

The Syntheses of Ethoxycarbonyl-1,3-dioxoles and Oxazoles from the Copper Catalyzed Thermolysis of Ethyl Diazopyruvate in the Presence of Ketones, Aldehydes and Nitriles

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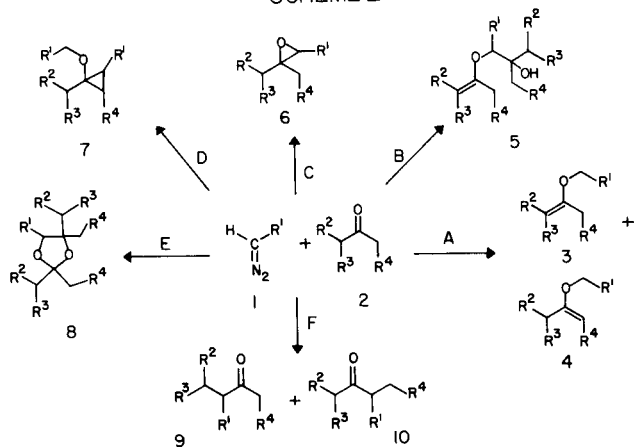
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The copper salt-catalyzed interaction of ethyl diazopyruvate with ketones, aldehydes and nitriles was examined. A variety of 1,3-dioxoles and oxazoles was obtained in moderate yield. The formation of enol ethers, epoxides, carbon-carbon insertion products, aziridines, and azetidines, typical products of carbene reactions with carbon-heteroatom multiple bonds, was not observed. Evidence for the operation of a 1,3-dipolar cycloaddition reaction is presented.

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The thermal transition metal catalyzed interaction of diazo compounds with carbonyl systems has been an attractive subject of investigation since Buchner and Curtius (1) first described the formation of ethyl 3-oxo-3-phenylpropionate from ethyl diazoacetate and benzaldehyde. In recent decades the reactions between diazomethane and ketones (2-4), and the interaction of alkyl diazoacetates with aldehydes (4-10) and ketones (9-16) have been thoroughly investigated. The synthetic use of this reaction, however, is often rendered unattractive because it furnishes poor yields and a variety of products (17). In Scheme I are collected the various typical adducts obtained from these transformations besides the aldol condensation products in which the diazo synthon is preserved (18). Yet, two workers (11,16) describe, among other products, the formation of enol ethers **3** and **4** in synthetically interesting yields (24-60%) (see Table I).

SCHEME I

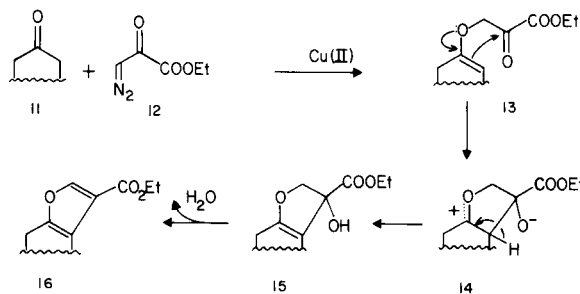


It was thought that glycolic ester (**4**) or some derivative thereof could conceivably be an intermediate *en route* to 3-substituted furans, if the enol ether moiety could be made to react in an intramolecular fashion with a strongly electrophilic carbonyl in the ester portion of the com-

pound, thus furnishing the required carbon-carbon bond. This, followed by electron reorganization in the five membered ring thereby produced and water elimination, would provide direct access to the desired heterocycle.

The thermal stability displayed by **4** (16) discouraged the use of ethyl diazoacetate and led us to explore other diazoesters that would supply a much more electrophilic carbonyl *en lieu* of the poorly polarized ester. This condition appeared to be met by the α -dicarbonyl group of ethyl diazopyruvate (**12**) (EDP) (19), which in principle would be capable of furnishing a 3-ethoxycarbonyl furan derivative (**16**), a family of compounds of difficult access, by way of the sequence portrayed in Scheme II.


