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ON THE QUESTION OF FREE RADICAL INTERMEDIACY IN CYCLOADDITION REACTIONS OF DIAZOCARBONYL COMPOUNDS TO OLEFINS UNDER COPPER(II) CHELATE CATALYSIS.[1]

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The Copper(II) chelate catalyzed thermal cycloaddition of ethyl diazoacetate, dimethyl diazomalonate, ethyl-2-diazo-3-oxobutyrate, and ethyl diazopyruvate, representatives of diazocarbonyl additions that yield cyclopropanes and dihydrofurans, respectively, to olefins, has been examined in terms of the possible participation of radical species in intermediary stages. To this purpose, the title diazocarbonyl compounds were exposed to 1-methyl-1-cyclopropylethylene and 1,1-dicyclopropylethylene under catalytic conditions. The absence of cyclopropylcarbinyl radical to butenyl radical rearrangement products in cyclopropanations as well as in those reactions that furnish heterocycles suggests that intermediates of free radical nature may not be involved in the cycloaddition process. In turn, the strong electron donor capability of cyclopropyl substituents is interpreted as allusive of a non synchronous 1,3-dipolar cycloaddition of transient metal carbenes to the olefin with possible charge polarization.

The concertedness of singlet carbene additions has been scrutinized and proved many times in the past.[3] The experimental probes to reach this conclusion are based mainly on carbene selectivity[4] and stereospecificity[5] of additions to olefins. Their employment continues to be a lively scenario. However, shades of imperfection of this universal picture appear occasionally. A limited number of reports have suggested that these carbene additions may not necessarily take place via strictly synchronous mechanisms. These go as far as proposing either diradical[6] or zwitterionic[7] intermediates in some instances, in spite of the occurrence of stereospecific cycloadditions of the same carbenic species. This paradox has been explained in terms of a singlet triplet intersystem crossing[8,9] that allows a portion of the carbenes to react in a concerted fashion to give stereospecific addition while the rest interacts with the double bond to give the hypothetical diradical. However, Skell's rule of carbene stereospecificity is not devoid of criticism[5,10] and cannot be overemphasized to the point of using it to rule out any degree of non-concert.

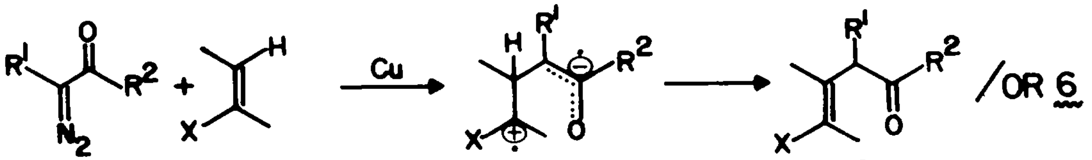
The mechanism picture is considerably more complex for those reactions where carbenes and carbenoids are generated by means of transition metal catalysis. Not only the actual identification of transient species is a difficult problem that still awaits clarification, but the diverse reaction modes of C-H insertion, cyclopropanation, addition-elimination and 1,3-dipolar cycloaddition make mechanistic generalizations more the consequence of sound intuition rather than theory at present.[11] Further, the interconversion of resulting 1:1 adducts introduces labyrinthine obstacles to the mechanistic interpretation.[12]

Not surprisingly, recent years have seen a wealth of proposals which base their claims on the classical regioselectivity [13] and stereospecificity qualifications of a given carbenoid-substrate system.[14] Great gaps exist in the accumulated knowledge of the reactions of diazocarbonyl compounds -as sources of putative metal carbenes- and alkenes under transition metal catalysis. In this concern, the question of concertedness is of central importance. It is to this topic that the present work is directed, in particular what touches the free radical character that might develop in the transition state of a potentially non-synchronous addition reaction.

