An Unusual Reaction of a Diazo Ester with Arylacetylenes and New Thermal and Photochemical Transformations of a 3H-Pyrazole

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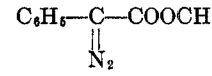
The reaction of methyl 1-phenyldiazoacetate (1) with diphenylacetylene gives methyl 1,2,3-triphenylcyclopropene-3-carboxylate (3) in 34% yield *via* a carbenic addition reaction. When the carboxylate group is separated from the reaction center by two methylene groups, 1,3-dipolar addition of diazo group to a triple bond predominates; thus the reaction of methyl 4-diazo-4-phenylbutyrate (2) with phenylacetylene gives 3-(2′-carbomethoxyethyl)-3,5-diphenyl-3H-pyrazole (6) in 59% yield. In contrast, the reaction of 2 with diphenylacetylene produces an unusual addition product, 3,4,5-triphenylpyrazole (4), in 29% yield. Unexpectedly, the 2′-carbomethoxyethyl group of 2 has been lost during the reaction. When the 3H-pyrazole 6 is heated at 160°, the rearrangement of phenyl and hydrogen proceeds smoothly without loss of the side chain and 5-(2′-carbomethoxyethyl)-3,4-diphenyl-3H-pyrazole (10) is obtained in 91% yield. A photochemical transformation of the 3H-pyrazole 6 unexpectedly gives no cyclopropene derivative, but a mixture of *trans*- and *cis*-styryl-2-phenylcyclopropane-1-carboxylic acid methyl esters (14) (14%) and 5,6-di(2′-carbomethoxyethyl)-2,3,5,6-tetraphenylbicyclo[2.2.0]hex-2-ene (7.5%) is obtained.

A one-step synthesis of various cyclopropenes by an addition of carbene to acetylenes has interested us, and some acylcyclopropenes[1] have been prepared successfully. In the course of this study, we investigated reactions of methyl 1-diazo-1-phenylacetate (1) and methyl 4-diazo-4-phenylbutyrate (2) with arylacetylenes.[2] No cyclopropene derivative was obtained in the reaction of 2 with diphenylacetylene, but an unexpected product was isolated, which was presumably derived from a 3H-pyrazole intermediate. Accordingly, the thermal and photochemical transformations of a related 3H-pyrazole were also investigated.



$C_6H_5{-}\underset{\| \atop N_2}{C}{-}COOCH_3$

1

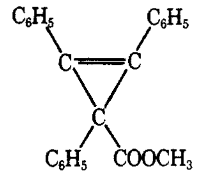
$C_6H_5{-}\underset{\| \atop N_2}{C}{-}CH_2CH_2COOCH_3$

2

Addition Reaction of 1 and 2 to Diphenylacetylene.—The diazo esters 1 and 2 were prepared from the corresponding *p*-toluenesulfonylhydrazone according to the Bamford–Stevens method.[3] There was obtained 1 of 63% purity in 55% yield from *p*-toluenesulfonylhydrazone of methyl benzoylformate.

When a diglyme solution of 1 was added dropwise to melted diphenylacetylene at 140°, a carbenic addition product, methyl 1,2,3-triphenylcyclopropene-3-carboxylate (3), was obtained in 34% yield.[4] The structural determination of 3 is based on the elemental analysis, molecular weight determination,[5] and spectroscopic data. The presence of a cyclopropene skeleton in 3 is indicated by the characteristic peaks in the infrared (ir) and ultraviolet (uv) absorption spectra.[6]

In contrast, a similar addition of 2 to diphenylacetylene did not result in the formation of a cyclopropene derivative, but the compound isolated in 29% yield was 3,4,5-triphenylpyrazole (4); unexpectedly the 2′-carbomethoxyethyl side chain had been lost during the reaction. The structure of 4 was unambiguously established by the comparison with an authentic specimen prepared from benzaldesoxybenzoin and hydrazine followed by oxidation.[7] The 3H-pyrazole 5, which is produced by the 1,3-dipolar addition of 2 to diphenylacetylene, might be unstable under the reaction condition and eliminate methyl acrylate to afford the pyrazole 4. In an attempt to isolate the 3H-pyrazole 5, the reaction of 2 with diphenylacetylene was carried out at 55°, but the only product isolated was again 4.



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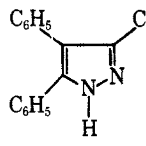

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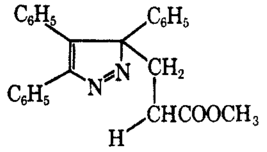

5

Reaction of 2 with Phenylacetylene.—In the reaction of diazo ester 2 with phenylacetylene at 55°, a normal 1,3-dipolar addition[8,9] proceeded smoothly and 3-(2′-carbomethoxyethyl)-3,5-diphenyl-3H-pyrazole (6) was obtained in 59% yield. The structure was deduced from elemental analysis, spectroscopic data, and its thermal rearrangement to 5-(2′-carbomethoxyethyl)-3,4-diphenylpyrazole[11] (see next section). An isomeric

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[1] (a) I. Moritani and N. Obata, *Tetrahedron Lett.*, 2817 (1965); (b) N. Obata and I. Moritani, *Bull. Chem. Soc. Jap.*, **39**, 1975 (1966); (c) N. Obata and I. Moritani, *Tetrahedron Lett.*, 1503 (1966); (d) N. Obata and I. Moritani, *Bull. Chem. Soc. Jap.*, **39**, 2250 (1966).

[2] As a leading reference for the reaction of diazo acetic ester with acetylenes, see W. Krimse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 95.

