Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.45; H, 12.39.

B. From the Hydrogenation of Phenanthrene.—Separation of the first (a) of the two isomers obtained from the hydrogenation of phenanthrene by preparative vpc gave a product which was identical by its vpc retention time, index of refraction, and nmr spectrum with that obtained from the reduction of the tosylate **23**. After separation by vpc, this isomer was chromatographed on 5 g of neutral, activity I Woelm alumina in pentane. The material obtained gave a negative TNM test and had $n^{25}\mathrm{D}$ 1.5015.

Anal. Calcd $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.37; H, 12.78.

Registry No.—**1**, 2108-89-6; **2**, 27425-35-0; **3**, 27389-73-7; **4**, 27389-74-8; **5**, 26634-41-3; **6**, 27389-76-0; **23**, 27389-77-1; **29**, 27389-78-2; **30**, 27389-79-3.

Studies of Acenaphthene Derivatives. XXI.[1] Reaction of 2-Diazoacenaphthenone with Olefins and Acetylenes

OTOHIKO TSUGE,*[2] ICHIRO SHINKAI, AND MASAHIRO KOGA

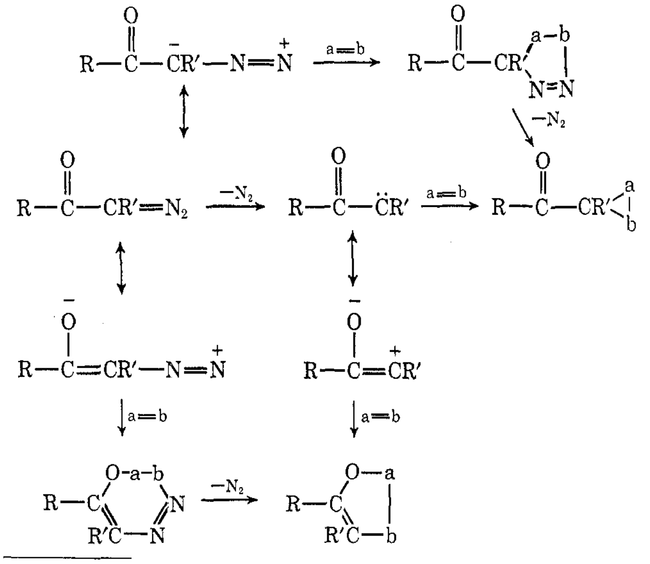
Research Institute of Industrial Science, Kyushu University, Hakozaki, Fukuoka 812, Japan

Received July 20, 1970

No thermal decomposition of 2-diazoacenaphthenone (**1**) occurred in boiling benzene or toluene for a long while. Copper-catalyzed thermolysis of **1** in boiling toluene led to the formation of biacenedione, although **1** was not decomposed in boiling benzene under the influence of copper powder. On the other hand, thermolysis of **1** in boiling xylene gave biacenedione, together with a trace amount of acenaphthenequinone ketazine. Reactions of **1** with ethyl acrylate (**2a**), acrylonitrile (**2b**), ethyl α-bromoacrylate (**2c**), methyl vinyl ketone (**2d**), and diethyl fumarate and maleate in refluxing benzene gave the corresponding spiro[acenaphthenone-2,1′-cyclopropanes] (**3a–d**, **4a–c**, **7**); with **2a**, **2b**, and **2c**, two stereoisomers obtained respectively. Although **1** did not react with cyclohexene and indene, the reaction with bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride gave the spiro-[acenaphthenone-2,3′-tricyclooctanedicarboxylic anhydride] (**8**). However, **1** reacted with acrolein to give two isomers of 2′-hydroxymethylspiro[acenaphthenone-2,1′-cyclopropanes] (**5**, **6**) corresponding to dihydro derivatives of the expected 2′-formyl compounds. On the other hand, addition of **1** to phenylacetylene and to diethyl acetylenedicarboxylate gave the corresponding spiro[acenaphthenone-2,3′(3′H)-pyrazoles] (**9**, **10**).

The thermal and photochemical reactions of α-diazo ketones, such as diazoacetophenone, azibenzil, and *o*-benzoquinone diazide, have received considerable attention.[3] Although α-diazo ketones exhibit a different behavior depending on their nature and reaction conditions, the reaction can be classified into three categories from a viewpoint of the cycloaddition, as illustrated in Scheme I. Little attention has been paid to the reaction of α-diazo ketone with olefins under such conditions that the ketocarbene is not generated, although the low temperature reactions of diazomethanes have been investigated considerably.

