Thermal Cleavage of I.—Crystalline I (0.20 g.) was placed in a small glass tube open to the atmosphere and heated in an oil-bath for one hour between 190–230°. On cooling a clear yellow liquid was obtained, which, on treatment in 40 ml. of ethanol with 2,4-dinitrophenylhydrazine, gave 0.06 g. of the corresponding hydrazone of benzophenone. Recrystallization from ethanol yielded pure material; m.p. 238–239°. Mixed m.p. with authentic 2,4-dinitrophenylhydrazone produced no depression.

The Grignard reaction was repeated with 38 g. of methyl dehydroabietate, and the crude product was freed of biphenyl by steam distillation. The impure carbinol was then subjected to *evaporative distillation* at 3 mm. in a modified Hickman still. At 90° a small amount of residual biphenyl, m.p. 67–69°, collected on the cold finger. Between 140–150° 2.5 g. of distillate was collected which slowly crystallized. Recrystallization from methanol yielded unreacted methyl dehydroabietate, m.p. 60.5–61.5°. Another cut (3 g.), distilling in the same range, was also crystalline ester. An increase in temperature to 180° produced 5 g. of a non-crystallizing oil. The main fraction was evaporatively distilled between 190–200° and consisted of 12 g. of a clear, colorless liquid. An additional amount (5 g.) was obtained in the same temperature range. A portion of the main fraction (1 g.) with 1.5 g. of 2,4-dinitrophenylhydrazine in 100 ml. of ethanol and 2 ml. of hydrochloric acid yielded 0.5 g. of benzophenone 2,4-dinitrophenylhydrazone.

Isolation of Hydrocarbon Fraction (IIa).—A portion of the main fraction (5 g.) from the above distillation was redistilled evaporatively at 3 mm. Between 60–90° two fractions were separated which deposited benzophenone on standing. The fraction collected between 90–100° (2.2 g.) was dissolved in 200 ml. of petroleum ether (b.p. 30–60°) and passed through a column of aluminum oxide (h = 8″, d = 1″). The column was washed with an additional 500 ml. of petroleum ether, and the solvent ether removed. The residual oil was again evaporatively distilled between 90–100° (3 mm.): 0.9 g.; $n^{25}{}_D$ 1.5428; $d^{25}{}_4$ 0.961; $[\alpha]^{25}{}_D$ + 102° (α = + 1.04°, c = 1.02).

Anal. Calcd. for $C_{19}H_{28}$: C, 88.99; H, 11.01. Found: C, 89.46; H, 10.53.

The hydrocarbon did not decolorize potassium permanganate in acetone solution but reacted with bromine in carbon tetrachloride with the evolution of hydrogen bromide.

Oxidation of IIa.—Ten grams of the hydrocarbon (IIa) was oxidized at 80° with chromic acid as described.[2] From the oxidation mixture there was obtained 2.8 g. of ketone (IIIa), $n^{27}{}_D$ 1.5560. Its 2,4-dinitrophenylhydrazone, after recrystallization from ethyl acetate, melted between 196–197.5°; mixed with 2,4-dinitrophenylhydrazine, the m.p. was depressed.

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Comment on Mechanism of Photolysis of Acetaldehyde

BY PAUL D. ZEMANY AND MILTON BURTON[1]

The banded absorption of acetaldehyde at longer wave lengths (3400 Å.) and the continuous absorption in the shorter ultraviolet (2800–2400 Å.) with gradual transition between suggest two different mechanisms of the photolytic process.[2] Gorin introduced iodine into samples photolyzed at 25°; assuming that iodine would react with any methyl radicals primarily formed and that all methane produced under such circumstances comes from a primary rearrangement, he concluded that the free radical split preponderates at 3130 Å. but that the rearrangement is the major reaction at 2537 Å.[3] Comparison of the high-temperature quantum yield data of Rollefson and Grahame[4] may also be used as evidence that the free radical split occurs more readily at the longer wave length. Blacet and his co-workers[5] used methods similar to those of Gorin but arrived at results quantitatively different. If we note the probabilities of radical split and molecular rearrangement as p_r and p_m, respectively, the data for p_r/p_m may be compared

λ, Å.	Gorin	Blacet, *et al.*
3130	2.6	20
2537	0.34	1.1

By a different method which is described in detail elsewhere[6] we have obtained data which permit an independent estimate of the probabilities of the competing photolytic mechanisms.

Equimolar mixtures of CH_3CHO and CD_3CDO at a total pressure of 37.8 cm. were photolyzed at a temperature of 25° to the extent of 3 or 4 per cent. In the first sample in a quartz bulb irradiated by a Germicidal lamp, photolysis was caused largely by the 2537 Å. mercury line. In a second sample in a Pyrex bulb, with GE H4 lamp as illuminant, photolysis was effected by radiation longer than 3000 Å.

Consider the competing reactions

$$CD_3CDO \xrightarrow{h\nu} CD_3 + CDO \qquad (1)$$

$$CD_3CDO \xrightarrow{h\nu} CD_4 + CO \qquad (2)$$

The succeeding reactions for the energetic radical primarily produced include two important reactions for our consideration

$$CD_3 + CD_3CDO \longrightarrow CD_4 + CD_3CO \qquad (3)$$

$$CD_3 + CH_3CHO \longrightarrow CD_3H + CH_3CO \qquad (4)$$

Reaction (2) can yield only CD_4 but reaction (1) can yield both CD_4 and CD_3H. If only rearrangement occurs in the photolysis of the mixture, the product methane should be exclusively CD_4 and CH_4. Using mass spectrographic methods of analysis the following results were obtained.

λ, Å.	3130	2537
CD_4/CD_3H	1.08	2.4

No CD_2H_2 was formed.

The interpretation of these results involves certain considerations of the nature of the reactions. The very existence of CD_3H in relatively large yield shows that reaction (3) can occur at 25°. However, the best data we have[3] indicate that the chain length can at most be unity at room temperature. A reasonable conclusion is that CD_3 as initially formed in reaction (1) has excess energy, even when produced with light of λ > 3000 Å., sufficient to provide activation energy for reaction (3) in a first collision. To complete our estimate we make assumptions regarding reactions (3) and (4): (a) They have approximately the same steric factors. (b) Their activation energies are not high.[7] (c)

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[2] P. A. Leighton and F. E. Blacet, THIS JOURNAL, **55**, 1766 (1933).

[3] E. Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[4] G. K. Rollefson and D. C. Grahame, *ibid.*, **7**, 775 (1939).

[5] F. E. Blacet and J. D. Heldman, THIS JOURNAL, **64**, 889 (1942); F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942).

[6] P. D. Zemany and M. Burton, *J. Phys. Colloid Chem.*, forthcoming publication.

[7] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, gives 8-10 kcal./mole.

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.

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[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.