amounts of *N,N*-dimethylformamide gave high yields of **5**. This compound was converted to the azide **6** by treatment with NaN_3 in acetone or acetonitrile, and on thermolysis (or photolysis) the isocyanatophthalic anhydride **3**, mp 80–82°, was obtained in high yield.

If carbonyl chloride was used instead of thionyl chloride in the conversion **4** to **5**, the trichloride **8** was formed in high yield. This method of synthesis of **8** is superior to the one described previously.[4]

The anhydride isocyanate **3** reacted selectively on the isocyanate group when treated with 1 equiv of methanol in toluene, giving the carbamate **7** in high yield. Studies to evaluate **3** or the more stable **7** as useful precursors of condensation polymers are underway.

Experimental Section

4-Chloroformylphthalic Anhydride (5).[4]—A suspension of 100 g (0.52 mol) of trimellitic anhydride in 100 g (0.85 mol) of thionyl chloride and 100 mg of *N,N*-dimethylformamide was stirred under reflux (bath temperature 115°) until the gas evolution ceased and a clear yellow solution was formed (2.0–2.5 hr). The excess thionyl chloride was removed under reduced pressure and vacuum distillation of the residue gave 105 g (96%) of **5**, bp 120–124° (0.1 mm), mp 69°.

4-Azidoformylphthalic Anhydride[5] **(6).**—To a solution of 10.2 g (0.048 mol) of freshly distilled 4-chloroformylphthalic anhydride in 60 ml of acetone, 3.25 g (0.05 mol) of sodium azide and 2 drops of triethylamine were added. The suspension was stirred rapidly at room temperature and the progress of the initially exothermic reaction was followed by ir (maximum absorption of the azide band at 2150 cm^{-1} with shoulder at 2200 cm^{-1} which occurred after approximately 2 hr). The precipitated sodium chloride was removed by filtration and the solvent was evaporated under vacuum, care being taken not to exceed a bath temperature of 50–55°.[6] Thus, 10.60 g (97%) of colorless needles of **6** were obtained, mp 100–103°.

Anal. Calcd for $C_9H_3N_3O_4$: C, 49.79; H, 1.39; N, 19.35. Found: C, 49.57; H, 1.32; N, 19.40.

4-Isocyanatophthalic Anhydride[5] **(3).**—To a solution of 31.5 g (0.15 mol) of 4-chloroformylphthalic anhydride in 100 ml of acetone, 11.3 g (0.175 mol) of sodium azide was added. After stirring for 2 hr at room temperature, 100 ml of toluene was added to the suspension, and the reaction flask was immersed in an oil bath and slowly heated to a bath temperature of 115°. During the heating period (1–2 hr) acetone was removed by distillation. Overheating and splashing of concentrated liquid onto hot surfaces of the apparatus has to be avoided because of the danger of explosion. After the evolution of nitrogen ceased the precipitated sodium chloride was removed by filtration, and the filtrate was evaporated under reduced pressure (bath temperature 60°). The crude product, 28.4 g (quantitative), mp 70–75°, can be purified by sublimation to give colorless crystals, mp 80–82°, ir (KBr) 2260 cm^{-1} (NCO).

Anal. Calcd for $C_9H_3NO_4$: C, 57.16: H, 1.60; N, 7.40. Found: C, 57.16; H, 1.49; N, 7.28.

4-Methylcarbamatophthalic Anhydride (7).—A solution of 4.8 g (0.15 mol) of methanol in 30 ml of toluene was added dropwise with stirring to a solution of 28.4 g (0.15 mol) of 4-isocyanatophthalic anhydride in 100 ml of toluene over a period of 15–20 min. The slightly exothermic reaction was controlled at 40–50°, and the reaction product precipitated as a yellow amorphous solid. Filtration and washing with diethyl ether gave 27.5 g (83%) of **7**, mp 150–154° dec.

Anal. Calcd for $C_{10}H_7NO_5$: C, 54.30; H, 3.19; N, 6.33. Found: C, 53.97; H, 3.07; N, 6.03.

