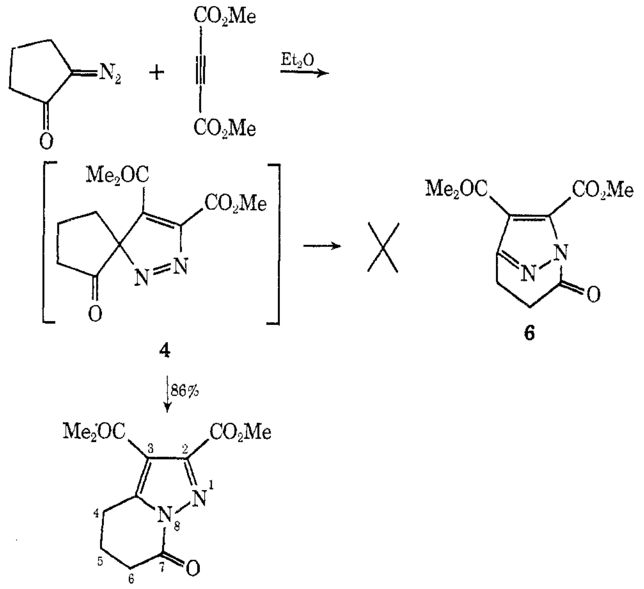
Table III

Compd	λ_{max}, nm (ϵ)[a]
A (**2a**)	237 (8700)
5	240 (8200)
B (**2b**)	251 (13,400)

[a] In 95% EtOH.

studied the reaction of 2-diazocyclopentanone[7] with DMAD.[8] Physical data confirmed that the product was dimethyl-4,5-dihydro-7(6*H*)-oxopyrazolo[1,5-*a*]pyridine-2,3-dicarboxylate (**5**) (rearrangement of the intermediate 3*H*-pyrazole **4** to **6** would violate Bredt's rule).



The similarity between the uv spectra of **5** and A (Table III) provides considerable support for the assignment of the dimethyl 1-acetyl-5-methylpyrazole-3,4-dicarboxylate (**2a**) structure to the 2-diazo-3-butanone–DMAD product (isomer A) and the dimethyl 1-acetyl-3-methylpyrazole-4,5-dicarboxylate (**2b**) structure to isomer B.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected. Nmr spectra were recorded on Varian A-60A and HA60 instruments at 60 MHz in 5–10% deuteriochloroform solution with tetramethylsilane as an internal standard. Infrared spectra were obtained with a Perkin-Elmer Model 21 in chloroform solution, and ultraviolet spectra were determined in 95% ethanol solution on a Carey Model 15. Vpc analyses were performed on a Hewlett-Packard Model 402 instrument equipped with a flame ionization detector. A 4 ft × 4 mm, 3% OV-1 on Chromosorb W (HP) 80/100 mesh column at 125° and a He flow rate of 60 ml/min were used. Mass spectral data were obtained on a CEC Model 110 spectrometer.

Dimethyl 3(5)-Methylpyrazole-4,5(3,4)dicarboxylate (3).—A solution of 2.5 g (10.4 mmol) of the 2-diazo-3-butanone–DMAD adduct[1] in 140 ml of methanol and 0.5 ml of concentrated HCl was heated under reflux for 20 min and poured into 500 ml of water. The mixture was extracted with 3 × 50 ml of CH_2Cl_2. The combined extracts were dried (Na_2SO_4) and concentrated. The residual oil was crystallized from benzene–hexane to give 1.7 g (82%) of **3** as tan crystals: mp 104–106° alone and mixed with an authentic specimen prepared from the reaction of diazoethane with DMAD;[6] ir 3425, 3180 (broad, NH), 1724 cm^{-1} (broad, C=O); nmr δ 2.52 (s, 3 H), 3.87 (s, 3 H), 3.91 (s, 3 H); mass spectrum *m/e* 198 (M^+).

Anal. Calcd for $C_8H_{10}N_2O_4$: C, 48.49; H, 5.09; N, 14.14. Found: C, 48.70; H, 5.34; N, 14.33.

