

SYNTHESIS OF DIETHYL 1-[(^{13}C)METHYL]-3-PHENYL(1,3- $^{13}\text{C}_2$)BICYCLO[1.1.0]-
BUTANE-exo,exo-2,4-DICARBOXYLATE

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SUMMARY

The synthesis of the triply ^{13}C labeled molecule, diethyl 1-[(^{13}C)methyl]-3-phenyl(1,3- $^{13}\text{C}_2$)bicyclo[1.1.0]butane-exo,exo-2,4-dicarboxylate is described. The unique feature of the synthesis is that in three instances we employed $^{13}\text{CO}_2$ (from $\text{Ba}^{13}\text{CO}_3$) without using a high vacuum line. We found that excellent yields were obtained in two Grignard reagent carbonations and in a CO_2 reduction using a mechanical pump which produced a vacuum of 0.05 torr. The synthetic sequence involved carbonation of phenylmagnesium bromide to give (α - ^{13}C)benzoic acid, reduction with LiAlH_4 , conversion to the corresponding benzyl chloride followed by preparation of the Grignard reagent and carbonation to produce phenyl(1,2,- $^{13}\text{C}_2$)acetic acid. Reaction with $^{13}\text{CH}_3\text{Li}$ provided 1-phenyl-2-(1,2,3- $^{13}\text{C}_3$)-propanone which, after conversion to its hydrazone and reaction with mercurous trifluoroacetate, yielded 1-phenyl-1-(1,2,3- $^{13}\text{C}_3$)propyne. Reaction twice with carbethoxycarbene (from ethyl diazoacetate) gave the desired triply ^{13}C labeled bicyclobutane.

Key Words: (α - ^{13}C)Benzoic acid, phenyl(1,2- $^{13}\text{C}_2$)acetic acid, 1-phenyl-2-(1,2,3- $^{13}\text{C}_3$)propanone, 1-phenyl-1-(1,2,3- $^{13}\text{C}_3$)propyne.

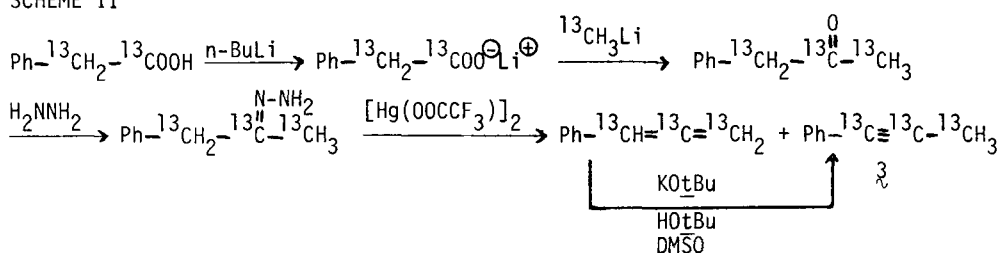
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out in a reasonably straightforward manner in 44% overall yield. The most significant difference between the present synthesis and those in the literature reported for monolabeled benzoic(6) and phenylacetic(7) acids is that we have carried out the carbonation of the corresponding Grignard reagents without the use of a high vacuum line. Instead we have adapted the procedures to the use of a mechanical pump (0.05 torr) and a leak free system and have essentially maintained the same yields as with the more elaborate high vacuum systems. Indeed, it seems apparent that this method could be readily applicable to the synthesis of a large variety of carboxylic acids from other organometallic precursors.

