EPR Spectroscopy. EPR spectra of powdered samples in frozen solutions (about 0.01 M in MeOH at 77 K) were recorded on a Varian E3 instrument. Field calibrations were done using DPPH. EPR spectra with varying amounts of exogenous ligands were performed by controlled addition of Bu_4NF and NaIm (Im = imidazolate) to the EPR solution before rapid cooling to 77 K, and warming up after each spectrum.

Acknowledgment. We thank Akzo International research BV for financial support and Mr. F. B. Hulsbergen (Leiden University, Department of Chemistry) for recording the EPR spectra. Of the Department of Chemical Analysis (University of Twente) we thank J. M. Visser and J. L. M. Vrielink for recording the ^1H and ^{13}C NMR spectra and IR spectra, T. Stevens for recording the mass spectra, and A. Montanaro-Christenhusz and H. Weber for the elemental analyses.

Registry No. 1, 24677-78-9; 2, 7460-82-4; 3a, 121073-78-7; 3b, 130642-27-2; 4, 108059-04-7; 5, 130642-25-0; 6, 130642-26-1; 7, 130668-80-3; 8, 95-54-5; 9b, 121073-80-1; 9c, 130669-02-2; 9e, 130669-00-0; 10a, 121073-84-5; 10a·2H_2O, 130668-86-9; 10b, 121073-82-3; 10b·(H_2O, DMSO), 130668-83-6; 10c, 130668-98-3; 10d, 130668-96-1; 10e, 130668-94-9; 10f, 130668-92-7; 10h, 130668-90-5; 10i, 130668-88-1; $BrCH_2CH_2Br$, 106-93-4; $HOCH_2CH_2OH$, 107-21-1.

Supplementary Material Available: Tables of positional and thermal parameters of all atoms, bond distances, and bond angles in the dinickel/barium complex 10b·(H_2O,DMSO) (8 pages). Ordering information is given on any current masthead page.

Mechanistic Investigations Aided by Isotopic Labeling. 10.[1] Investigations of Novel Furan-2,3-dione Rearrangements by Oxygen-17 Labeling[2]

Gert Kollenz,* Heinz Sterk, and Gerald Hutter

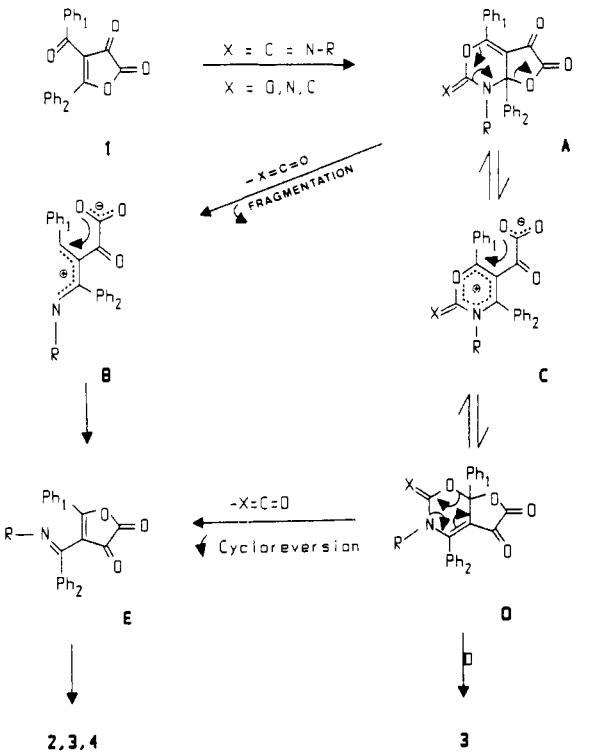
Institute of Organic Chemistry, Isotope Department and Spectroscopic Department, Karl Franzens University Graz, Heinrichstrasse 28, A-8010 Graz, Austria

Received February 27, 1990

The oxa 1,3-diene moiety in 4-benzoyl-5-phenylfuran-2,3-dione (1) adds aryl isocyanides or heterocumulenes via formal [4 + 1] or [4 + 2] cycloaddition processes. The unstable primary adducts undergo novel furandione rearrangements to intermediates in which the two oxygen atoms of the lactone moiety in 1 are equivalent. This equivalence was confirmed by ^{17}O-labeling experiments using ^{17}O NMR spectroscopic and mass spectroscopic measurements. Comparison of the ^{17}O chemical shifts in 1, labeled either at the benzoyl and ring oxygens (1a-^{17}O) or at both exocyclic ring-carbonyl oxygens (1b-^{17}O), with those in the products 2-4 confirmed the proposed pathways of these rearrangements. Reactions involving carbodiimides, isocyanates, and ketene imines were investigated.

