the time of data collection, (Table II).

The positions of the two sulfur atoms in **9a** were determined from a Patterson synthesis. The rest of the structure was determined by heavy-atom methods and refined by a full-matrix least-squares routine using anisotropic thermal parameters for the non-hydrogen atoms.[20] All of the hydrogen atoms were located from a difference Fourier map and were refined isotropically. Scattering factors were obtained from "International Tables for X-Ray Crystallography" (Vol. 4, 1974). The refinement converged to a final $R$ ($=\sum||F_o| - |F_c||/\sum|F_o|$) of 0.026 for 1787 observed reflections [$I > 2\sigma(I)$] and $R_w$ ($=\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ of 0.028. An analysis of the variance after refinement of the data revealed no systematic variation of $\sum w(|F_o| - |F_c|)^2$ with either $\sin\theta$ or $F$. The final atomic coordinates are listed in Table III. Thermal parameters and hydrogen atomic parameters for **9a** are listed in Tables IV and V, respectively (supplementary material). The atom numbering scheme is given in Figure 1.

**Reaction of 9 with Triethylamine.** To a solution of **9** (mixture of isomers, 27.42 g, 0.1 mol) in dry acetonitrile (100 mL) under argon was added dry triethylamine (35 mL, 0.25 mol), and the reaction mixture was refluxed under argon (24 h). The reaction mixture was then cooled to room temperature and concentrated in vacuo. The residue was diluted with pentane (200 mL) and stirred vigorously (15 min). The resulting mixture was filtered, and the residue was washed thoroughly with pentane. The filtrate was then concentrated in vacuo to afford a yellow oil (17.61 g). This material was purified by distillation at 58–62 °C (0.02 mm) to afford a mixture of isomeric alkenes **10** and **11** (colorless oil, 14.62 g, 78%). Elemental microanalysis was performed on this mixture of isomers.

Anal. Calcd for $C_9H_{16}S_2$: C, 57.39; H, 8.56; S, 34.05. Found: C, 57.48; H, 8.67; S, 33.95.

Compound **10** was isolated from this mixture in pure form via careful column chromatography on silica gel impregnated with 13% (w/w) silver nitrate (1:3 methylene chloride–pentane eluent). Under these conditions, most of **10** and all of **11** remained on the column after elution: $^1$H NMR ($CDCl_3$) $\delta$ 1.24 (d, $J$ = 7.2 Hz, 3 H), 1.47–2.26 (m, 4 H), 2.35–3.48 (m, 7 H), 5.06 (s, 1 H), 5.24 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 23.13 (q), 26.44 (t), 27.14 (t), 29.04 (t), 29.63 (t), 33.48 (t), 41.01 (d), 114.58 (t), 145.68 (s); IR (film) 3077 (w), 2917 (s), 1600 (s), 1455 (s), 1379 (m), 1288 (m), 1253 (m), 887 (s), 761 cm$^{-1}$ (m); mass spectrum (70 eV), $m/e$ (relative intensity) 190.1 (M + 2, 3.8), 189.1 (M + 1, 5.4), 188.1 (molecular ion, 39.6), 146.0 (25.7), 127.1 (10.2), 115.0 (13.0), 114.0 (95.3), 113.0 (32.0), 106.0 (40.3), 99.0 (58.1), 85.0 (11.8), 81.1 (24.7), 79.0 (31.9), 77.0 (11.3), 74.0 (11.3), 71.0 (25.0), 65.0 (12.9), 61.0 (12.3), 60.0 (12.8), 59.0 (43.3), 58.0 (37.8), 55.1 (12.2), 53.0 (30.8), 47.0 (35.6), 46.0 (34.3), 45.0 (84.3), 42.0 (11.6), 41.0 (100.0).

The $^1$H and $^{13}$C NMR spectra of **11** can be inferred by subtracting the absorption patterns in the spectrum of **10** from the absorption patterns in the corresponding spectra of the mixture of **10** and **11**, given above. However, separation of **10** and **11** was possible by GC/MS: mass spectrum of **11** (70 eV), $m/e$ (relative intensity), 190.1 (M+2, 4.7), 189.2 (M+1, 5.7), 188.2 (molecular ion, 49.3), 146.1 (22.9), 127.1 (10.8), 115.1 (15.8), 114.1 (100.0), 113.1 (71.4), 106.1 (35.1), 99.1 (54.2), 87.1 (17.8), 85.1 (18.7), 81.1 (25.3), 79.1 (28.7), 77.1 (10.7), 74.1 (13.4), 73.1 (18.3), 71.1 (20.3), 65.1 (11.2), 60.1 (11.0), 59.1 (42.8), 58.1 (19.8), 55.1 (10.2), 53.1 (24.4), 47.1 (22.9), 46.1 (19.9), 45.1 (55.3), 41.1 (68.1).