Results and Discussion:

The extreme case in the spectrum of non-synchronous to synchronous additions of diazocarbonyl compounds to olefins is represented by those instances where only one C-C bond is constructed. This is the case of the formation of addition-elimination compounds such as 2. These are, in fact, the major reaction products of the copper catalyzed reaction of dimethyl diazomalonate (MDM) 1 with enol ethers (X= OR in 2).[15] Further, some cyclopropanations of electron-rich olefins might proceed in a stepwise fashion. This is suggested by the exclusive formation of cyclopropane 4 from enol ether 3 and MDM.[15] This probably occurs owing to the inability of putative intermediate 5 to evolve in the addition-elimination mode. Furthermore, products of formal 1,3-dipolar cycloaddition such as dihydrofuran 6 could result also[16] from a non-concerted construction of C-C and C-O bonds, as recent evidence from this laboratory has indicated.[17] Finally. allowance must be made for possible *in situ* interconversion of these 1:1 adducts. Indeed, in the structural and geometrical isomerization of cyclopropanes as well as the thermal rearrangement of cyclopropane ketones to dihydrofurans, diradicals are frequently invoqued as intermediates.[18]

A test for the presence of free radicals in the metal catalyzed cycloaddition of diazocarbonyl compounds to olefins, therefore, not only would provide evidence for the existence of such a structure in an intermediary stage between diazocompound and adducts, but also would bring about information as to the extent of interconversion of products by way of radical structures.



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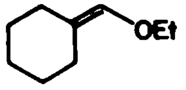
1a: $R^1 = H$, $R^2 = OEt$

1b: $R^1 = COOMe$, $R^2 = OMe$



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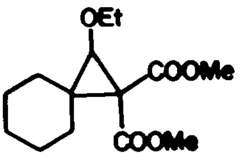

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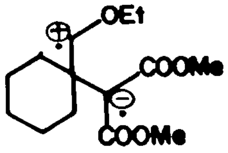

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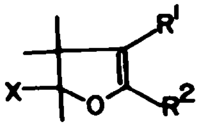
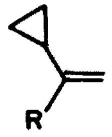


6

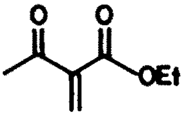
Wulfman and coworkers have postulated a number of possible structures of intermediates arising from non-synchronous reactions of diazocarbonyl compounds to olefins under copper catalysis.[19] Radical as well as zwitterionic species are suggested. However, no experimental evidence to prove this interesting scheme has appeared ever since. The existence of free radical intermediates has been explored by a number of methods. Within the realm of product analysis, cyclobutene,[20] dihaloethylenes,[21] and cyclopropyl ethylenes[22,23] have been used to detect these transient species with photochemically and thermally generated carbenes. However, there is a paucity of data regarding the transition metal catalyzed carbenoid formation and their reaction with free radical-sensitive olefinic substrates, besides our previous report in this connection.[24]

We have exposed 1-methyl-1-cyclopropylethylene 7a and 1,1-dicyclopropyl ethylene 7b to ethyl diazoacetate 1a, MDM 1b, ethyl 2-diazo-3-oxobutyrate 8, and ethyl diazopyruvate 9, under copper(II) chelate catalysis, and examined in detail the resulting products. The universe of addition-elimination, cyclopropanation, and formal 1,3-dipolar cycloaddition is represented in these reactions. The outcome of these experiments is now described:



7a: R=CH_3

7b: R=



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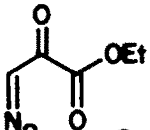

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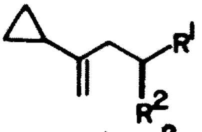