The addition of aryl isocyanides[3] or heterocumulenes[4] to the oxa diene moiety in 4-benzoyl-5-phenylfuran-2,3-dione (1) has been reported to afford various mono- and bicyclic heterocyclic systems. Their molecular skeletons were elucidated by single-crystal X-ray diffraction analyses and ^{13}C NMR measurements.[3,4] All the reaction pathways obviously include formal [4 + 1] or [4 + 2] cycloaddition processes (intermediate A, Scheme I) accompanied by novel furandione rearrangements. The latter should proceed via ring opening of the furan ring with formation of an oxo carboxylic side chain (B or C), which undergoes free rotation around the single bond to give heterocyclic systems by relactonization at the former benzoyl carbon. The net result is the exchange of the two phenyl groups in 1. Ring opening could be initiated by attack of the heterocumulene on the heterodiene system in 1, leading to intermediate E by a cycloreversion process (reaction pathway A → C → D → E). This cycloreversion could be effected either by the re-formation of the furandione ring or through intermediate D. Alternatively, fragmentation of the primary adduct A would lead to E via intermediate B

Scheme I



(reaction pathway A → B → E). In both reaction pathways the lactone oxygens in 1 become equivalent by free rotation in the ring-opened intermediates B or C, irrespective of

(1) For part 9, see: Kollenz, G.; Seidler, P. *Monatsh. Chem.* 1984, *115*, 623.

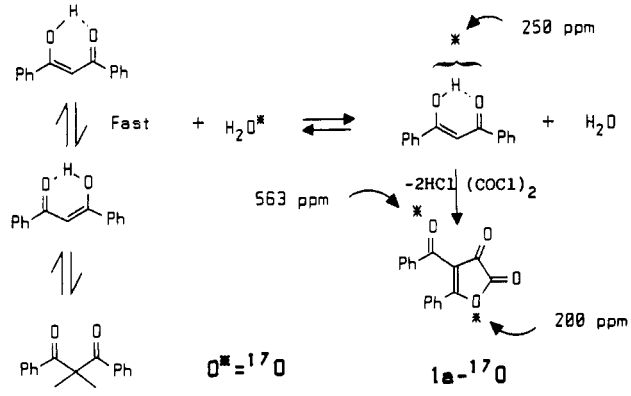
(2) Presented, in part, at the 2nd International Symposium on Synthetic Applications of Isotopically Labeled Compounds, Kansas City, 1985.

(3) Kollenz, G.; Ott, W.; Ziegler, E.; Peters, E.-M.; Peters, K.; von Schnering, H. G.; Formacek, V.; Quast, H. *Justus Liebigs Ann. Chem.* 1984, 1137.

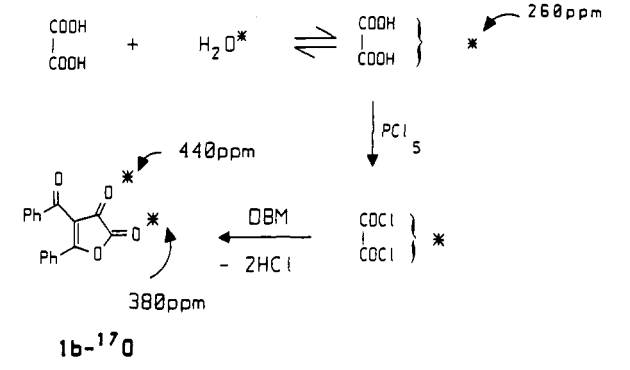
(4) (a) Kollenz, G.; Penn, G.; Dolenz, G.; Akcamur, Y.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Chem. Ber.* 1984, *117*, 1299. (b) Kollenz, G.; Penn, G.; Ott, W.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Chem. Ber.* 1984, *117*, 1310. (c) Kollenz, G.; Penn, G.; Ott, W.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Heterocycles* 1987, *26*, 625.

0022-3263/91/1956-0235$02.50/0

Scheme II



Scheme III

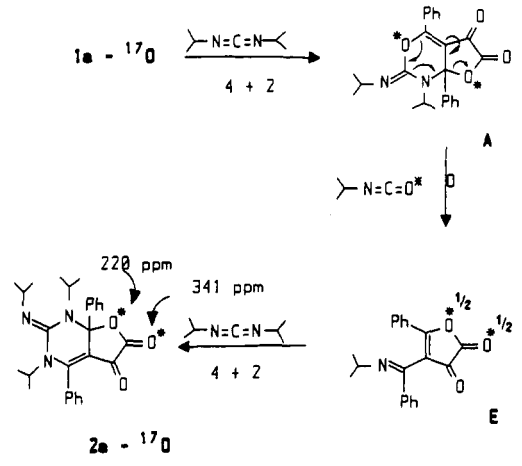


their ionic or radical nature. In view of the polarity of the educts and reaction products, as well as the mild reaction conditions[4] (no solvent, 30–60 °C), formation of ionic intermediates seems to be reasonable. Further evidence for this equilibration process was obtained by ^{17}O-labeling experiments comparing the distribution of the label in **1** with that in the products **2**–**4**. Two differently labeled educts (**1a**-^{17}O, **1b**-^{17}O, Schemes II and III) have been prepared and reacted to afford products bearing the label at different positions as expected from the proposed reaction mechanism to ensure the assignment of the oxygen shifts in the educt and the rearranged products. From these experiments the chemical shift assignments of all oxygens involved could easily be made.