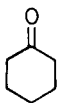
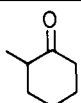

SCHEME II

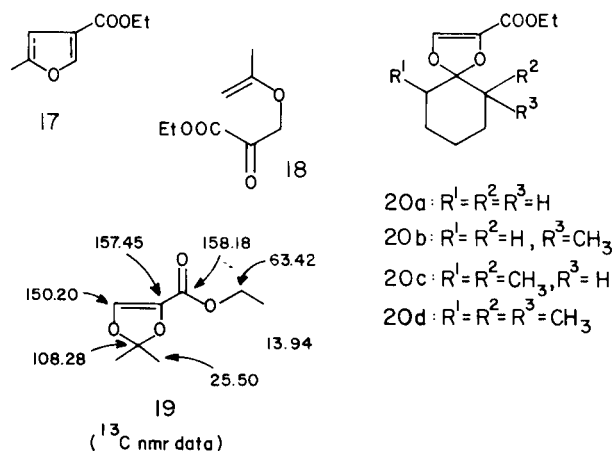
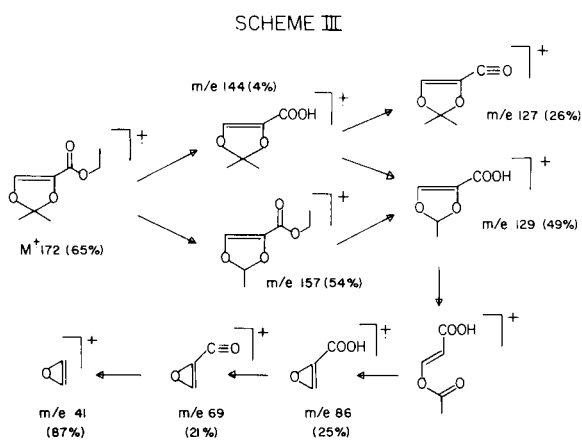


To this end the *bis*-copper(II) acetylacetonate catalyzed decomposition of EDP in the presence of a five mole excess of acetone in benzene was examined. A 55% yield of a single distillable material showing ir 1730 and 1640 cm^{-1} and nmr signals at δ 1.30 (t, 3H), 1.58 (s, 6H), 4.18 (q, 2H), and 6.86 (s, 1H) ppm was obtained. The lack of a second vinyl proton, an integration of six protons at 1.58 ppm and a molecular weight of 172 ruled out the formation of the expected furan nucleus (**17**) or enol ether (**18**). The carbon-13 nmr data and the fragmentation pattern shown

TABLE I

REACTION PRODUCTS FROM THE COPPER CATALYZED INTERACTION OF ETHYL DIAZOACETATE AND KETONES.

ENTRY	REF	SUBSTRATE	CATALYST	SUBSTITUENTS				PRODUCTS / YIELDS (%)				
				R ¹	R ²	R ³	R ⁴	3	4	5	7	8
1	11		Cu ⁰	COOEt	H	H	H	24		5	23	4
2	11		Cu ⁰	COOEt	H	-(CH ₂) ₃		43		16	1	4
3	16		CuCl	COOEt	H			57		—	—	—
4	16		CuCl	COOEt	CH ₃			5	60		—	—
5	16		CuCl	COOEt	CH ₃	CH ₃	H	—	38		—	—



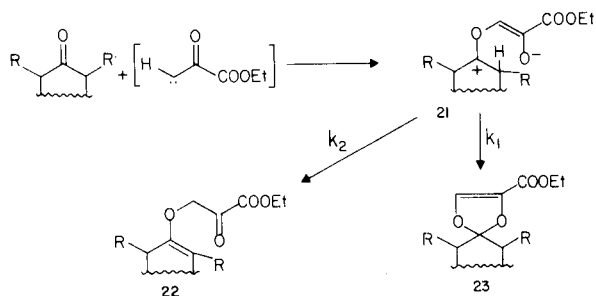
20a: R¹=R²=R³=H
 20b: R¹=R²=H, R³=CH₃
 20c: R¹=R²=CH₃, R³=H
 20d: R¹=R²=R³=CH₃

in Scheme III (20) best accommodate for ethyl 2,2-dimethyl-1,3-dioxole-4-carboxylate (19) as the most probable structure. Analogously, cyclohexanone gave 1,3-dioxole (20a) in 48% yield on exposure to the EDP-derived copper carbenoid.