14a: R^1=H, R^2=COOEt

14b: R^1=R^2=COOMe

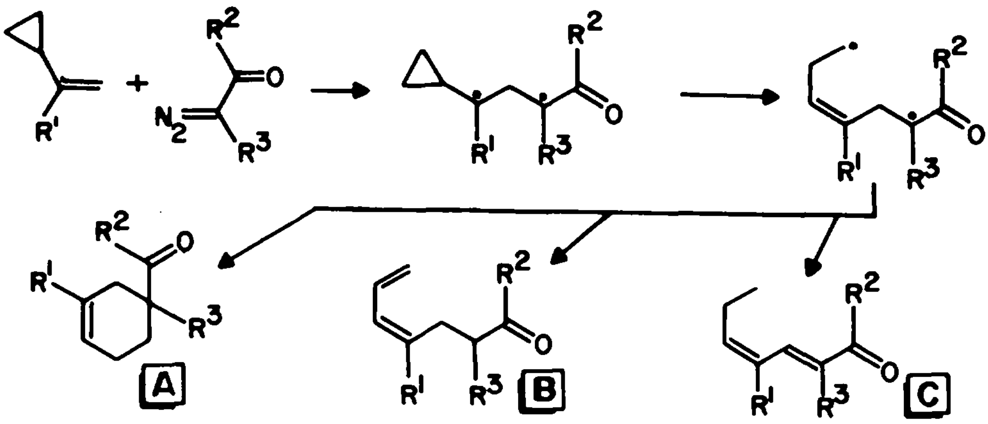
The bis(acetoacetonato)copper(II) catalyzed decomposition of ethyl diazoacetate with 7a and 7b in refluxing benzene gave the corresponding cyclopropyl derivatives 10 and 11 in 79 and 89% yield, respectively, as the only volatile adducts. Similarly, diazoester 1b gave adducts 12 and 13 in 79 and 95% yield, respectively. The results appear collected in table I (entries 1-4). Neither ethyl diazoacetate nor MDM afforded C-H insertion products 14a,b (<1%) in their addition to 7a. Their reaction was accompanied only by dimerization of intermediate carbenoids and small amounts of tarrish material. A free radical intermediate would be likely to evolve in the way indicated on Scheme I, whereby olefinic products A-C would be expected.[22] No trace of olefinic material could be detected, however. The yield of product 13 was found strongly dependent on the ratio of copper catalyst to diazocarbonyl compound, though adduct composition remained constant. The results are indicated in Figure I.

Then, our attention turned to other diazocarbonyl compounds with a grater chance for non-synchronous additions, by virtue of their electronic structure favoring the estabishment of a radical carbon in their vicinity. On the one hand, diazoöxobutyrate 8 reacts with polarizable alkenes to give formal 1,3-dipolar cycloaddition products of type 6[17]. In its reaction with benzo|B|furan and with 1-phenyl-1-methoxyethylene, addition-elimination products of type 2 appear also, thus suggesting a certain degree of non concert in the coupling reaction.[17]

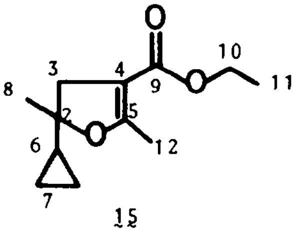
The bis(hexafluoroacetoacetonato)copper(II) assisted addition of 8 to 7a and 7b in fluorobenzene was thus examined. Only dihydrofuroic ester derivatives 15 and 16 were obtained in 44 and 86% yield, respectively (entries 5 and 6 of Table I). Their structures were secured on the basis of spectral data (see experimental) and ^{13}C-nmr spectra (see below). Products of cyclopropanation, addition-elimination, C-H insertion, and rearrangement in the mode indicated on Scheme I were absent within our limits of detection (2%).

On the other hand, ethyl diazopyruvate 9 was also deemed of interest since it furnishes dihydrofurans upon addition to electron rich alkenes.[16] The thermal

SCHEME I



decomposition of 9 catalyzed by bis(acetoacetonato)copper(II) in the presence of alkene 7b afforded only dihydrofuroic ester 17 as the only isolable product (59%). By contrast, olefinic adduct 19 accompanied the formation of 1,3-dipolar cycloadduct 18 in comparable quantity (1:2) in the reaction of 9 with 7a. Although 19 could be interpreted as an allylic C-H insertion product, there is also the possibility of an addition-elimination process preceeding it. In fact, in the various cyclopropanation and other reactions that have been examined in the past with compound 9,[25] no indication of a true C-H insertion was detected. Rather, the formation of seemingly C-H insertion compounds has been traced to the rearrangement -either 1,3- (addition-elimination) or 1,5-hydrogen transfer of a cyclopropyl derivative. It is likely, therefore, that 19 is the consequence of such a process. This statement carries within the suggestion that a cyclopropyl derivative precedes the formation of both 18 and 19, and possibly of 15 and 16 by way of a 1,3-sigmatropic rearrangement. Nothing would remain of the hypothetical trimethylene because of its inability to survive reaction conditions (refluxing benzene). However, the thermal fission of cyclopropanes has been attributed to trimethylene diradicals.[18] The absence of rearrangement products (Scheme I), consequently, precludes this possibility. This reinforces earlier conclusions on the independent origin of dihydrofurans from similar reaction processes.[17] Conversely, product 19 could be the consequence of ring fission of 18 followed by proton transfer. The control experiment of heating compound 18 under those conditions required for the thermocatalytic decomposition of 9, however, revealed its stability without trace of rearranged products.



