aqueous sodium carbonate at room temperature and then bubbling carbon dioxide in the aqueous solution for several hours, whereby the salt of the enolic form of the diketo ester is quantitatively decomposed. The copper chelate was prepared by addition of 2 g of the β-diketo ester in ethanol solution to an excess of copper acetate dissolved in 50% ethanol and extraction with chloroform. After recrystallization from benzene the melting point was 252.5–253.5°.

*Anal.* Calcd for $C_{20}H_{18}O_{10}Cu$: C, 49.85; H, 3.76; Cu, 13.18. Found: C, 49.69; H, 3.61; Cu, 13.08.

**Ethyl 5-Acetoacetyl-2-furoate.**—This ester was prepared through two different ways.

(1) By the aforementioned procedure the ethyl ester was prepared with similar results, but the yield was slightly lower because more difficulties were experienced in the sublimation of the low melting brown residue. Melting point and analysis are given in Table I. The copper chelate, obtained under the same conditions as above, melted at 234.5–235.5°.

*Anal.* Calcd for $C_{22}H_{22}O_{10}Cu$: C, 51.85; H, 4.35; Cu, 12.46. Found: C, 52.02; H, 4.46; Cu, 12.61.

(2) When the reactions was carried out as originally proposed by Gilman, *et al.*,[1] (benzene as solvent, 250 ml; ethyl 2-furoate, 56 g, 0.4 mole; acetic anhydride, 40.8 g, 0.4 mole; stannic chloride, 208.5 g, 0.8 mole; molar ratios 1:1:2) keeping the temperature at 13–20° and hydrolyzing the reaction mixture 90 min after the addition of stannic chloride, the crude mixture contained much unreacted ethyl 2-furoate, chiefly ethyl 5-acetyl-2-furoate and ethyl 5-acetoacetyl-2-furoate, and little higher boiling products.

By fractional distillation under reduced pressure were collected at 85–120° at 20 mm 44 g of ethyl 2-furoate unreacted and at 100–150° (0.1–1 mm) 11 g of the keto and β-diketo esters. The infrared quantitative analysis of the mixture showed that approximately a 2:1 ratio was obtained. The two components were actually separated by repeatedly stirring the benzene solution with aqueous sodium carbonate and regenerating the β-diketo ester by bubbling carbon dioxide for several hours into the aqueous layer; 3.5 g of ethyl 5-acetoacetyl-2-furoate (4% yield) was recovered.

**Methyl or Ethyl 5-Acetyl-2-furoate.**—The keto esters were obtained by the short time reaction as described in method 2 above, it being difficult to obtain them in the pure state under the reaction conditions usually described in literature (very long reaction time). For the ethyl 5-acetyl-2-furoate the benzene layer, previously exhausted with aqueous sodium carbonate, was dried and evaporated under reduced pressure. The residue (7 g, 10% yield) was sublimated and the sample for the analysis was further purified by crystallization from ethanol. Analyses and melting points of the keto esters are given in Table I.

*Anal.* Calcd for $C_8H_8O_4$: equiv sapon, 168.15. Found: equiv sapon, 169. Calcd. for $C_9H_{10}O_4$: equiv sapon, 182.2. Found: equiv sapon, 182.5.

The presence of the ketonic group was also substantiated by the preparation of the oximes. The white oxime of methyl 5-acetyl-2-furoate after recrystallization from water melted at 89.5–93.5°.

*Anal.* Calcd for $C_8H_9NO_4$: C, 52.46; H, 4.95; N, 7.65. Found: C, 52.35; H, 5.00; N, 7.47.

The oxime of ethyl 5-acetyl-2-furoate after crystallization from 35% ethanol melted at 129–131°.

*Anal.* Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.11. Found: C, 54.99; H, 5.71; N, 7.41.

**5-Acetoacetyl-2-furoic Acid.**—The hydrolysis of the β-diketo esters to the corresponding acid required some caution because of the easy splitting of the acetoacetyl group and therefore it was not a clear-cut reaction. Ethyl 5-acetoacetyl-2-furoate (3.03 g) was dissolved in 30 ml of 1 *N* sodium hydroxide and warmed to 95–98° for 15 min. After cooling carbon dioxide was bubbled into the solution until the formation of the precipitate was stopped. On filtration, 0.45 g of the unaltered diketo ester was collected. The solution was then acidified with a little excess of 1 *N* hydrochloric acid; after filtration and drying, 1.58 g of crude impure acid was obtained (yield *ca.* 70%). By crystallization from 220 ml of boiling water, 0.87 g of pure 5-acetoacetyl-2-furoic acid was obtained (mp 228–230° dec).