1,2,4-Benzenetricarboxylic Acid Trichloride (8).—A suspension of 50 g (0.26 mol) of trimellitic anhydride in 250 ml of benzene containing 100–200 mg of *N,N*-dimethylformamide was heated to 65° and carbonyl chloride was added until a clear yellow solution was obtained (approximately 90 min). Excess carbonyl chloride was removed with nitrogen and vacuum distillation yielded 60.4 g (87%) of **8**, bp 124° (0.1 mm) [lit.[4] bp 143–148° (3 mm)].

Anal. Calcd for $C_9H_3Cl_3O_3$: C, 40.72; H, 1.14; Cl, 40.06. Found: C, 40.51; H, 1.06; Cl, 39.2.

Registry No.—**3**, 40139-36-4; **4**, 552-30-7; **5**, 1204-28-0; **6**, 40139-39-7; **7**, 40139-40-0; **8**, 3867-55-8; sodium azide, 12136-89-9; thionyl chloride, 7719-09-7; carbonyl chloride, 75-44-5.

(4) G. Drechsler and S. Heidenreich, *J. Prakt. Chem.*, **27**, 152 (1965).

(5) *Caution!* All reactions involving azides should be carried out behind safety shields.

(6) Impure samples of azide, obtained by using undistilled acid chloride in the reaction, decomposed sometimes spontaneously during the drying process.

Photochemical Deconjugation as a Synthetic Route to 1,2,3,6-Tetrahydropyridine-4-acetic Acid Esters from $\Delta^{4,\alpha}$-Piperidine-4-acetic Acid Esters[1]

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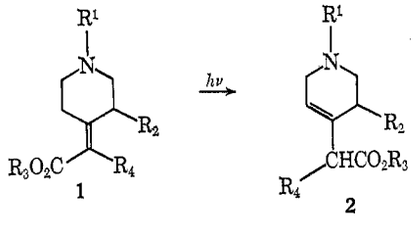
The Wittig reaction employing carbalkoxymethylphosphonates makes esters of $\Delta^{4,\alpha}$-piperidine-4-acetic acids readily available from the corresponding substituted 4-piperidones.[2] These α,β-unsaturated esters can subsequently be converted to the endocyclic isomers by acid- or base-catalyzed equilibration.[2a–f] We report here that photochemical deconjugation[3] constitutes an alternative method for effecting this transformation and that the photochemical method often has the advantage of effecting complete conversion in contrast to the catalytic equilibration procedures.

Ethyl 1-methyl-$\Delta^{4,\alpha}$-piperidine-4-acetate (**1a**) can be prepared in good yield from 1-methyl-4-piperidone.[2b] The compound is isomerized by base or heat to a mixture of **1a** and **2a**. A 4:7 mixture was obtained on isomerization with sodium ethoxide[2f] while a 25:75 mixture was obtained by the thermal method.[2b] The conversion to pure **2a** is 36% in the base-catalyzed method. Irradiation of **1a** in methanol or ethanol effected complete conversion to **2a**, identified by spectral data. The most informative spectral change which accompanies the isomerization is a shift in the carbonyl frequency from 1715 cm^{-1} for **1a** to 1740 cm^{-1} for **2a**. In the nmr spectrum, the singlet at δ 5.62 due to the exocyclic vinyl hydrogen is replaced by a broad unresolved multiplet at δ 5.5. The *N*-benzyl analog **1b** was isomerized to **2b** under similar conditions

(1) Supported by NSF Grant GP-19374 and NCI Grant 12940.

(2) (a) R. J. Sundberg, W. V. Ligon, Jr., and L.-S. Lin, *J. Org. Chem.*, **36**, 2471 (1971); (b) L. D. Quin, J. W. Russell, Jr., R. D. Prince, and H. E. Shook, Jr., *ibid.*, **36**, 1495 (1971); (c) R. J. Sundberg and F. O. Holcombe, Jr., *ibid.*, **34**, 3273 (1969); (d) N. Whittaker, *J. Chem. Soc. C*, 94 (1969); (e) H. T. Openshaw and N. Whittaker, *J. Chem. Soc.*, 1461 (1963); (f) R. F. Borne and H. Y. Aboul-Enein, *J. Heterocycl. Chem.*, **9**, 869 (1972); (g) C. Szantay, L. Töke, and P. Kolonits, *J. Org. Chem.*, **31**, 1447 (1966); (h) S. Sugasawa and H. Matsuo, *Chem. Pharm. Bull.*, **8**, 819 (1960); (i) F. O. Holcombe, Ph.D. Thesis, University of Virginia, 1971.