**Acknowledgment.** Financial support of our study by the Naval Air Systems Command, the Air Force Office of Scientific Research (Grant No. AFOSR-84-0085), The Robert A. Welch Foundation (Grant B-963), and the North Texas State University Faculty Research Committee is gratefully acknowledged. The X-ray crystallographic structure determination of **9a** was supported in part by a grant from the DHHS, National Cancer Institute, CA17562 (to D. v. d. H); we also thank the University of Oklahoma Computing Center for providing computing facilities and service in this connection.

**Registry No.** **2**, 87830-51-1; **5a**, 100296-39-7; **5b**, 100206-70-0; **6a**, 100206-72-2; **6b**, 100296-02-4; **7**, 100206-74-4; **8**, 100206-73-3; **9** (isomer 1), 100206-76-6; **9** (isomer 2), 100296-04-6; **10**, 100206-77-7; **11**, 100206-78-8; 5-hexen-2-one, 109-49-9; 1,3-propanedithiol, 109-80-8; boron trifluoride etherate, 109-63-7; methanethiol, 74-93-1.

**Supplementary Material Available:** A list of atomic positional parameters, thermal parameters, and hydrogen atomic parameters for **9a** (3 pages). Ordering information is given on any current masthead page.

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# Reactions of *o*-Quinone Monoimides with Sulfoxides, Diazoalkanes, and Triphenylphosphine

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*Received July 25, 1985*

*o*-Quinone monoimides react with dialkyl sulfoxides to produce *N*-(2-(aroyloxy)phenyl)-*S*,*S*-dialkylsulfoximines. Analogously, *o*-quinone diimides and dialkyl sulfoxides combine to form *N*-(2-(dibenzoylamino)phenyl)-*S*,*S*-dialkylsulfoximines. *o*-Quinone monoimides when admixed with phenyldiazomethane and diphenyldiazomethane afford 2-(aroyloxy)-*N*-(phenylmethylene)- and 2-(aroyloxy)-*N*-(diphenylmethylene)benzenamines. Similarly, *o*-quinone monoimides treated with ethyl diazoacetate form 2-(aroyloxy)-*N*-(carbethoxymethylene)benzenamines. *o*-Quinone monoimides are converted by triphenylphosphine into benzoxazoles.

Until recently only two publications on the reactions of *o*-quinone monoimides had appeared. Adams and Stewart[1] reported that hydrogen chloride added 1,4 across the enimide system of **1** to produce **2** (Scheme I). Mustafa and Kamel[2] described the twofold addition of arylmagnesium bromides to the carbonyl and imido moieties of **3** which gave rise to **4**. In 1984[3] we demonstrated that **5** underwent Diels–Alder reactions across the heterodiene system with

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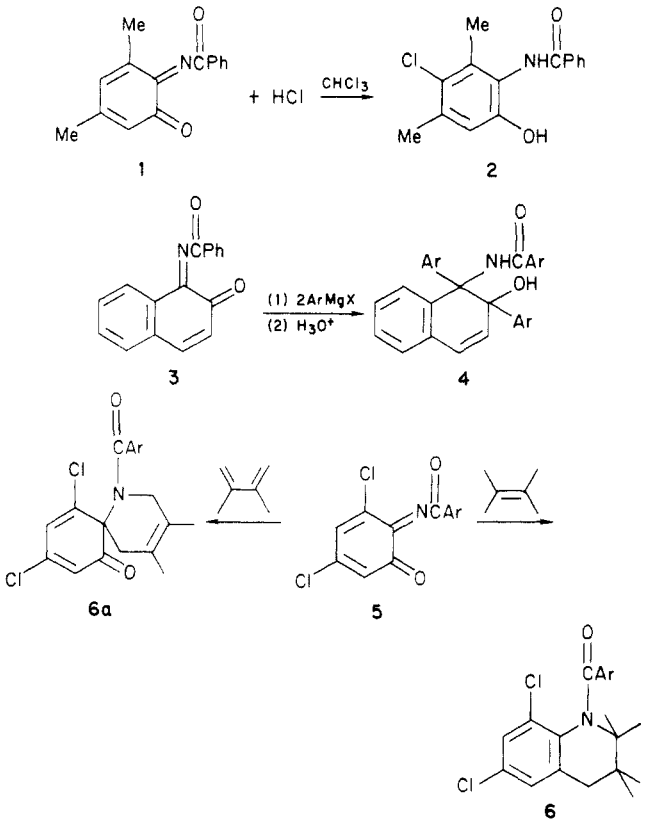
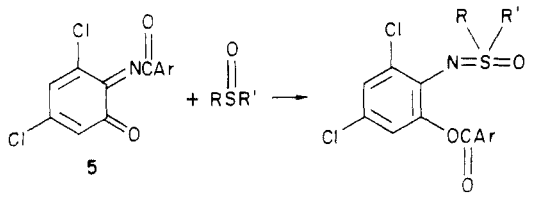
0022-3263/86/1951-0829$01.50/0 