Dimethyl 1-Acetyl-5-methylpyrazole-3,4-dicarboxylate (2a, Isomer A).—A solution of 0.7 g (3.54 mmol) of **3** in 20 ml of acetic anhydride was heated under reflux for 2 hr and then concentrated at 50° under reduced pressure. The residual oil was shown by vpc to contain isomers A (retention time 16 min) and B (retention time 12 min) in an 80:20 ratio (Table I). Crystallization from ether/Skelly B gave 0.5 g (59%) of **2a** (isomer A) (homogeneous by vpc) as colorless needles, mp 64–66° alone and mixed with 2-diazo-3-butanone–DMAD adduct.[1] Ir and nmr are presented in Table I and uv in Table III.

Acetylation of **3** in acetic anhydride at 24° for 24 hr gave a 72:28 mixture of isomers A and B (vpc, Table I).

Dimethyl 1-Acetyl-3-methylpyrazole-4,5-dicarboxylate (2b, Isomer B).—A mixture of 1 g (5.05 mmol) of **3**, 0.75 g of pyridine, 0.75 g of acetyl chloride, and 50 ml of ether was stirred for 2.5 hr at 22°. Water (40 ml) was added and after stirring for 0.5 hr the ether layer was separated, washed with water (2 × 50 ml) and brine (50 ml), and dried (Na_2SO_4). Removal of solvent under reduced pressure at <25° left a pale yellow oil which crystallized on standing. Vpc indicated that the product was a mixture of isomers A and B in the ratio 8:92 (Table I). Recrystallization from ether–hexane gave 0.5 g (41%) of **2b** (isomer B), mp 51–53°. This material was homogeneous by vpc. Ir and nmr are shown in Table I and uv in Table III; mass spectrum *m/e* 240 (M^+).

Anal. Calcd for $C_{10}H_{12}N_2O_5$: C, 50.00; H, 5.04; N, 11.66. Found: C, 49.90; H, 5.21; N, 11.79.

Dimethyl 4,5-Dihydro-7(6*H*)oxopyrazolo[1,5-*a*]pyridine-2,3-dicarboxylate (5).—A solution of 2.8 g (25.5 mmol) of 2-diazocyclopentanone[7] and 3.7 g (26.0 mmol) of DMAD in 70 ml of ether was warmed to boiling and then allowed to stand at ambient temperatures for 72 hr. The crystalline product (5.5 g, 86%) was separated and washed with a little ether: mp 108–110°; ir 1739 cm^{-1} (broad, C=O); nmr δ 2.28 (m, 2 H), 2.95 (t, 2 H, J = 6.25 Hz), 3.29 (t, 2 H, J = 6.25 Hz), 3.87 (s, 3 H), 3.94 (s, 3 H); uv 240 nm (ε 8200); mass spectrum *m/e* 252 (M^+).

Anal. Calcd for $C_{11}H_{12}N_2O_5$: C, 52.38; H, 4.80; N, 11.11. Found: C, 52.17; H, 5.02; N, 10.96.

Registry No.—**1**, 37387-70-5; **2a**, 37387-71-6; **2b**, 37387-72-7; **3**, 37387-73-8; **5**, 37387-74-9; 2-diazo-3-butanone, 14088-58-5; 2-diazocyclopentanone, 14088-61-0; dimethyl acetylenedicarboxylate, 762-42-5.

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[7] M. Regitz and J. Rüter, *Chem. Ber.*, **101**, 1263 (1968).

[8] Note Added in Proof.—Additional examples of the reactions of acetylenes with five-membered ring α-diazo ketones have recently been described by T. Yamazaki and H. Shechter, *Tetrahedron Lett.*, 4533 (1972).

Sulfur–Oxygen Bond Cleavage in the Condensation of Cinnamyl Tosylate with Carbonium Ions

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The enormous utility of tosyl esters as substrates in nucleophilic substitution reactions arises from the extreme readiness with which the tosyl residue departs as an anion, after cleavage of the C–O bond. Cleavage of the S–O bond in tosylates has been reported, but only in special cases, as for example during electrolytic reduction,[1] or where the tosylate carbon atom is not susceptible to nucleophilic attack for steric or other reasons,[2] or where loss of the tosylate anion would lead

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[1] P. Yousefzadeh and C. K. Mann, *J. Org. Chem.*, **33**, 2716 (1968).