If the mechanism proposed by Kharasch (11) is correct, namely that the copper carbenoid is first bonded to the oxygen atom to give carbonyl ylide (21) (Scheme IV), one would expect a favorable enol ether formation on thermodynamic grounds with increasing substitution of the α -carbon of the starting ketone. In addition, the increased

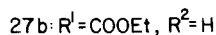
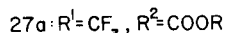
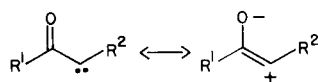
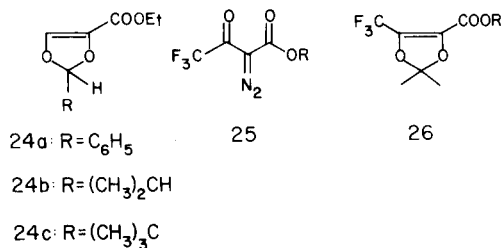
steric bulk of the substrate should retard the rate of cyclization of the intermediate zwitterion appreciably enough (21) making $k_2 > k_1$. The reaction of EDP with 2-methylcyclohexanone was thus looked upon. Again, however, only dioxole (20b) was isolated (48%) as a diastomeric mixture. Further, 2,6-dimethylcyclohexanone and 2,2,6-trimethylcyclohexanone gave only dioxole derivatives (20c) and (20d) respectively, on exposure to EDP under copper salt catalysis (22). The low yields recorded were probably the consequence of an increasing steric interference of proliferating substituents in the substrate.

SCHEME IV



Aliphatic and aromatic aldehydes reacted with EDP in a similar fashion, furnishing dioxoles (**24a-c**) in satisfactory yields. Notably, no Wagner-Meerwein rearrangement products expected from the development of a low electron density center at the carbonyl carbon were detected in the crude reaction mixtures of **20d** and **24c**, thus casting doubt on the existence of a truly zwitterionic intermediate in this sort of cycloaddition. It is also noteworthy that the **3-10** type adducts were not observed in any of the EDP additions studied indicating that dioxole production is the most favorable process of the several ones involved.

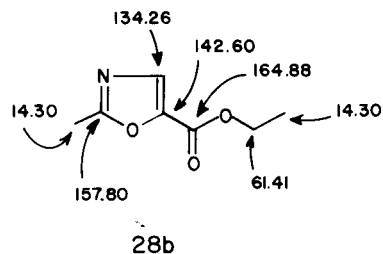
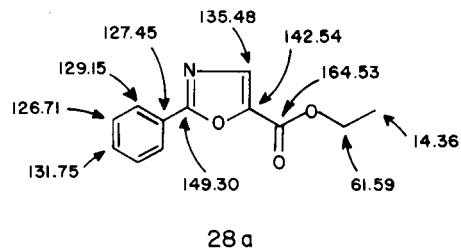
To our knowledge only one example of dioxole production from a diazocarbonyl derivative and a ketone has been reported previously (12,14). It involves the photo-induced interaction of ethyl 4-trifluoro-2-diazo-3-oxobutylate (**25**) with acetone. This compound shares with EDP the fact that both may in principle lead to stabilized 1,3-dipoles *via* delocalization of the carbene or metal carbenoid intermediate, due to the strong electron withdrawing power of the respective vicinal carbonyl units. Therefore, the operation of a genuine 1,3-dipolar cycloaddition (23) to account for the production of dioxole from some ketocarbenes is particularly appealing at this point.



Our original intentions were therefore stymied, although these efforts have led to an efficient synthesis of the little known 1,3-dioxole-4-carboxylates. In view of this

prior art it was deemed worth investigating further the interaction of EDP with other carbon-heteroatom multiple bonds.