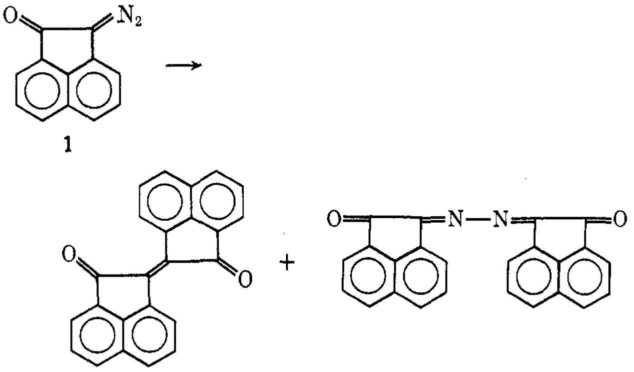
SCHEME I



In order to clarify whether 2-diazoacenaphthenone (**1**) reacts with an olefin to lead to the spiropyrazoline or -cyclopropane ring formation, or to give the dihydro-1,4,5-oxadiazepine or dihydrofuran, the reaction of **1** with various olefins in refluxing benzene has been investigated. Also, this paper deals with the reaction of **1** with acetylenes.

Results and Discussion

The diazo ketone **1** was not decomposed in boiling benzene or toluene for a long while; **1** was recovered quantitatively. Thermolysis of **1** in boiling toluene was greatly accelerated by copper powder and led to the formation of diacenaphthylidenedione (biacenedione), although the decomposition of **1** did not take place in the presence of copper powder in boiling benzene. As shown by Ried and Lohwasser,[4] thermolysis of **1** in boiling xylene gave biacenedione as the main product, accompanied by a trace amount of acenaphthenequinone


1

---

[1] (a) Presented in part at the 22th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1969. (b) Part XX of this series: O. Tsuge and I. Shinkai, *Bull. Chem. Soc. Jap.*, **43**, 3514 (1970).

[2] Author to whom correspondence should be directed.

[3] For reviews, see M. Regitz, *Angew. Chem.*, **79**, 786 (1967); see also G. Pfundt and G. O. Schenck, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York and London, 1967, p 405.

[4] W. Ried and H. Lohwasser, *Justus Liebigs Ann. Chem.*, **683**, 118 (1965).

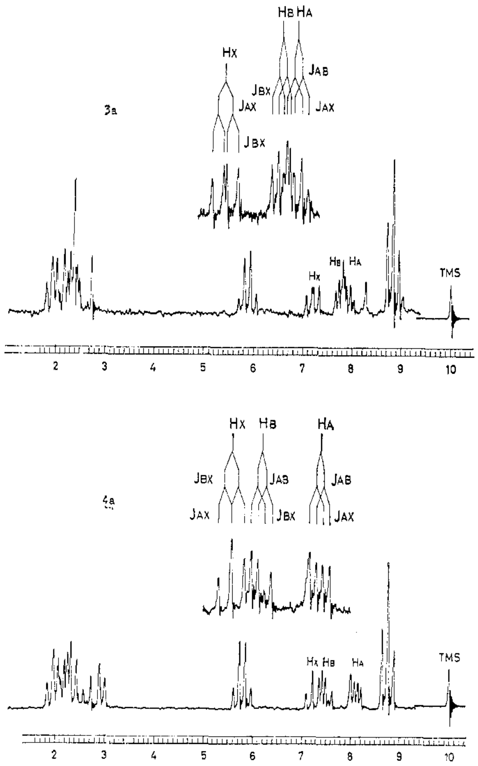


Figure 1.—Nmr spectra of **3a** and **4a**.

ketazine. The ketazine was not converted into biacenedione under the above conditions.[5] Although the mechanism of these decompositions has not been established, biacenedione appears to be derived from the reaction of **1** with the ketocarbene intermediate and/or dimerization of the ketocarbene.

It has been found that, in refluxing benzene or in xylene at the temperature at which benzene boils, **1** reacted with olefins under the elimination of nitrogen and no biacenedione was formed.

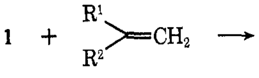
When a solution of **1** and ethyl acrylate (**2a**) in benzene was refluxed for 10 hr, two products, **3a** (mp 74–75°) and **4a** (mp 110–111°), were obtained in 30 and 35% yields, respectively. Elemental analyses and molecular weight (M^+ m/e 266) of both **3a** and **4a** agreed with the molecular formula ($C_{17}H_{14}O_3$) derived from a 1:1 adduct of **1** and **2a** under the elimination of nitrogen. The ir spectrum of **3a** showed the bands ascribed to carbonyl groups at 1710 and 1728 cm^{-1}, while the bands appeared at 1713 and 1740 cm^{-1} in that of **4a**. However, the mass spectrum of **4a** was very similar to that of **3a**. The compound **3a** was proved, by a mixture melting point determination and by the ir spectrum, to be identical with an authentic sample of 2′-ethoxycarbonylspiro[acenaphthenone-2,1′-cyclopropane] previously[1b] prepared from ethoxycarbonylmethyleneacenaphthenone and dimethyloxosulfonium methylide.