The preparation of (α - ^{13}C)benzoic acid(6) proceeded in 83% yield while the lithium aluminum hydride reduction(8,9) produced (α - ^{13}C)benzyl alcohol in 81% yield which was, in turn, converted to (α - ^{13}C)benzyl chloride with SOCl_2 ,(9,10) in 81% yield. Pmr analysis showed ca. 93% ^{13}C and $^1\text{J}_{\text{CH}} = 150 \text{ Hz}$ (lit.(11) 152 Hz). The preparation of the Grignard reagent followed by carbonation produced an 81% yield of phenyl(1,2- $^{13}\text{C}_2$)acetic acid (ζ). Mass spectral analysis showed, after taking into account the natural abundance ^{13}C in six (phenyl) carbon atoms, that the remaining two carbons were (ca. 2%): 4% $^{13}\text{C}_0$, 17% $^{13}\text{C}_1$, and 80% $^{13}\text{C}_2$. This compares extremely well with the following calculated distribution assuming 90% ^{13}C at each of two carbon atoms: 1% $^{13}\text{C}_0$, 18% $^{13}\text{C}_1$, and 81% $^{13}\text{C}_2$.

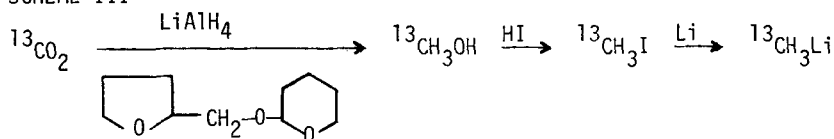
The next molecule we set out to synthesize was 1-phenyl-1-(1,2,3- $^{13}\text{C}_3$)-propyne (ζ), since the unlabeled material was known to produce the unlabeled bicyclobutane corresponding to λ .(12,13) Scheme II outlines the preparation of

SCHEME II



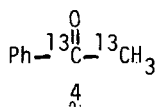
ζ from the phenylacetic acid, ζ , while Scheme III provides the synthetic route used to prepare $^{13}\text{CH}_3\text{Li}$.

SCHEME III



In this latter scheme, the methanol synthesis(14) deserves some comment. Tetrahydrofurfuryloxytetrahydropyran is the solvent of choice(14) since it is stable in alkaline solution, has low volatility, will dissolve LiAlH_4 and is easily prepared. As a result of having used the LiAlH_4 directly without purification we found that the methanol was only 72% ^{13}C labeled, by pmr spectroscopy. We attribute this dilution of the label to an impurity of methoxide on the LiAlH_4 formed by reduction of atmospheric CO_2 . Thus, while the other two labeled carbons are about 90% ^{13}C this methyl group is only about 72% ^{13}C . The $^{13}\text{CH}_3\text{OH}$ was produced in 104% yield confirming the contamination suggestion. In fact, if not for the 18% contamination the yield of methanol would have been 85-90%. The same (non-high-vacuum line) system was used here as was used for the Grignard carbonations. A 73% yield of (^{13}C)methyl iodide was obtained by treatment of the methanol with 57% HI,(15) and conversion to methyllithium gave a 0.45 M solution in 74% yield.

The methyllithium thus produced was reacted with the lithium salt of phenyl(1,2- $^{13}\text{C}_2$)acetic acid to give a 60% yield of 1-phenyl-2-(1,2,3- $^{13}\text{C}_3$)prop- anone. Pmr analysis of this ketone indicated about 86% ^{13}C at C-1, 71% ^{13}C at C₃, $^1J_{\text{C}_1\text{H}} = 128$ Hz and $^1J_{\text{C}_3\text{H}} = 127$ Hz. In addition, both the hydrogens on C₁ and C₃ were each long range coupled to one additional carbon with $J = 6$ Hz. This coupling is probably $^2J_{\text{CH}}$ based on Bernstein's report(16) that $^2J_{\text{CH}} = 6.2 \pm 0.1$ Hz in (α, β - $^{13}\text{C}_2$)acetophenone (4), a somewhat analogous compound. This

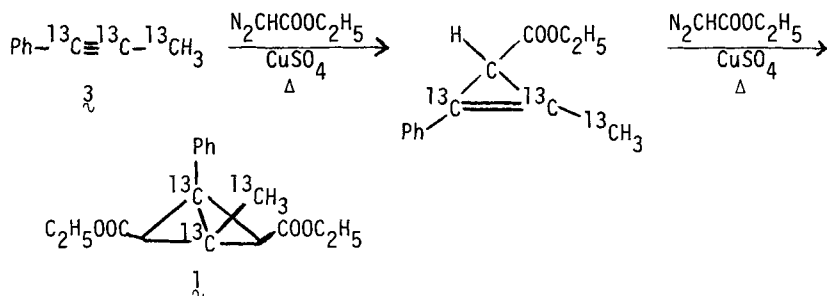


assignment, however, must remain tentative. The peaks all appear broad (width at half height=3-4 Hz) so there are other couplings which we are unable to determine.