On the one hand, addition of EDP to benzonitrile under copper catalysis led to a 52% yield of ethyl 2-phenyl-oxazole-5-carboxylate (**28a**) as the only tractable product. Thus, the nmr spectrum showed a singlet at δ 7.78 (1H) assigned to the olefinic proton which appears at such a low field because of its being β to the ester group; further, a quartet and a triplet at 4.38 (2H) and 1.39 (3H) ppm, respectively, which are characteristic of the ethoxycarbonyl synthon, and the aromatic protons grouped in two multiplets at 7.50 and 8.20 ppm were detected. The mass spectrum showed a molecular ion peak (73%) at *m/e* 217 and a base peak at *m/e* 144 due to the loss of the ester grouping (24). A similar reaction performed with acetonitrile furnished, not surprisingly, 2-methyl oxazole derivative (**28b**) (35%). The carbon-13 nmr data indicated below secured the proposed structures of **28a** and **28b**.

¹³C NMR DATA

Oxazoles have also been reported in the photochemical and metal catalyzed reaction of ethyl diazoacetate (23,25-28), diazomalonnate and diazomalonanilate (27) with nitriles, presumably with the participation of 1,3-dipoles (27-30), although the mechanism issue is far from settled (30). Oxazoles, however, are accompanied by azetidines, and the products ratio appears to be dependent on the catalyst and reaction conditions used (30), a phenomenon not recorded during EDP cycloadditions to nitriles.

EXPERIMENTAL

Infrared spectra were measured on a Perkin-Elmer 337 spectrophotometer. Nmr spectra were obtained from a Varian Associates

EM-390 spectrometer operating at 90 MHz, using tetramethylsilane as internal standard and in carbon tetrachloride solutions unless otherwise stated. Carbon-13 nmr spectra were measured in a Bruker WP-60 instrument operating at 15.03 MHz, using tetramethylsilane as internal standard in deuteriochloroform solutions and a deuterium lock. Mass spectra were obtained from a DuPont 21-492 instrument (32). The experimental conditions described furnish maximum yields of adducts. Ethyl diazopyruvate was prepared as reported earlier (19) and purified by sublimation at ca. 70° (2 torr). Elemental analyses were performed by Dr. H. Malissa and G. Reuter in Germany.

Ethyl 2,2-Dimethyl-1,3-dioxole-4-carboxylate (19)

Ethyl diazopyruvate (1.5 g., 10.6 mole) dissolved in anhydrous benzene (20 ml.) was added dropwise over a four-hour period to a stirred suspension of *bis*-copper acetylacetonate (II) (4 mg.) in benzene (2 ml.) and 3.0 g. (52 mmoles) of anhydrous acetone, at reflux temperature under a nitrogen atmosphere. After the addition was complete, heating was continued for an additional one half-hour period. The cold reaction mixture was filtered through a pad of neutral alumina activity IV and solvents evaporated. The remaining tar was distilled under vacuum to give 1.0 g. of pure dioxole (19), b.p. 65-68°/3 torr; ir (neat): 1720 (s), 1650 (s) cm^{-1} ; uv (acetonitrile): λ max 277 ($\epsilon = 7200$) nm; nmr (deuteriochloroform): δ 1.30 (t, 3H, J = 7.0 Hz), 1.58 (s, 6H, methyls), 4.18 (q, 2H, J = 7.0 Hz), 6.86 (s, 1H) ppm.

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{O}_4$: C, 55.79; H, 7.03; O, 37.18. Found: C, 55.69; H, 7.09; O, 37.26.

3'-Ethoxycarbonyl- $\Delta^{3',4'}-2',5'$ -dioxaspiro[5,4]decane (20a)

This compound was prepared from cyclohexanone and ethyl diazopyruvate by the method described for 19. From 1.5 g. of EDP 1.08 g. (48%) of 20a was obtained as a colorless oil, b.p. 110° (bath)/0.5 torr; ir (neat): ν max 1720 (s), 1650 (s) cm^{-1} ; nmr: δ 1.28 (t, 3H, J = 7.0 Hz, CH_3CH_2), 1.40-1.90 (m, 10H, 5 \times CH_2), 4.18 (q, 2H, J = 7.0 Hz, CH_3CH_2), 6.99 (s, 1H) ppm; ms: m/e (%) 212 (56) (M^+), 169 (100) ($\text{C}_6\text{H}_8\text{O}_2$), 167 (21) ($\text{M}^+\text{OC}_2\text{H}_5$).

