum oxide, and the progress of the separation was followed by ultraviolet absorption spectroscopy (Fig. 4).

The recrystallized mixture of III and IV above could be hydrogenated further to a mixture richer in III but never to pure III. Pure III can, however, be obtained from the mixture by reduction with stannous chloride. Similarly, both pure 2,2'-dinitroso-4,4'-bis-(trifluoromethyl)-biphenyl (V) and pure IV can be hydrogenated, but the product is always a mixture of III and IV and contains no diamine, II. The benzo(c)cinnoline, III, is not reduced further under our conditions.

The mixtures of III and IV obtained are not all of the same composition, and the failure to reduce all of the benzo(c)cinnoline oxide to III is probably ascribable to catalyst poisoning. From the results described above, it is nevertheless, clear that the reduction proceeds along two distinct paths, one leading to compounds containing the benzo(c)cinnoline ring system and the other to the diamine, II. Although there are other possible intermediates in the reduction of I to III and IV, a high degree of probability attaches to the dioxide, V, as the critical intermediate, since this compound was actually isolated in the sodium sulfide reduction, and since it gives III and IV on catalytic reduction. It seems, to us, probable that in a symmetrical dinitro com-

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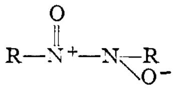
(3) For numbering the benzo(c)cinnoline system see A. M. Patterson and L. T. Capell, "The Ring Index," Reinhold Publishing Corp., 1940, p. 258. English workers have called the benzo(c)cinnoline-5-oxide the 6-oxide.

(4) (a) F. Ullman and P. Dieterle, *Ber.*, **37**, 23 (1904); (b) S. Sako, *Bull. Chem. Soc. Japan*, **9**, 393 (1934); (c) R. E. King and T. J. King, *J. Chem. Soc.*, 824 (1945).

(5) For other preparative methods leading to compounds containing the benzo(c)cinnoline ring system see the following: (a) E. Tauber, *Ber.*, **24**, 3081 (1891); (b) Th. Wohlfahrt, *J. prakt. Chem.*, [2] **65**, 295 (1902); (c) P. Z. Slack and R. Slack, *Nature*, **160**, 437 (1947).

(6) (a) K. E. Calderbank and R. J. W. LeFevre, *J. Chem. Soc.*, 1949 (1948); (b) A. H. Cook, D. G. Jones and J. B. Polya, *ibid.*, 1315 (1939).

(7) The recent study by C. F. Fenimore (THIS JOURNAL, **72**, 3226 (1950)) of the crystal structure of dimeric 2,4,6-tribromonitrosobenzene reconciles the previous difficulties and makes it possible to represent the nitroso dimers as



$$\mathrm{R}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{N}}{}^{+}-\mathrm{N}\genfrac{}{}{0pt}{}{\mathrm{R}}{\mathrm{O}^-}$$

and other resonance forms. For an excellent discussion of the problem see N. V. Sidgwick, "Organic Chemistry of Nitrogen," Oxford University Press, London, 1942, p. 213.

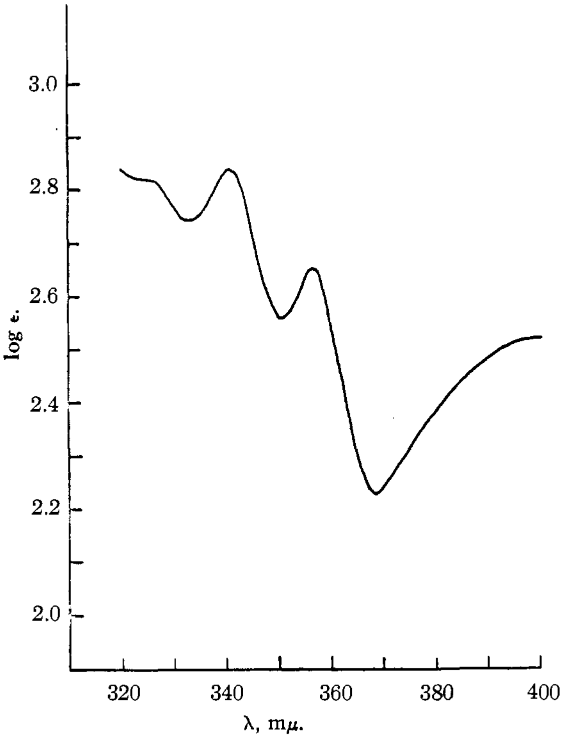


Fig. 1.—Absorption spectrum in dioxane of 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline.