The nmr spectra of **3a** and **4a** are illustrated in Figure 1. A typical ABX pattern for cyclopropyl protons appears in the nmr spectrum of **4a** as well as in that of **3a**. It is well known that *cis*-cyclopropanes exhibit higher coupling constants (8–10,[6] 7.9–9.3 Hz[7]) than those (4–7,[6] 5.3–6.6 Hz[7]) of the corresponding trans isomers. Also, Graham and Rogers[7] have reported that the values of $J_{cis} + J_{trans}$ and $J_{cis} + J_{trans} + J_{gem}$ in 1,1,2-trisubstituted cyclopropanes are virtually constant (about 16 and 21 Hz, respectively), regardless of the nature of substituents. The respective values in **3a** and **4a** are shown in Table II.

From the above observations, it may be deduced that **4a** is a stereoisomer of **3a**. Two stereoisomers owing to the conformation of the spirocarbon atom are possible for 2′-ethoxycarbonylspiro[acenaphthenone-2,1′-cyclopropane]. It has previously been reported that **3a** is consistent with the configuration in which H_A and H_X are situated cis and the ethoxycarbonyl group sees the acenaphthene ring.

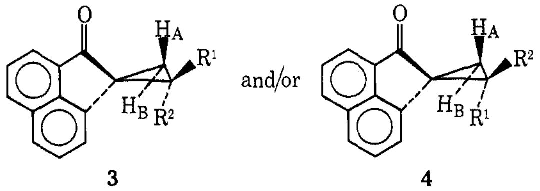
As Figure 1 shows, the methyl protons signal of the ethoxycarbonyl group in **3a** appears at a field higher than that in **4a**. This fact can be understood in terms of the shielding effect of acenaphthene ring and supports the proposed configuration for **3a**.

From a comparison of chemical shifts of methyl protons in two stereoisomeric ethoxycarbonylmethyleneacenaphthenones[8] with those in **3a** and **4a**, and from a study of coupling constants of cyclopropyl protons in **3a** and **4a**, it may be considered that **4a** is the spiro[acenaphthenone-2,1′-cyclopropane] in which H_A and H_X are situated trans and the ethoxycarbonyl group overlooks the carbonyl group in the acenaphthenone ring.



1 + $\mathrm{R^1R^2C{=}CH_2} \longrightarrow$

2a, $R^1 = H$; $R^2 = CO_2Et$
b, $R^1 = H$; $R^2 = CN$
c, $R^1 = Br$; $R^2 = CO_2Et$
d, $R^1 = H$; $R^2 = COCH_3$



3 **4**

a, $R^1 = H_X$; $R^2 = CO_2Et$
b, $R^1 = H_X$; $R^2 = CN$
c, $R^1 = Br$; $R^2 = CO_2Et$
d, $R^1 = H_X$; $R^2 = COCH_3$

Similar reactions of **1** with acrylonitrile (**2b**) and ethyl α-bromoacrylate (**2c**) gave the corresponding spiro[acenaphthenone-2,1′-cyclopropanes] (**3b** and **4b**, **3c** and **4c**), respectively. However, **1** reacted with methyl vinyl ketone (**2d**) to give only one 2′-acetylspiro[acenaphthenone-2,1′-cyclopropane] (**3d**). The respective configurations for **3** and **4** were assumed on the basis of spectral studies.

The yields, physical properties, elemental analyses, and spectral data of **3** and **4** are summarized in Tables I and II.

---

[5] When acenaphthenequinone ketazine was decomposed at 300° for 1 hr, biacenedione was obtained in 65% yield.

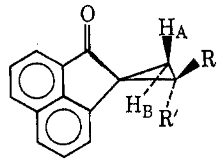
[6] K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **85**, 2788 (1963).

[7] J. D. Graham and M. T. Rogers, *ibid.*, **84**, 2249 (1962).

[8] In the nmr spectrum ($CDCl_3$) of ethoxycarbonylmethyleneacenaphthenone whose ethoxycarbonyl group overlooks the carbonyl group in acenaphthenone ring, methyl and methylene protons appeared at τ 8.60 (t, 3) and 5.60 (q, 2), while the respective protons appeared at τ 8.75 (t, 3) and 5.70 (q, 2): O. Tsuge, M. Tashiro, and I. Shinkai, *Bull. Chem. Soc. Jap.*, **42**, 181 (1969).