[3] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952). This preparation was found to be much better than that of the Curtius and Müller procedure; see T. Curtius and E. Müller, *Chem. Ber.*, **37**, 1261 (1904).

[4] Yields of the reaction of diazo compounds which appear hereafter in this paper are all based on the amount of diazo compound utilized.

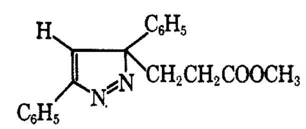
[5] All other compounds which appear hereafter in this paper also showed satisfactory elemental analysis and molecular weight.

[6] (a) R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, **80**, 5991 (1958); (b) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *ibid.*, **87**, 1320 (1965).

[7] (a) E. Ectors, *Chem. Zentr.*, **I**, 914 (1924); (b) W. E. Parham and W. R. Hasek, *J. Amer. Chem. Soc.*, **76**, 799 (1954).

[8] R. Huisgen, *Angew. Chem. Intern. Ed. Eng.*, **2**, 565, 633 (1963).

[9] R. Hüttel, J. Riedl, H. Martin, and K. Franke, *Chem. Ber.*, **93**, 1425 (1960).



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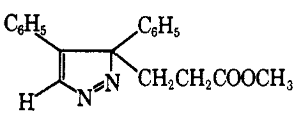
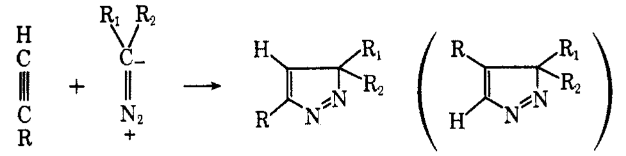


7

structure **7** for this compound can be eliminated because of the following reasons.[10] Hüttel and his coworkers[9] have studied the reaction of acetylene derivatives with disubstituted diazomethane compounds and, for the direction of addition of some diazo compounds to terminal acetylenes, they have shown that the additions have taken a mode to give **8** without exceptions. This mode of addition is said to be both electronically and sterically more favored than that giving 3H-pyrazole **9**.

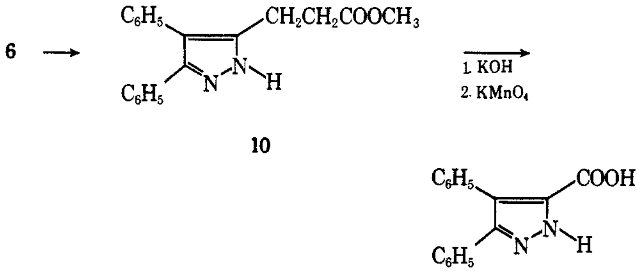


8 **9**

In sharp contrast to the addition of **2** to diphenylacetylene, the side chain is preserved in this case.

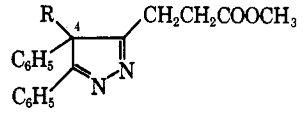
Accordingly, we were interested in the investigation of thermochemical behavior of 3H-pyrazole **6** in a relation to the unusual pyrazole formation in the reaction of **2** with diphenylacetylene.

Thermal Rearrangement of 6.—A diglyme solution of **6** was heated at 160° for 3 hr. The rearrangement proceeded smoothly and 5-(2′-carbomethoxyethyl)-3,4-diphenylpyrazole (**10**) was obtained in 91% yield. The structure of **10** was confirmed by converting it into 3,4-diphenylpyrazole-5-carboxylic acid (**11**) by potassium permanganate oxidation[7b] after hydrolysis. The acid **11** was found to be the same with an authentic sample prepared from phenyldiazomethane and methyl phenylpropiolate followed by hydrolysis.[9]



10 **11**

It is clearly established that the thermal rearrangement of **6** proceeds with a preservation of the side chain; a phenyl group migrates from C-3 to C-4 and hydrogen from C-4 to C-2.[11] This result is in marked contrast to that observed in the case of 3H-pyrazole **5**, in which the side chain is eliminated with great ease. The difference in the reaction of **5** and **6** might be due to the different substituents at C-4 position of 3H-pyrazole ring. In the case of **6**, the 1,2-phenyl migration will produce an intermediate **12a** which can easily transform into a stable pyrazole derivative by a simple prototropic rearrangement.



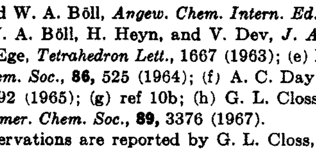
12a, R = H
b, R = C_6H_5

On the contrary, the intermediate **12b** has no hydrogen at C-4 and therefore it cannot be stabilized in the same way as **12a**. The reaction of **5** thus results in a retro Michael reaction[12] in which the side chain is eliminated as methyl acrylate to afford the pyrazole **4**. Steric strain produced by an accumulation of bulky groups on a 3H-pyrazole ring might also play a role in the above transformation of **5**.

Photodecomposition of 6.—As the attempt to prepare the cyclopropene derivative by the thermal decomposition of **2** in diphenylacetylene was not successful, we now turn our attention to investigate the photochemical decomposition of 3H-pyrazole **6**. Recently several workers[13] have carried out photodecompositions of 3H-pyrazoles and obtained cyclopropene derivatives.