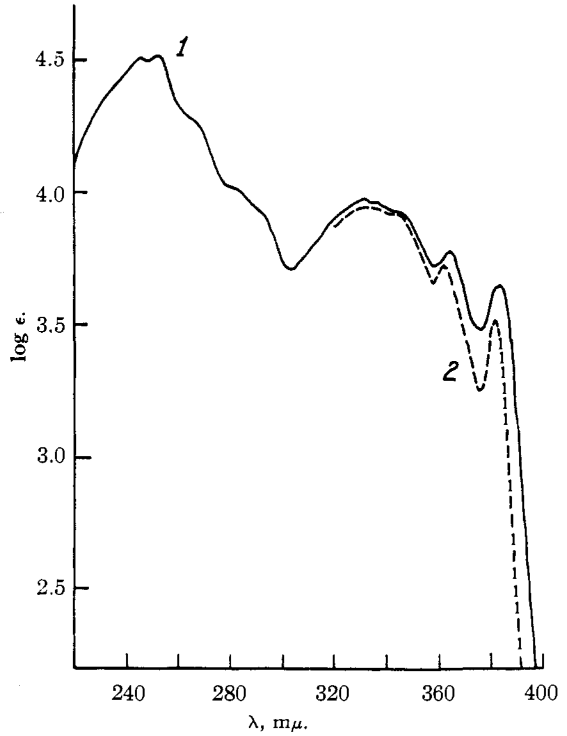


Fig. 2.—Absorption spectra of benzo(c)cinnoline-5-oxide in ethanol (1, solid line); 3,8-bis-(trifluoromethyl)-benzo-(c)cinnoline-5-oxide in dioxane (2, dashed line).

pound such as I both nitro groups can be reduced at rates such that V is formed. This intermediate is particularly attractive, since its two nitrogen atoms are so situated that intramolecular nitroso dimer formation is favored. There is thus some

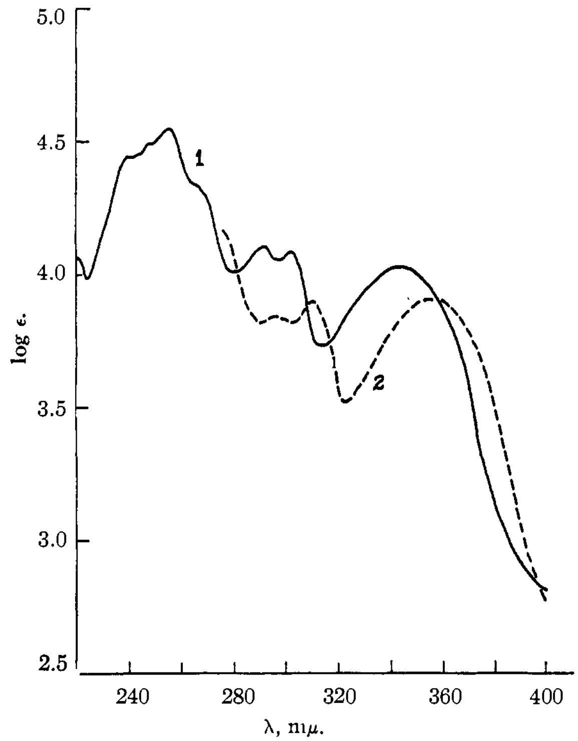


Fig. 3.—Absorption spectra of benzo(c)cinnoline-5,6-dioxide in ethanol (1, solid line); 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline-5,6-dioxide in dioxane (2, dashed line).