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_4$: C, 62.23; H, 7.60; O, 30.16. Found: C, 62.05; H, 7.67; O, 30.26.

3'-Ethoxycarbonyl- $\Delta^{3',4'}-2$ -methyl-2',5'-dioxaspiro[5,4]decane (20b)

This product was prepared as above from 2-methylcyclohexanone (4 g.) and ethyl diazopyruvate (1.5 g.); 0.490 g. (47.5%) of 20b was isolated by vacuum distillation, b.p. 130-135° (bath)/0.5 torr; ir (neat): ν max 1730 (s), 1650 (s) cm^{-1} ; nmr: δ 0.93 (d, 3H, J = 6 Hz, $\text{CH}_3\text{-CH}$), 1.26 (t, 3H, J = 7.0 Hz, CH_3CH_2), 4.16 (q, 2H, J = 7.0 Hz, CH_3CH_2), 6.96 (s, 1H) ppm; ms: m/e 226 (87) (M^+), 197 (9) ($\text{M}^+\text{-C}_2\text{H}_5$), 181 (7) ($\text{M}^+\text{-ethoxy}$), 95 (100).

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_4$: C, 63.68; H, 8.02; O, 28.29. Found: C, 63.60; H, 8.06; O, 28.33.

3'-Ethoxycarbonyl- $\Delta^{3',4'}-2,5$ -dimethyl-2',5'-dioxaspiro[5,4]decane (20c)

This compound was prepared as above from 2,6-dimethylcyclohexanone (1.5 g.) and ethyl diazopyruvate (1.0 g.); the crude material was distilled under reduced pressure yielding 0.645 g. of a mixture of desired dioxol and the starting ketone. Purification was accomplished by preparative (hexane) thin layer chromatography; yielding 0.497 g. (30%) of pure dioxol (20c), b.p. 95-100° (bath)/0.25 torr; ir (neat): ν max 1730 (s), 1650 (s) cm^{-1} ; nmr: δ 0.95 (d, 6H, J = 6.5 Hz, 2 \times CH_3CH), 1.28 (t, 3H, J = 7 Hz, CH_3CH_2), 4.18 (q, 2H, J = 7 Hz, CH_3CH_2), 6.99 (s, 1H) ppm.

Anal. Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_4$: C, 64.96; H, 8.39; O, 26.64. Found: C, 64.79; H, 8.43; O, 26.71.

Ethyl 2-Phenyl-1,3-dioxole-4-carboxylate (24a)

This product was obtained as above from ethyl diazopyruvate (1.42 g.) and freshly distilled benzaldehyde (1.16 g.) previously washed with 10% aqueous sodium carbonate, in benzene and *bis*-copper(II) acetylacetonate (4 mg.) as catalyst, at 80°. After removal of the catalyst, the crude product was distilled under vacuum, yielding 0.728 g. (47%) of pure dioxol, (24a) as a pale yellow oil; b.p. 120-123°/0.2 torr; ir (neat): ν max 1720 (s),

1640 (s), 1140 (s), 1010 (s), 965 (s), 745 (s), 693 (s) cm^{-1} ; nmr: δ 1.28 (t, 3H, J = 7 Hz, CH_3), 4.22 (q, 2H, J = 7 Hz, CH_2), 6.80 (s, 1H, benzylic methyne), 7.10 (s, 1H, vinyl proton), 7.43 (m, 5H, aromatic protons) ppm.

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_4$: C, 65.43; H, 5.50; O, 29.07. Found: C, 65.50; H, 5.51; O, 29.02.

Compound 24a was found to decompose back to benzaldehyde and polymeric material when exposed to alumina or silica gel.