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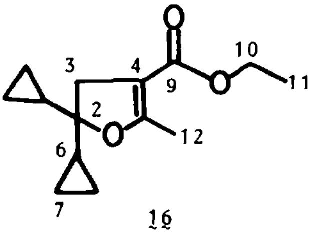

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^{13}C-NMR DATA:

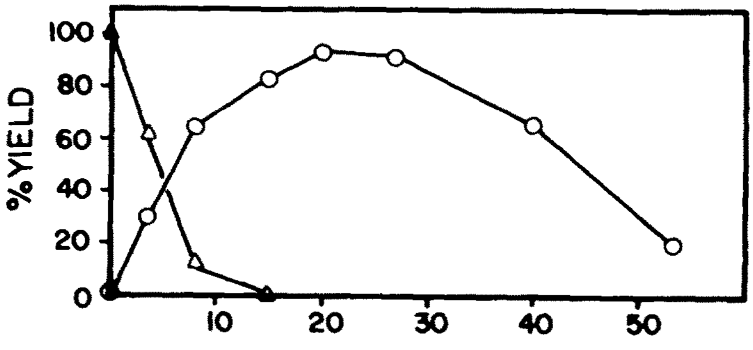
	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12
15:	87.5	40.5	101.3	166.5⁑	20.2	0.4	26.4	166.8⁑	59.3	14.2*	14.4*
16:	82.2	38.2	101.5	165.6⁑	19.0	0.4	--	166.7⁑	58.9	14.2	13.4

* and ⁑: These signals may be interchanged.

Mechanistic Considerations:

Although no direct evidence to support the existence of copper-carbene complexes has ever been produced, the hypothesis of metal carbene species mediating between diazocompound and cycloadduct in copper chelate catalyzed reactions may be assumed on the basis of homologation of the methylene transfer reactions recorder for the various Re, Mn, Fe, and W carbene complexes to olefins.[26] Also, recent evidence has portrayed a parallel behavior of $(CO)_5$WCHPhe and dirhodium tetraacetate catalyzed reactions of ethyl diazoacetate with several olefins.[27] Further, methylene transfer appears to occur in a non concerted fashion.[17b] Our recent proposition in this concern contends that the ketocarbenoid undergoes electrophilic attack by the olefin with initial formation of a C-C bond between the carbenic carbon and the alfa-carbon of the alkene. By alfa carbon is meant either the least substituted trigonal atom or that carbon in conjugation with electron donor substituents on the olefin e.g. methoxy. Conceptually similar, belabored models have appeared since,[27,28] which emphasize the distinctive role of the carbons alfa and beta of the alkene in determining the steric outcome of the cyclopropanation reaction. However, these models are not specific as to charge development or whether one electron transfer during the alkene-carbenoid interaction takes place prior to the alfa carbon-carbenic carbon bond consolidation. If this were the case, a free radical would be expected to develop at the beta carbon of the alkene. This is precisely the carbon atom that has been monitored through the present work. The failure to observe cyclopropyl carbinyl rearrangement indicates that one electron transfer is not involved in the coupling process, at least in the time domain of this reaction, 10^{-8} seconds. The formation of dihydrofurans from 8 and 9 proceeds also without rearrangement of the cyclopropyl fragment, making unlikely the participation of diradicals during the addition itself or a hypothetical rearrangement of a primary cyclopropane. The cyclopropanation behavior of 8 and 9 with other non polarizable hydrocarbon alkenes indicates that in 7a,b the cyclopropyl substituent acts as a potent donor of electron density,[29] comparable to the alkoxy group of alkyl vinyl ethers. It is conceivable, therefore, that the formation of dihydrofurans follows a reaction course with significant charge separation. This hypothesis is actively being investigated.