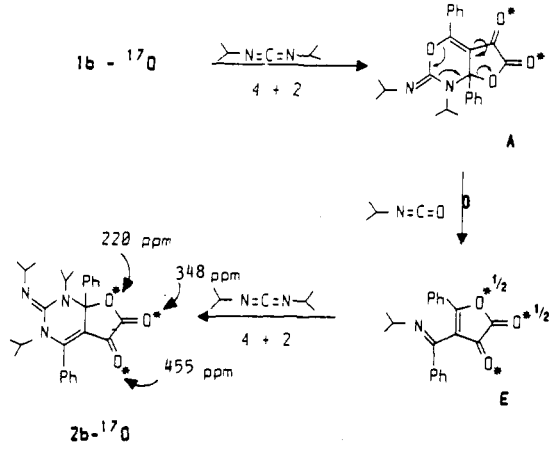
Results and Discussion

Synthesis of 1-^{17}O. **1a**-^{17}O, labeled at the ring oxygen (δ = 200 ppm) and the benzoyl oxygen (δ = 563 ppm), is easily obtained by the reaction of dibenzoylmethane-^{17}O and oxalyl chloride according to an improved synthesis of unlabeled **1**.[4a,5] Both chemical shift values are within the region found for either aryl carbonyl[6a] or lactone ring oxygens.[6b] The label is introduced into the dibenzoylmethane by a simple isotope exchange reaction[6c] involving hydration of the two carbonyl groups with $H_2{}^{17}O$ (labeling degree 23%) in methanol. Dibenzoylmethane exists almost exclusively in its enolic form and the rate of interconversion of the two possible enols is obviously high enough to give only one signal (δ = 250 ppm) in the ^{17}O NMR spectrum, which represents an average value of the C=O and the OH groups. The ^{17}O signals of similar β-diketones are found in the same region.[7] From the MS data (M, M + 1, M + 2) of the reisolated ^{17}O-labeled dibenzoylmethane, the ratio of bilabeled to monolabeled molecules was calculated to be approximately 2.5 to 1. The overall labeling degree was 20–22% in several dibenzoylmethane-^{17}O samples prepared in this manner.

Scheme IV



Scheme V



1b-^{17}O, labeled at both of the exocyclic carbonyl oxygens (lactone oxygen at 380 ppm, C-3 carbonyl oxygen at 440 ppm), was prepared from labeled oxalic acid via the oxalyl-^{17}O chloride and subsequent cyclization with dibenzoylmethane as in the preparation of **1a**-^{17}O. Both ^{17}O signals of **1b**-^{17}O are reasonable; the significant upfield shift of the C-3 carbonyl oxygen has been observed in several cyclic enone systems.[6e] Labeling of the oxalic acid was also done by an exchange reaction of anhydrous oxalic acid and $H_2{}^{17}O$ (labeling degree 27%). After sublimation the labeled oxalic acid exhibited one signal (260 ppm), again representing an average value of the C=O and OH groups. This agrees well with the chemical shifts of several carboxylic acids.[6c,d]

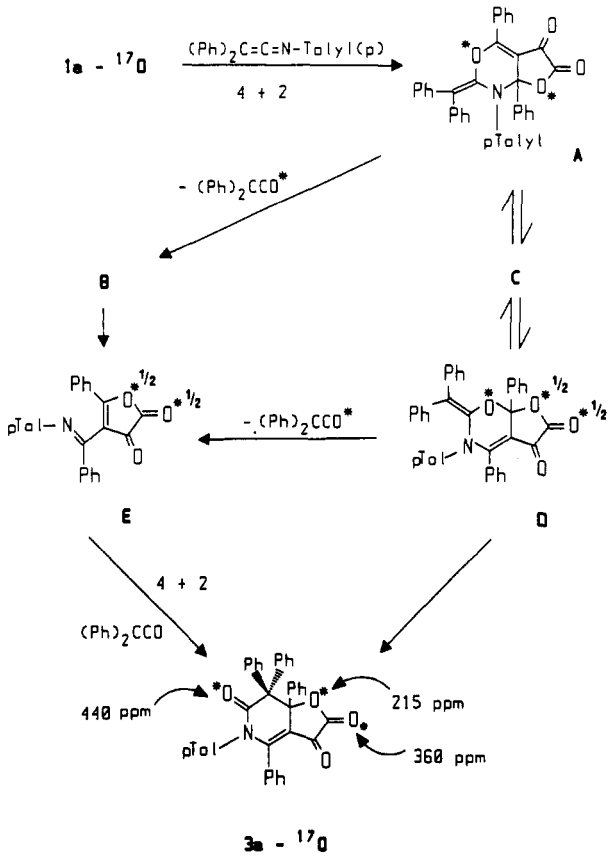
Reaction of 1-^{17}O with Diisopropylcarbodiimide.[4b] 1-^{17}O and diisopropylcarbodiimide produce the furo[2,3-*d*]pyrimidine **2**-^{17}O as the main reaction product (Schemes