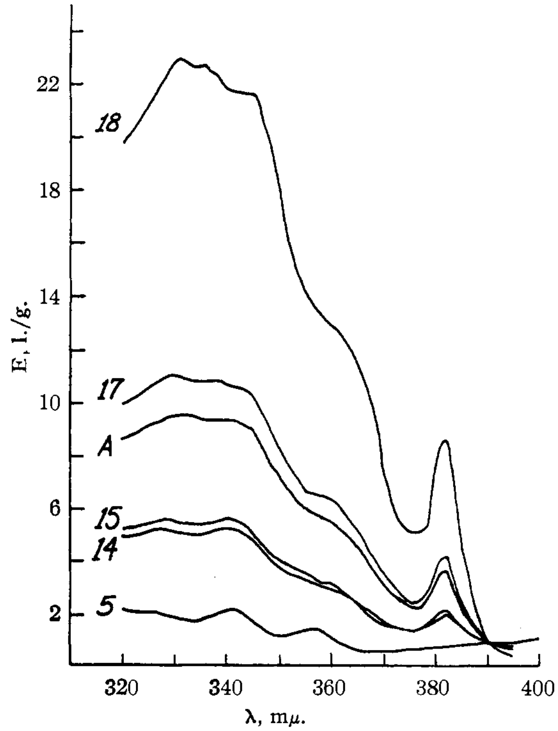


Fig. 4.—Absorption spectra in dioxane of the various chromatographic elutions of the benzo(c)cinnoline–benzo(c)-cinnoline oxide product obtained by catalytic reduction of 2,2'-nitro-4,4'-bis-(trifluoromethyl)-biphenyl. Curve A is that of the initial mixture and the other curves are numbered in accordance with the order in which the samples were eluted from the column.

partial N, N bonding in V, and this may well be the necessary precondition for facile benzo(c)cinnoline ring formation on further reduction.

As we have previously noted, the failure of III or IV to reduce to diamine makes it certain that at least one other reduction path obtains in the catalytic reduction. While it is true that reduction to the diamine probably proceeds in steps *via* nitroso and hydroxylamino stages, it is, nevertheless possible to offer a plausible explanation for the observed results. Of the many possible orientations of the dinitro compound, II, on the catalyst surface let us consider the two extreme configurations. The first is the one in which both nitro groups are seated on the catalyst surface and oriented *cis* to one another. The other extreme configuration is that in which either or both nitro groups are on the catalyst surface but are oriented *trans* to one another. It is, we feel, apparent that the first configuration could result in facile benzo(c)cinnoline ring formation. The latter configuration is, however, more likely to be reduced all the way to the diamine, since the *trans* configuration prevents interaction of either the nitro groups or their reduction products.

In the course of this work we also had occasion to run the hypophosphorus acid deamination of II, using both the more common procedure involving the amine hydrochloride and the procedure of Kornblum and Iffland[8] which utilizes the hypophosphorous acid salt. The former procedure gave 46% of III and traces of another product, the structure of which is not established, but no products free of nitrogen. The latter procedure gave 13.2% of III and 27.6% of 4,4′-bis-(trifluoromethyl)-biphenyl.[9]

Experimental[10,11]

2,2′-Dinitro-4,4′-bis-(trifluoromethyl)-biphenyl (I).—3-Nitro-4-chlorobenzotrifluoride (451 g., 2 moles, from Hooker Electrochemical Co.) was heated to 165° in a flask fitted with a stirrer, thermometer and reflux condenser. Copper powder (127 g.) was added cautiously over a 15-minute period, and the reaction mixture was heated to reflux. After two hours, copper powder (31 g.) was added, and this addition was repeated twice again after the same time intervals. After 17 hours of reflux the reaction mixture was poured into water, and the aqueous mixture was extracted portionwise with benzene (1 liter). The combined benzene extracts were washed with 10% hydrochloric acid and water and dried over anhydrous magnesium sulfate. After removal of the solvent, the residue was distilled, with slight accompanying decomposition, at 1.5 mm. to give 130 g. of yellow product; b.p. 163–170°. Recrystallization from ethanol yielded 112 g. (30%) of yellow needles; m.p. 124–125°; reported m.p. 121–122°.[2]

2,2′-Diamino-4,4′-bis-(trifluoromethyl)-biphenyl (II).—A mixture of II (8.5 g., 0.022 mole) and concentrated hydrochloric acid (115 cc., sp. gr. 1.18) was warmed to 50°. Mossy tin (28 g.) and concentrated hydrochloric acid (46 cc.) were added over a one-half hour interval. After addition of sufficient ethanol to effect solution of the organic material, the reaction mixture was refluxed three hours. It was then poured into ice water and made basic to litmus with sodium hydroxide. The basic solution was extracted with benzene; the extract was washed and dried; the solvent was removed at reduced pressure and the residue was crystallized from ligroin (b.p. 90–100°) to give 4.6 g. (65%) of the diamine, colorless needles, m.p. 130–134°. Recrystallization from ligroin raised the m.p. to 134–135°.