FIG. 1



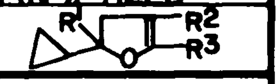
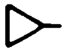
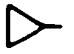
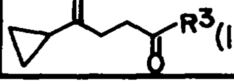
% Yield of 13 vs. catalyst to 1b molar ratio, Reaction of 1b+7b and bis-(acetoacetonato)copper(II) in benzene. Conditions: 24 hrs at 80°C. (○): yield of 13. (△): yield of recovered 1b.

Experimental Section:

Diazocompounds MDM and 8 were synthesized from the esters and tosyl azide.[30] Compounds 7a,b were obtained as reported [22] and ethyl diazopyruvate was synthesized as indicated before.[16c]

General method for the addition of diazocarbonyl compounds to cyclopropyl ethylenes

A mixture of freshly distilled diazocarbonyl compound (17 mmol) and the substrate olefin (24 mmol) in dry benzene (25 mL) is added dropwise with vigorous stirring to a suspension of the copper catalyst (5-15 mg) in dry benzene (2 mL) containing some of the alkene (1 mmol), at reflux temperature, under a nitrogen atmosphere. After the addition is complete, the mixture is tested for presence of diazocompound by means of its infrared band at 2150 cm^{-1}. Usually, heating must be continued for

TABLE I						PRODUCT (N°)/YIELD			
#	OLEF.	DIAZO.	R^1	R^2	R^3				
1	7a	Ia	CH_3	H *	COOEt	(10)	79 %	—	—
2	7b	Ia		COOEt	H	(11)	89	—	—
3	7a	Ib	CH_3	COOMe	COOMe	(12)	79	—	—
4	7b	Ib		COOMe	COOMe	(13)	95	—	—
5	7a	8	CH_3	COOEt	CH_3	—	—	(15)	44%
6	7b	8		COOEt	CH_3	—	—	(16)	86
7	7b	9		H	COOEt	—	—	(17)	59
8	7a	9	CH_3	H	COOEt	—	—	(18) +	58
* MIXTURE OF CIS AND TRANS									(19)

0.5 to 4 hrs until complete decomposition. The mixture, then is ice cooled and passed through a short column of neutral alumina act III to separate organic material from catalyst. Solvents are evaporated in vacuo and the residue is examined by nmr spectroscopy and GLC. The residue is distilled at reduced pressure to obtain the purified volatile fraction. The non-volatile residue is examined chromatographically for other separable heavier components.

Z,E-2-methyl-2-cyclopropyl-1-ethoxycarbonyl cyclopropane (10):

From ethyl diazoacetate (2.5 g) and 7a (2.9 g) compound 10 was obtained (2.92 g, 79%) by distillation as a colorless liquid. Bp 81°C (0.25 torr); ir (neat) 2970 (s) 1730 (s), 1310 (s), 1250 (s), 1160 (s), 1020 (s), 970 (s) cm^{-1}; nmr: δ 1.00 (s, 3H, Me-C of E-epimer), 1.23 (s, 3H, idem of Z epimer), 1.23 (t, 3H, J= 7.0 Hz, O-Et), 4.03 (q, 2H, J= 7.0 Hz, O-Et) ppm. Mass spectrum m/e: 168 (M^+, 5%), 140 (17%), 139 (18%), 95 (100%). Anal.: Calcd for $C_{10}H_{16}O_2$: C, 71.38; H, 9.59; O, 19.03. Found: C, 71.27; H. 9.62; O, 19.10.