A benzene solution of 3H-pyrazole **6** was irradiated by a high pressure mercury lamp at 10–12°. After 5 min, the benzene solution became red and evolution of nitrogen gas started. The ir spectrum of this red solution showed a sharp peak at 2010 cm^{-1} indicating the formation of a diazo compound.[14] The nitrogen evolution was completed after about 3 hr. A distillation of the product gave a fraction of bp 132–136° (0.002 mm) and a residue. From the residue, a crystalline material **13** (mp 199–200°) was obtained in 7.5% yield. The distillate was subjected to an alumina column chromatography and two crystalline products **14a** (mp 105°) and **14b** (mp 65–67°) were obtained in 7.5 and 6.5% yield, respectively. None of the intermediate fractions showed the characteristic ir absorption of a mono-substituted double bond of cyclopropenes.[13c]

The compounds **14a** and **14b** are found to be isomeric compounds of a formula $C_{19}H_{18}O_2$ by the analytical and spectroscopic examinations. Careful analyses of the available data suggest to us that **14a** and **14b** could be



14

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[10] (a) Although the nmr spectrum could not give a conclusive evidence to differentiate the structures **6** and **7**,[10b] the nmr absorptions of **6** and 3-methyl-3,5-diphenyl-3H-pyrazole were found to be almost identical except for the signals due to the side chains. 3-Methyl-3,5-diphenyl-3H-pyrazole was prepared according to the Hüttel's procedures[9] and hence its structure was assured. (b) A. C. Day and M. C. Whiting, *J. Chem. Soc., C*, 1719 (1967).

[11] For the rearrangement of 3H-pyrazoles, see (a) J. van Alphen, *Rec. Trav. Chim. Pays-Bas*, **62**, 485 (1943); (b) R. Hüttel, K. Frank, H. Martin, and J. Riedel, *Chem. Ber.*, **93**, 1433 (1960).

[12] A similar type of elimination of acrylic acid ester has been reported in heterocyclic chemistry; see E. Bullock, B. Gregory, A. W. Johnson, P. J. Brignell, U. Eisner, and H. Willams, *Proc. Chem. Soc.*, 122 (1962).

[13] (a) G. L. Closs and W. A. Böll, *J. Amer. Chem. Soc.*, **85**, 3904 (1963); (b) G. L. Closs and W. A. Böll, *Angew. Chem. Intern. Ed. Eng.*, **2**, 399 (1963); (c) G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, **90**, 173 (1968); (d) G. Ege, *Tetrahedron Lett.*, 1667 (1963); (e) R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 525 (1964); (f) A. C. Day and M. C. Whiting, *Chem. Commun.*, 292 (1965); (g) ref 10b; (h) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967).

[14] Similar observations are reported by G. L. Closs, *et al.*,[13a,c] and A. C. Day, *et al.*[10b,13f]

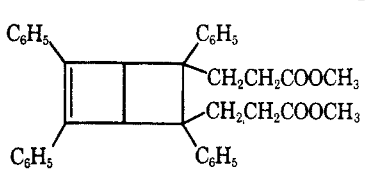
stereoisomers of methyl 2-styryl-2-phenylcyclopropane-1-carboxylate.[15] The vicinal coupling constant of two vinylic protons in **14a** was 16 cps while that in **14b** was nearly 0. From these values, it can be assigned that **14a** has a *trans*-styryl group[16] and **14b** has a *cis*-styryl.[17]

The compounds **14a** and **14b** were hydrogenated catalytically at the double bond, but again they gave a pair of isomeric methyl 2-(2′-phenylethyl)-2-phenylcyclopropane-1-carboxylates. Namely, **14a** gave a crystalline compound **15a** (mp 44–46°) while **14b** gave a low melting **15b** (mp 10–12°). Consequently, it may be concluded that the two isomers **14a** and **14b** differ geometrically not only at the double bond but also at the cyclopropane ring.

To confirm further the parent structure of **14**, the hydrogenated products (**15a** and **15b**) were compared with authentic samples prepared from the decomposition of methyl diazoacetate in 2,4-diphenylbut-1-ene. A cuprous chloride catalyzed decomposition of methyl diazoacetate in a boiling ether solution of 2,4-diphenylbut-1-ene produced two isomeric addition products, which were found to be the same compounds in all respects as **15a** and **15b**. Unfortunately, the available data did not allow the determination of the strict stereochemistry about the cyclopropane ring for **14** and **15**.

The crystalline material **13** was found to be a compound of a formula $C_{38}H_{36}O_4$ from elemental analysis and mass spectroscopy (*m/e* 556); namely, the compound is a dimeric material resulted from **6** with loss of N_2. The ir and nmr spectra of this compound clearly indicate the presence of 2′-carbomethoxyethyl side chain. In addition, the nmr spectrum exhibited 20 aromatic hydrogens and two hydrogens at τ 4.28 as a singlet peak.