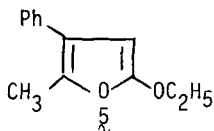
The route we chose from the ketone to 1-phenyl-1-(1,2,3- $^{13}\text{C}_3$)propyne (**3**) involved an overall "dehydration" by first preparing the hydrazone and then oxidizing this with mercurous trifluoroacetate(17) (Scheme II). This was after a procedure involving reduction to the alcohol, dehydration, bromination and dehydrobromination proved totally unsuccessful in our hands.

Unfortunately, although reactions with unlabeled material gave better results, we obtained a mixture of **3** and 1-phenyl-1,2-(1,2,3- $^{13}\text{C}_3$)propadiene. This mixture was converted completely to the alkyne by isomerization using KOtBu/tBuOH/DMSO . The overall yield of 1-phenyl-1-(1,2,3- $^{13}\text{C}_3$)propyne (**3**) was only 18%.

The preparation of 1-[(^{13}C)-methyl]-3-phenyl(1,3- $^{13}\text{C}_2$)bicyclo[1.1.0]butane-exo,exo,2,4-dicarboxylate (**1**) involved the thermal reaction of the alkyne (**3**) with ethyl diazoacetate, in the presence of anhydrous CuSO_4 , to produce the corresponding cyclopropene, followed by further reaction with ethyl diazoacetate- CuSO_4 .(12,13) We found that better yields of the bicyclobutane could be



obtained than were obtained previously(12,13) by chromatographing the cyclopropene prior to reaction with ethyl diazoacetate. In addition, contrary to the previous reports,(12,13) we found that none of the furan (**5**) was obtained



even when relatively large amounts of CuSO_4 were employed. The overall yield of **1** from **3** was about 21%. By comparison, Wolf(13) reports a 2.4% yield of the bicyclobutane from the alkyne in a reaction that did not involve isolation or purification of the intermediate.

Mass spectroscopy indicated that **1** had the following distribution (\pm ca. 2%) of ^{13}C in three carbon atoms after taking into account the natural abundance of ^{13}C in the other 14 carbon atoms: 3% $^{13}\text{C}_0$, 7% $^{13}\text{C}_1$, 35% $^{13}\text{C}_2$, and 55% $^{13}\text{C}_3$. This compares extremely well with the following distribution calculated assuming two carbons are 89% ^{13}C and one is 71% ^{13}C : 0.4% $^{13}\text{C}_0$, 7% $^{13}\text{C}_1$, 37% $^{13}\text{C}_2$, and 55% $^{13}\text{C}_3$. Thus, except for the methanol preparation, the ^{13}C labels were completely retained in the synthesis.