**5-Acetyl-2-furoic Acid.**—The keto ester was hydrolyzed by refluxing the alcoholic solution with 100% excess of sodium hydroxide 1 *N* in water–ethanol solution. After gentle boiling for 1 hr the solution was evaporated under reduced pressure. The residue was diluted with a small quantity of water, filtered, and acidified. The acid was collected and recrystallized from water–ethanol. Analysis and melting point are given in Table I.

*Anal.* Calcd for $C_7H_6O_4$: neut equiv, 154.1. Found: neut equiv, 154.

**Note.**—While this paper was ready for publication, we became acquainted with the surprising results obtained by G. C. Robinson[7] on the directive effects in acylation of methyl furan-2-carboxylate. Although we agree that the reaction is more complex than was previously assumed, we can confirm that, at least in the acylations with acetic anhydride, significant amounts of furan derivatives acylated in position 4 cannot be isolated and identified among the reaction products. We will refer to the results obtained with other anhydrides in a subsequent Note.

**Registry No.**—A, 13341-77-0; B, 13341-78-1; C, 13341-79-2; oxime of C, 13341-80-5; D, 13341-81-6; E, 13318-36-0; oxime of E, 13341-82-7; F, 13341-83-8.

**Acknowledgments.**—The authors wish to thank the Italian National Council for Research (C.N.R.) for financial support and Dr. A. L. Segre for the registration and interpretation of the nmr spectra.

---

[7] G. C. Robinson, *J. Org. Chem.*, **31**, 4252 (1966).

---

## Synthesis of Oxetanes by Photoaddition of Benzophenone to Furans

CARLOS RIVAS AND ELISEO PAYO

*Department of Chemistry, Instituto Venezolano de Investigaciones Cientificas, Caracas, Venezuela*

*Received February 21, 1967*

The direct 1,2 photoaddition of benzophenone to furan was observed independently by two groups of workers[1] to lead an oxetane. The product was later identified unequivocally by nuclear magnetic resonance (nmr) as the 6,6-diphenyl-2,7-dioxabicyclo[3.2.0]-$\Delta^3$-heptene (1).[2] We have carried out the photoaddition of benzophenone to 3-methylfuran, 2-methylfuran, 2-furfuryl alcohol, and 2,4-dimethylfuran. The results of the irradiations of solutions of benzophenone in each one of these furans are shown in Table I.

In contrast to the product mixture of the two isomeric oxetanes obtained by Toki, Shima, and Sakurai[3] from the photolysis of aldehydes such as benzaldehyde, acetaldehyde, and propionaldehyde in 2-methylfuran which result from addition of the carbonyl compound to either double bond of the furan, we have in each case isolated one single product. It is interesting to note that in this work benzophenone invariably adds to the double bond having the methyl substituent and, if the furan carries two methyl groups as in 2,4-dimethylfuran, the resulting product mixture consists of 50% bicyclic adduct to one double bond and 50% bicyclic adduct to one double bond and 50% bicyclic adduct to the other. Apart from the oxetanes no

---

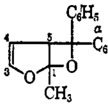
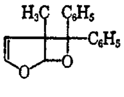
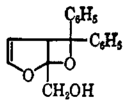
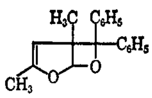
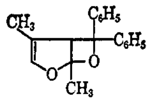
[1] G. O. Schenck, W. Hartmann, and R. Steinmetz, *Ber.*, **96**, 498 (1963); G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963).

[2] D. Gagnaire and Eliseo Payo-Subiza, *Bull. Soc. Chim. France*, 2623 (1963).

[3] S. Toki, K. Shima, and H. Sakurai, *Bull. Chem. Soc. Japan*, **38**, 760 (1965).