Anal. Calcd. for $C_{14}H_{10}N_2F_6$: C, 52.51; H, 3.15; N, 8.75. Found: C, 52.64, 52.78; H, 3.20, 3.09; N, 8.84, 8.73.

From the reaction of 0.1 g. of II, 2 cc. of pyridine and 2 cc. of acetic anhydride there was isolated 0.08 g. (70%) of **2,2′-diacetamino-4,4′-bis-(trifluoromethyl)-biphenyl**; colorless needles; m.p. 162–165° from ligroin (b.p. 90–100°). Further recrystallization from ligroin raised the m.p. to 174–175°.

Anal. Calcd. for $C_{18}H_{14}N_2O_2F_6$: C, 53.47; H, 3.49; N, 6.93. Found: C, 53.70, 53.49; H, 3.46, 3.54; N, 6.95, 7.11.

Reduction of I with Sodium Sulfide. A. 1 Mole Na_2S/Mole NO_2.—The procedure was patterned on the King and King[4c] modification of the preparation of benzo(c)cinnoline oxide.[4a] To a stirred solution of I (25 g., 0.066 mole) in ethanol (500 cc.), which had been heated to 60°, there was added a solution of sodium sulfide nonahydrate (31.6 g., 0.132 mole) and sodium hydroxide (6.3 g.) in water (55 cc.). The addition was made at a rate such that the temperature of the reaction mixture was maintained at 60–70° and required 45 minutes. After the reducing solution had been added, the reaction mixture was refluxed two hours, after which time ethanol (300 cc.) was removed by distillation. On pouring the dark residue into water a tan solid separated. This was filtered and crystallized from methanol to yield 18.8 g. of yellow crystals; m.p. 189–191°. Further recrystallization gave bright yellow-green plates; m.p. 192–193°. From analytical data (Found: C, 52.49, 52.61) we estimate that this product contains 75% III and 25% IV. The separation of such a mixture will be described in detail in connection with the catalytic hydrogenation study.

The above mixture of III and IV (9.9 g.) and ethanol (400 cc.) was added to a solution of stannous chloride dihydrate (18 g.) in concentrated hydrochloric acid (150 cc.), and the mixture was refluxed three hours. After removal of the ethanol by distillation, the reaction mixture was poured into ice-water, made basic to litmus with sodium hydroxide, and the yellow-brown solid which deposited was collected by suction filtration. Recrystallization from ethanol gave 7.7 g. of III; yellow-green plates; m.p. 192.5–193°.

Anal. Calcd. for $C_{14}H_6N_2F_6$: C, 53.21; H, 1.91. Found: C, 52.93, 53.14; H, 1.75, 1.83.

B. 0.25 Mole Na_2S/Mole NO_2.—A mixture of I (5 g.) sodium sulfide nonahydrate (1.58 g.) and sodium hydroxide (0.32 g. in 10 cc. water) in ethanol (100 cc.) was refluxed three hours. The crude product was isolated as in A above and crystallized from ethanol to yield 2,2′-dinitroso-4,4′-bis-(trifluoromethyl)-biphenyl (V) (2.0 g., 43.6%). Recrystallization from dioxane gave colorless needles; m.p. 267° d. (into copper block at 220°; temperature rise 5° per minute). This product yellows before melting and gives, on recrystallization, yellow mother liquors, the color intensity of which increases with prolonged heating.

Anal. Calcd. for $C_{14}H_6N_2O_2F_6$: C, 48.29; H, 1.74. Found: C, 48.02, 48.19; H, 1.87, 1.79.

3,8-Bis-(trifluoromethyl)-benzo(c)cinnoline-5-oxide (IV) (1.3 g, 31.1%), was obtained from the ethanolic liquors as colorless plates of m.p. 211–213°. This material did not give a depression on mixed melting with IV obtained by the other methods to be described, and its ultraviolet absorption spectrum was superposable with those of other samples of this compound.