The proton nmr spectrum of **1** was as follows: δ 0.86-3.02 ppm (2H, ddd, $^1J_{\text{CH}} = +129$ Hz, $^2J_{\text{CCH}} = -7.3$ Hz, $^3J_{\text{CCCH}} = +2.7$ Hz, $\text{>C-}^{13}\text{CH}_3$), 1.03 (6H, t, $J = 7$ Hz, OCH_2CH_3), 1.56 (2H, broad s, half width = 6 Hz, >C-H), 1.94 (1H, dd, $^2J_{\text{CCH}} = -7.3$ Hz, $^3J_{\text{CCCH}} = +2.7$ Hz, $\text{>C-}^{12}\text{CH}_3$), 3.93 (4H, q, $J = 7$ Hz, $-\text{OCH}_2\text{CH}_3$) and 7.18-7.25 (5H, m, ArH). The cmr spectrum (proton noise decoupled; CDCl_3) displayed the following: δ (TMS) 4.22 ppm ($\text{>C-CH}_3, \text{C}_M$), 24.05 ($\text{>C-CH}_3, \text{C}_1$), 29.00 ($\text{>C-Ph}, \text{C}_3$); $^1J_{\text{C}_1-\text{C}_M} = +53.2 \pm 0.5$ Hz, $^2J_{\text{C}_3-\text{C}_M} = -2.4 \pm 0.5$ Hz, $^1J_{\text{C}_1-\text{C}_3} = -5.4 \pm 0.5$ Hz.

The unlabeled analog of **1** showed the following proton noise decoupled ^{13}C nmr spectrum (CDCl_3): δ (TMS) 4.22 ppm (>C-CH_3), 13.93 ($-\text{OCH}_2\text{CH}_3$), 24.00 (>C-CH_3), 29.04 (>C-Ph), 41.17 (>CH-COO), 60.16 (OCH_2CH_3), 127-131 (arom. C), 166.82 (C=O).

EXPERIMENTAL

Melting points and boiling points are uncorrected. Nuclear magnetic resonance spectra were determined with a Varian A-60A, Varian XL-100, Varian CFT-20 or a JEOL PFT-100 spectrometer using 5-10% solutions in CCl_4 except where otherwise noted. Mass spectra were obtained on a Finnigan 3200 GC/MS instrument.

(α - ^{13}C)Benzoic Acid. The procedure was a modification of that in the literature for the ^{14}C labeled molecule,⁽⁶⁾ where a high vacuum line was not used. Into a 250 mL round bottomed flask equipped with a magnetic stirring bar was placed 97 mL of a 0.60 M(18) ethereal solution of phenylmagnesium bromide (58 mmol). The flask was connected via a 3-way stopcock to a vacuum pump and to a CaCl_2 drying tube placed atop a pressure equalized addition funnel which

was on a 100 mL round bottomed flask. This latter flask contained 15.0g of 90% labeled $\text{Ba}^{13}\text{CO}_3$ (68 mg-atom ^{13}C , 76 mmol) while the addition funnel contained 100 mL of concd sulfuric acid. The system was filled with dry N_2 (via a second 3-way stopcock), the Grignard reagent was frozen in liq. N_2 and the entire system evacuated to 0.05 torr. The system was isolated from the pump and the Grignard solution was thawed and stirred while being kept at -30°C with a Dry-Ice-acetone bath. The H_2SO_4 was then added dropwise to the $\text{Ba}^{13}\text{CO}_3$ over a period of ca. 0.5 hr. After the addition was complete, stirring was continued for an additional 0.5 hr at -20°C . Workup consisted of hydrolysis (140 mL of 2 N HCl), separation of layers, extraction of the aqueous layer with 2 75 mL portions of ether, and washing the combined ether solution with 20 mL of saturated NaCl. The ether was then extracted with 1N NaOH which was subsequently warmed to remove the residual ether, acidified with concd HCl, and cooled. Filtration provided 7.7 g (6.3 mmol), 83% (based on $\text{Ba}^{13}\text{CO}_3$). Recrystallization from water gave 7.3 g of pure (α - ^{13}C)benzoic acid, m.p. 120-122°C (lit.(19) 121.5-122.2°C for 66% labeled benzoic acid).

(α - ^{13}C)Benzyl Alcohol. The reduction of 7.2 g (59 mmol) of (α - ^{13}C)benzoic acid with 2.8 g (74 mmol) of LiAlH_4 in a total of 220 mL of ether was carried out in the usual manner. (8,9) Workup and evaporation of the ether afforded 5.2 g (48 mmol) of (α - ^{13}C)benzyl alcohol (81%).