2,2-Dicyclopropyl-1-ethoxycarbonylcyclopropane (11):

From ethyl diazoacetate (2.5 g) and 1,1-dicyclopropylethylene 7b, compound 11 was obtained as a colorless liquid after distillation (3.79 g, 89%). Bp 100-110°C (bath) (0.25 torr). Ir (neat) 1725 (s), 1310 (s), 1255 (s) cm^{-1}; nmr: δ 0.30-0.6 (m, 8H, cyclopropyl protons), 1.26 (t, 3H, J= 7.0 Hz, OEt), 1.3-1.5 (m, 1H, cyclopropane methyne), 4.12 (q, 2H, J= 7.0 Hz, OEt) ppm. Anal.: Calcd for $C_{12}H_{18}O_2$: C, 74.18; H, 9.35; O, 16.48. Found: C, 74.28; H, 9.30; O, 16.42.

2-Methyl-2-cyclopropyl-1,1-dimethoxycarbonyl cyclopropane (12):

From dimethyl diazomalonate (2.0 g) and 7a (2.0 g) with bis(acetoacetonato)copper(II) (130 mg) product 12 was obtained by distillation as a colorless liquid (1.90 g, 71% isolated yield). GLC analysis of crude material indicated 79% yield of 12. Bp. 73.5 (0.1 torr). Ir (neat) 1730 (s), 1445 (s), 1255 (s), 1105 (s), 870 (m) cm^{-1}; nmr δ 0.2-0.7 (m, 4H, cyclopropane protons), 0.85-1.2 (m, 1H, cyclopropane methyne), 1.38 (s, 3H, Me on cyclopropyl C-2), 3.80 (s, 6H, 2xCOOMe) ppm. Anal.: Calcd. for $C_{11}H_{16}O_4$: C, 62.23; H, 7.60; O, 30.16. Found: C, 62.16; H, 7.56; O, 30.28.

2,5-Dimethyl-2-cyclopropyl-4-ethoxycarbonyl-2,3-dihydrofuran (15):

From ethyl 2-diazo-3-oxobutyrate (1.0 g) and 7a (1.0 g) with bis(hexafluoroacetoacetonato)copper(II) (100 mg), compound 15 was obtained as a colorless liquid by distillation (0.56 g, 44%). Bp. 72-3 (0.3 torr). Ir (neat) 1710 (s), 1650 (s), 1390 (s) 1295 (s), 1250 (s), 1070 (s), 975 (s), 760 (s) cm^{-1}; nmr δ 0.3-0.5 (m, 4H, cyclopropyl methylenes), 0.9-1.2 (m, 1H, cyclopropyl methyne), 1.33 (t, 2H, J= 6.5 Hz, OEt), 1.40 (s, 3H, Me on C-2), 2.17 (t, 3H, J-1.5 Hz, Me on C-5), 2.65 (2xdq, 2H, J_1= 13.8 Hz, J_2= 1.5 Hz, methylene on C-3), 4.17 (q, 2H, J= 6.5 Hz, OEt) ppm. For ^{13}C data see text. Anal. Calcd. for $C_{12}H_{18}O_3$: C, 68.53; H, 8.63; O, 22.84. Found: C, 68.50; H, 8.51; O, 22.99.

2,2-Dicyclopropyl-4-ethoxycarbonyl-5-methyl-2,3-dihydrofuran (16):

From Diazocompound 8 and 7b using bis(hexafluoroacetoacetonato)copper(II) in fluorobenzene, compound 16 was obtained upon distillation as a colorless liquid (1.30 g, 86%). Bp. 80-85 °C (0.3 torr). Ir (neat) 1700 (s), 1640 (s), 1380 (s), 1340 (m), 1290 (s), 1240 (s), 1075 (s), 1020 (m), 972 (m), 950 (m), 760 (m) cm^{-1}; nmr δ 0.3-0.6 (m, 8H, cyclopropyl methylenes), 0.9-1.2 (m, 2H, cyclopropyl methynes), 1.24 (t, 3H, J= 6.5 Hz, OEt), 2.10 (t, 3H, J= 1.5 Hz, Me at C-5), 2.57 (d, 2H, J= 1.5 Hz C-3 methylene), 4.13 (q, 2H, J=6.5 Hz, OEt) ppm. For ^{13}C nmr data see text. Anal. calcd. for $C_{14}H_{20}O_3$: C, 71,14; H, 8.53; O, 20.32. Found: C, 71.21; H, 8.49; O, 20.30