Anal. Calcd. for $C_{14}H_6N_2OF_6$: C, 50.61; H, 1.82. Found: C, 50.33, 50.08; H, 1.72, 1.79.

C. 3.0 Moles Na_2S/Mole NO_2.—A mixture of I (5 g.), sodium sulfide nonahydrate (18.7 g.) and sodium hydroxide (1.5 g. in 50 cc. water) in ethanol (120 cc.) was refluxed 20 hours. Isolation of the product in the usual fashion yielded 4.0 g. of III; m.p. 192.8–193.5°. The ultraviolet spectrum of this sample was superposable with the spectra of those prepared by other methods to be described.

From the alcoholic mother liquors from the above product there was obtained 2,2′-diamino-4,4′-bis-(trifluoromethyl)-

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[8] N. Kornblum and D. C. Iffland, THIS JOURNAL, **71**, 2137 (1949).

[9] For earlier work on the deamination of 2,2′-dinitrobiphenyls see the following: (a) J. J. Dobie, J. J. Fox and A. J. H. Gauge, *J. Chem. Soc.*, **99**, 1615 (1911); (b) R. B. Sandin and T. L. Cairns, THIS JOURNAL, **58**, 2019 (1936); (c) K. H. Saunders and W. A. Waters, *J. Chem. Soc.*, 1154 (1946); (d) H. H. Hodgson, *ibid.*, 348 (1948).

[10] Boiling points and melting points are uncorrected.

[11] The microanalyses and molecular weight determinations were performed by Dr. Carl Tiedcke.

biphenyl (II); yield 0.1 g., 2.4%; m.p. 133–135°—no depression on mix-melting with an authentic sample of I.

3,8-Bis-(trifluoromethyl)-benzo(c)cinnoline-5-oxide (IV).—A solution of III (1.79 g., 0.0057 mole) in chloroform (20 cc.) was treated with peracetic acid (1.85 g. of a 40% solution of the peracid in acetic acid; obtained from the Becco Sales Corp.). After standing at room temperature for two days, during which time the reaction mixture was shaken occasionally, the chloroform solution was washed with 10% sodium hydroxide, then water, and dried over anhydrous magnesium sulfate. Removal of the solvent gave IV; colorless solid; m.p. 208–210°; yield 1.71 g. (90%). Crystallization from ethanol–benzene gave colorless plates of m.p. 210.5–212°.

Anal. Calcd. for $C_{14}H_6N_2OF_6$: C, 50.61; H, 1.82. Found: C, 50.42, 50.58; H, 1.67, 1.49.

The ultraviolet spectrum of IV obtained in this manner was superposable on the spectra of samples obtained both by the sodium sulfide reduction and catalytic hydrogenation.

Catalytic Hydrogenation of 2,2′-Dinitro-4,4′-bis-(trifluoromethyl)-biphenyl (I).—A solution of I (53.8 g., 0.14 mole) in ethyl acetate (140 cc.) was shaken in a Parr low-pressure hydrogenation apparatus at 2–3 atmospheres hydrogen pressure with 0.1 g. of platinum oxide catalyst (Baker and Co., Lot No. 7021) at room temperature. Initially, hydrogen uptake was rapid, and the reaction bottle became warm. After 2.5 hours no further hydrogen uptake was observed. Addition of fresh catalyst and renewed shaking for several hours did not lead to any perceptible pressure drop. After filtration of the catalyst most of the ethyl acetate–water azeotrope was removed by distillation at atmospheric pressure. When the final traces of solvent were removed *in vacuo* the residue set to a solid yellow cake weighing 50 g. This crude product began to melt at 125°, was liquid at 140° but not completely clear until 175°.

The crude solid was suspended in refluxing absolute ethanol (200 cc.). Rapid filtration of the hot solution led to the isolation of 3.1 g. of an insoluble yellow material; m.p. 229–235°. Repeated recrystallization from ethanol–benzene (1:1) and charcoal treatment gave butter-yellow needles, m.p. 248–249°.