(3) For studies of the synthetic utility of photochemical deconjugation in aliphatic systems see (a) R. R. Rando and W. v. E. Doering, *J. Org. Chem.*, **33**, 1671 (1968). For mechanistic studies see (b) J. R. Scheffer and B. A. Boire, *J. Amer. Chem. Soc.*, **93**, 5490 (1971); (c) M. J. Jorgenson, *ibid.*, **91**, 198 (1969); (d) J. A. Barltrop and J. Wills, *Tetrahedron Lett.*, 4987 (1968); (e) M. J. Jorgenson and L. Gundel, *ibid.*, 4991 (1968); (f) R. Noyori, H. Inoue, and M. Kato, *J. Amer. Chem. Soc.*, **92**, 6699 (1970); (g) J. K. Crandall and C. F. Mayer, *J. Org. Chem.*, **35**, 3049 (1970); P. J. Kropp and H. J. Krauss, *ibid.*, **32**, 3222 (1967).



	R_1	R_2	R_3	R_4
a	CH_3	H	C_2H_5	H
b	$PhCH_2$	H	C_2H_5	H
c	PhCO	H	C_2H_5	H
d	PhCO	C_2H_5	C_2H_5	H
e	$PhCH_2OCO$	H	CH_3	H
f	$PhCH_2OCO$	C_2H_5	CH_3	H
g	PhCO	H	C_2H_5	C_2H_5

but the reaction was not so clean. Extensive decomposition of product to undefined materials was observed when the photoisomerization was carried beyond 60% completion.

Ethyl 1-benzoyl-$\Delta^{4,\alpha}$-piperidine-4-acetate is partially converted to the isomeric 1,2,3,6-tetrahydropyridine with ethanolic sodium ethoxide and the mixture can be separated by chromatography. We have observed about 75% conversion to **2c** at room temperature. Borne and Aboul-Enein[2f] report a higher **2c**:**1c** ratio by treatment of a Wittig reaction mixture containing **1c** with sodium ethoxide at reflux, but the net conversion to **2c** is lower (39%). Photodeconjugation effects complete conversion to pure endocyclic ester **2c**.

The 3-ethyl derivative **1d** is converted to an equilibrium mixture containing about 45% **2d** by base-catalyzed isomerization.[2c] The photochemical procedure effects complete transformation of **1d**. The spectral properties of the residual material, which consists of a single component according to tlc, establish that it is primarily **2d**. The integration of the vinyl proton region is only about 70% of what is expected. This suggests that the photochemical reaction has resulted in the formation of as much as 30% of the alternative endocyclic ester, ethyl 1-benzoyl-5-ethyl-1,2,3,6-tetrahydropyridine-4-acetate. Although **1d** can be assigned the structure shown with confidence on the basis of the steric factors which govern olefin geometry in the Wittig reaction, it is likely that **1d** is photoequilibrated with the double bond geometric isomer at a rate exceeding the deconjugation reaction.[4]

Methyl 1-carbobenzyloxy-$\Delta^{4,\alpha}$-piperidineacetate is converted cleanly to the endocyclic isomer **2e**. The reaction has been used preparatively and has routinely provided 80–90% yield of pure product on up to 15-g quantities of **1e**.

Photolysis of **1f** leads to complete disappearance and quantitative conversion to isomeric material. As in the case of **1d**, although the product is primarily **2f** it may contain some of the alternative endocyclic isomer. The distilled product analyzes correctly and appears homogeneous to tlc. The integration of the vinyl proton region is only approximately 70% of what is expected. The 1-acylpiperidines **1d** and **1f**, therefore, do not appear to show the very high selectivity for trisubstituted endocyclic olefin which Jorgenson and Patumtevapibal observed in the carbocyclic system, ethyl 2-methylcyclohexylideneacetate.[4]

Base-catalyzed isomerization of the tetrasubstituted olefin **1g** to **2g** in 81% yield has been carried out directly on a Wittig reaction mixture containing **1g**.[2f] Photochemical isomerization was complete and the spectral properties of the crude product were identical with those of a pure sample prepared by a base-catalyzed isomerization.