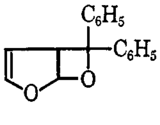
TABLE I

PHOTOLYSIS OF BENZOPHENONE AND FURAN DERIVATIVES AT −10°

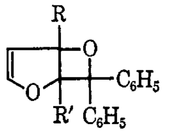
| | | | | | | Nmr spectral data on the oxetanes | | | |
|---|---|---|---|---|---|---|---|---|---|
| Furan | Oxetane | Registry No. | Yield, % | Mp, °C | Protons | Chemical shift, ppm | Integral protons | Multiplicity | Coupling constants, cps |
| 2-Methyl |  | 13341-73-6 | 98 | 129–130 | 1-$CH_3$ | 1.60 | 3 | s | |
| | | | | | C-3 | 6.40 | 1 | q | $J_{3,4} = 2.9$ |
| | | | | | C-4 | 5.00 | 1 | t | $J_{4,5} = 2.9$ |
| | | | | | C-5 | 4.2 | 1 | q | $J_{3,5} = 1.2$ |
| 3-Methyl |  | 13341-74-7 | 98 | 142–143 | C-1 | 6.10 | 1 | d | $J_{1,3} = 0.8$ |
| | | | | | C-3 | 6.30 | 1 | q | $J_{3,4} = 2.9$ |
| | | | | | C-4 | 5.00 | 1 | d | |
| | | | | | 5-$CH_3$ | 1.10 | 3 | s | |
| 2-Carbinol |  | 13341-75-8 | 80 | 134–135 | OH | 1.50 | 1 | s | |
| | | | | | 1-$CH_2$ | 3.50 | 2 | s | |
| | | | | | C-3 | 6.40 | 1 | q | $J_{3,4} = 2.9$ |
| | | | | | C-4 | 4.80 | 1 | t | $J_{4,5} = 2.8$ |
| | | | | | C-5 | 4.40 | 1 | q | $J_{3,5} = 1.2$ |
| |  | | 50 | 145 | C-1 | 6.10 | 1 | s | |
| | | | | | 3-$CH_3$ | 1.80 | 3 | d | $J_{3\text{-}CH_3,4} = 1.2$ |
| | | | | | C-4 | 4.80 | 1 | q | |
| | | | | | 5-$CH_3$ | 1.10 | 3 | s | |
| 2,4-Dimethyl |  | 13341-76-9 | 50 | 135 | 1-$CH_3$ | 1.35 | 3 | s | |
| | | | | | C-3 | 6.05 | 1 | quint | $J_{4\text{-}CH_3,3} = 1.8$ |
| | | | | | 4-$CH_3$ | 0.90 | 3 | q | $J_{4\text{-}CH_3,5} = 1.2$ |
| | | | | | C-5 | 3.80 | 1 | quint | $J_{3,5} = 1.2$ |

[a] The chemical shift for the aromatic protons in all these compounds is found between 7.0 and 7.7 ppm; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet.

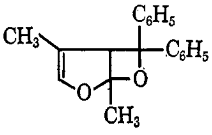
other products were found. As in previous publications, the possible formation of compounds with structure II has been ruled out[2,3] by inspection of the nmr spectra.



I

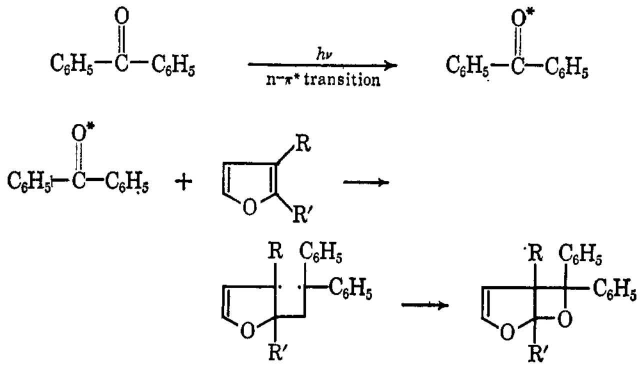


II



III

The reaction path in the formation of the oxetanes most likely goes through the excitation of the carbonyl compound, *via* an excited singlet, to a low-lying triplet state[4] and subsequent addition of the biradical species to the most labile double bond in the furan system.



R = R′ = $CH_3$ or H

The formation of two isomeric oxetanes from benzaldehyde as opposed to one single product from benzophenone may be due to the fact that the excited-triplet benzaldehyde molecule has a higher energy content ($E_{T_1} \simeq 71$ kcal/mole) than the excited-triplet benzophenone ($E_{T_1} = 68.7$ kcal/mole) according to data based on phosphorescence spectra.[5] The more energetic excited benzaldehyde consequently would not entirely discriminate between the two double bonds.

Owing to the great selectivity of benzophenone in its mode of addition to substituted furans compared with the aldehydes, other ketones and aldehydes are being studied in this laboratory.