TABLE I

SYNTHESES OF **3** AND **4**



Olefin	Reaction time, hr	Compd	R	R′	Yield, %	Mp, °C	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Mol wt, *m/e*
2a	10	**3a**	H	CO_2Et	30	74–75	76.67	5.30		76.78	5.04		266
		4a	CO_2Et	H	35	110–111	76.67	5.30		76.48	5.11		266
2b	13	**3b**[a]	H	CN	39	118–119	82.17	4.14	6.39	81.99	4.17	6.30	219
		4b[a]	CN	H	44	163–164	82.17	4.14	6.39	81.92	3.97	6.45	219
2c	8	**3c**	Br	CO_2Et	57	120–121	59.13	3.77		59.25	3.81		344, 346
		4c	CO_2Et	Br	12	160–162	59.13	3.77		59.06	3.82		344, 346
2d	2	**3d**	H	$COCH_3$	65	106–107	81.34	5.12		81.17	4.91		236

[a] It was temporarily assigned that the compound with lower melting point was **3b** and that with higher melting point was **4b**.

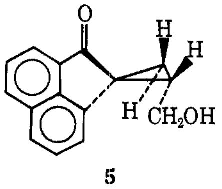
TABLE II

SPECTRAL DATA OF **3** AND **4**

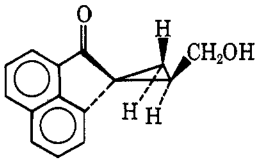
Compd	$\nu_{C=O}^{KBr}$, cm^{-1}	Chemical shift, τ H_A	H_B	R or R′ (H_X)	R or R′ (CH_3)	R or R′ (CH_2)	Coupling constant, Hz J_{trans}	J_{cis}	J_{gem}	$J_{trans} + J_{cis}$	$J_{trans} + J_{cis} + J_{gem}$
3a	1728, 1710	7.95	7.75	7.25	8.82	5.86	6.5	9.9	4.5	16.4	20.9
4a	1740, 1713	8.08	7.48	7.21	8.76	5.78	8.1	8.4	4.2	16.5	20.7
3b	1700, 2240[a]	8.02	7.80	7.46			7.2	8.4	4.5	15.6	20.1
4b	1713, 2260[a]	7.94	7.73	7.52			6.9	9.6	3.6	16.5	20.1
3c	1716	7.60	7.14		8.82	5.84			6.9		
4c	1736, 1710	7.86	7.10		8.72	5.72			6.9		
3d	1705, 1690	7.95	7.66	6.90	7.84		7.1	8.4	5.1	15.5	20.6

[a] $\nu_{C\equiv N}^{KBr}$.

Although a similar reaction of **1** with acrolein gave also two products, **5** (mp 134–136°) and **6** (mp 114–116°), in 13 and 24% yields, respectively, the molecular formula of both **5** and **6** did not agree with the expected 2′-formylspiro[acenaphthenone-2,1′-cyclopropanes] but agreed with their dihydro derivatives. The ir spectra of **5** and **6** displayed the bands ascribed to the hydroxyl and carbonyl groups; the absorption of hydroxyl group in **5** appeared as a sharp band at 3620 cm^{-1} and that in **6** was revealed as a broad band at 3450 cm^{-1} in the respective spectrum in a dilute benzene solution. The nmr spectrum of **5** showed signals at τ 8.10 (1 H, OH, exchanged with D_2O) and 6.00 (2 H, CH_2OH), while that of **6** exhibited signals at τ 7.54 (1 H, OH, exchanged with D_2O) and 5.93 (2 H, CH_2OH), besides signals ascribed to cyclopropyl and aromatic protons. The appearance of the hydroxyl proton in **6** at a higher field than that in **5** may be attributable to the shielding effect of acenaphthene ring in **5** and to the hydrogen bonding between the hydroxyl and carbonyl groups in **6**.



5

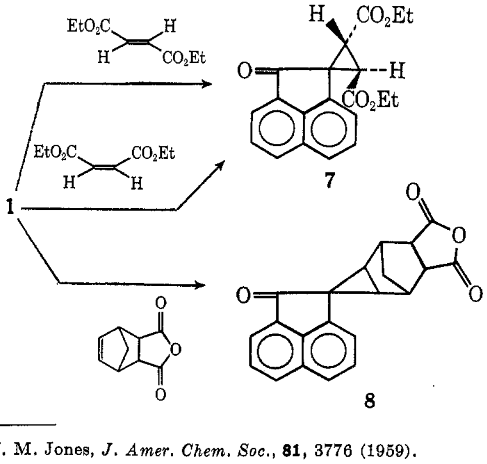


6

From a consideration of the above results, it seems reasonable to assume that **5** is 2′-hydroxymethylspiro[acenaphthenone-2,1′-cyclopropane] in which the hydroxymethyl group sees the acenaphthene ring, while **6** is the isomer in which the hydroxymethyl group overlooks the carbonyl group in the acenaphthenone ring. However, the reduction course of the formyl to hydroxymethyl group is not clear yet.