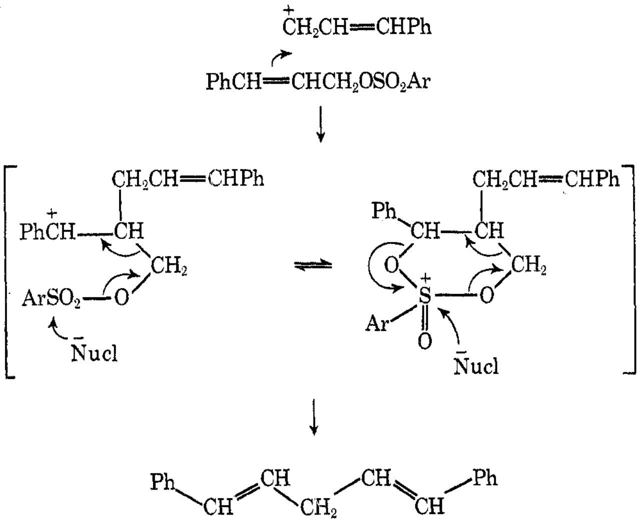
[2] (a) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 1371 (1949); (b) H. M. Walborsky, *ibid.*, **36**, 1251 (1953); (c) F. G. Bordwell, B. M. Pitt, and M. Knell, *J. Amer. Chem. Soc.*, **73**, 5004 (1951).

to an unstable carbonium ion, as in aryl tosylates.[3] Even then, attack on the sulfur atom requires the use of powerful nucleophiles. We wish to report a condensation reaction of cinnamyl tosylate which proceeds under very mild conditions, and which appears to involve an unusual S–O bond cleavage with loss of formaldehyde in the tosylate intermediate.

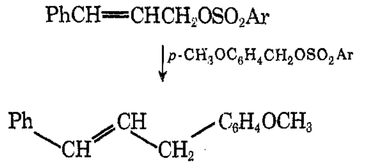
The tosyl ester of *trans*-cinnamyl alcohol may be isolated as a white, crystalline solid, but it decomposes within minutes at room temperature to a red oil.[4,5] A freshly prepared solution of it, prepared *in situ* by treating cinnamyl alcohol in ether with sodium hydride followed by tosyl chloride, was heated under reflux for 6 hr. Chromatographic separation of the products afforded dicinnamyl ether, cinnamyl alcohol, cinnamyl chloride, and some unreacted tosyl chloride, together with a nonpolar polymeric material. In addition, however, an unsaturated hydrocarbon, *trans,trans*-1,5-diphenylpenta-1,4-diene (I), was obtained in 20% yield. Its structure was shown by ir, uv, and nmr spectroscopy, by its mass spectrum, by hydrogenation to 1,5-diphenylpentane, and by comparison of it with an authentic sample of the diene prepared[6] by the Wittig reaction of 1,3-di(triphenylphosphonium)propane dibromide with benzaldehyde.

Formation of 1,5-diphenylpenta-1,4-diene (I) in this reaction may be explained by an initial condensation of a cinnamyl cation with the double bond of a molecule of cinnamyl tosylate. Decomposition of the resulting intermediate by S–O bond cleavage and elimination of a molecule of formaldehyde would yield diene I. This decomposition could be concerted, as shown, or could proceed by initial cleavage to give the cationic species $ArSO_2O{=}CH_2^+$, which could then lose formaldehyde. To test this mechanism, a carbonium ion incapable of self-condensation was generated in the presence of cinnamyl tosylate. Thus a cooled ethereal solution of the highly unstable tosylate[5] of *p*-methoxybenzyl alcohol was added to an ethereal solution of cinnamyl tosylate and the mixture was allowed to warm up to room temperature. Among other products, the expected condensation product *trans*-1-*p*-methoxyphenyl-3-phenylprop-2-ene (II) was isolated.