**Scheme I**[a]




[a] 5, 6, 6a, Ar = $p$-$O_2NC_6H_4$.

**Scheme II**[a]




[a] Ar = $p$-$O_2NC_6H_4$.

electron-rich alkenes to form 2,3-dihydro-4*H*-1,4-benzoxazine derivatives **6** (Scheme I). We also observed that the imino group of **5** acted as a dienophilic site when **5** was treated with 2,3-dimethyl-1,3-butadiene. The product of the latter reaction was the spiro compound **6a**.

The work detailed here involves the interaction of some *o*-quinone monoimides with sulfoxides, diazoalkanes, and triphenylphosphine. The products in the case of the sulfoxides are *N*-arylsulfoximines. *N*-Arylsulfoximines have been made by (1) reacting azidopentafluorobenzene with dimethyl sulfoxide,[4] (2) oxidizing sulfilimines,[5,6] and (3) treating a complex of dimethyl sulfoxide and *tert*-butyl hypochlorite with an aryl amine.[7] Several comprehensive reviews on the chemistry of sulfoximines have appeared.[8-14]

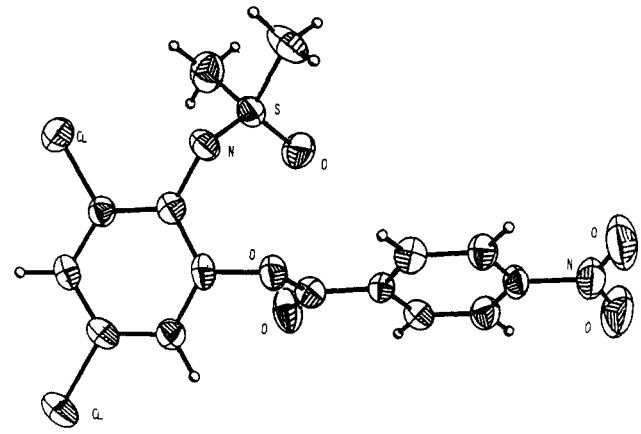
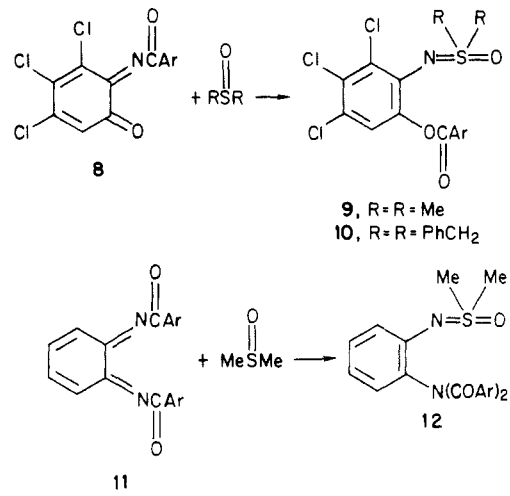


**Figure 1.** Thermal ellipsoid (50% probability) plot of *N*-[2,4-dichloro-6-[(4-nitrobenzoyl)oxy]phenyl]-*S*,*S*-dimethylsulfoximine (**7a**).