Jones[9] has reported that the reaction of ethyl diazoacetate with *cis*- or *trans*-stilbene at 180–200° gave the *cis*- or *trans*-cyclopropane, respectively.

When the reaction of **1** with diethyl fumarate or maleate was conducted in refluxing benzene, the same product, *trans*-2′,3′-diethoxycarbonylspiro[acenaphthenone-2,1′-cyclopropane] (**7**), was obtained in 89 or 37% yield. The compound **7** was identical with an authentic sample[1b] prepared from ethoxycarbonylmethyleneacenaphthenone and dimethylethoxycarbonylsulfonium methylide. Also, the reaction of **1** with diethyl fumarate in the presence of copper in refluxing toluene gave **7** in 65% yield, together with a small amount of biacenedione.



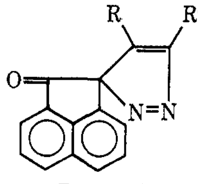
---

[9] W. M. Jones, *J. Amer. Chem. Soc.*, **81**, 3776 (1959).

Similar reactions of **1** with cyclohexene and indene did not take place, but **1** was quantitatively recovered. On the other hand, **1** reacted with bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride to give spiro[acenaphthenone-2,3′-tricyclo[3.2.1.0$^{2',4'}$]octane-6′,7′-dicarboxylic anhydride] (**8**), mp 274–276° dec, in 25% yield. The structure of **8** was confirmed by ir, nmr, and mass spectra as well as by the elemental analysis. Unfortunately its configuration could not be clarified yet.

It has been reported that disubstituted diazomethanes reacted with acetylenes to give pyrazolenines or pyrazoles depending on the nature of reagents and reaction conditions.[10] Also, diazoacetophenone reacted with phenylacetylene at 100°, affording 3-benzoyl-5-phenylpyrazole in a good yield.[11] Recently, Snatzke and Langen[12] have observed that 3,3-diphenylpyrazolenine obtained from diphenyldiazomethane and acetylene, isomerized to 3,4-diphenylpyrazole on treatment with acetic acid, and gave 1,1-diphenylcyclopropene on photolysis.

When the reactions of **1** with phenylacetylene and with diethyl acetylenedicarboxylate were performed in refluxing benzene, 5′-phenyl- (**9**), mp 243–244°, and 4′,5′-diethoxycarbonylspiro[acenaphthenone-2,3′(3′H)-pyrazole] (**10**), mp 147.5–148.5°, were obtained in 25 and 80% yields. The structures of **9** and **10** were confirmed by ir, nmr, and mass spectra as well as by elemental analyses.



9, R = H; R′ = Ph
10, R = R′ = CO_2Et

The compounds **9** and **10** were stable on heating in boiling *o*-dichlorobenzene for 8 hr. Also, when a benzene solution of **9** or **10** was irradiated by a 100-W high-pressure mercury lamp with a Pyrex filter at room temperature for 8 hr, **9** or **10** was recovered quantitatively.

Experimental Section[13]

Materials.—2-Diazoacenaphthenone (**1**) was prepared by the reported method[14] and purified by chromatography (alumina), mp 93–94° (lit.[14] 94°). Olefins purchased from Wako Pure Chemical Co. were purified by distillation.

Thermolysis of 2-Diazoacenaphthenone (1). A. In Xylene.—After a solution of **1** (580 mg, 3 mmol) in xylene (25 ml) was refluxed for 24 hr, the solvent was removed under vacuum. The residue was triturated with benzene (10 ml) and then filtration gave acenaphthenequinone ketazine, mp 295° dec, whose ir spectrum was identical with that of an authentic sample, yield 15 mg (2.8%). The filtrate was chromatographed on alumina using benzene as eluent. The foreband gave unreacted **1** (160 mg, 28%), and further elution with chloroform afforded 210 mg (42%) of biacenedione, mp 294°, which was identical with the authentic sample prepared from acenaphthenequinone and acenaphthenone.

B. Copper-Catalyzed Decomposition in Toluene.—A solution of **1** (500 mg, 2.6 mmol) in toluene (20 ml) was refluxed over copper powder (300 mg) for 1 hr. The reaction mixture was filtered and washed with hot toluene to leave copper (300 mg). After the filtrate and washings were concentrated under vacuum, the residue was purified by chromatography on alumina in a similar manner as above; unreacted **1** (80 mg, 16%) and biacenedione (340 mg, 79.5%) were obtained.

In refluxing benzene for 6 hr in the presence of copper powder, **1** was not decomposed but recovered quantitatively. Also, no decomposition of **1** occurred in refluxing toluene for 24 hr in the absence of copper powder.