(α - ^{13}C)Benzyl Chloride. The procedure was similar to that reported(9,10) (for ^{14}C labeled material) except that 12.5 g of thionyl chloride (0.105 mol) and 5.2g (48 mmol) of (α - ^{13}C)benzyl alcohol were refluxed for 4 hr, benzene was added and the benzene-thionyl chloride mixture was distilled. The (α - ^{13}C)benzyl chloride was distilled, b.p. $120^\circ\text{C}/60$ torr. Yield: 5.0g (39 mmol; 81%). Nmr: δ 3.20 and 5.70 ppm (1.86H, d, $J=150$ Hz, $\text{Ph}-^{13}\text{CH}_2\text{Cl}$), 4.45 (0.14H, s, $\text{Ph}-^{12}\text{CH}_2\text{Cl}$), and 7.20-7.23 (5H, m, ArH).

Phenyl(1,2- $^{13}\text{C}_2$)acetic Acid (2). The procedure was, once again, a modification of that reported for ^{14}C labeled material(7) in that a high vacuum system was not employed. (α - ^{13}C)Benzylmagnesium chloride was prepared from 1.5 g

(62 mg-atom) of Mg, 5.0g (39 mmol) of (α - ^{13}C)benzyl chloride in a total of 110 mL of ether. Titration(18) showed the solution to be 0.36 M. Carboxylation was carried out as described for the preparation of (α - ^{13}C)benzoic acid. In this case 8.1g (41 mmol) of 90% $\text{Ba}^{13}\text{CO}_3$ and 60 ml of concd H_2SO_4 were used to produce the $^{13}\text{CO}_2$ which was reacted with the Grignard reagent. Hydrolysis (75 mL of 2 N HCl), separation layers, extraction of the aqueous layer with 45 mL of ether, extraction of the combined ether solution with 1N NaOH, heating and acidification with concd HCl produced 4.5g (33 mmol) of phenyl(1,2- $^{13}\text{C}_2$)-acetic acid (2), after filtration (81%). Recrystallization from water afforded pure 2 (4.0g), m.p. 75-77°C (lit. (7) 75.5-76.5°C).

(^{13}C)Methanol. The procedure was similar to that reported for the ^{14}C labeled molecule (14) except, once again, a high vacuum line was not used. The basic setup was the same as in the benzoic acid synthesis except that the reaction flask contained 370 mL of tetrahydrofurfuryloxytetrahydropyran (distilled from LiAlH_4) and 11.4g of LiAlH_4 (0.30 mol) and was cooled in a Dry-Ice-acetone bath rather than in liq. N_2 while being evacuated to 0.05 torr. The $^{13}\text{CO}_2$ was produced from 30.0g of $\text{Ba}^{13}\text{CO}_3$ (0.15 mol) and 160 mL of concd H_2SO_4 over a one hour period and allowed to react with the LiAlH_4 solution which was kept at 0°C. The reaction mixture was stirred at 0° for an additional 20 minutes and then it was allowed to come to room temperature. The vacuum was released, an addition funnel and an efficient condenser were attached and a Dry-Ice-acetone cooled trap was connected to the top of the condenser. The air was replaced with N_2 and 200 mL of tetrahydrofurfuryl alcohol was added over a 2 hr period while keeping the temperature below 100°C. After the addition was complete the (^{13}C)methanol was distilled into the trap using an oil bath temperature of 100°C and 60 torr pressure. Yield: 5.1g (0.156 mol); 104%. NMR: δ 2.20 and 4.55 (2.18H, d, $J=141$ Hz, $^{13}\text{CH}_3\text{OH}$), 2.56 (1H, s, CH_3OH) and 3.38 (0.82H, s, $^{12}\text{CH}_3\text{OH}$). (Lit. (10) $^1J_{\text{CH}} = 141, 144$ Hz.)