Now, the uv spectrum of this compound, two broad bands at 207 mμ (log ε 4.56) and 314 mμ (log ε 4.46), suggests that it has an extended conjugated system, but both ir and nmr spectra indicate that this compound has not a condensed aromatic system; the four phenyls are clearly monosubstituted. Consequently, it might have a kind of stilbene chromophore. Recently, White and Anhalt[18] have studied the uv spectra of a series of 1,2-diphenylcycloalkenes and they have shown that 1,2-diphenylcyclobutene absorbs at unusually long wavelengths, at 297 and 307 mμ (sh). The present compound also absorbs at far longer wavelength than those observed in the ordinary *cis*-stilbenes and, therefore, it might be considered that it has either a 1,2-diphenylcyclopropene or a 1,2-diphenylcyclobutene structure. When the spectrum is examined carefully, it can be seen that no fine structure is present in the 300–330-mμ region; 1,2-diphenylcyclopropenes are known to exhibit more fine structures in this region than 1,2-diphenylcyclobutenes.[6a] In addition, Blomquist and LaLancette[19] have pointed out that the strongest absorption is at longer wavelength for the cyclopropenes while the reverse is true for 1,2-diphenylcyclobutene systems. In the present compound, the intensity of absorption at 207 mμ was higher than that observed at 314 mμ. Accordingly, one can conclude that this compound might have 1,2-diphenylcyclobutene structure. After these discussions, we propose a structure of bicyclo[2.2.0]hexene for compound **13**. Although the compound did not exhibit the C═C vibration in the ir region, it decolorized testing solutions of bromine in carbon tetrachloride and potassium permanganate in water. These observations are also in agreement with the proposed highly symmetrical structure for **13**. Moreover, the compound **13** could not be hydrogenated under catalytic conditions. A similar difficulty in the catalytic hydrogenation of **16** has been experienced by Nagarajan, Caserio, and Roberts.[20] A point which seems to be inconsistent with the proposed structure is a sharp singlet peak of τ 4.28 observed in the nmr spectrum. The τ value observed here is too low for tertiary protons of similar compounds,[21] but we believe that the protons in **13** might suffer unusual deshielding effects by the phenyl- and methoxycarbonyl side chains. Similar low field resonances have been observed in the case of tricyclo[3.1.0.0^{2,4}]hexane derivatives.[1,23] The tertiary protons in **18** have appeared at τ 4.80[1d] and those in **19** (*trans* form) at 4.90.[23b]



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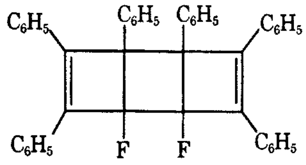

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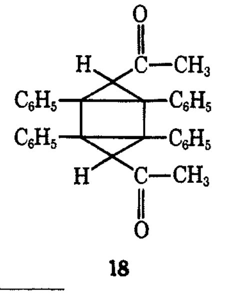

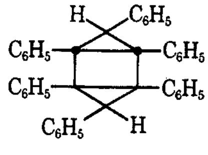

18 **19**

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[15] There are four stereoisomers for this compound, but only two of them have been isolated in the present experiment.

[16] L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p 85.

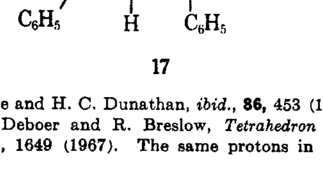
[17] In this compound, vinylic protons appeared as a singlet at τ 4.08. Similar results have been reported for *cis*-1,3-diphenyl-1,3-butadiene; see G. M. Badger, P. Cheuychit, and W. H. F. Sasse, *Aust. J. Chem.*, **17**, 353 (1964).

[18] For the study of the uv spectra of 1,2-diphenylcycloalkenes, see E. H. White and J. P. Anhalt, *Tetrahedron Lett.*, 3937 (1965).

[19] A. T. Blomquist and E. A. LaLancette, *J. Org. Chem.*, **29**, 2331 (1964).

[20] K. Nagarajan, M. C. Caserio, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 449 (1964).

[21] Tertiary protons in the compound **17** appear at τ 6.13.[22]

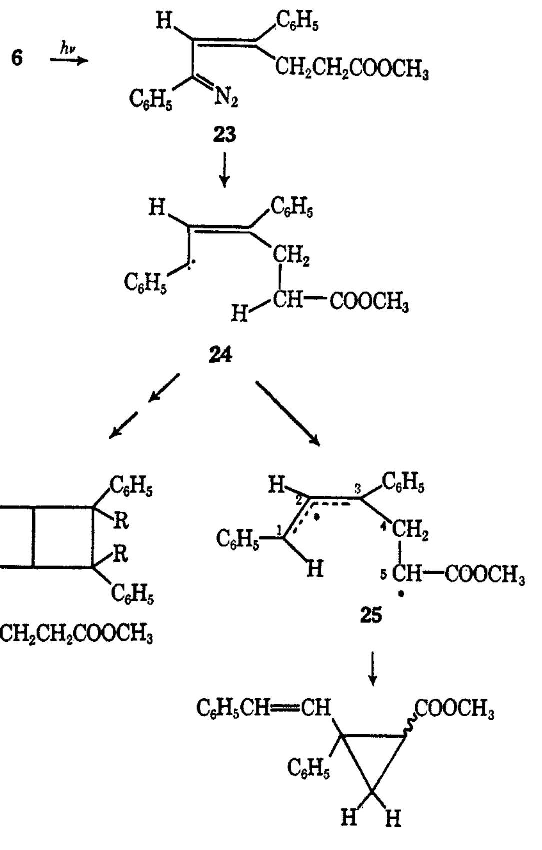


17

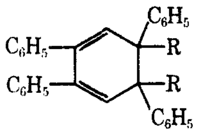
[22] E. H. White and H. C. Dunathan, *ibid.*, **86**, 453 (1964).

[23] (a) C. R. Deboer and R. Breslow, *Tetrahedron Lett.*, 1033 (1967); (b) H. Dürr, *ibid.*, 1649 (1967). The same protons in *cis* form have been reported at τ 5.86.