Anal. Found: C, 51.71, 51.53; H, 2.52, 2.67; N, 8.67, 8.54; F, 36.69, 36.98.

The ultraviolet absorption spectrum of this material in dioxane shows a single maximum ($E(1/g)$, 18.2) at 310 mμ. We have not assigned a structure to this product.

The filtrate from the hot ethanol treatment described above set to an almost solid mass on cooling. Filtration and crystallization from a smaller volume of ethanol gave 17 g. of yellow needles; m.p. 190–192°. This was shown to be a mixture of III and IV by chromatography. A 2-g. sample of the mixture was deposited on an alumina column (1.5 cm. × 50 cm.). Elution at 30–50 mm. of mercury pressure above atmospheric was carried out with varying concentrations of ethanol in hexane, initially 0.5%, then 1% and finally 20%. The benzo(c)cinnoline oxide, IV, was finally liberated from the column with absolute alcohol. The course of the separation was followed by determining the spectrum of each fraction eluted from the column (Fig. 4). From the 2-g. sample we obtained 0.41 g. of III, m.p. 192–193°, 1.11 g. of mixtures of III and IV at various stages of separation and 0.45 g. of IV, m.p. 201–204°. The 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline thus obtained was crystallized from ethanol; yellow-green plates; m.p. 192–193°.

Anal. Calcd. for $C_{14}H_6N_2F_6$: C, 53.21; H, 1.91. Found: C, 53.01, 52.86; H, 1.96, 1.75.

Crystallization of the above 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline-5-oxide from hexane–ethanol gave colorless plates; m.p. 211–212.5°.

Anal. Calcd. for $C_{14}H_6N_2OF_6$: C, 50.61; H, 1.82. Found: C, 50.81, 50.65; H, 1.76, 1.82.

By comparison of the spectrum of the initial mixture of III and IV with the spectra of pure III and pure IV it is possible to estimate that this mixture contains 30 ± 2% by weight of IV.

Evaporation of the solvent from the mother liquors from the isolation of the mixture of III and IV and crystallization of the crude product from ligroin (b.p. 90–100°) gave colorless crystals of 2,2-diamino-4,4′-bis-(trifluoromethyl)-biphenyl (II); yield 22 g. (49%); m.p. 134–135°; no depression on mix-melting with an authentic sample of II. The diacetyl derivative, prepared as above, had the same m.p. as an authentic sample and gave no depression on mix-melting with it.

Anal. Calcd. for $C_{18}H_{14}N_2O_2F_6$: C, 53.47; H, 3.49. Found: C, 53.04, 53.19; H, 3.49, 3.29.

Catalytic Reduction of Intermediate Reduction Products.—Small amounts of material (0.2–0.5 g.) in ethyl acetate (100 cc.) were shaken for two hours under 2–3 atmospheres hydrogen pressure in the presence of platinum oxide (0.1 g.), and the products were isolated in the usual manner

(1) **3,8-Bis-(trifluoromethyl)-benzo(c)cinnoline** (III).—Several reduction attempts led only to the quantitative recovery of starting material.

(2) **3,8-Bis-(trifluoromethyl)-benzo(c)cinnoline-5-oxide (IV).**—An almost quantitative yield of yellow-green plates of m.p. 192–193° was obtained. The spectrum indicates this is a mixture of III and IV.

(3) **3,8-Bis-(trifluoromethyl)-benzo(c)cinnoline-5,6-dioxide (V).**—Reduction of 0.46 g. of V gave 0.34 g. of yellow-green product; m.p. 190–192°. The spectrum indicates that this product, too, is a mixture of III and IV. No trace of a basic product could be isolated.

(4) **The Mixture of III and IV Obtained by Catalytic Reduction.**—A recrystallized portion of the mixture of III and IV containing 31 ± 2% IV by weight gave an almost quantitative yield of yellow-green plates; m.p. 191.5–193°. The spectrum of the product indicates that IV was still present but much reduced in concentration.