(^{13}C)Methyl Iodide. A modification of the reported (for $^{14}\text{CH}_3\text{I}$) procedure (15) employing HI was used. A 250 mL round bottomed flask equipped with a magnetic stirrer and condenser, containing 100 mL of 57% HI, was frozen in a Dry-Ice-

acetone bath and 5.0g (0.15 mol) of (^{13}C)methanol was added. After the solution was brought to room temperature it was refluxed for 3 hr and cooled. The condenser was replaced with a distilling head connected through a drying tube containing anhydrous lime and P_2O_5 to a condenser. Distillation produced 15.0g (0.11 mol) of (^{13}C)methyl iodide, b.p. 40°C ; yield: 73%.

(^{13}C)Methyl lithium. The procedure was essentially that used by Meinwald(20) for the ^{14}C labeled material. We employed 2.5g (0.36 g-atom) of Li, 15.0g (0.11 mol) of (^{13}C)methyl iodide and a total of 200 mL of ether. About 180 mL of a 0.45 M(21) solution of (^{13}C)methyl lithium was obtained (74%).

1-Phenyl-2-(1,2,3- $^{13}\text{C}_3$)propanone. In a 500 mL 3-necked flask equipped with a mechanical stirrer, addition funnel and drying tube, was placed 6.5g (48 mmol) of phenyl(1,2- $^{13}\text{C}_2$)acetic acid (2) in 300 mL of ether. The reaction mixture was cooled to 0°C , and maintained at this temperature during the addition of 18 mL of 2.6 M n-butyllithium (47 mmol) in 30 mL of ether, followed by 180 mL of 0.45 M (81 mmol) (^{13}C)methyl lithium in ether. The addition lasted one hour, and after that the reaction mixture was stirred at room temperature overnight. The turbid white reaction mixture was pipeted into a solution of ice water containing 20 mL of concd HCl. The aqueous layer was extracted several times with ether, the combined ether layer was washed with a dilute solution of sodium carbonate, then with water, dried (MgSO_4) and evaporated to yield 6.0g of impure ketone. Distillation produced, after a forerun, pure 1-phenyl-2-(1,2,3- $^{13}\text{C}_3$)propanone, 4.0g (20 mmol; 60%), b.p. $125^\circ\text{C}/45$ torr.

1-Phenyl-1-(1,2,3- $^{13}\text{C}_3$)propyne 3. The method was similar to that described for the unlabeled compound. (17) In a 25 mL 3-necked flask equipped with a magnetic stirrer, condenser, drying tube and addition funnel, was placed 4.0g(29 mmol) of 1-phenyl-2-(1,2,3- $^{13}\text{C}_3$)propanone and 4.0g (0.13 mol) of 95% hydrazine. The reaction mixture was refluxed at 100°C for 3 hr, extracted with ether, the ethereal solution was washed with a small amount of water and dried (K_2CO_3). Solvent evaporation gave 4.0g (27 mmol) of the hydrazone of 1-phenyl-2-(1,2,3- $^{13}\text{C}_3$)propanone (93%).

Into a 500 mL 3-necked flask equipped with a mechanical stirrer, condenser, drying tube and addition funnel, were placed 34g (54 mmol) of mercurous tri-fluoroacetate (22) and 100 mL of ether. To this was added, while stirring and under gentle reflux, 4.0g (27 mmol) of the hydrazone in 100 mL of ether over a period of 1 hr. After the addition was complete the reaction mixture was refluxed for an additional 0.5 hr, cooled and filtered. The ether layer was washed with 5% ammonium hydroxide (to neutralize acid and destroy unreacted mercurous salt), then with water and dried (K_2CO_3). The ether was evaporated to leave 2.5g of a red oil, which was chromatographed on neutral alumina (40g; 0.75 in. diam) using pentane to elute. Solvent evaporation of the first 500 mL of eluent collected gave 1.0g of a mixture of 1-phenyl-1-(1,2,3- $^{13}C_3$)propyne and 1-phenyl-1,2-(1,2,3- $^{13}C_3$)propadiene. I.R. (neat; unlabeled): 1920 cm^{-1} (-C=C-), 2260 and 2220 cm^{-1} (-C≡C-).