(5) Ziegler, E.; Eder, M.; Belegratis, C.; Prewedourakis, E. *Monatsh. Chem.* **1967**, *98*, 2249.

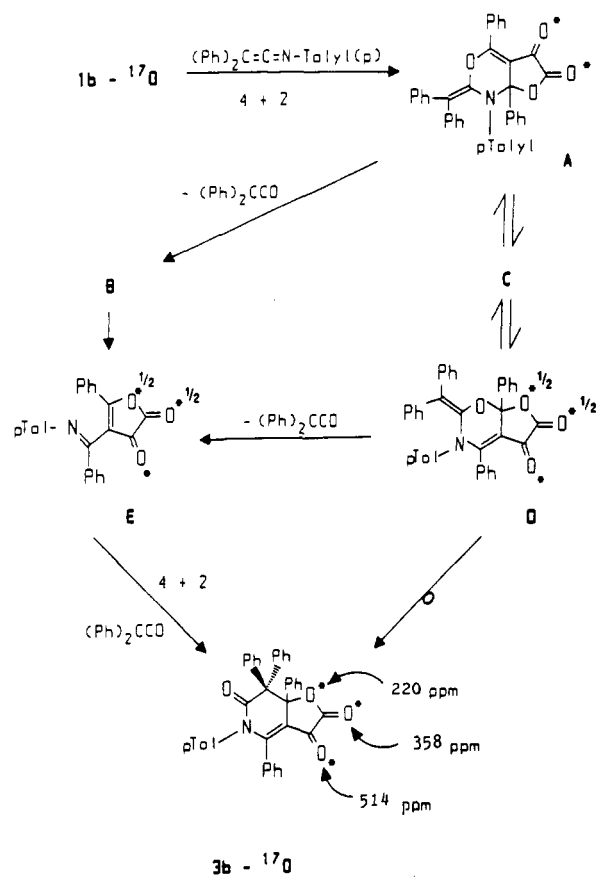
(6) (a) Boykin, D. W.; Baumstark, A. L. *Tetrahedron* **1989**, *45*, 3613. (b) Boykin, D. W.; Sullins, D. W.; Eisenbraun, E. J.; *Heterocycles* **1989**, *29*, 301. (c) Kintzinger, J.-P. In *NMR Basic Principles and Progress, Oxygen-17 and Silicon-29*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer: Berlin-Heidelberg-New York, 1981; Vol. 17, p 1 ff. (d) Ponnusamy, E.; Fotadar, U.; Spisni, A.; Fiat, D. *Synthesis* **1986**, 48. (e) Chandrasekaran, S.; Wilson, D. W.; Boykin, D. W. *Org. Magn. Reson.* **1984**, *22*, 757.

(7) (a) Gorodetsky, M.; Luv, Z.; Mazur, Y. *J. Am. Chem. Soc.* **1967**, *89*, 1183. (b) Winter, W.; Zeller, K. P.; Berger, S. *Z. Naturforsch.* **1979**, *34B*, 1607.

Scheme VI



Scheme VII



IV and V). In the ^{17}O NMR spectra the chemical shifts of all labeled oxygens are found in the expected regions,[6a-c] and are in good agreement with those of the corresponding oxygens in the educts **1a**-^{17}O and **1b**-^{17}O. Detection of the label in both oxygens of the lactone group in **2a**-^{17}O confirms that the furandione rearrangement proceeds via intermediates in which the oxygens of the lactone group in **1a**-^{17}O are equilibrated.

2a-^{17}O is an equimolar mixture of two molecules, each bearing a labeled oxygen at one of the two positions indicated. Double-labeled species were not present as shown by the MS spectra (no increase of the M + 2 ion intensity). A semiquantitative calculation involving electronic and plane-calculated integration of the signals of the substrate and the product indicated that the signal intensities should have a nearly equal distribution of the remaining ^{17}O label in the product. One label of **1a**-^{17}O is lost during elimination of isopropyl-^{17}O isocyanate.