Reaction of 1 with Ethyl Acrylate (2a).—A solution of **1** (290 mg, 1.5 mmol) and **2a** (450 mg, 4.5 mmol) in benzene (25 ml) was refluxed for 10 hr; during this time an initial orange solution became pale yellow. Solvent was removed under vacuum, leaving a semicrystalline residue which was triturated with *n*-pentane (20 ml) to give crystals. The crystals were collected by filtration and recrystallized from petroleum benzine (bp 42–60°), giving 140 mg (35%) of **4a**, mp 110–111°, as colorless prisms.

The *n*-pentane filtrate was concentrated to dryness under vacuum, leaving a semicrystalline compound. Purification by chromatography (alumina) using benzene as eluent followed by recrystallization from petroleum ether (bp 38–50°) gave 120 mg (30%) of **3a**, mp 74–75°, as colorless prisms. This compound was identical with an authentic sample[1b] prepared from ethoxycarbonylmethyleneacenaphthenone and dimethyloxosulfonium methylide.

Similar reactions of **1** with acrylonitrile (**2b**), ethyl α-bromoacrylate (**2c**), and methyl vinyl ketone (**2d**) gave the corresponding spiro[acenaphthenone-2,1′-cyclopropanes] **3** and **4**. The yields, physical properties, elemental analyses, and spectral data are summarized in Tables I and II.

Reaction of 1 with Acrolein.—After a solution of **1** (870 mg, 4.5 mmol) and acrolein (1.12 g, 20 mmol) in benzene (25 ml) was refluxed for 10 hr, the reaction mixture was concentrated under vacuum. The residue was chromatographed (alumina), eluting with chloroform. The obtained crystals were recrystallized twice from benzene, giving 90 mg (13%) of **5**, mp 134–136°, as colorless needles: ir (KBr) 3390 (OH), 1680 cm^{-1} (C=O); ir (dilute benzene solution) 3620 (OH), 1722 cm^{-1} (C=O); nmr τ 8.55–7.5 (m, 3, cyclopropyl ring protons), 8.10 (s, 1, OH, exchanged with D_2O), 6.00 (m, 2, CH_2OH), 2.85–1.8 (m, 6, aromatic protons); mass spectrum *m/e* (rel intensity) 224 (50), 206 (10), 205 (21), 194 (16), 181 (29), 180 (100), 178 (14), 168 (37), 166 (13), 165 (72), 164 (19), 163 (23), 153 (17), 152 (82), 151 (26), 150 (14), 139 (13).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 80.30; H, 5.21.

The benzene filtrate was concentrated under vacuum, and three recrystallizations of the residue from ligroin (bp 80–110°) gave 170 mg (24%) of **6**, mp 114–116°, as colorless prisms: ir (KBr) 3430 (OH), 1680 cm^{-1} (C=O); ir (dilute benzene solution) 3450 (OH), 1717 cm^{-1} (C=O); nmr τ 8.55–7.5 (m, 3, cyclopropyl ring protons), 7.54 (s, 1, OH, exchanged with D_2O), 5.93 (m, 2, CH_2OH), 3.05–1.8 (m, 6, aromatic protons); mass spectrum *m/e* (rel intensity) 224 (72), 206 (11), 205 (26), 194 (13), 181 (43), 180 (100), 178 (24), 168 (48), 166 (14), 165 (73), 164 (26), 153 (24), 151 (28), 150 (16), 139 (16).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39. Found: C, 80.38; H, 5.48.

***trans*-2′,3′-Diethoxycarbonylspiro[acenaphthenone-2,1′-cyclopropane] (7). A. In Benzene.**—A solution of **1** (870 mg, 4.5 mmol) and diethyl fumarate (1.55 g, 9 mmol) in benzene (25 ml) was refluxed for 6 hr. Solvent was removed under vacuum, giving a semicrystalline residue which was triturated with petroleum benzine (bp 42–60°). The crystals were collected by filtration and then recrystallized from methanol, giving 1.35 g (89%) of **7**, mp 109–110° (lit.[1b] 110–111°), as colorless prisms. This compound was proved, by the mixture melting point and by the ir spectrum, to be identical with an authentic sample[1b] prepared from ethoxycarbonylmethyleneacenaphthenone and dimethylethoxycarbonylsulfonium methylide. A similar reaction of **1** with diethyl maleate for 12 hr gave **7** in 37% yield.

B. In Toluene in the Presence of Copper Powder.—After a solution of **1** (500 mg, 2.6 mmol) and diethyl fumarate (660 mg, 3.8 mmol) in toluene (20 ml) was refluxed over copper powder (300 mg) for 3 hr, the hot reaction mixture was filtered to leave

---

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

[11] W. Ried and J. Omran, *Justus Liebigs Ann. Chem.*, **666**, 144 (1963).