## Experimental Section

**Materials.**—Benzophenone was used as received from Eastman Kodak. 2-Methylfuran and 2-furfuryl alcohol (Eastman Kodak) were carefully distilled before the irradiations. 3-Methylfuran was prepared according to the procedure of Burness[6] and 2,4-dimethylfuran was prepared according to the method of Morel and Verkade.[7]

A typical experiment will suffice to illustrate the technique.

**Photolysis of Benzophenone in 3-Methylfuran.**—A solution of 2 g (0.0109 mole) of benzophenone in 60 ml of 3-methylfuran was placed in a 70-ml reaction vessel. A quartz immersion well was fitted into the reaction vessel and a Hanovia 450-w lamp was placed in the immersion well. The solution was then irradiated at −10° (Colora Kälte thermostat) while nitrogen gas was passed through the irradiation vessel until no carbonyl band was detected in the infrared spectrum (2 hr). After the solvent was distilled, the residue solidified into a mass of yellowish crystals. The nmr spectrum of the crude product exhibited the characteristic bands of the adduct with traces of 3-methylfuran (total yield, virtually quantitative). The solid was crystallized from a mixture of benzene–petroleum ether (bp 60–65): mp 142–143°.

*Anal.* Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 82.04; H, 6.14.

**Other Photolysis Reactions.**—These reactions were carried out as illustrated above for benzophenone and 3-methylfuran. The total yields calculated on the basis of benzophenone consumed

---

(4) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **83**, 2789 (1961), and related papers.

(5) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 298.

(6) D. M. Burness, *Org. Syn.*, **39**, 46 (1959).

(7) Th. Morel and P. E. Verkade, *Rec. Trav. Chim.*, **70**, 35 (1951).

are given in Table I. The infrared spectra exhibited bands characteristic of a vinyl ether group (1150–1240 cm$^{-1}$) and of a trimethylene oxide ring (995, 980 cm$^{-1}$).[8] The separation of the two adducts formed from benzophenone and 2,4-dimethylfuran was achieved by washing the crude product with carbon tetrachloride: the 1,4-dimethyl-6,6-diphenyl-2,7-dioxabicyclo[3.2.0]-$\Delta^3$-heptene (III) remained on the filter and the other adduct dissolved in the carbon tetrachloride.

Nmr spectra were measured at approximately 30° with a Varian A-60 nmr spectrometer; tetramethylsilane was used as an external standard. The long distance coupling ($J$ = 1.2 cps) between the C-5 and the 4-methyl group in 1,4-dimethyl-6,6-diphenyl-2,7-dioxabicyclo[3.2.0]-$\Delta^3$-heptene (III) was determined by the usual decoupling techniques.

**Registry No.**—Benzophenone, 119-61-9.

[8] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, pp 117–119.

## 2,3-Dicyanoquadricyclane. Synthesis and Isomerization

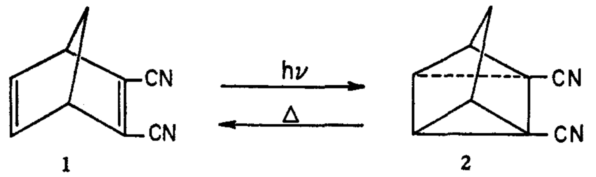
J. R. EDMAN

*Contribution No. 1289, Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898*

*Received January 25, 1967*

The first isomerization of a norbornadiene to a quadricyclane was that of norbornadiene-2,3-dicarboxylic acid.[1] Since then, the isomerizations of norbornadiene and a number of other substituted norbornadienes have been reported.[2] Although the reverse thermal reaction has frequently been observed, the only kinetic work in this area was done by Frey.[3] He studied the isomerization of quadricyclane to norbornadiene in the vapor phase and pointed out that the Arrhenius parameters he obtained were more closely related to those of the cyclobutene to diene[4] rearrangements than the cyclobutanes to two molecules of olefin rearrangements.[5] The only photosensitized isomerization reported is that of quadricyclane to norbornadiene.[6]

Analogous to norbornadiene-2,3-dicarboxylic acid,[1] we find that 2,3-dicyanonorbornadiene (2,3-dicyanobicyclo[2.2.1]hepta-2,5-diene)[7] (**1**) isomerizes cleanly to 1,5-dicyanotetracyclo[3.2.0.0.$^{2,7}$0$^{4,6}$]heptane[8] (2,3-dicyanoquadricyclane) (**2**) when irradiated in ether without a sensitizer.