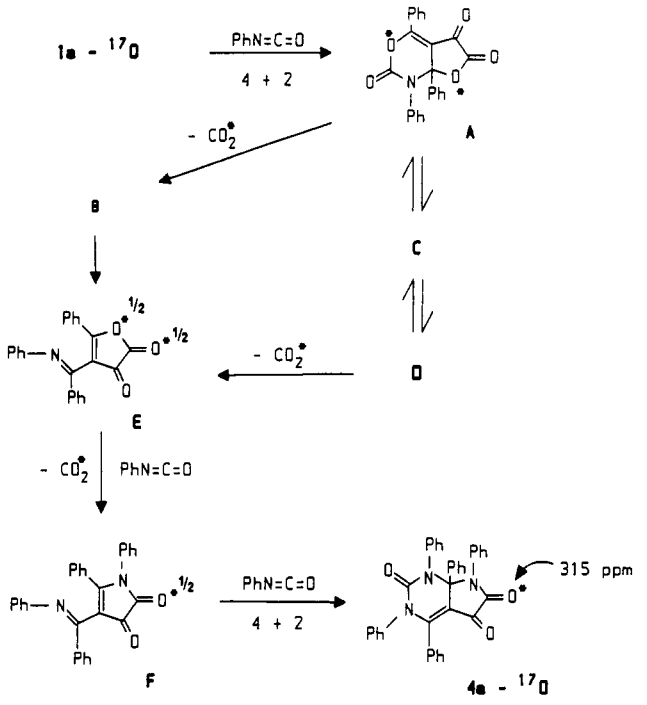
The ^{17}O NMR spectrum of **2b**-^{17}O from **1b**-^{17}O indicates the presence of three labeled oxygens (Scheme V). The chemical shifts of the lactone oxygens are in excellent agreement with those of **2a**-^{17}O, thus confirming their assignments. The shift of the C-3 carbonyl oxygen in **2b**-^{17}O (455 ppm) is also close to that of the corresponding oxygen in **1b**-^{17}O (440 ppm).

Reaction of 1-^{17}O with Diphenylketene *N*-*p*-Tolylimine.[4c] Addition of diphenylketene *N*-*p*-tolylimine to **1a**-^{17}O leads to the furo[3,2-*c*]pyridine **3a**-^{17}O (Scheme VI). Signals at δ = 440, 215, and 360 ppm in the ^{17}O NMR spectrum show three labeled positions in the molecule. These findings are in full agreement with the proposed reaction mechanism. The chemical shifts of the lactone oxygens are in excellent agreement with those of the corresponding shifts of the educts **1a**-^{17}O and **1b**-^{17}O. The lactam oxygen is shifted somewhat beyond the downfield end of the reported range for cyclic amides.[8a] This shift is due to the facts that (a) phenyl groups attached to nitrogen can cause downfield shifts of the amide oxygen of ~30 ppm[8a] by electronic effects and (b) the lactam carbonyl is influenced by steric interactions with four phenyl groups, thus possibly producing additional deshielding.[8b] The steps after the initial [4 + 2] addition of the ketene imine (intermediate A) cannot be distinguished. There is some experimental evidence for both pathways to **3a**-^{17}O. Unlabeled (*N*-*p*-tolylimino)benzylfuran-2,3-dione, intermediate E, was synthesized independently[4c] and found to add diphenylketene to give **3**.[4c] On the other hand, with dimethylketene *N*-*p*-tolylimine as a dienophile, the reaction with 1 stops at D, the primary rearranged product of the alternative route to **3**. Again a plane-calculated integration shows the expected distribution of the label. The signal intensities of the lactone oxygens (δ = 215 and 360 ppm) together are approximately equal to that of the amide oxygen (δ = 440 ppm).