**Scheme III**[a]




[a] Ar = $p$-$O_2NC_6$

## Results and Discussion

The *o*-quinone monoimide **5** reacts with sulfoxides to give the sulfoximines **7a–e** (Scheme II). The structures of **7a–e** were initially deduced from spectral data. The infrared spectrum of **7a**, for example, exhibited absorption peaks at 1295, 1200, and 1060 $cm^{-1}$, which are characteristic of the —N=S(=O) < moiety.[7,15-18] An intense ester carbonyl stretch at 1745 $cm^{-1}$ was also present. Mass spectra showed molecular ions and fragmentation patterns in harmony with structures **7a–e**. The $^{13}C$ NMR spectra were consistent with the proposed structures. Known substituent effects[19] were used to calculate the expected

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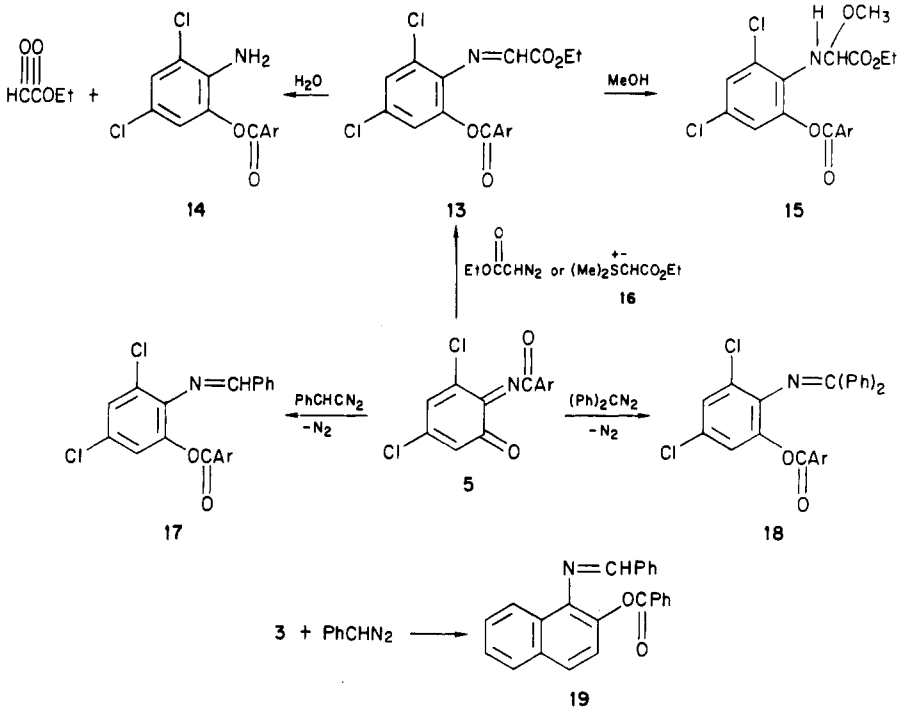
**Scheme IV**[a]




[a] Ar = $p$-$O_2NC_6H_4$.

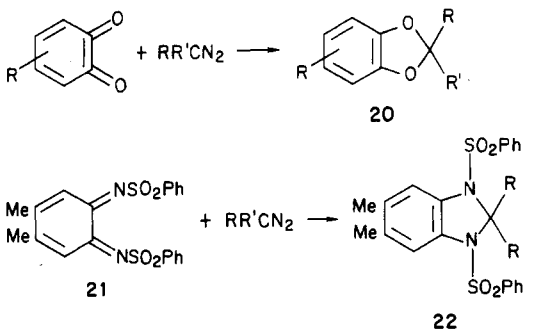
values of the chemical shifts for the chlorinated aromatic ring and the $p$-nitrobenzoyl substituent. The observed chemical shifts gave good agreement with the calculated values. Unequivocal evidence for the structure of **7a** was forthcoming by an X-ray crystallographic study (Figure 1).

Treatment of dimethyl sulfoxide and dibenzyl sulfoxide with the $o$-quinone monoimide **8** afforded the sulfoximines **9** and **10**, respectively (Scheme III). Attempts to react the $o$-quinone monoimide **3** with dimethyl sulfoxide resulted in recovery of the starting reagents. The reaction of $o$-quinone monoimides with sulfoxides was extended to the $o$-quinone dibenzimide **11**. Heating a mixture of dimethyl sulfoxide and **11** gave **12** (Scheme III). The identity of **12** was determined by spectral data, mass spectroscopy, and elemental analyses.