Scheme I



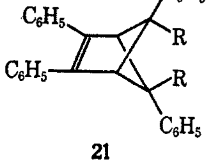
Alternative structures for **13** can hardly explain the available data mentioned above. For example, diphenylcyclohexadienes (**20**) are not likely because



20, R = $CH_2CH_2COOCH_3$

2,3-diphenyl-1,3-butadiene[24] shows an uv maximum at 243 mμ, and 1,4-diphenyl-1,4-cyclohexadiene absorbs at 272 mμ and is hydrogenated easily over platinum catalyst.[25]

Other structures such as **21** and **22** are also unlikely because these should exhibit the uv maxima at much shorter wavelengths than that observed for **13**; for example, 1,2-diphenylcyclopent-1-ene shows a maximum at 272 mμ[18] and tricyclo[3.1.0.0^{2,4}]hexane derivatives show their maxima at 226[1d] and 214–271 mμ.[23b]



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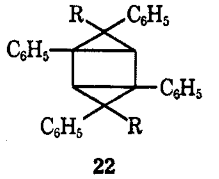

22

R = $CH_2CH_2COOCH_3$

Now, we propose reaction paths for the formation of styrylcyclopropane and bicyclo[2.2.0]hexene as shown in Scheme I. The formation of the diazo compound **23** on the irradiation of **6** is indicated by the ir check of the irradiating solution as mentioned already. This diazo compound undergoes a photochemical decomposition to the carbene **24**.[26] The carbene **24** may dimerize to give a hexa-1,3,5-triene derivative which produces bicyclohexene **13** on the further irradiation. A photochemical transformation of hexatriene to bicyclo[2.2.0]hexene is a known reaction.[27,28]

In the other way, the carbene **24** might abstract a hydrogen from C-5 to produce the biradical **25**. This biradical is stabilized by the allylic resonance and hence it might be possible to cyclize between C-3 and C-5 to give **14a** and **14b**.

Experimental Section[29]

Methyl Phenyldiazoacetate (1).—The tosylhydrazone of methyl benzoylformate[30] was prepared by refluxing a solution of methyl benzoylformate (3.2 g, 20 mmol) and *p*-toluenesulfonylhydrazine[31] (3.8 g, 20 mmol) in methanol (100 ml) for 3 hr. The crystalline tosylhydrazone was recrystallized from benzene–methanol and the pure tosylhydrazone (5.6 g, 84%) melted at 128.5–129°.

Anal. Calcd for $C_{16}H_{16}O_4N_2S$: C, 57.81; H, 4.85; N, 8.42. Found: C, 57.88; H, 4.81; N, 8.76.

Sodium methoxide (4.3 g, 80 mmol) was added to a solution of the tosylhydrazone (18.5 g, 56 mmol) in dry pyridine (150 ml). After the solution stirred for 20 min at 55°, the reaction mixture was poured onto a large amount of ice–water. The organic material was washed with several portions of water and dried over anhydrous magnesium sulfate. The solvent was removed by evaporation, giving an orange-yellow oil (7.6 g). This oil exhibited characteristic ir absorptions at 2075 (diazo) and 1705 cm^{-1} (carbonyl). It decomposed smoothly at 130° and evolved nitrogen gas. Based on the volume of nitrogen gas, this oily diazo compound was found to be 63% pure; the yield based on the starting tosylhydrazone was 56%. Further reactions were carried out in this purity. Decomposition of this diazo compound with benzoic acid gave methyl benzoyloxyacetate: bp 161–162° (1 mm); n^{25}D 1.5438 [lit.[32] bp 165° (2 mm); n^{25}D 1.5439].

Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.05; H, 5.49.

The ir spectrum of this compound was superimposable with that of an authentic material prepared from the reaction of methyl mandelate and benzoyl chloride.[32]

Reaction of Methyl Phenyldiazoacetate (1) **with Diphenylacetylene.**—A solution of methyl diazoacetate (18 mmol) added dropwise under stirring to a melt of diphenylacetylene (12.5 g, 70 mmol) at 140° for 2 hr. After nitrogen evolution was completed, the reaction mixture was poured onto a large amount of ice–water and the organic material was extracted with several portions of ether. After the combined ethereal solution was dried with anhydrous magnesium sulfate, the solution was concentrated. The residue was chromatographed on a column of alumina (600 g). From a fraction eluted with benzene, methyl 1,2,3-triphenylcyclopropene-3-carboxylate (3) was obtained (2.0 g, 34%). After recrystallization from ethanol, this ester melted at 140.5–141.5°: nmr (CCl_4) 2.50 (15) m, 6.40 (1) s; uv max (95% C_2H_5OH) 227 mμ (log ε 4.63), 233 (4.58), 296

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[24] A. C. Cope and D. S. Smith, *J. Amer. Chem. Soc.*, **74**, 5136 (1952). This compound was chosen for a model compound because the uv spectrum of 2,3-diphenyl-1,3-cyclohexadiene has not been reported.

[25] C. E. Griffin and G. Witschard, *J. Org. Chem.*, **27**, 3334 (1962).

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(4.48), 310 (4.64), and 326 (4.57); ir (Nujol) 1865 (C=C) and 1720 cm^{-1} (ester C=O).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.74; H, 5.61.

Hydrolysis of **3** gave 1,2,3-triphenylcyclopropene-3-carboxylic acid, mp 219–220° (recrystallized from acetone).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.53; H, 5.16.

Methyl 4-Phenyl-4-diazobutyrate (2).—The tosylhydrazone of methyl β-benzoylpropionate[33] was prepared by 4-hr reflux of a solution of methyl β-benzoylpropionate (104 g, 0.54 mol) and *p*-toluenesulfonylhydrazine (132 g, 0.71 mol) in methanol (400 ml). The crystalline tosylhydrazone (183 g, 94%) was recrystallized from benzene–methanol and the pure tosylhydrazone melting at 123–124° was obtained.