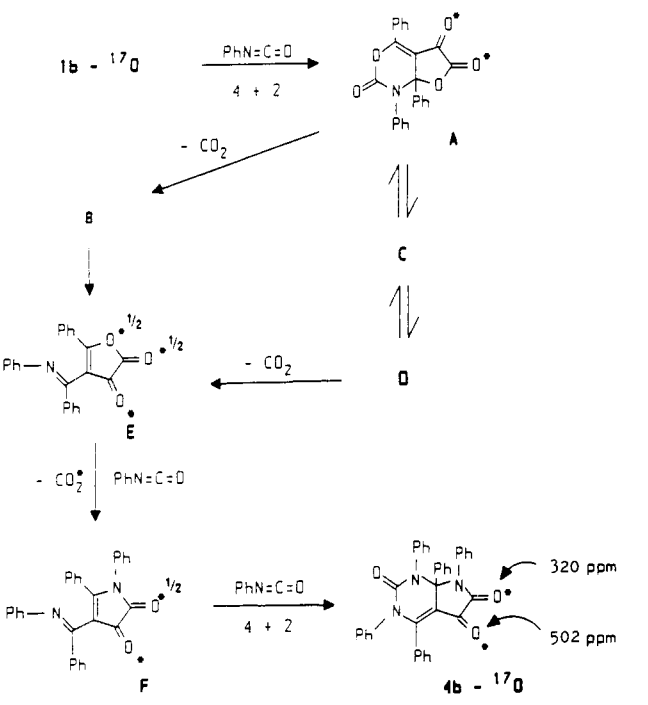
The overall reaction pathway **1** → **3** was investigated using the differently labeled **1b**-^{17}O as educt to confirm these results. The distribution of the label was found as expected from the proposed reaction mechanism (Scheme VII). The ^{17}O chemical shifts of the lactone moiety in **3b**-^{17}O are in good agreement with those of **3a**-^{17}O. The keto oxygen (514 ppm) is strongly deshielded compared with the corresponding signals of the educt (440 ppm) and the close analogue **2b**-^{17}O (455 ppm). This could be explained by the varying influence of the N substituent in the enamino ketone system (C-3–C-3a–C-4–N) of **2b**-^{17}O

(8) (a) Boykin, D. W.; Sullins, D. W.; Pourahmady, N.; Eisenbraun, E. J. *Heterocycles* **1989**, *29*, 307. (b) Baumstark, A. L.; Dotrong, M.; Oakley, M. G.; Sherk, R. R.; Boykin, D. W. *J. Org. Chem.* **1987**, *52*, 3640. (c) St. Amour, Th. E.; Burgar, M. I.; Valentine, B.; Fiat, D. *J. Am. Chem. Soc.* **1981**, *103*, 1128. (d) Brownlee, R. T. C.; Sadek, M.; Craik, D. J. *Org. Magn. Reson.* **1983**, *21*, 616.

Scheme VIII



Scheme IX



on the one hand and **3b**-^{17}O, **4b**-^{17}O (Scheme IX) on the other hand. As mentioned earlier, an aryl group attached to a lactam nitrogen can cause a downfield shift of ~30 ppm in the carbonyl signal compared to the *N*-alkyl analogue.[8a] The extension of this conjugation in **3b**-^{17}O and **4b**-^{17}O could lead to even greater downfield shifts. Electron-withdrawing or electron-donating substituents conjugated to carbonyl groups can cause chemical shift differences of ~60 ppm.[8c,d,9]

Reaction of 1-^{17}O with Phenyl Isocyanate. **1a**-^{17}O and phenyl isocyanate react with loss of 2 molecules of $C^{17}O_2$ to give the pyrrolo[2,3-*d*]pyrimidine **4a**-^{17}O. By ^{14}C labeling it was shown that all the CO_2 was derived from the isocyanate.[4a] Furthermore, independently synthesized intermediates E and F react with isocyanates to give **4**,[4a,b] indicating that the reaction proceeds as shown in Schemes VIII and IX. Starting with **1a**-^{17}O, all the label should be eliminated as CO_2 except the amide carbonyl oxygen of the pyrroldione moiety in **4a**-^{17}O. In fact its ^{17}O NMR spectrum shows only one oxygen resonance peak at δ = 315 ppm, which is at a higher field than found with the lactam oxygen in **3a**-^{17}O but nevertheless is in good agreement with the usual chemical shifts of amides and lactams.[6c,8-10] Apparently, the electron-withdrawing effect of the vicinal C-3 carbonyl group influences the overall electronic situation within the pyrroldione moiety, thus increasing the single-bond character of the lactam carbonyl.

The reaction was repeated starting from **1b**-^{17}O, which should bring the label into both oxygens of the pyrroldione moiety of the product (Scheme IX), to verify this result. In fact the ^{17}O NMR spectrum of **4b**-^{17}O shows two labeled oxygens, which could be assigned to the lactam oxygen (320 ppm) and the C-3 keto oxygen (502 ppm). These chemical shifts again are close to those of the similar carbonyl oxygens of **4a**-^{17}O (315 ppm) and **3b**-^{17}O (C-3 keto oxygen at 514 ppm). The nearly identical *N*-arylenamino ketone moieties of the pyrrolopyrimidine and furopyridine skeletons of **3b**-^{17}O and **4b**-^{17}O show almost identical chemical shifts for the carbonyl oxygens (514 and 502 ppm), thus confirming their assignment.