Deamination of 2,2′-Diamino-4,4′-bis-(trifluoromethyl)-biphenyl (II). Procedure A.—A suspension of 5 g. of II in 10 cc. of concentrated hydrochloric acid and 45 cc. of water was boiled for five minutes. After cooling to room temperature and the addition of 8 cc. of concentrated hydrochloric acid the reaction mixture was cooled to 0°. A solution of 2.3 g. of 97% sodium nitrite in water (6 cc.) was then added over a 15-minute period while the temperature was maintained at 0–3°. The diazonium solution was then stirred for one hour at the same temperature. 50% hypophosphorous acid (60.3 g., 0.46 mole, precooled to 0°) was added to the yellow-orange tetrazonium solution over 15 minutes, and, after stirring at 0–3° for two hours, the deamination mixture was kept at 5–8° for 38 hours. Filtration of the yellow-brown solid, which separated during the reaction, and crystallization from ethanol gave 2.27 g. (46%) of yellow crystals of 3,8-bis-(trifluoromethyl)-benzo(c)cinnoline (III) (m.p. 190–193°). Recrystallization from ethanol gave yellow plates (m.p. 191–192.8°).

Anal. Calcd. for $C_{14}H_6N_2F_6$: C, 53.21; H, 1.91. Found: C, 53.26, 53.09; H, 1.72, 1.83.

From the filter paper used in the crystallization of III there was obtained 0.31 g. of a pale yellow solid of m.p. 240–243°. Recrystallization from dioxane gave poorly defined pale yellow crystals; m.p. 252–254°.[12]

Anal. Found: C, 53.04, 53.38; H, 1.89, 2.00; mol. wt. (Rast–Tiedcke), 277, 272, 304, 287.

Procedure B.—2,2′-Diamino-4,4′-bis-(trifluoromethyl)-biphenyl (5 g.) was dissolved in 50% hypophosphorous acid (123.6 g., 0.94 mole). Water (50 cc.) was added, and the solution was cooled to 5°. A solution of 97% sodium nitrite (2.3 g.) in water (10 cc.) was added, with stirring, over 15 minutes while the temperature of the reaction mixture was maintained at 0–5°. During the addition of the nitrite solution a tan-colored solid deposited. The reaction slurry was then stirred at 0° for one hour, allowed to come to room temperature and finally permitted to stand four hours. The crude product was filtered and steam distilled to yield 1.25 g. (27.6%) of 4,4′-bis-(trifluoromethyl)-biphenyl; colorless crystals; m.p. 82–87°. Crystallization from methanol–water gave colorless plates; m.p. 93–94.5°; no depression on mix-melting with an authentic sample of this compound.[13]

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[12] The analyses and molecular weight determinations indicate that this product has the same empirical formula as III. One structure which is consistent with these results is that of 2,7-bis-(trifluoromethyl)-4,5-iminocarbazole. The formation of carbazoles during the reactions of diazonium compounds has been observed previously (V. Niementowski, *Ber.*, **36**, 3329 (1901); J. J. Dobbie, J. J. Fox and A. H. H. Gauge, *J. Chem. Soc.*, **99**, 1615 (1911)). Our data, however, are not sufficient to permit a definite structural assignment.

[13] The preparation of 4,4′-bis-(trifluoromethyl)-biphenyl will be the subject of a separate communication from this Laboratory.

Anal. Calcd. for $C_{14}H_8F_6$: C, 57.92; H, 2.78. Found: C, 58.46, 58.19; H, 3.08, 3.12.

The solid residue from the steam distillation was boiled with methanol, and, from the hot alcoholic filtrate, there was obtained 0.65 g. (13.2%) of III. Leaching of the insoluble, red-brown tar, remaining from the methanol treatment, with hot dioxane gave 0.18 g. of yellow solid; m.p. 170–180° d. Several crystallizations from ethanol–benzene gave yellow-orange crystals of m.p. 185–187° d. which could not be purified further. This material appears to be III contaminated with the tarry by-product.

Anal. Found: C, 52.37, 52.50; H, 3.04, 2.77.

Ultraviolet Absorption Spectra.—A Beckman model DU quartz spectrophotometer was employed for the determinations. The dioxane employed as solvent was purified according to the procedure of Fieser.[14]

Acknowledgment.—We are indebted to Mr. William A. Leach of these laboratories for the determination of some of the ultraviolet absorption spectra reported herein.

[14] L. F. Fieser, "Experiments in Organic Chemistry," Second Edition, D. C. Heath and Co., Boston, Mass., 1941, p. 368.