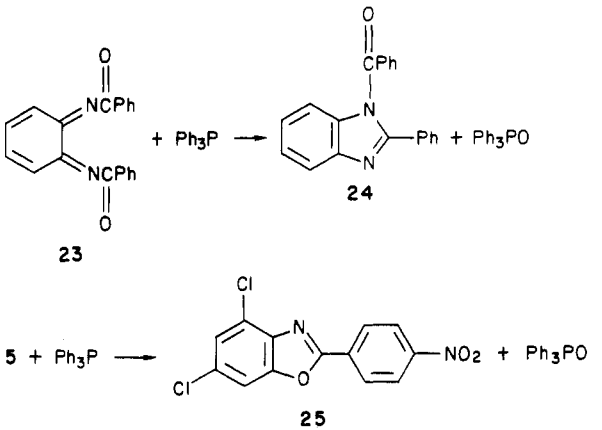
Addition of ethyl diazoacetate and phenyldiazo- and diphenyldiazomethanes in methylene chloride at ambient temperature to **5** led to the evolution of nitrogen and the formation of $N$-aryl imines (Scheme IV). For example, admixing of **5** and ethyl diazoacetate afforded **13**. Structural assignment to **13** was based on spectral information and upon hydrolysis of **13** to the known **14**[3] and ethyl glyoxylate. The infrared spectrum of **13** is quite similar to that reported for ethyl (phenylimino)acetate.[20] Further support for the structure of **13** was the easy addition of methanol to the electrophilic imino group to produce **15** (Scheme IV). Reaction of **5** with the sulfur ylide **16** also formed **13** in high yields. Reaction of **8** with **5** gave the trichloro analogue of **13**, namely, **13a** (see Experimental Section). Addition of phenyldiazomethane and diphenyldiazomethane to **5** afforded **17** and **18**, respectively, and hydrolysis of **17** generated **14** and benzaldehyde. The $o$-quinone monoimide **3** reacted with phenyldiazomethane to form **19** but no reaction occurred between **3** and ethyl diazoacetate.

It is of interest to note that $o$-benzoquinones react with diazoalkanes to yield, for the most part, 1,3-dioxoles **20** and

**Scheme V**




**Scheme VI**




in some instances spiro epoxy ketones[21] (Scheme V). Analogously, dihydrobenzimidazoles **22** are formed when diazoalkanes are treated with compound **21**[22,23] (Scheme V).

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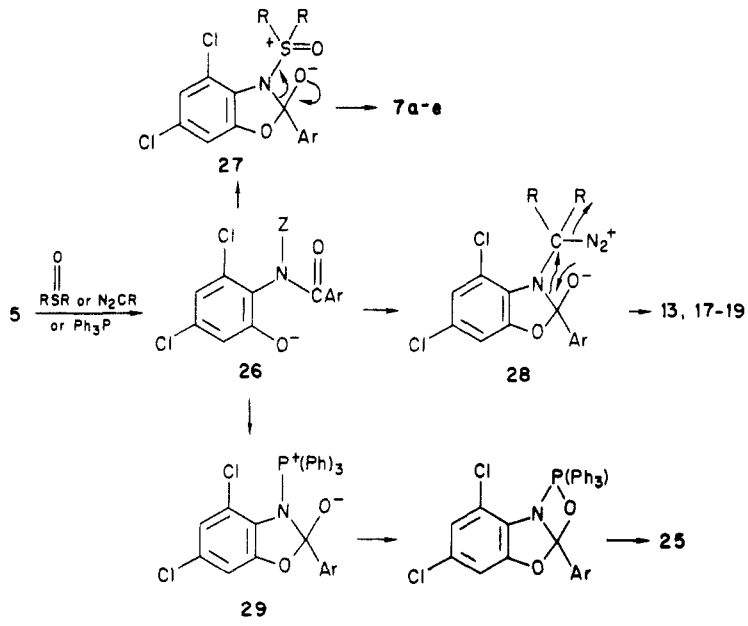
**Scheme VII**[a]




[a] Ar = $p$-$O_2NC_6H_4$; Z = $^+S(ORR)$; $C(N_2^+)RR$; $^+P(Ph)_3$.

It has been reported[24] that the *o*-benzoquinone dibenzimide **23** when reacted with triphenylphosphine formed triphenylphosphine oxide and 1-benzoyl-2-phenylbenzimidazole **24** (Scheme VI). Similar treatment of **5** with triphenylphosphine in methylene chloride at ambient temperature results in the formation of the oxazole **25** and triphenylphosphine oxide (Scheme VI).

The reactions of **5** with sulfoxides, diazoalkanes, and triphenylphosphine can be rationalized by mechanisms involving attack by the electron-rich sulfur, carbon, and phosphorus atoms of these reagents with the nitrogen atom of the *o*-quinone monoimide to give intermediates **26** (Scheme VII). The phenoxide ion of **26** then adds to the carbonyl carbon to give intermediates **27–29** which are the precursors to the sulfoxides (**7a–e**), the imines (**13**, **17**, **18**, **19**), and the oxazole **25**.