Table I. ^{17}O NMR Chemical Shifts and Line Widths of Enriched Samples

compound	δ O	$\nu_{1/2}$ (O)	solvent
DBM-^{17}O	250	150	CH_3CN, $CDCl_3$
oxalic-^{17}O acid	260	120	CH_3CN
1a-^{17}O	200	400	CH_3CN
	563	800	CH_3CN
1b-^{17}O	380	1000	CH_3CN
	440	800	CH_3CN
2a-^{17}O	220	1200	CH_3CN
	341	1000	CH_3CN
2b-^{17}O	220	750	CH_3CN
	348	720	CH_3CN
	455	860	CH_3CN
3a-^{17}O	215	1200	CH_3CN
	360	1200	CH_3CN
	440	1600	CH_3CN
3b-^{17}O	220	1200	CH_3CN
	358	1050	CH_3CN
	514	1400	CH_3CN
4a-^{17}O	315	1400	CH_3CN
4b-^{17}O	320	1050	CH_3CN
	502	900	CH_3CN

Experimental Section

The ^{17}O spectra were recorded at 22 °C on a Varian XL-200 spectrometer (**1a**-^{17}O–**4a**-^{17}O), a Bruker MSL 300 spectrometer, a Bruker AM 360 spectrometer (**1b**-^{17}O–**3b**-^{17}O), and a Bruker AM 400 spectrometer (**4b**-^{17}O), equipped with 10-mm broad-band probes operating at 27.1, 40.65, 48.78, and 54.25 MHz, respectively. The instruments settings were 20–40-kHz spectral width, 4, 6, or 8 K data points, 100-μs preacquisition delay, and 100–200-ms acquisition time. The spectra were recorded without proton decoupling and with sample spinning. The signal-to-noise ratio was improved by applying a broadening factor $\exp(-t/0.06)$ to the FID prior to Fourier transformation. The data point resolution was improved by zero filling to 8 K and 16 K datapoints. Chemical shifts are reported relative to external water at 22 °C. The error in the chemical shift is estimated to be ±3 ppm due to signal broadening problems, probably caused by association and/or diffusion phenomena. Attempts were made to overcome these problems by dilution (0.02–0.2 M solutions). The narrowest line

(9) Chandrasekaran, S.; Wilson, W. D.; Boykin, D. W. *J. Org. Chem.* **1985**, *50*, 829.
(10) Hunston, R. N.; Gerothanassis, I. P.; Lauterwein, J. *J. Am. Chem. Soc.* **1985**, *107*, 2654.

widths obtained for the signals are listed in Table I. Generally, 10^2–10^5 scans were accumulated. An acoust pulse sequence[11] was used to cancel out the acoustic ringing with the Varian XL 200 spectrometer. The degree of labeling in the enriched samples was determined by mass spectrometry, using the natural abundance correction of M + 1 and M + 2 peaks made either by calculation or by comparison with spectra of the corresponding unlabeled species.[12] The evaluation of data was made difficult by hydrogen capture and elimination processes, which could be responsible for small discrepancies between calculated and found values of labeling degrees in reaction products. All MS spectra were recorded on a Varian MAT 111 spectrometer. All experiments were performed in an inert gas atmosphere to minimize contact with moisture.

Dibenzoylmethane-^{17}O. To a solution of 0.5 g of dibenzoylmethane in 6 mL of dry methanol was added 0.5 g of $H_2{}^{17}O$ (Merck Sharp & Dohme Isotopes, 23% ^{17}O), molar ratio 1:12. Dry gaseous hydrogen chloride was passed through the mixture for a few seconds, and the flask was closed and warmed to 40–50 °C to keep the dibenzoylmethane dissolved. After 6 h the mixture was cooled to room temperature and allowed to stand overnight. The methanol and water were removed at 10^{-4} mmHg, and the recovered dibenzoylmethane-^{17}O was crystallized from methanol (yield 0.45 g, 90%). This procedure was repeated several times, and in all cases mass spectral analysis of peaks at m/e 224 (M), 225 (M + 1), and 226 (M + 2) indicated 20–23% ^{17}O incorporation.

Oxalic-^{17}O Acid. Anhydrous oxalic acid (1 g) was heated in 1 mL of $H_2{}^{17}O$ (Merck, Sharp & Dohme Isotopes, 27% ^{17}O) under reflux and stirring for 1 h. After cooling, the excess water was removed by lyophilization at 10^{-4} mmHg. The residual oxalic acid-^{17}O dihydrate was converted into the anhydrous form by sublimation at 140 °C/10 mmHg, yielding 0.8 g (80%) of pure oxalic acid-^{17}O (labeling degree ~20%).

Oxalyl-^{17}O Chloride. A mixture of 0.8 g of anhydrous oxalic-^{17}O acid and 3.5 g of PCl_5 was kept at room temperature for 3 days ($CaCl_2$ tube). The liquid phase was then pipetted off and fractionated through a distillation column. The fraction below 65 °C (1.05 g) contained all the oxalyl chloride; the yield was 45% in several nonlabeled experiments.