To show that these condensation products are not formed by reaction between the carbonium ion and cinnamyl alcohol, *p*-methoxybenzyl tosylate in ether solution was treated with cinnamyl alcohol. No 1-*p*-methoxyphenyl-3-phenylprop-2-ene (II) was obtained. Furthermore, when cinnamyl cations were generated by acid catalysis from cinnamyl alcohol in the presence of excess cinnamyl alcohol, we found that dicinnamyl ether was formed as previously reported[7] but no 1,5-diphenylpenta-1,4-diene (I) could be detected. This latter experiment also suggests that the condensation is not between cinnamyl cation and dicinnamyl ether. A related reaction mechanism has recently been suggested[8] for the decomposition of the tosylate of a β-hydroxy ketone system, involving cleavage of an S–O bond with subsequent loss of formaldehyde.



I



II

Experimental Section[9]

***trans,trans*-1,5-Diphenylpenta-1,4-diene** (I).—A solution of *trans*-cinnamyl *p*-toluenesulfonate in superdry ether (50 ml) at −70° was prepared *in situ* from cinnamyl alcohol (5.0 g) as previously described.[5] It was allowed to warm to room temperature and was then refluxed for 6 hr. The solution was diluted with ether, washed (H_2O), dried ($MgSO_4$), and evaporated, and the resulting black oil was chromatographed on a column of silica gel. Elution with ether:light petroleum (1:9) gave the diene I (0.68 g): bp 170° (0.5 mm) [lit.[6a] bp 205–211° (12 mm)]; uv max (EtOH) 208 nm (log ε 5.85), 259 (5.53), 279 (3.83), 293 (3.67), and 311 (3.25) [lit.[6b] 260 (5.39), 312 (3.25)]; ir (neat) 1642 (C=C), 1600, 1580, 1495 (Ph), and 965 cm^{-1} (CH=CH trans) (lit.[6b] ir 965 cm^{-1}); nmr (CCl_4) 2.81 (s, 10), 3.74 (m, 4), and 6.91 (br t, 2); mass spectrum (70 eV) *m/e* (rel intensity) 220 (37) M^+, 129 (100), 115 (80), 91 (78), 77 (48), and 51 (48). Also isolated from the column were a polymeric hydrocarbon material (0.05 g) (*Anal.* Found: C, 86.3; H, 14.2.), cinnamyl chloride (0.28 g), dicinnamyl ether (0.72 g), cinnamyl alcohol (0.60 g), and *p*-toluenesulfonyl chloride (0.70 g).

Hydrogenation of diene I in ethyl acetate over palladium on charcoal gave 1,5-diphenylpentane:[6a] nmr (CCl_4) 2.91 (s, 10), 7.50 (m, 4), 8.2–8.6 (m, 6); mass spectrum (70 eV) *m/e* (rel intensity) 224 (5) M^+, 154 (22), 91 (100), 65 (26); ir identical with that previously reported.[10]

***trans*-1-*p*-Methoxyphenyl-3-phenylprop-2-ene** (II).—Cooled (−70°), ethereal solutions of *trans*-cinnamyl *p*-toluenesulfonate (from 10 g of alcohol) and of *p*-methoxybenzyl *p*-toluenesulfonate[5] (from 10 g of alcohol) were mixed and allowed to warm to

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[3] (a) J. F. Bunnett and J. Y. Bassett, Jr., *J. Org. Chem.*, **27**, 2345, 1887 (1962); (b) C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1872 (1951).

[4] O. A. Prib, L. V. Glushkova, and R. V. Sendega, *Ukr. Khim. Zh.*, **34**, 497 (1968).

[5] P. H. Boyle, J. H. Coy, and H. N. Dobbs, *J. Chem. Soc., Perkin Trans. 1*, 1617 (1972).

[6] (a) G. Wittig, H. Eggers, and P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 10 (1958); (b) S. Brenner and J. Klein, *Israel J. Chem.*, **7**, 735 (1969).

[7] M. G. J. Beets and H. van Essen, *Recl. Trav. Chim. Pays-Bas*, **74**, 98 (1955).

[8] F. Nerdel, D. Frank, W. Metasch, K. Gerner, and H. Marschall, *Tetrahedron*, **26**, 1589 (1970).