## Experimental Section[25]

***N*-[2,4-Dichloro-6-[(4-nitrobenzoyl)oxy]phenyl]-*S*,*S*-dimethylsulfoximine (7a).** To a solution of 81 mg (0.25 mmol) of **5** in 3 mL of dry $CHCl_3$ was added 19.5 mg (0.25 mmol) of $Me_2SO$. After 6 h at ambient temperature the solvent was evaporated and the residual oil was triturated with MeOH. The crude **7a** (99 mg, 98%, mp 135–141 °C) was filtered and recrystallized from EtOH to give **7a** melting at 144–146 °C.

**Synthesis of 7b.** A mixture of 81 mg (0.25 mmol) of **5** and 57.5 mg (0.25 mmol) of dibenzyl sulfoxide in 2.0 mL of $CHCl_3$ was allowed to stand at ambient temperature for 48 h. Evaporation of the solvent gave crude **7b** (133 mg, 96%) melting at 125–133 °C. Recrystallization from EtOH gave **7b**, mp 147–149 °C.

**Synthesis of 7c.** A mixture of 162 mg (0.5 mmol) of **5**, 70 mg (0.5 mmol) of methyl phenyl sulfoxide, and 5.0 mL of dry $CHCl_3$ was kept at ambient temperature for 144 h. Evaporation of the $CHCl_3$ yielded a reddish brown oil which was dissolved in 2 mL of EtOAc. Elution of this solution through a column containing 250–400-mesh Merck 60 grade silica gel employing as a mobile phase hexane/EtOAc (5:1) afforded **7c** as an oil. Dissolution of the oil in a minimal quantity of $Et_2O$/hexane (2:1) followed by evaporation of the solvents gave 127 mg (55%) of **7c** melting at 106–108 °C. An analytical sample of **7c** (mp 117–119 °C) was prepared by precipitating it from MeCN with water.

**Synthesis of 7d.** To a solution of 81 mg (0.25 mmol) of **5** in 2 mL of dry $CHCl_3$ was added 38.5 mg (0.25 mmol) of benzyl methyl sulfoxide. After 96 h the $CHCl_3$ was evaporated and the residual oil was dissolved in 1.5 mL of EtOH. Petroleum ether (1.5 mL, bp 94–105 °C) was added and the mixture stirred at 60 °C until a precipitate appeared. Filtration gave 99 mg (82.9%) of **7d** melting at 130–139 °C. Recrystallization from $CHCl_3$–petroleum ether (bp 94–107 °C) afforded **7d**: mp 152–155 °C.

**Synthesis of 7e.** A mixture of 162 mg (0.5 mmol) of **5**, 52 mg (0.5 mmol) of tetramethylene sulfoxide, and 4 mL of dry $CHCl_3$ was allowed to stand for 48 h. Removal of the solvent and trituration of the residual oil with MeOH formed 142 mg (66.8%) of crude **7e**. Recrystallization from methanol gave **7e**: mp 120–121 °C.

**Synthesis of 9.** To a solution of 81 mg (0.25 mmol) of **5** in 6 mL of dry $CHCl_3$ was added 20 mg (0.25 mmol) of $Me_2SO$. The mixture was kept at ambient temperature for 48 h, the $CHCl_3$ was evaporated, and the residual oil was triturated with 2.0 mL of MeOH. Filtration gave 97 mg (96%) of crude **9** (mp 172–178 °C) which when recrystallized from $CH_2Cl_2$/MeOH formed **9** (mp 174–178 °C).

**Synthesis of 10.** A mixture of 81 mg (0.25 mmol) of **5**, 6 mL of dry $CHCl_3$, and 58 mg (0.25 mmol) of dibenzyl sulfoxide was kept at ambient temperature for 48 h. The solvent was removed and the residual oil triturated with 1.5 mL of $Et_2O$. Filtration yielded 129 mg (87%) of **10** melting at 132–138 °C. Recrystallization from EtOH gave **10**: mp 146–148 °C.