While our work indicates that the photochemical procedure has some limitations as indicated for **1b**, **1d**, and **1f**, it constitutes a major improvement over base-catalyzed isomerization in other cases studied and would appear to be a useful synthetic route to tetrahydropyridines from 4-piperidones.

(4) M. J. Jorgenson and S. Patumtevapibal, *Tetrahedron Lett.*, 489 (1970).

Experimental Section

General.—Hanovia mercury lamps (Type S, 200 W or Type L, 450 W) in water-cooled quartz or Vycor immersion wells (25–30°) were used. A Vycor filter sleeve was used with the quartz immersion well. No substantial reaction occurred when compound **1b** was irradiated with the Type S lamp using a Pyrex filter. The solutions were purged with nitrogen for 0.5 hr prior to commencing photolysis and the purge was continued during the photolysis. The photolysis periods cited in the individual experiments represent approximately the minimal time for complete conversion on the scale reported.

Isomerization of 1a.—A solution of **1a** (3.66 g, 2.1 mmol) in methanol (350 ml) was irradiated for 17 hr using the Type L lamp. Evaporation of the solvent left **2a** which was completely free of **1a**, as indicated by the absence of the conjugated CO absorbance. The nmr and infrared spectra of this material were identical with those of an analytically pure sample purified by distillation: bp 65° (0.2 mm); nmr ($CDCl_3$) δ 5.5 (broad s, 1), 4.1 (q, 2), 2.95 (broad, 4), 2.7–2.2 (NCH_3 singlet overlapping multiplets, 7), and 1.21 (t, 3).

Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.65; H, 9.38; N, 7.56.

The methiodide was prepared by reaction with excess methyl iodide in ether, mp 133–135° after recrystallization from ethanol–ether (lit.[5] mp 134–135°).

Synthesis of 1b[6] and 2b.—Triethyl phosphonoacetate (20.0 g, 84.7 mmol) was added to a solution of sodium ethoxide (1.95 g of sodium metal dissolved in 150 ml of ethanol) and the solution was stirred for 20 min. 1-Benzyl-4-piperidone (10.0 g, 53.0 mmol) was added and the mixture was stirred for 4 hr. Approximately half of the ethanol was removed on a rotary evaporator and the residue was diluted with cold brine (400 ml). The product was isolated by extracting with ether, drying, and evaporating. Two colorless oils were separated by chromatography on silicic acid. The more readily eluted product was the endocyclic isomer **2b** (2.80 g, 20%): ir (neat) 1750 cm^{-1} (CO); nmr ($CDCl_3$) δ 7.30 (s, 5), 5.52 (broad s, 1), 4.14 (q, 2), 3.54 (s, 2), 2.96 (broad, 4), 2.52 (m, 2), 2.20 (broad, 2), 1.22 (t, 3).

Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.01; H, 8.27; N, 5.46.

The less readily eluted product was the exocyclic isomer **1b** (5.3 g, 39%): ir (neat) 1720 cm^{-1} (CO); nmr ($CDCl_3$) δ 7.30 (s, 5), 5.61 (s, 1), 4.15 (q, 2), 3.50 (s, 2), 3.0 (distorted t, 2), 2.5 (m, 6), 1.25 (t, 3).

Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 74.32; H, 8.33; N, 5.61.

Photoisomerization of 1b.—Solutions of pure **1b** (~1 mmol) in methanol (60 ml) were irradiated with the Type S lamp. After 7.5 hr the product mixture (80% yield) was 40% **1b** and 60% **2b** as determined by the relative intensity of the carbonyl absorptions and confirmed by the size of the two vinyl hydrogen signals in the nmr. Continued photolysis led to complete disappearance of exo isomer but much decomposition also occurred

(5) S. M. McElvain and R. E. Lyle, Jr., *J. Amer. Chem. Soc.*, **72**, 384 (1950).

(6) Compound **1b** has been prepared previously and characterized as the methiodide, ref 2h.

with eventual disappearance of the nmr signals characteristic of **2b**.

Photoisomerization of 1c.—A solution of **1c**[2c] (0.50 g) in ethanol (60 ml) was irradiated using a Type L lamp for 5 hr. Evaporation of the solvent left pure **2c** having infrared and nmr spectral properties identical with those of previously characterized **2c**.[2c]

Photoisomerization of 1d.—Irradiation of **1d** (160 mg) in methanol (60 ml) for 3 hr using the Type S lamp resulted in complete disappearance of **1d** as shown by tlc. The material obtained by evaporation of the solvent had nmr and ir spectra which were very similar to those of an authentic sample of **2d**.[2c] The aromatic:vinyl integration ratio was about 7:1, however.