[9] Uv spectra were measured on a Unicam S. P. 800 recording spectrophotometer, ir spectra on a Perkin-Elmer 157 spectrophotometer, and nmr spectra on a Perkin-Elmer R.10 instrument. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-4 mass spectrometer. Light petroleum refers to the fraction of bp 40–60°.

[10] E. Kuss and P. Pollmann, Collection of the Institute for Petroleum Research, Hanover, ir card no. 16496.

room temperature. After standing for 6 hr the mixture was diluted with ether, washed (H_2O), dried ($MgSO_4$), and evaporated to give a black oil, which when chromatographed on silica (300 g), eluting with ether:light petroleum (1:9), gave the alkene II[11] (0.46 g): mass spectrum (70 eV) *m/e* (rel intensity) 224 (100) M^+, 209 (47), 193 (64), 115 (100), 91 (54), and 77 (42); uv, ir, and nmr spectral values correspond with those reported in the literature.[12] Also isolated from the column were the same polymeric hydrocarbon as mentioned previously (0.80 g), *p*-toluenesulfonyl chloride (1.3 g), di-*p*-methoxybenzyl ether (0.74 g), dicinnamyl ether (0.60 g), *p*-methoxybenzyl cinnamyl ether (1.00 g), cinnamyl alcohol (0.66 g), and *p*-methoxybenzyl alcohol (0.50 g).

Registry No.—I, 26057-48-7; II, 35856-80-5; *trans*-cinnamyl *p*-toluenesulfonate, 37611-16-8; *p*-methoxybenzyl *p*-toluenesulfonate, 14670-03-2.

Acknowledgment.—We are grateful to the Irish Government Department of Education for support of this work.

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(11) C. S. J. Rondestvedt, Jr., *J. Amer. Chem. Soc.*, **73**, 4509 (1951).

(12) T. Hase, *Acta Chem. Scand.*, **23**, 2403 (1969).

Anhydrous Hydrofluoric Acid as a Cyclizing Agent in the Preparation of Several Substituted Oxazoles from *N*-Aroyl-α-amino Ketones[1a]

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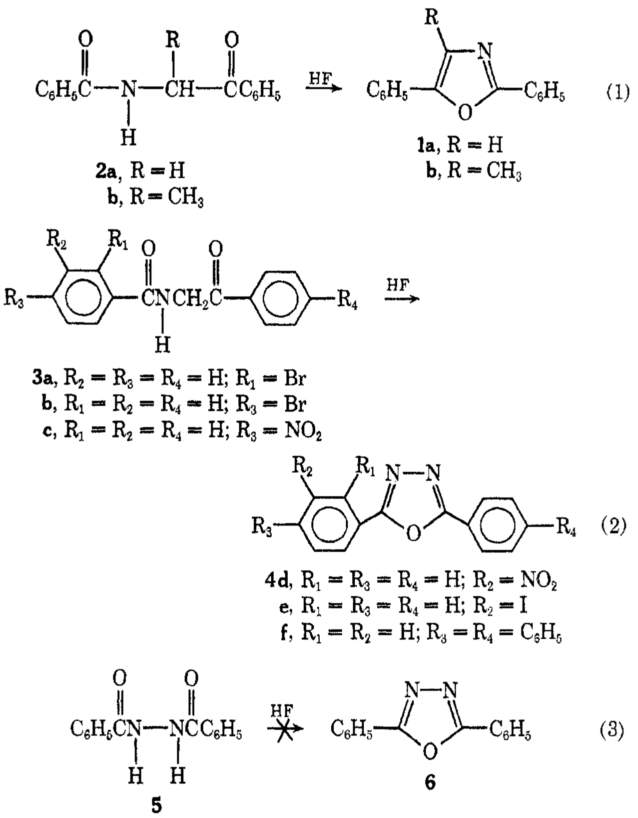
In the course of our studies of the photooxidation of 2,5-diphenyloxazole (PPO) (**1a**) it was necessary to prepare 4-methyl-2,5-diphenyloxazole (**1b**).[2] Attempts to cyclize α-benzamidopropiophenone (**2b**) to **1b** (Scheme I, eq 1) with concentrated sulfuric acid in accordance with the procedure given by Cleland and Nieman[3] gave a maximum yield of 12.5% of the desired product. Consequently, it was decided to try anhydrous hydrofluoric acid as a condensing agent in this reaction, and a 95% yield of the oxazole **1b** was isolated.