Ethyl 2-Isopropyl-1,3-dioxole-4-carboxylate (24b)

This compound was obtained as described above from ethyl diazopyruvate (1.065 g.) and freshly distilled isobutyraldehyde (3.9 g.) in refluxing benzene, using *bis*-copper(II) acetylacetonate (4 mg.) as catalyst. Compound 24b was isolated by vacuum distillation as a colorless oil (0.560 g., 41%), b.p. 85-90° (bath)/0.05 torr; ir (neat): ν max 1735 (s), 1640 (s), 1150 (s), 955 (s), 750 (s) cm^{-1} ; nmr: δ 1.05 (d, 6H, J = 7.5 Hz, $(\text{CH}_3)_2\text{CH}$), 1.30 (t, 3H, J = 7.0 Hz, CH_3CH_2), 2.10 (seven doublets, 1H, J₁ = 7.5, J₂ = 4.0 Hz, $(\text{CH}_3)_2\text{CH}$), 4.19 (q, 2H, J^s 7.0 Hz, CH_3CH_2), 5.69 (s, 1H, J = 4.0 Hz, CH-O), 6.99 (s, 1H, HC=) ppm.

Anal. Calcd. for $\text{C}_9\text{H}_{14}\text{O}_4$: C, 58.04; H, 7.58; O, 34.38. Found: C, 58.09; H, 7.60; O, 34.32.

Ethyl 2-*t*-Butyl-1,3-dioxole-4-carboxylate (24c)

This product was obtained as described above from ethyl diazopyruvate (1.21 g.) and 2,2-dimethylpropanol (1.60 g.) in refluxing benzene using *bis*-copper(II) acetylacetonate (4 mg.) as catalyst. Compound 24c was isolated from the crude reaction mixture by vacuum distillation as a colorless oil (0.346 g., 20%), b.p. 82-83°/0.30 torr; ir (neat): ν max 1720 (s), 1625 (s), 1330 (s), 1135 (s), 1030 (s), 956 (s), 745 (s) cm^{-1} ; nmr: δ 1.00 (s, 9H, $(\text{CH}_3)_3$), 1.28 (t, 3H, J = 7.0 Hz, CH_3CH_2), 4.18 (q, 2H, J = 7.0 Hz, CH_3CH_2), 5.53 (s, 1H, CHO), 6.80 (s, 1H, HC=) ppm.

Anal. Calcd. for $\text{C}_{10}\text{H}_{16}\text{O}_4$: C, 59.97; H, 8.06; O, 31.97. Found: C, 60.00; H, 8.06; O, 31.95.

Ethyl 2-Phenyloxazole-5-carboxylate (28a)

To a stirred suspension of *bis*-copper(II) acetylacetonate (4.5 mg.) in benzene (2 ml.) and benzonitrile (2.0 g.) at reflux temperature and under a nitrogen atmosphere, was added ethyl diazopyruvate (1.5 g.) in benzene (20 ml.) during a period of four hours. After the usual work-up, the crude reaction mixture was distilled under vacuum to remove excess benzonitrile and the residue was chromatographed through neutral alumina activity III. Elution with hexane-ether 6:1 gave 1.192 g. (52%) of crystalline material, m.p. (hexane) 56-57° identified as oxazole (28a) (31); ir (potassium bromide): ν max 1720 (s), 1315 (s), 1150 (s), 1025 (s), 800 (s), 712 (s) cm^{-1} ; nmr (deuteriochloroform): δ 1.40 (t, 3H, J = 7.0 Hz, CH_3CH_2), 4.38 (q, 2H, J = 7.0 Hz, CH_3CH_2), 7.50 (m, 3H, aromatic CH), 7.78 (s, 1H, CH=), 8.82 (m, 2H, aromatic CH) ppm; ms: m/e (%) 217 (73) (M^+), 189 (20) ($\text{M}^+\text{-C}_2\text{H}_5$, McLafferty), 172 (12) ($\text{M}^+\text{-OC}_2\text{H}_5$), 144 (100) ($\text{M}^+\text{-COOEt}$).