Anal. Calcd for $C_{18}H_{20}O_4N_2S$: C, 59.98; H, 5.59; N, 7.77. Found: C, 60.31; H, 5.58; N, 7.74.

Sodium methoxide (8.7 g, 0.16 mol) was added to a solution of the tosylhydrazone (45.4 g, 0.12 mol) in dry pyridine (400 ml). After the solution had stirred for 4 hr at 55–60°, the resulting reddish mixture was extracted with petroleum ether as described before; the organic solution was dried over anhydrous sodium sulfate. The solvent was removed by evaporation giving a wine-red oil (5.2 g). This oil exhibited characteristic ir absorptions at 2048 (diazo) and 1725 cm^{-1} (carbonyl). It decomposed rapidly at 90° with nitrogen evolution. In this case, the purity of this diazo compound was found to be 60% and the yield 12%. Further reactions were carried out in this purity.

Reaction of Methyl 4-Phenyl-4-diazobutyrate (2) with Diphenylacetylene. 3,4,5-Triphenylpyrazole (4).—A solution of methyl 4-phenyl-4-diazobutyrate (**2**) (14 mmol) was added dropwise under stirring to a diglyme solution (10 ml) of diphenylacetylene (18.7 g, 0.11 mol) at 100° in 2 hr. The volume of nitrogen gas evolved was 60% of theoretical amount. The reaction mixture was extracted with ether. The ethereal solution was washed with water, dried over anhydrous magnesium sulfate, and concentrated. The residue was chromatographed on a column of alumina (230 g). From a fraction eluted by petroleum ether, diphenylacetylene (17.8 g) was recovered and elution with ether–ethanol gave 3,4,5-triphenylpyrazole (**4**) (1.2 g, 29%). After recrystallization from benzene–ethanol, this pyrazole melted at 260–261°. It exhibited characteristic ir absorption at 3200 cm^{-1} (N—H stretching). An ir spectrum of this compound was superimposable with an authentic material prepared from benzaldesoxybenzoin and hydrazine followed by the oxidation with bromine[7] and mixture melting point was undepressed.

Anal. Calcd for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45. Found: C, 84.96; H, 5.50; N, 9.24.

Elution with ether resulted in tarry material, but this was not studied.

The same reaction was carried out at 55°. A solution of the diazo compound (**2**, 6.1 mmol) in *n*-hexane (15 ml) was added to an *n*-hexane solution (10 ml) of diphenylacetylene (12.3 g, 69 mmol). After the mixture was stirred for 17 hr, the resulting yellow solution was subjected to alumina column chromatography (300 g). Elution with ether–ethanol gave the same pyrazole (**4**, 0.18 g, 10%).

Reaction of 2 with Phenylacetylene. 3,5-Diphenyl-3-(2′-carbomethoxyethyl)-3H-pyrazole (6).—A solution of methyl 4-phenyl-4-diazobutyrate (**2**, 16 mmol) in phenylacetylene (30 ml) was added dropwise to phenylacetylene (18.3 g) with stirring for 30 min at 55°. After stirring for an additional hour, the solution decolorized and the excess phenylacetylene was removed under vacuum. The residual oil was allowed to crystallize in a refrigerator. Recrystallization from petroleum ether–benzene gave 3,5-diphenyl-3-(2′-carbomethoxyethyl)-3H-pyrazole (**6**): 2.9 g, 59%; mp 100.5–101.5°; uv max (95% C_2H_5OH) 273 mμ (log ε 4.07) and 280 (sh) (3.25); ir (Nujol) 1733 (ester C=O), 1180 (ester C—O), and 1623 cm^{-1} (C=C); nmr (CCl_4) 1.95–2.28 (11) m, 6.53 (3) s, 7.15–7.65 (2) m, 7.80–8.03 (2) m.

Anal. Calcd for $C_{19}H_{18}O_2N_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.58; H, 5.75; N, 9.11.

Thermal Rearrangement of 3H-Pyrazole 6 to 5-(2′-Carbomethoxyethyl)-3,4-diphenylpyrazole (10).—A solution of 3H-pyrazole (**6**, 0.36 g, 1.2 mmol) in diglyme (15 ml) was heated under reflux for 3 hr. The reaction mixture was poured into water and the organic layer was extracted with ether, dried over anhydrous magnesium sulfate, and concentrated. The residue crystallized. Recrystallization from petroleum ether–benzene gave 5-(2′-carbomethoxyethyl)-3,4-diphenylpyrazole: 0.33 g, 92%; mp 124–125°; uv max (95% C_2H_5OH) 220 mμ (log ε 4.08) and 250 (3.88); ir (Nujol) 3150 (N—H), 1730 (ester C=O), and 1150 cm^{-1} (ester C—O); nmr ($CDCl_3$) 2.50–2.90 (10) m, 6.36 (3) s, 7.03 (2) t (J = 8 Hz), and 7.37 (2) t.

Anal. Calcd for $C_{19}H_{18}O_2N_2$: C, 74.49; H, 5.92; N, 9.15. Found: C, 74.56; H, 5.92; N, 9.09.

Hydrolysis of Pyrazole 10.—A solution of pyrazole (**10**, 1.19 g, 3.8 mmol) and potassium hydroxide (1.05 g, 19 mmol) in methanol (30 ml) was refluxed for 2.5 hr on a water bath. The mixture was poured into water (100 ml) and acidified with 10% hydrochloric acid (50 ml); then the crude 3,4-diphenyl-5-(2′-carboxyethyl)pyrazole precipitated (1.07 g, 96%). Recrystallization from water–acetone gave the pure pyrazole which decomposed at 233–234°.