4-Benzoyl-5-phenyl-2,3-dihydrofuran-2,3-dione-^{17}O. (a) 1a-^{17}O.[4a] A solution of dibenzoylmethane-^{17}O (2 g, labeling degree ~5%) and oxalyl chloride (1.1 g) in 30 mL of dry diethyl ether was kept in a dry nitrogen atmosphere at 20 °C for 1 day. The liquid phase was pipetted from the yellow crystals, which were washed with anhydrous ether several times and dried by lyophilization at 10^{-4} mmHg at 20 °C, affording **1a**-^{17}O (42%).

(b) 1b-^{17}O. The oxalyl-^{17}O chloride solution, obtained from fractional distillation as described above, was added to 0.72 g of dibenzoylmethane dissolved in anhydrous ether under a stream of dry nitrogen. After 1 day at 20 °C a yellow precipitate formed, which was isolated and purified as described for **1a**-^{17}O, yielding 0.32 g (33%) of **1b**-^{17}O.

1,2,3,7a-Tetrahydro-1,3-diisopropyl-2-(isopropylimino)-4,7a-diphenylfuro[2,3-*d*]pyrimidine-5,6-dione-^{17}O (2a,b-^{17}O).[4b] Under dry nitrogen **1a**-^{17}O or **1b**-^{17}O was dissolved in an excess of diisopropylcarbodiimide (molar ratio 1:10). After 16 h at 20 °C the mixture was diluted with 1 mL of anhydrous ether, precipitating yellow crystals, which were washed with ether and crystallized from anhydrous ethanol to afford the products in 60% yield.

7,7a-Dihydro-5-(4-methylphenyl)-4,7,7,7a-tetraphenyl-5*H*-furo[3,2-*c*]pyridine-2,3,6-trione-^{17}O (3a,b-^{17}O).[4c] In an atmosphere of dry nitrogen a solution of **1a**-^{17}O or **1b**-^{17}O and diphenyl-*N*-(4-methylphenyl)ketenimine (molar ratio 1:3) in 10 mL of anhydrous toluene was kept at 60 °C for 4 h. Then the solvent was evaporated under vacuum, and the oily residue was treated with anhydrous ether to afford the yellow products **3a**-^{17}O and **3b**-^{17}O in 55% yield (anhydrous ethanol).

7,7a-Dihydro-1,3,4,7,7a-pentaphenyl-1*H*-pyrrolo[2,3-*d*]-pyrimidine-2,5,6(3*H*)-trione-^{17}O (4a,b-^{17}O).[4a] In a flask flushed with dry nitrogen and sealed by a $CaCl_2$ tube, a mixture of **1a**-^{17}O or **1b**-^{17}O and phenyl isocyanate (molar ratio 1:5) was kept in a drying oven at 60 °C for 24 h. By treating the cooled melt with anhydrous ether, a yellow product was formed, which was extensively washed with anhydrous ether to remove the excess phenyl isocyanate before crystallizing from acetic acid. After lyophilization under vacuum pure **4a,b**-^{17}O were obtained in 45% yield.

Acknowledgment. We are grateful to Doz. Dr. H. Hönig, Institute of Organic Chemistry, Technical University of Graz, for ^{17}O NMR measurements of the samples **1b**-^{17}O, **2b**-^{17}O, and **3b**-^{17}O, and Mag. H. P. Kählig, Institute of Organic Chemistry, University of Vienna, for providing the ^{17}O NMR spectrum of **4b**-^{17}O.

Registry No. 1, 17571-17-4; **1a**-^{17}O, 130762-42-4; **1b**-^{17}O, 130762-43-5; **2**, 90140-46-8; **2a**-^{17}O, 130762-44-6; **2b**-^{17}O, 130762-45-7; **3**, 130762-41-3; **3a**-^{17}O, 130762-46-8; **3b**-^{17}O, 130762-47-9; **4**, 90140-26-4; **4a**-^{17}O, 130762-48-0; **4b**-^{17}O, 130762-49-1; dibenzoyl methane, 120-46-7; dibenzoylmethane-^{17}O, 130762-50-4; diisopropylcarbodiimide, 693-13-0; diphenyl-*N*-(4-methylphenyl)-ketenimine, 5110-45-2; oxalic-^{17}O acid, 130762-51-5; oxalyl chloride, 79-37-8; oxalyl-^{17}O chloride, 130762-52-6; phenyl isocyanate, 103-71-9.

(11) Canet, D.; Brondeau, J.; Marchal, J. P.; Lherbier, B. R. *Org. Magn. Reson.* **1982**, *20*, 51.

(12) Schmidt, H. L. In *Anwendung von Isotopen in der Organischen Chemie und Biochemie, Messung von radioaktiven und stabilen Isotopen*; Simon, H., Ed.; Springer: Berlin-Heidelberg-New York, 1974; Vol. II, p 359 ff.