[12] G. Snatzke and H. Langen, *Chem. Ber.*, **102**, 1865 (1969).

[13] All melting points are uncorrected. The ir spectra were measured in KBr disks, and the nmr spectra were determined in $CDCl_3$ at 60 MHz with a Hitachi R-20 nmr spectrometer using TMS as an internal reference. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer using a direct inlet and an ionization energy of 70 eV.

[14] M. P. Cava, R. L. Litle, and D. R. Napier, *J. Amer. Chem. Soc.*, **80**, 2257 (1958).

copper (300 mg). The filtrate was cooled and then filtration gave 40 mg (9.3%) of biacenedione. The filtrate was concentrated under vacuum, and the residue was triturated with petroleum ether (bp 38–50°) (20 ml) to give pale yellow crystals. Recrystallization from methanol gave 565 mg (65%) of **7** as colorless prisms.

Spiro[acenaphthenone-2,3'-tricyclo[3.2.1.$0^{2',4'}$]octane-6',7'-dicarboxylic anhydride] (**8**).—A solution of **1** (580 mg, 3 mmol) and bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (660 mg, 4 mmol) in benzene (30 ml) was refluxed for 40 hr. Concentration of the solution was followed by addition of methanol (20 ml). After standing overnight, the product was collected by filtration. Recrystallization from chlorobenzene gave 250 mg (25%) of **8**, mp 274–276° dec, as colorless prisms: ir (KBr) 1845, 1770, 1708 cm^{-1} (C=O); mass spectrum *m/e* 330 (M^+).

Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.35; H, 4.27. Found: C, 76.32; H, 4.32.

Reaction of 1 with Phenylacetylene.—After a solution of **1** (580 mg, 3 mmol) and phenylacetylene (2.0 g, 19.6 mmol) in benzene (25 ml) was refluxed for 48 hr, the solvent was removed under vacuum to leave a semicrystalline residue. A solution of the residue in 20 ml of petroleum benzine (bp 42–60°) was heated under reflux for 30 min and then allowed to stand overnight. Filtration gave yellow crystals, which on two recrystallizations from ethanol afforded 200 mg of **9**, mp 243–244°, as pale yellow needles. The petroleum benzine filtrate was concentrated under vacuum, and the residue was chromatographed over alumina (elution with benzene and chloroform), giving 400 mg of **1** and 20 mg of **9**: yield of **9**, 220 mg (25%); ir (KBr) 1710 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) 296 (100), 268 (34), 267 (12), 240 (21), 239 (70), 238 (11), 237 (18), 120 (10).

Anal. Calcd for $C_{20}H_{12}N_2O$: C, 81.06; H, 4.08; N, 9.45. Found: C, 81.12; H, 4.10; N, 9.35.

Reaction of 1 with Diethyl Acetylenedicarboxylate.—After a solution of **1** (970 mg, 5 mmol) and diethyl acetylenedicarboxylate (1.2 g, 7 mmol) in benzene (20 ml) was refluxed for 16 hr, the same procedure as above gave crude **10**. Two recrystallizations from ethyl acetate gave 1.45 g (80%) of pure **10**, mp 147.5–148.5°, as pale yellow prisms: ir (KBr) 1742, 1712 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) 364 (39), 320 (15), 291 (25), 258 (26), 257 (26), 221 (26), 220 (100), 180 (31), 152 (20).

Anal. Calcd for $C_{20}H_{16}N_2O_5$: C, 65.93; H, 4.43; N, 7.69. Found: C, 65.65; H, 4.49; N, 7.70.

Registry No.—**1**, 2008-77-7; **3a**, 27544-92-9; **3b**, 27544-93-0; **3c**, 27610-03-3; **3d**, 27610-04-4; **4a**, 27544-94-1; **4b**, 27544-95-2; **4c**, 27544-96-3; **5**, 27544-97-4; **6**, 27544-98-5; **8**, 27544-99-6; **9**, 27545-00-2; **10**, 27545-01-3.

Synthesis of 3-Substituted 1,4-Pentadiyn-3-ols

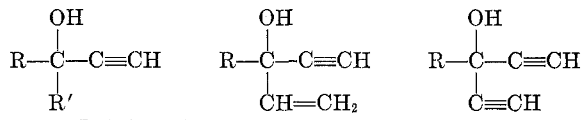
R. D. DILLARD* AND D. E. PAVEY

The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana 46206

Received July 25, 1969

A convenient synthesis of 3-substituted 1,4-pentadiyn-3-ols is described. This synthesis employs the treatment of a phenyl ester with a metal acetylide in liquid ammonia, using dichloromethane as cosolvent. Triethynylmethanol was synthesized by a similar method.