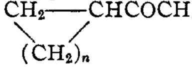
NORTH ADAMS, MASS. RECEIVED JULY 30, 1951

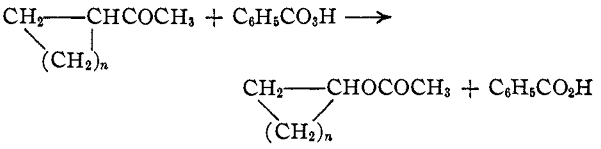
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Reactions of Peracids. VI. The Reaction of Acetylcyclanes with Perbenzoic Acid[1]

BY S. L. FRIESS[2] AND REX PINSON, JR.

Acetate esters are obtained in yields of 58 to 72% from the reaction of acetylcyclanes, varying in ring size from four to seven members, with perbenzoic acid in chloroform solution. Kinetic studies indicate that the reaction is a second order, acid-catalyzed process which is accelerated by an increase in the polarity of the medium. Energies, enthalpies and entropies of activation have been determined. The relative reactivities of the ketones are discussed in terms of the electronic character and steric environment of the carbonyl group.

It has previously been observed[3] that cyclohexyl acetate is formed in 67% yield from the reaction of cyclohexyl methyl ketone with perbenzoic acid in chloroform, and that no analogous product can be isolated from similar treatment of cyclopropyl methyl ketone. It was therefore of interest to extend the study of the peracid reaction to a series of acetylcyclanes  CH_2—$CHCOCH_3$ $(CH_2)_n$ in which the ring size was systematically varied, and note the effect of ring size on both the yield of acetate esters produced and the relative rates of reaction. Extension of the reaction represented by the general equation



n = 1, 2 · · · · 5
Compounds I, II · · · V

to other members of the homologous series has now shown that, with the exception of cyclopropyl methyl ketone (I), the reaction proceeds readily and provides the corresponding acetates in yields of 58 to 72%.

In accord with the previous work,[3] it was found that the peracid activity of a chloroform solution of perbenzoic acid containing I disappears very slowly, and that no ester product indicative of a normal reaction can be isolated.

Isopropyl methyl ketone (VI), taken as a typical open-chain ketone having certain features of structural similarity to the members of the cyclic series was also allowed to react with perbenzoic acid, for comparison purposes. It provided the single product isopropyl acetate in normal yield.

The results of these experiments, summarized in Table I, point to the synthetic utility of the peracid reaction in the transformation $-COCH_3 \rightarrow -OCOCH_3$ for the acetyl group attached to an alicyclic system. In no case was there evidence for the formation of the isomeric methyl ester, corresponding to migration of the methyl group from carbon to oxygen.

Over a limited range of initial ketone and peracid concentrations in chloroform solution, the reaction for each ketone in the series II–V was observed to be a second order process. The data of each run gave excellent linearity in second order plots, and relative constancy of the specific reaction rates (k_2) with varying initial concentrations was observed for each ketone. Data representative of a typical ketone of the series are given in Table II.

Also included in Table II are data illustrating the catalytic effect of acetic or benzoic acid initially added to a reaction mixture. These and similar data for the other ketones indicate that for all reactive members of the series there is a marked increase in the observed rate constants of reactions run in the presence of either acetic or benzoic acid. This second order, acid-catalyzed behavior parallels that observed in the perbenzoic acid oxidation of acetophenones[4] and cyclanones.[5]

Since different preparations of perbenzoic acid contain varying amounts of benzoic acid, a uniform catalytic effect could be obtained only by using identical aliquots of the same peracid solution. Evaluation of any single factor therefore necessitated the use of the same stock solution of perbenzoic acid throughout all runs in which that factor was under consideration. This procedure ensures the reliability of relative rate values, and the dependence of rate on catalyst content explains cer-

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[1] Presented in part before the Division of Organic Chemistry at the 118th Meeting of The American Chemical Society, Chicago, Ill., September 3–8, 1950.

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[3] S. L. Friess, THIS JOURNAL, **71**, 14 (1949).

[4] S. L. Friess and A. H. Soloway, *ibid.*, **73**, 3968 (1951).

[5] S. L. Friess, *ibid.*, **71**, 2571 (1949).