The 1g mixture of phenylallene and 1-phenylpropyne was placed in a 25 mL round bottomed flask equipped with a magnetic stirrer and a drying tube. To this was added 50 mg of potassium *t*-butoxide, 1.4g of *t*-butanol and 2 mL of DMSO. The orange colored mixture was stirred for ca. 3 hr at room temperature. Water (50 mL) was added, and the reaction mixture was extracted 5 times with 30 mL portions of pentane. The pentane extract was washed with water, dried ($MgSO_4$) and evaporated to yield 600 mg of 1-phenyl-1-(1,2,3- $^{13}C_3$)propyne (3; 5.1 mmol; 18% overall) I.R. (neat, unlabeled): 2260 and 2220 cm^{-1} (-C≡C-). (Lit. (23) 2260 and 2220 cm^{-1}).

Diethyl 1-[(^{13}C)Methyl]-3-phenyl(1,3- $^{13}C_2$)bicyclo[1.1.0]butane-exo,exo-2,4-dicarboxylate (1). (12,13) In a 25 mL 3-necked flask equipped with a magnetic stirrer, condenser, bubble counter and nitrogen inlet, were placed 600 mg (5.1 mmol) of 1-phenyl-1-(1,2,3- $^{13}C_3$)propyne (3) and a few mg of anhydrous $CuSO_4$. To this was added dropwise, under a nitrogen atmosphere, at 95-100°C, 1.5g (13 mmol) of freshly prepared ethyl diazoacetate (24) over 0.5 hr. After the addition, the reaction mixture was heated for an additional 10 minutes, cooled and placed on a 30g silica gel column (0.75 in. diam), prepared with benzene and eluted with a 1:9 chloroform:benzene mixture. Evaporation of the

first 500 mL of eluent gave 1.1g of material. This material was not analyzed, but, based on reactions with unlabeled compounds, it was assumed to consist of a mixture in which the major component was the cyclopropene derivative, some diethyl fumarate and diethyl maleate and a small amount of the bicyclobutane derivative, **1**.

Into a 25 mL 3-necked flask equipped with a magnetic stirrer, condenser, bubble counter and nitrogen inlet, were placed 1.1g of the above mixture and a few mg of anhydrous CuSO_4 . To this was added dropwise 1.8g (16 mmol) of freshly prepared ethyl diazoacetate (**24**) under a nitrogen atmosphere, at 95-100°C, over a 0.5 hr period. After the addition was complete, the reaction mixture was heated for an additional 10 minutes, cooled, and placed on a 40g silica gel column (0.75 in. diam) prepared and eluted with benzene. Upon evaporation of the first 500 mL of eluent 800 mg of material was obtained. This material was distilled using a modified Hickman still, and the first fraction (260 mg) was collected at 58°C and 0.05 torr. It contained mostly diethyl fumarate and diethyl maleate, as determined by nmr analysis. The second fraction, 380 mg, was collected at 70-80°C and 0.05 torr. This consisted of about 80% pure (nmr analysis) diethyl 1-[(^{13}C)methyl]-3-phenyl(1,3- $^{13}\text{C}_2$)bicyclo[1.1.0]butane-exo, exo-2-dicarboxylate (**1**). The overall yield of **1**, from, 1-phenyl-1-(1,2,3- $^{13}\text{C}_3$)-propyne (**3**) was ca. 21%. Proton and ^{13}C nmr spectra are presented in the text.

ACKNOWLEDGEMENTS

We wish to thank the Alfred P. Sloan Foundation for partial support of this work and a research fellowship to M.P. and also the University of Texas at Arlington Organized Research Fund for partial support. We are grateful to the following people for ^{13}C nmr spectra: Dr. G. A. Gray, Dr. T. Witherup, Dr. R. Rodebaugh and Mr. A. Temps, and to Dr. R. A. Caldwell for his help in obtaining the mass spectra.

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