Anal. Calcd. for $\text{C}_{12}\text{H}_{11}\text{NO}_3$: C, 66.34; H, 5.11; N, 6.45; O, 22.11. Found: C, 66.40; H, 5.09; N, 6.40.

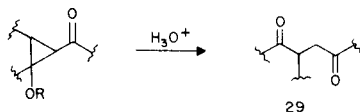
Ethyl 2-Methyloxazole-5-carboxylate (28b)

This compound was prepared as described for 28a from ethyl diazopyruvate (1.5 g.) and freshly distilled spectroscopic grade acetonitrile (5 g.). After a similar work-up procedure and evaporation of solvent, the tarry residue was passed through a column of neutral alumina activity III eluting with ether. The collected fractions were mixed, solvents evaporated and the clear residue distilled under vacuum, to yield 0.377 g. (23%) of pure 28b as a colorless oil; b.p. 75-80° (bath)/0.15 torr; ir (neat): ν max 1730 (s), 1550 (s), 1305 (s), 1145 (s), 1020 (s), 963 (s), 760 (s) cm^{-1} ; uv (acetonitrile): ν max 239 (ϵ 7150); nmr: δ 1.36 (t, 3H, J = 7.0 Hz, CH_3CH_2), 2.52 (s, 3H, CH_3), 4.30 (q, 2H, CH_3CH_2), 7.51 (s, 1H, HC=) ppm.

Anal. Calcd. for $\text{C}_7\text{H}_9\text{NO}_3$: C, 54.17; H, 5.85; N, 9.03; O, 30.95. Found: C, 54.22; H, 5.84; N, 9.09.

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was rediscovered years later, becoming the elegant and well known Julia-Wenkert synthesis of 1,4-diketones and γ -ketoesters, useful intermediates in the construction of five-membered rings. See, E. Wenkert, R. A. Mueller, E. J. Reardon, Jr., S. S. Sathe, D. J. Scharf, and G. Tosi, *J. Am. Chem. Soc.*, **92**, 7428 (1970) and references cited.

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(20) These decomposition pathways were confirmed by metastable ion analysis.

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which cycloaddition is overcome by "insertion" of the carbene yielding a α -trisubstituted ketone equivalent; M. E. Alonso and P. Jano, to be published elsewhere.

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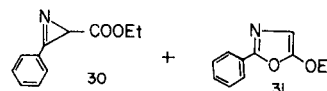
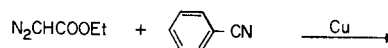
(26) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963).

(27) N. T. Buu and J. T. Edward, *Can. J. Chem.*, **50**, 3730 (1972).

(28) K. Kitatani, T. Hiyama and H. Nozaki, *Tetrahedron Letters*, 1531 (1974).

(29) Notably, in the copper catalyzed decomposition of ethyl diazoacetate in acrylonitrile addition occurred only at C=C bond and not at the nitrile. See, V. I. Ivanskii, I. A. D'Yakonov, and A. P. Kuleshov, *J. Org. Chem., USSR*, **7**, 2190 (1971). This result is in conflict with other observations (R. Paulissen and P. Teyssie, unpublished results).

(30) This is a subject of much debate. Komendantov and co-workers found that the copper-catalyzed reaction of ethyl diazoacetate with benzonitrile actually provided not only oxazole **31** but in addition a variable proportion of azetidine **30** depending on the type of catalyst used. They concluded that a triplet carbene is required for the



production of **31** whereas singlet carbenes yield **30** preferably. See, M. I. Komendantov, V. N. Novinskii and R. R. Bekminkhamentov, *J. Org. Chem. USSR*, **9**, 431 (1973).

(31) L. F. Zerilli, G. Tuan, G. Tarzia and G. G. Gallo, *Proc. Int. Symp. Gas Chromatogr., Mass Spectrom.*, **229** (1972); *Chem. Abstr.*, **78**, 92286j (1973).

(32) We thank Ms. Carmen Cabello for making the mass spectral measurements and Dr. Karl Döppert for the Carbon-13 nmr spectra.