Anal. Calcd for $C_{18}H_{16}O_2N_2$: C, 73.95; H, 5.52. Found: C, 73.91; H, 5.69.

Oxidation of 3,4-Diphenyl-2-(2′-carboxyethyl)pyrazole.—To a solution of 3,4-diphenyl-2-(2′-carboxyethyl)pyrazole (0.56 g, 1.9 mmol) in *t*-butyl alcohol (8 ml) was added potassium permanganate (1.50 g, 9.5 mmol) in water (10 ml). After the mixture was heated under reflux for 3 hr, excess permanganate was decomposed with methanol. The hot mixture was filtered and the filtrate was acidified with 10% hydrochloric acid, then the crude 3,4-diphenylpyrazole-5-carboxylic acid precipitated (0.06 g, 12%). Two recrystallizations from water–methanol gave the pure pyrazolecarboxylic acid, mp 259–260°. The ir spectrum of this compound was superimposable with that of an authentic material prepared from the reaction of phenyldiazomethane and methyl phenylpropiolate followed by hydrolysis,[9] and mixture melting point was undepressed.

Photolysis of 3H-Pyrazole 6.—A solution of 3H-pyrazole (**6**, 4.08 g, 13 mmol) in dry benzene (300 ml) was irradiated with a 500-W high pressure mercury lamp at 10–12° in a quartz reaction vessel (500 ml). A red coloration developed after 5 min. Part of the reaction mixture was examined by ir spectroscopy. The characteristic absorption for diazo group was observed at 2010 cm^{-1}. Nitrogen evolution was completed after about 3 hr. The solvent was removed under vacuum. Distillation gave a fraction of bp 132–136° (0.002 mm) (2.15 g) and a residue (1.51 g). The yellow distillate was purified by a column chromatography on 50 g of alumina. Elution with petroleum ether (140 ml) afforded *trans*-2-styryl-2-phenylcyclopropane-1-carboxylic acid methyl ester (**14a**, 0.25 g). An analytically pure sample was obtained by recrystallization from benzene–petroleum ether: mp 105°; uv max (95% C_2H_5OH) 261 mμ (log ε 4.44), 286 (sh) (3.85), and 296 (3.61); ir (CCl_4) 1730 (ester C=O), 1638 (C=C), and 1180 cm^{-1} (ester C—O); nmr ($CDCl_3$) 2.63 (5) s, 2.78 (1) s, 3.44 (1) d (J = 16 Hz), 4.12 (1) d (J = 16 Hz), 6.25 (3) s, 7.63 (1) d (J = 5.9 Hz) of d (J = 8.2 Hz), 8.10 (1) d (J = 4.9 Hz) of d (J = 5.9 Hz), and 8.32 (1) d (J = 4.9 Hz) of d (J = 8.2 Hz).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.72; H, 6.23.

Further elution with petroleum ether (350 ml) and petroleum ether–ether (3:7, 140 ml) gave a yellow mixture (0.84 g). Finally, elution with methanol gave a glassy material,[34] which was not further investigated. The yellow mixture was rechromatographed on alumina (5 g). Elution with petroleum ether gave a yellow oil (0.31 g) and *cis*-2-styryl-2-phenylcyclopropane-1-carboxylic acid methyl ester (**14b**, 0.11 g). The analytical sample was purified by recrystallization from benzene–petroleum ether: mp 65–67°; uv max (95% C_2H_5OH) 262 mμ (log ε 4.33), 287 (sh) (3.69), and 296 (3.36); ir (CCl_4) 1730 (ester C=O), 1632 (C=C), and 1160 cm^{-1} (ester C—O); nmr (CCl_4) 2.80 (5) s, 2.91 (5) s, 4.08 (2) s, 6.14 (3) s, 7.73–8.05 (2) m, and 8.57 (1) q.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.02; H, 6.50.

The yellow oily substance from petroleum ether elution was rechromatographed, yielding compounds **14a** (0.03 g) and **14b**

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(33) L. F. Somerville and C. F. H. Allen in "Organic Syntheses," Coll. Vol. II, N. Rabjohn, Ed., John Wiley & Sons, Inc, New York, N. Y., 1963, p 81.

(34) Recently it has been reported by G. L. Closs, *et al.*,[13c] that 1-phenyl-3,3-dimethylcyclopropene polymerized rapidly in a condensed phase at room temperature. There is a possibility that the glassy material obtained in the present experiment might be produced by the polymerization of cyclopropene derivative.

(0.13 g) isolated in 7.5 and 6.5% total yield, respectively. The residue at distillation described above was crystallized from ether. Recrystallization from benzene–petroleum ether yielded the colorless needles (0.28 g, 7.5%). Recrystallizations afforded a pure analytical bicyclo[2.2.0]hexene derivative (**13**): mp 199–200°; uv max (95% C_2H_5OH) 207 mμ (log ε 4.56), 314 (4.46); and *ca.* 230 (sh) (4.14); ir (Nujol) 1730 (ester C=O), 1160 (ester C—O), 760, and 700 cm^{-1} (monosubstituted phenyl); nmr ($CDCl_3$) 2.70–3.10 (20) m, 4.28 (2) s, 6.58 (6) s, 7.50 (4) t (J = 7 Hz), and 7.90 (4) (J = 7 Hz).