2,2-Dicyclopropyl-5-ethoxycarbonyl-2,3-dihydrofuran (17):

From ethyl diazopyruvate (1.5 g) and 7b (1.8 g) with bis(acetoacetonato)copper(II) (120 mg), compound 17 was obtained as a light yellow oil (1.38 g, 59%). Bp. 110°C (0.1 torr). Ir (neat) 1745 (s), 1640 (s), 1340 (s), 1260 (s), 1245 (s), 1125 (s), 1020 (s), 730 (m) cm^{-1}; nmr δ 0.3-0.7 (m, 8H, cyclopropyl methylenes), 0.9-1.3 (m, 2H, cyclopropyl methynes), 1.30 (t, 3H, J= 7.0 Hz, Oet), 2.55 (d, 2H, J= 3.0 Hz,C-3 methylene), 4.28 (q, 2H, J= 7.0 Hz, OEt), 5.80 (t, 1H, J= 3.0 Hz, HC=) ppm. Mass spectrum m/e: 222 (M$^+$, 38%), 149 (40%), 121 (46%), 79 (100%). Exact mass calcd. for $C_{13}H_{18}O_3$: 222.1256. Found: 222.1264.

2-Methyl-2-cyclopropyl-5-ethoxycarbonyl-2,3-dihydrofuran (18).

From ethyl diazopyruvate (2.0 g) and 7a (2.5 g) and bis(acetoacetonato)copper(II) (160 mg), 1.6 g of distillable material was obtained bp. 100-105°C (0.1 torr). The nmr spectrum (H) indicated the presence of compounds 18 and 19 in a 2:1 ratio. Fractional distillation in vacuo and column chromatography using neutral alumina or silica gel failed to separate this mixture, causing only partial decomposition of 19, which was also found unstable under GLC separation conditions (180°C, nitrogen, SE-30 or Carbowax supports). Purification of 18 was achieved by chromatography through silica gel impregnated with silver nitrate, and elution with hexane-benzene mixtures. Ir (neat) 1740 (s), 1640 (s), 1240 (s), 1120 (s), 1020 (s) cm^{-1}; nmr δ 0.35-0.65 (m, 4H, cyclopropyl methylenes), 0.90-1.20 (m, 1H, cyclorpopyl methyne), 1.31 (t, 3H, J= 7.0 Hz, OEt), 1.40 (s, 3H, Me on C-2), 2.60 (2xdd, 2H, J_1= 13.0 Hz, J_2= 3.0 Hz, methylene at C-3), 4.20 (q, 2H, J= 7.0 Hz, OEt), 5.83 (t, 1H, J= 3.0 Hz HC=) ppm. Mass spectrum m/e: 196 (M$^+$, 23%), 123 (23%), 95 (100%), 55 (94%). Anal. calcd. for $C_{11}H_{16}O_3$: C, 67.31; H, 8.22; O, 24.47. Found: C, 67.28; H, 8.28; O,24.44 Compound 19 was characterized on the basis of its H nmr data: 0.9-1.21 (m, 4H, cyclopropyl methylenes), 1.31 (t, 3H, J=7.0 Hz, OEt), 2.35 (t, 2H, J= 7.5 Hz, allylic methylene), 2.95 (t, 2H, J= 7.5 Hz, CH_2-C=O), 4.21 (q, 2H, J= 7.0 Hz, OEt), 4.65 (s, 2H, =CH_2) ppm. Irradiation (0.3 G) at 2.95 collapsed signal at 2.35 ppm to a broad singlet. Each individual peak of signal at 2.35 ppm showed a wider meanhight than the signal at 2.95, indicating its coupling with the terminal methylene. Irradiation of this methylene's signal (4.65) caused the broad triplet at 2.35 to become a fine triplet. 19 proved too unstable to withstand further isolation.

References and Notes:

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