**Synthesis of 12.** A solution of 201 mg (0.5 mmol) of **11** in 3 mL of $Me_2SO$ was stirred and warmed. After a few minutes the color of the mixture went from yellow to dark brown and finally to light brown. After 10 min the solvent was evaporated. The residual brown oil was dissolved in 3 mL of a 1:1 mixture of EtOAc/hexane. This solution was chromatographed on a column composed of 250–400-mesh Merck 60 grade silica gel employing a solution of EtOAc/hexane as the eluting solvent. Three fractions were obtained, the last of which collected proved to be crude **12** (110 mg, 45.8%), melting at 116–121 °C. Recrystallization from $Et_2O$/hexane gave an analytical sample of **12** melting at 118–122 °C. Mass spectrum, $M^+$ 482.

**Reaction of 5 with Ethyl Diazoacetate. Synthesis of 13.** A mixture of 584 mg (1.80 mmol) of **5**, 2 mL of $CH_2Cl_2$, and 577 mg (5.06 mmol) of ethyl diazoacetate was kept at ambient temperature for 4 h. Evaporation of the solvent gave 724 mg (98%) of crude **15**, mp 125–130 °C. Recrystallization from MeCN afforded **15** melting at 129–132 °C.

**Alternate Synthesis of 13.** Compound **13** was also prepared by the dropwise addition of 302 mg (2.04 mmol) of $Me_2SCHCO_2Et$ in 40 mL of $CH_2Cl_2$ to a solution of 593 mg (1.84 mmol) of **5** in

(24) Sprecher, M.; Levy, D. *Tetrahedron Lett.* **1969**, 4957.
(25) Satisfactory analytical data for C, H, and N were reported for all new compounds described in the Experimental Section (Ed.).

40 mL of $CH_2Cl_2$. The solvent was evaporated, the residue redissolved in $CH_2Cl_2$, and the solvent was evaporated. The crude **15** weighed 740 mg (98%) and was recrystallized from MeCN. The infrared spectra of **15** prepared from **5** with $EtO_2CCHN_2$ and with $Me_2SCHCO_2Et$ were identical.

**Synthesis of 13a.** To a stirred suspension of 211 mg (0.59 mmol) of **8** in 6.43 g of $CH_2Cl_2$ was added 253 mg (2.22 mmol) of $N_2CHCO_2Et$. After 17 h the solvent was evaporated, the residue was dissolved in 4 mL of $CH_2Cl_2$, and the solvent was evaporated. The crude **13a** weighed 232 mg (89%) and melted at 145–141 °C. Recrystallization from MeCN gave **13a**: mp 148–131 °C.

**Hydrolysis of 13.** A suspension of 123 mg (0.30 mmol) of **13**, 393 mg MeCN, and 369 mg of $H_2O$ was stirred for 29 h during which time the color of the mixture changed from creamy white to yellow. Filtration gave 77 mg (79%) of **14**.[3] The filtrate was subjected to GC–mass spectroscopy. The presence of $EtO_2CCHO$ was verified by its molecular ion $m/e$ 102 and by a comparison with an authentic sample with its fragmentation pattern and retention time.

**Synthesis of 15.** A mixture of 95 mg (0.23 mmol) of **5** in 2 mL of MeOH was refluxed for 45 min. The solution was cooled and filtered. The crude **15** weighed 94 mg (92%). Recrystallization from MeOH gave **15**: mp 109–112 °C; IR (Nujol) 3330, 1730, 1725, 1620, 1325, 1365, 1260, 1135, 1095, 1060, 1040, 1010, 870, 862, 848, 713 $cm^{-1}$; $^1H$ NMR (90 MHz) ($CDCl_3$) $\delta$ 1.25 (t, 3 H), 3.11 (s, 3 H), 4.22 (q, 4 H), 5.24 (d, 1, CH), 5.45 (d, 1, NH), 7.09 (d, 1 H), 7.32 (d, 1 H), 8.37 (s, 4 H).

**Synthesis of 17.** Compound **17** was prepared by the dropwise addition of a solution of 45.7 mg (0.39 mmol) of $PhCHN_2$ in 0.3 mL of $CH_2Cl_2$ to a solution of 122 mg (0.38 mmol) of **5** in 2.5 mL of $CH_2Cl_2$. Nitrogen evolution was instantaneous and the orange color of **5** was discharged. The solvent was evaporated and the 131 mg (96%) of **17** was recrystallized from MeCN to give **17**: mp 198–201 °C.