Reports in the literature on the preparation of tertiary ethynyl carbinols have been numerous, and a wide variety of reagents and reaction conditions have been described. For compounds having an unsubstituted terminal acetylenic group, the most familiar method has involved the use of a metal acetylide in liquid ammonia.[1,2] These include monoethynyl carbinols with various alkyl or aryl substituents on the α carbon.



$$R-\overset{OH}{\underset{R'}{C}}-C\equiv CH \qquad R-\overset{OH}{\underset{CH=CH_2}{C}}-C\equiv CH \qquad R-\overset{OH}{\underset{C\equiv CH}{C}}-C\equiv CH$$

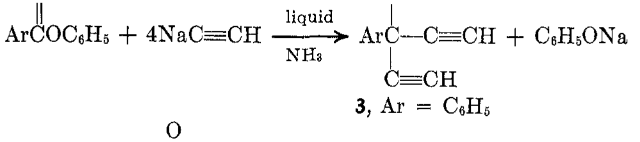
R, R' = alkyl or aryl

1, R = H
2, R = CH_3
3, R = C_6H_5

Although several diethynyl carbinols that are terminally substituted on the triple bond have been described,[3] only a few examples of diethynyl carbinols that are not substituted at this position have been reported. Jones, *et al.*,[4] developed the ethynyl Grignard reagent which was reacted with EtO_2CH to give **1**. The methyl derivative **2** was obtained by treating diethynyl ketone with MeMgBr or by reacting 3-butyn-2-one with ethynylmagnesium bromide.[5] The phenyl compound **3** was obtained similarly from phenyl ethynyl ketone.[6] All of these methods employ the ethynyl Grignard which is not always successful.

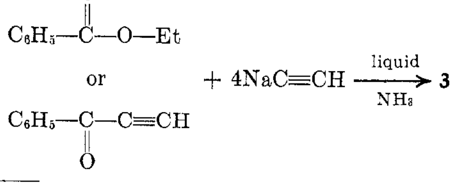
We wish to report a convenient synthesis of tertiary diethynyl carbinols using a metal acetylide in liquid ammonia. Earlier work in these laboratories has shown that CH_2Cl_2 is a very effective cosolvent in ethynylation reactions involving liquid ammonia.[7] Use of this cosolvent in the ethynylation of appropriately substituted phenyl esters proved to be beneficial in obtaining a large variety of 3-substituted 1,4-pentadiyn-3-ols.

3-Aryl-1,4-pentadiyn-3-ols.—Phenyl benzoate dissolved in CH_2Cl_2 was added to 4 equiv of sodium acetylide in liquid ammonia to give 3-phenyl-1,4-pentadiyn-3-ol (**3**) in 20–30% yield. Lithium acetylide



$$Ar\overset{O}{\overset{\|}{C}}OC_6H_5 + 4NaC\equiv CH \xrightarrow[NH_3]{liquid} Ar\overset{OH}{\underset{C\equiv CH}{C}}-C\equiv CH + C_6H_5ONa$$

3, Ar = C_6H_5



$$\left.\begin{matrix} C_6H_5-\overset{O}{\overset{\|}{C}}-O-Et \\ \text{or} \\ C_6H_5-\underset{O}{\underset{\|}{C}}-C\equiv CH \end{matrix}\right. + 4NaC\equiv CH \xrightarrow[NH_3]{liquid} 3$$

---

[1] K. N. Campbell, B. K. Campbell, and L. T. Eby, *J. Amer. Chem. Soc.*, **60**, 2882 (1938).

[2] W. M. McLamore, M. Harfenist, A. Bavley, and S. Y. P'An, *J. Org. Chem.*, **19**, 570 (1954).

[3] H. G. Viehe, *Chem. Ber.*, **92**, 1950 (1959); K. Hess and W. Weltzien, *Ber.*, **54B**, 2511 (1921).

[4] E. R. H. Jones, L. Skattebol, and M. C. Whiting, *J. Chem. Soc.*, 4765 (1956); E. R. H. Jones, H. H. Lee, and M. C. Whiting, *ibid.*, 3483 (1960).

[5] T. Bohm-Gossl, W. Hunsmann, L. Rohrschneider, W. M. Schneider, and W. Ziegenbein, *Chem. Ber.*, **96**, 2504 (1963).

[6] J. G. Noltes and G. J. M. Van der Kerk, *Recl. Trav. Chim. Pays-Bas*, **81**, 41 (1962).

[7] It was noted in these laboratories that ethynylation of diaryl ketone in liquid NH_3-CH_2Cl_2 solvent consistently gave complete conversions to the 1,1-diaryl-2-propynyl-1-ols which was not the case when NH_3-ether solvent was employed.