Preparation of 1e.—A mixture of **1c** and **2c** (80 g) prepared by the method of Sundberg, Ligon, and Lin[2a] was refluxed for 24 hr with 300 ml of 10% sodium hydroxide solution. The cooled alkaline solution was extracted with ether to remove organic impurities and then made strongly acidic with concentrated hydrochloric acid and extracted with ether to remove benzoic acid. The aqueous layer was made alkaline with concentrated sodium hydroxide and treated at 0° with small portions of benzyl chloroformate with vigorous shaking (total 40 ml). The solution was kept alkaline by addition of small portions of concentrated sodium hydroxide during the acylation. The reaction mixture was extracted with ether and acidified, and then the mixture of exocyclic and endocyclic acids was extracted with chloroform (93% yield). Crystallization from absolute ether gave the exocyclic isomer, 1-carbobenzyloxy-$\Delta^{4,\alpha}$-piperidineacetic acid: mp 127.5–128.5°; nmr ($CDCl_3$) δ 11.35 (s, 1), 7.4 (s, 5), 5.8 (s, 1), 5.2 (s, 2), 3.6 (broad t, 2).

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.28; H, 6.30; N, 5.01.

Esterification with diazomethane gave **1e**.

Photoisomerization of 1e.—Irradiation of a solution of **1e** (8.3 g) in methanol (150 ml) for 22 hr using the Type L lamp gave after evaporation of the solvent 7.8 g of **2e** having spectral properties identical with those of an analytical sample prepared by bulb-to-bulb distillation: ir 1750 (ester CO), 1720 cm^{-1} (carbamate CO); nmr ($CDCl_3$) δ 7.35 (s, 5), 5.48 (broad, 1), 5.12 (s, 2), 3.6 (overlapping multiplet and singlet, 5), 2.98 (s, 2) and 2.1 (broad, 2).

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.58; H, 6.78; N, 4.84.

For routine preparative work the mixture of exocyclic and endocyclic acids described in the previous experiment was esterified with diazomethane and the resulting mixture of esters was converted to pure **2e** by irradiation.

Synthesis of 1f.—A mixture of **1d** and **2d** was prepared from 1-benzoyl-3-ethyl-4-piperidone as described by Sundberg, Ligon and Lin.[2a] Conversion to **1f** was carried out as described for **1e**. The analytical sample was purified by chromatography on Florisil: ir (neat) 1720 cm^{-1} (CO, broad, overlapping carbamate and conjugated ester); nmr ($CDCl_3$) δ 7.3 (s, 5), 5.68 (s, 1), 5.11 (s, 2), 3.62 (s, 3), 1.4 (q, 2), and 0.82 (t, 3).

Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.31; N, 4.41. Found: C, 68.19; H, 7.45; N, 4.47.

Isomerization of 1f.—A solution of **1f** (15.5 g, 0.049 mol) in methanol (500 ml) was irradiated with the Type L lamp for 20 hr. Evaporation of the solvent gave a residue which was eluted from Florisil F-100 (200 g) with 10% ether in benzene. Evaporation of the solvent gave a quantitative yield of material having spectral properties identical with those of the analytical sample, prepared from a center fraction: ir (neat) 1749 (CO) and 1720 cm^{-1} (carbamate CO); nmr ($CDCl_3$) δ 7.4 (s, 5), 5.5 (broad s, ~1), 5.18 (s, 2), 3.68 (s, 3), 3.08 (s, 2), 2.1 (broad q, 2) and 1.0 (m, 2).

Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.31; N, 4.41. Found: C, 68.35; H, 7.35; N, 4.34.

Although there were no other indications of the presence of a second component, the vinyl proton integration was about 70% of the expected value, indicating that the product might contain up to 30% of the alternative endocyclic isomer.

