In general CD_3 as initially formed possesses sufficient energy to make the reaction go on the first collision if steric requirements are met. (d) If the reaction does not go on the first collision, CD_3 is sufficiently deactivated so that the reaction occurs with very low probability on a succeeding collision.

We can then write

$$p_r \propto 2CD_3H$$
$$p_m \propto CD_4\text{–}CD_3H$$

Thus, we have for the ratio p_r/p_m for the photolysis of CD_3CDO

λ, Å.	>3000	~2537
p_r/p_m	25	1.4

This result is in reasonably good agreement with that of Blacet, *et al.*, when we note the slight differences in wave length of light employed and the fact that our data are for the d_4 compound. The assumptions employed in arrival at this estimate are rough. More careful consideration might include note of the fact that $E_4 < E_3$[8]; such more precise considerations would lead to the conclusion that our estimates of p_r/p_m tends to be high. The details of a more reliable calculation are not readily apparent.

[8] Data given in reference 6 indicate that the CD_4/CD_3H ratio at 140–200°, where the chain reaction overwhelmingly predominates, is 0.62. Thus, E_4 is ~0.4 kcal./mole less than E_3.

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NEW COMPOUNDS

Some Derivatives of Biphenyl

4-Ethoxy-2′-nitrobiphenyl was prepared by a crossed Ullmann synthesis.[1] A mixture of 92 g. of *o*-iodonitrobenzene and 65 g. of commercial copper–bronze powder was added slowly with stirring to a mixture of 92 g. of *p*-iodophenetole and 50 g. of sand, while the temperature was maintained at 220–235°. After 15 minutes, an additional 65 g. of copper–bronze was added, and heating and stirring were continued for 2.5 hours. The desired product was isolated from the reaction mixture by successive ether extraction, vacuum distillation, chromatographic separation on alumina, recrystallization from alcohol and vacuum sublimation. The yield was 12 g. (13%) of yellow solid, m.p. 52–52.5°. *Anal.*[2] Calcd. for $C_{14}H_{13}NO_3$: C, 69.12; H, 5.39. Found: C, 69.32; H, 5.16.

2-Amino-4′-ethoxybiphenyl was obtained in 76% yield by the reduction of 3 g. of 4-ethoxy-2′-nitrobiphenyl with tin and hydrochloric acid.[3] After three vacuum sublimations, the product was a white solid which darkened on standing and melted at 54–55°. *Anal.* Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09. Found: C, 78.81; H, 7.00.

4-Ethoxy-2′-hydroxybiphenyl.—A solution of 1.0 g. of 2-amino-4′-ethoxybiphenyl in 200 ml. of dilute sulfuric acid was diazotized at −5° with 0.4 g. of sodium nitrite. After standing for three days at room temperature the solution was extracted with ether. Evaporation of the ether and vacuum sublimation of the remaining tar gave 0.7 g. (70% yield) of an oil which later solidified. After three further vacuum sublimations and a recrystallization from petroleum ether, the product was obtained as a white solid which melted at 53.5–54.5°. A mixture of equal amounts of 2-amino-4′-ethoxybiphenyl and 4-ethoxy-2′-hydroxybiphenyl melted at 43–47°. *Anal.* Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.43; H, 6.67.

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Preparation of 2-Pyrroyltrifluoroacetone[1]

To 0.3 mole of sodium ethoxide suspended in 150 ml. of anhydrous ether in a three-necked flask fitted with a stirrer, reflux condenser and separatory funnel, 43 g. (0.3 mole) of ethyl trifluoroacetate was added slowly with stirring. To the resulting clear, light brown, solution, 32.7 g. (0.3 mole) of 2-acetylpyrrole,[2] m.p. 89–91°, dissolved in 350 ml. of anhydrous ether was added. When approximately one-half of the solution had been added, a precipitate appeared which redissolved as more of the ketone was added to give a clear yellowish-brown solution. The reaction mixture then was stirred for about 5 hours and allowed to stand overnight. Five hundred ml. of a copper acetate solution (0.23 mole of copper) was added and the mixture stirred for 3 hours more. On standing, two layers separated, a bluish-green ether layer containing most of the copper chelate, and a bluish aqueous layer containing some suspended copper chelate. The ether was then stripped and the precipitated copper chelate filtered and air-dried. The yield was 68 g., 95% of the theoretical amount. When some of the copper chelate was steam distilled to remove any unreacted 2-acetylpyrrole, no unreacted ketone was recovered. A solution containing 31 g. of the copper chelate in 800 ml. of ether, in a 2000-ml. erlenmeyer flask, was treated under pressure with dry hydrogen sulfide. Two 30-minute treatments were required before all the blue color of the copper compound had disappeared. The precipitated copper sulfide was filtered after each treatment with the aid of Filter Cel. The resulting clear, brown solution when stripped of the ether gave a pasty brown product. The crude product was distilled twice, under vacuum, with the fraction between 112–117° (5 mm.) collected. The distillate was a dark yellow liquid which solidified as it came in contact with the receiving flask. The yield was 14 g. The melting point range 59–69° indicated that the diketone was still impure, thus it was recrystallized, twice, from petroleum ether (60–68° fraction) to give long light yellow needles. The yield was 8.7 g. of the purified material. The melting point, after drying in a vacuum at room temperature for three hours, was 68.5–70.0°.

Anal.[3] Calcd. for $C_8H_6NO_2F_3$: C, 46.83; H, 2.95; N, 6.83. Found: C, 47.06, 47.20; H, 2.90, 2.95; N, 7.41, 7.22.

Further identification was provided by the metal analysis of bis-(1,1,1-trifluoro-4-(2-pyrryl)-2,4-butanediono)-copper. For analysis, the copper chelate, prepared as above, was recrystallized from hot 95% ethyl alcohol and dried at 110° for 24 hours after a preliminary drying for 12 hours at room temperature *in vacuo*, m.p. (dec.) 160°.

Anal. Calcd. for $CuC_{16}H_{10}N_2O_6F_6$: Cu, 13.47. Found: Cu, 13.43.

The isoxazole was produced by placing 1.33 g. of 2-pyrroyltrifluoroacetone in 15 ml. of 0.5 *N* HCl and adding enough ethyl alcohol to effect solution. Then a solution, containing 0.9 g. of hydroxylamine hydrochloride in 5 ml. of water, was added and the solution allowed to stand overnight. The solution was heated on a steam-bath until a precipitate appeared, at which time the heating was stopped and the mixture cooled in a water–ice mixture. The product was filtered and air-dried giving a yellow colored com-

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[1] For a review of the Ullman synthesis of biaryls see P. E. Fanta, *Chem. Revs.*, **38**, 139 (1946).

[2] All analyses by Micro-Tech Laboratories, Skokie, Illinois.

[3] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 144.

[1] Based on research carried out under Task Order 4 of Contract N 7onr-28504 between the Office of Naval Research and the University of Wisconsin.

[2] A. A. Berlin, *J. Gen. Chem.* (*U. S. S. R.*), **14**, 438–46 (1944); *C. A.*, **39**, 4606[8].

[3] Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.