1 2

In contrast to compound **1**, compound **2** is a stable white solid which can be stored at room temperature for at least 1 year. Its structure was verified by spectroscopic[9] and analytical data. The nmr spectrum consists of a multiplet with peaks at 147, 144, and 137 cps and an integrated intensity of 2 and a second multiplet with peaks at 165 and 159 cps and an integrated intensity of 1. The infrared spectrum exhibits cyclopropyl C–H stretching at 3070 and 3080 cm$^{-1}$, $-C\equiv N$ at 2220 cm$^{-1}$, and no HC=CH stretching. The ultraviolet spectrum shows only end absorption with a shoulder at 2070 A ($\epsilon$ 1140).

When attempts were made to react dicyanoquadricyclane with various dienophiles,[10] the observed product was **1**. This was true for electron-rich and electron-poor olefins and for acetylenes in polar and nonpolar solvents. Since the thermal isomerization of **2** to **1** appeared to go quite readily (80–100°) and could be followed by nmr, it seemed of interest to examine it more closely. The isomerization was studied at three temperatures and plots of ln ($C_0/C$) ($C$, concentration of quadricyclane as determined by integration of the nmr spectrum) *vs.* time gave straight lines from which the rate constants in Table I were calculated. An Arrhenius plot of these data gave a good straight line from which the activation energy ($E_a$ = 33.8 kcal) and entropy ($\Delta S^{\ddagger}$ = +8.5 eu) were calculated. In order to compare these results with quadricyclane,[11] we determined $E_a$ and $\Delta S^{\ddagger}$ for the isomerization of quadricyclane to norbornadiene in deuterioacetonitrile. The values obtained were $E_a$ = 38.3 kcal and $\Delta S^{\ddagger}$ = +7.5 eu. We feel the decrease in activation energy in going from quadricyclane to 2,3-dicyanoquadricyclane and the positive $\Delta S^{\ddagger}$ values are more consistent with the known isomerizations of cyclobutanes to two molecules of olefin[5] than with the isomerizations of cyclobutenes to dienes.[4] However, any attempt to define a reaction mechanism on the basis of existing data seems premature. Additional work should be done with substituted quadricyclanes in various solvents and the vapor phase.

TABLE I
ISOMERIZATION OF DICYANOQUADRICYCLANE

| | Temperature, °C | | |
|---|---|---|---|
| | 123 | 111 | 101 |
| $10^4k$, sec$^{-1}$ | 3.8 | 0.97 | 0.30 |

The similarity in behavior of the thermal isomerization of 2,3-dicyanoquadricyclane to that of quadricyclane prompted an investigation of the possible photoisomerization of 2,3-dicyanoquadricyclane. Hammond, Wyatt, DeBoer, and Turro[6] report that benzophenone ($T_1$ = 68.5 kcal), 2-naphthaldehyde ($T_1$ = 59.5 kcal), and benzil ($T_1$ = 53.7 kcal) sensitize the isomerization of quadricyclane to norbornadiene. In substantiating this point, we find that pyrene ($T_1$ = 48.7 kcal) and anthracene ($T_1$ = 42.5 kcal) also work

---

[1] S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958).

[2] J. R. Edman, *ibid.*, **88**, 3454 (1966). See ref 1 for a partial listing of work in this area.

[3] H. M. Frey, *J. Chem. Soc.*, 365 (1964).

[4] (a) W. Cooper and W. D. Walters, *J. Am. Chem. Soc.*, **80**, 4220 (1958); (b) H. M. Frey, *Trans. Faraday Soc.*, **58**, 957 (1962).

[5] M. Zupan and W. D. Walters, *J. Am. Chem. Soc.*, **86**, 173 (1964), and references cited therein.

[6] G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964).

[7] (a) A. T. Blomquist and A. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945); (b) we appreciate the generous gift by Dr. E. Ciganek of the 2,3-dicyanonorbornadiene used in this work.

[8] Named in accordance with IUPAC rules as suggested by J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966).

[9] Nmr spectrum run in CDCl$_3$–TMSi on a Varian A-60 spectrometer. Infrared spectrum run in Nujol on Perkin-Elmer 237. Ultraviolet spectrum run in acetonitrile.

[10] C. D. Smith, *J. Am. Chem. Soc.*, **88**, 4273 (1966).

[11] Frey[3] obtained $E_a$ = 33.5 kcal and $\Delta S^{\ddagger}$ = −2.6 eu (calculated from his data) for the vapor phase reaction.