Preparation of 1g.—Sodium hydride (2.1 g of 50% mineral oil dispersion) was rinsed with hexane and then covered with anhydrous ether (80 ml). A solution of triethyl 2-phosphonobutyrate[7] (12.6 g) in ether (20 ml) was added slowly. When hydrogen evolution had ceased, a solution prepared by dissolving 1-benzoyl-4-piperidone (10.15 g) in ether (100 ml) and benzene (20 ml) was added. The reaction mixture was then refluxed for 17 hr under nitrogen. The reaction mixture was filtered and the organic filtrate was dried and evaporated. Chromatography gave **1g** (10.2 g, 68%). The analytical sample was prepared by bulb-to-bulb distillation: bp 174–175° (0.1 mm); ir (neat) 1725 (ester CO), 1640 cm^{-1} (amide CO); nmr ($CDCl_3$) δ 7.5 (s, 5), 4.25 (q, 2), 3.7 (broad, 4), 2.46 (m, 6), and 1.25 and 1.0 (overlapping t, 6).

Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.94; H, 7.65; N, 4.47.

Photoisomerization of 1g.—A solution of **1g** (100 mg) in ethanol (60 ml) was irradiated for 3.5 hr using the Type S lamp. Evaporation of the solvent left **2g** having spectral properties identical with those of the analytical sample prepared by bulb-to-bulb distillation: ir (neat) 1745 (ester CO), 1640 cm^{-1} (amide CO); nmr ($CDCl_3$) δ 7.48 (s, 5), 5.60 (bs, 1), 4.15 (q overlapping m, 4), 3.60 (b, 2), 2.90 (t, 1), 2.20 (b, 2), 1.75 (broadened q, 2), 1.25 (t, 3), 0.90 (t, 3).

Anal. Calcd for $C_{18}H_{23}NO_3$: C, 71.73; H, 7.69; N, 4.65. Found: C, 71.55; H, 7.86; N, 4.50.

Base-Catalyzed Isomerization of 1c.—A solution of **1c** (40.0 g) was dissolved in ethanol (200 ml) and treated with a sodium ethoxide solution prepared by dissolving sodium metal (0.75 g) in ethanol. After stirring for 3 hr at room temperature the solution was poured into acidic brine and extracted with ether. The product obtained by drying and evaporation of solvent was shown by nmr to be a 1:2.9 mixture of **1c** and **2c** (92% yield). Separation and characterization of **1c** and **2c** have been reported previously.[2c]

Registry No.—**1a**, 28399-82-8; **1b**, 40110-55-2; **1c**, 21363-69-9; **1d**, 21363-68-8; **1e**, 40112-93-4; **1f**, 40112-94-5; **1g**, 40112-95-6; **2a**, 37123-97-0; **2b**, 40112-97-8; **2c**, 21363-70-2; **2d**, 21389-71-9; **2e**, 30338-85-3; **2f**, 40113-01-7; **2g**, 37124-04-2; triethyl phosphonoacetate, 867-13-0; 1-benzyl-4-piperidone, 3612-20-2; 1-carbobenzyloxy-$\Delta^{4,\alpha}$-piperidineacetic acid, 40113-03-9; triethyl 2-phosphonobutyrate, 17145-91-4; 1-benzoyl-4-piperidone, 24686-78-0.

Acknowledgment.—Some of the compounds utilized in this work were originally prepared in our laboratory by Dr. F. O. Holcombe.

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Formamoylation of Some Azo Compounds and the Characterization of Reaction Products

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The free-radical addition of formamide to olefins has been reported.[1] The reaction proceeds with good yields in the presence of peroxide or ultraviolet radiation (2000–2500 Å).[2] Likewise, the addition of a number of free-radical species to azo compounds has been observed.[3] We wish to report here the first addition of the formamoyl radical to azo compounds.

Formamide adds to 1,1′-azobisformamide (ABFA) in the presence of decomposing benzoyl peroxide (BPO)

(1) (a) D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964); (b) D. Elad, *Chem. Ind. (London)*, 362 (1962); (c) L. Friedman and H. Schechter, *Tetrahedron Lett.*, 238 (1961); *Chem. Abstr.*, **55**, 20934*d* (1961).

(2) The addition also proceeds in sunlight.[1a,b]

(3) (a) A. Jones, E. R. Morris, and J. C. J. Thynne, *J. Phys. Chem.*, **72**, 2677 (1968); (b) D. Mackay, U. F. Marx, and W. A. Waters, *J. Chem. Soc.*, 4793 (1964).