**Synthesis of 18.** To a solution of 145 mg (0.45 mmol) of **5** in 2 mL of $CH_2Cl_2$ was added dropwise a solution of 88 mg (0.45 mmol) of diphenyldiazomethane in 0.2 mL of $CH_2Cl_2$. Nitrogen evolution was complete in a few minutes. After about 4 h pentane was added and then the solvent was evaporated. The residue was slurried in pentane and the crude **18** (140 mg, 28.5%) was filtered off. Recrystallization from MeCN gave **18**: mp 204–208 °C.

**Synthesis of 19.** A solution of 276 mg (1.06 mmol) of **3** in 25 mL of $CH_2Cl_2$ was added dropwise and with stirring to a solution containing a slight excess of phenyldiazomethane in 100 mL of $CH_2Cl_2$. After 3 h the solvent was evaporated to about 13 mL. The solution was filtered and the crude **19** (230 mg, 65.4%) recrystallized from methanol to give **21** melting at 114–117 °C.

**Synthesis of 25.** A mixture of 164 mg (0.50 mmol) of **5** and 131 mg (0.50 mmol) of $(C_6H_5)_3P$ in 2 mL of $CH_2Cl_2$ stood 17 h at ambient temperature. The solvent was evaporated and the residue slurried with methanol. Filtration gave 111 mg (0.36 mol, 72%) of crude **25**, mp 168–176 °C. Recrystallization from 2-propanol gave **25** melting at 183–187 °C.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by The American Chemical Society, and to the National Science Foundation for Grant CHE-84058555. We thank Professor Xavier Creary for running the reaction of **5** with diphenyldiazomethane and Mr. Jim Spriggle for mass spectral data.

**Registry No.** **5**, 90388-37-7; **7a**, 100189-94-4; **7b**, 100189-95-5; **7c**, 100189-96-6; **7d**, 100189-97-7; **7e**, 100189-98-8; **8**, 100205-35-4; **9**, 100189-99-9; **10**, 100190-00-9; **11**, 67944-81-4; **12**, 100190-01-0; **13**, 100190-02-1; **13a**, 100190-03-2; **14**, 90368-43-7; **15**, 100190-04-3; **16**, 7380-81-6; **17**, 100190-05-4; **18**, 100190-06-5; **19**, 100190-07-6; **25**, 100190-08-7; $PhCHN_2$, 21113-61-1; $Me_2SO$, 67-68-5; methyl phenyl sulfoxide, 1193-82-4; benzyl methyl sulfoxide, 824-86-2; tetramethylene sulfoxide, 1600-44-8; dibenzyl sulfoxide, 621-08-9; ethyl diazoacetate, 623-73-4; diphenyldiazoethane, 883-40-9; triphenylphosphine, 603-35-0.

**Supplementary Material Available:** Crystal structure data for **7a** and $^{13}C$ NMR spectral data for **7a** and **12**, IR spectral data for **7a–e**, **10**, and **12** (8 pages). Ordering information is given on any current masthead page.

# Kinetics of Reversible Endothermic Elimination Reactions: β-Amino Carboxylic Esters and Amides

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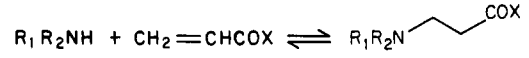
*Received June 7, 1985*

The kinetics of the elimination reactions of substituted β-amino carboxylic esters and amides, to give amines and the α,β-unsaturated esters and amides, have been studied in several model systems. The reaction was studied by trapping the olefin formed with another nucleophile capable of competing with the amine formed by elimination. The rate constant for elimination of methyl 3-(*N*-methyl-*N*-butylamino)propionate, in methanol at room temperature, is $1.8 \times 10^{-6}$ $s^{-1}$. The corresponding amide has an elimination rate constant of $8.8 \times 10^{-8}$ $s^{-1}$. Rate constants for the forward reaction were also measured and combined with the reversion rate constants to yield equilibrium constants for the same two systems. The equilibrium constant for the methyl esters is $2.0 \times 10^4$ L $mol^{-1}$ and for the amides is $7.3 \times 10^3$ L $mol^{-1}$. These were confirmed by measurement of the equilibrium concentrations of olefins by $^1H$ NMR spectroscopy.

The addition reaction of amines with α,β-unsaturated ketones, esters, amides, and sulfones is a well-known reaction whose kinetics have been studied in some detail.[1] It has been recognized that this reaction is reversible, and this reversion reaction has been used in the synthesis of substituted acrylamides[2] and certain β-amino ketones.[3]




Similar reversion reactions with oxygen and sulfur nucleophiles have been studied,[4] and in some cases the kinetics as well as the equilibrium concentrations of the

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