Anal. Calcd for $C_{38}H_{36}O_4$: C, 81.98; H, 6.52; mol wt, 556. Found: C, 81.79; H, 6.54; mol wt, 556.

This compound **13** discolored the solutions of both potassium permanganate in acetone and bromine in carbon tetrachloride at room temperature. On the contrary, it could not be hydrogenated under the conditions in which *trans-trans*-1,4-diphenylbutadiene in ethanol was hydrogenated on platinum black at room temperature.

Hydrogenation of Methyl *trans*-2-Styryl 2-phenylcyclopropanecarboxylate (14a).—Methyl *trans*-2-styryl-2-phenylcyclopropanecarboxylate (0.078 g, 0.28 mmol) was hydrogenated in ethanol–ether (18:1, 90 ml) with palladium black catalyst (70 mg) at room temperature under atmospheric pressure. Hydrogen uptake (1 mol equiv) was complete after 1 hr. After the solvent was removed, the residual oil was subjected to an alumina column chromatography (7.8 g). Elution with ether gave methyl 2-(2′-phenylethyl)-2-phenylcyclopropanecarboxylate (**15a**, 0.058 g, 71%). Recrystallization from petroleum ether gave a pure analytical sample: mp 44–46°; nmr (CCl_4) 2.70–3.18 (10) m, 6.40 (3) s, 7.55–7.71 (2) m, 7.90–8.20 (3) m, and 8.46–8.82 (2) m.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.60; H, 7.17.

Hydrogenation of Methyl *cis*-2-Styryl-2-phenylcyclopropanecarboxylate (14b).—Methyl *cis*-2-styryl-2-phenylcyclopropanecarboxylate (**14b**, 0.233 g, 0.83 mmol) was hydrogenated in ethanol (40 ml) with palladium black catalyst (90 mg). Theoretical amount of hydrogen was absorbed after 1 hr. After the solvent was removed, the residual oil was chromatographed on alumina (30 g). Elution with petroleum ether gave colorless oil, methyl 2-(2′-phenylethyl)-2-phenylcyclopropanecarboxylate (**15b**, 0.166 g, 71%), which crystallized in an ice box. An analytical sample was obtained by preparative vpc (Apiezon L, 2 m, 264°) and recrystallized from petroleum ether: mp 10–12°; nmr (CCl_4) 2.80–3.11 (10) m, 6.69 (3) s 7.32–8.50 (6) m, and 8.82–9.10 (1) m.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19 Found: C, 81.53; H, 7.19.

Preparation of Authentic Materials.—To a stirred solution of 2,4-diphenylbut-1-ene[35] (7.0 g, 34 mmol) in dry ether (10 ml) containing cuprous chloride (2.5 g) was added a solution of methyl diazoacetate (6.2 g, 62 mmol) in dry ether (10 ml) for a period of 1 hr at 35° and the mixture was stirred for an additional 1 hr. After cuprous chloride was filtered off, the ether was evaporated, and residual oil was chromatographed on an alumina column (130 g). From a fraction eluted by petroleum ether (150 ml), colorless oily material was obtained, which was rechromatographed to give the starting olefin (4.8 g) and **15a** (0.52 g). Further elution with the same solvent (150 ml) gave the oily substance which was purified by rechromatography on alumina, yielding the starting olefin (0.2 g) and cyclopropanecarboxylate **15b** (0.58 g). Compounds **15a** and **15b** obtained in this reaction were identical in all respects with hydrogenated products of **14a** and **14b**, respectively.

Registry No.—**1** tosylhydrazone, 18793-81-2; **2** tosylhydrazone, 18793-82-3; **3**, 18793-83-4; 1,2,3-triphenylcyclopropene-3-carboxylic acid, 18793-84-5; **4**, 18076-30-7; **6**, 18793-86-7; **10**, 18793-87-8; 3,4-diphenyl-5-(2′-carboxyethyl)pyrazole, 18793-88-9; **13**, 18793-89-0; **14a**, 18793-91-4; **14b**, 18793-90-3; **15**, 18793-92-5.

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Sugar Lactams. III. Synthesis of Five-, Six-, and Seven-Membered Analogs[1-3]

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Sugar lactams having five-, six-, and seven-membered rings have been prepared by the reductive cyclization of appropriate azido lactones or carboxylic acids. The synthesis of sugar lactim ethers, a new group of sugars containing nitrogen in the ring, is described.

In earlier communications[5,6] we investigated newer methods for the synthesis of 5-amino-5-deoxypentopyranoses[7-9] by the reductive ring expansion of 5-azido-5-deoxypentofuranoses.[5,6] The reaction is an excellent preparative route to 3,4,5-trihydroxypiperidines[6,9] which are formed as sole products in the presence of excess catalyst. Anticipating that the reduction of certain azido aldonolactones would also proceed with ring enlargement of the intermediate amino aldonolactones, we synthesized sugar lactams of various ring sizes and studied their transformations.

Oxidation of 5-azido-2,3-*O*-benzylidene-5-deoxy-β-D-ribofuranose (**1**)[8] with pyridine–chromium trioxide proceeded very readily to give crystalline 5-azido-2,3-*O*-benzylidene-5-deoxy-D-ribonolactone (**2**)[3] (Scheme I). It should be noted that, whereas the oxidation of a secondary hydroxyl group in a furanose derivative with the pyridine–chromium trioxide reagent has been unsuccessful,[10] the anomeric hydroxyl group in **1** is readily oxidized. Hydrogenation of the azido lactone **2** afforded crystalline 5-amino-2,3-*O*-benzylidene-5-deoxy-D-ribo-

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