The customary condensing agents used by Hayes and coworkers[4] in the preparation of oxazoles from the corresponding *N*-aroyl-α-amino ketones were phosphorus oxychloride or concentrated sulfuric acid and the recorded yields generally ranged from 50 to 80%. In another paper[5] we reported yields of 39–62% of 2,5-diaryloxazoles when phosphorus oxychloride was used as a cyclizing agent. The nearly quantitative yield of 4-methyl-2,5-diphenyloxazole (**1b**) obtained when anhydrous hydrofluoric acid was used led to a study of the general efficiency of the acid in condensations of this type.

SCHEME I



Anhydrous hydrofluoric acid was used for the cyclization of α-benzamidoacetophenone (**2a**), α-(2-bromobenzamido)acetophenone (**3a**), α-(4-bromobenzamido)acetophenone (**3b**), α-(4-nitrobenzamido)acetophenone (**3c**), α-(3-nitrobenzamido)acetophenone (**3d**), α-(3-iodobenzamido)acetophenone (**3e**), and 2-aza-1,4-di(4-biphenylyl)-1,4-butanedione (**3f**) to the corresponding oxazoles, **1a** and **4a–f** (Scheme I, Table I).

TABLE I

CYCLIZATION OF *N*-AROYL-α-AMINO KETONES TO OXAZOLES

Substrate	Product	Yield,[a] %
α-Benzamidopropiophenone (**2b**)	4-Methyl-2,5-diphenyloxazole (**1b**)	95
α-Benzamidoacetophenone (**2a**)	2,5-diphenyloxazole (**1a**)	91[b]
α-(2-Bromobenzamido)-acetophenone (**3a**)	2-(2-Bromophenyl)-5-phenyloxazole (**4a**)	61[c]
α-(4-Bromobenzamido)-acetophenone (**3b**)	2-(4-Bromophenyl)-5-phenyloxazole (**4b**)	62
α-(4-Nitrobenzamido)-acetophenone (**3c**)	2-(4-Nitrophenyl)-5-phenyloxazole (**4c**)	Trace
α-(3-Nitrobenzamido)-acetophenone (**3d**)	2-(3-Nitrophenyl)-5-phenyloxazole (**4d**)	64
α-(3-Iodobenzamido)-acetophenone (**3e**)	2-(3-Iodophenyl)-5-phenyloxazole (**4e**)	79
2-Aza-1,4-di(4-biphenylyl)-1,4-butanedione (**3f**)	2,5-Di(4-biphenylyl) oxazole (**4f**)	96[d]
1,2-Dibenzoylhydrazine (**5**)	2,5-Diphenyloxadiazole (**6**)	0[e]

[a] In all cases the yield reported is of crystallized product (or crude product) having a melting point corresponding to that of pure material reported in the literature. [b] Using sulfuric acid yields of 53–81% are obtained. [c] Treated with two portions of HF. [d] Using phosphorus oxychloride the yield was 51%. [e] Using phosphorus oxychloride the yield was 55%.

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(1) (a) From the Ph.D. dissertation of Margaret E. Ackerman (1971). This investigation was supported in part by a research grant from the Division of Biology and Medicine of the U. S. Atomic Energy Commission, Contract No. AT (29-2) 915. (b) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) We are indebted to Arapahoe Chemicals, Inc., for their generous gift of 100 g of the α-benzamidopropiophenone for use in this synthesis.

(3) G. H. Cleland and C. Niemann, *J. Amer. Chem. Soc.*, **71**, 841 (1949).

(4) F. N. Hayes, B. S. Rogers, and D. G. Ott, *ibid.*, **77**, 1850 (1955).

(5) M. D. Barnett, G. H. Daub, F. N. Hayes, and D. G. Ott, *ibid.*, **82**, 2282 (1960).