under reduced pressure. Distillation of the residue gave 154.9 g of **4** (92% yield): bp 109–110° (7 mm); mp 16° uncor; $n^{25}D$ 1.4794 (lit. bp 117°–118° (10 mm),[1b] mp 15°,[8] $n^{20}D$ 1.4810[9]). The infrared spectrum of **4** compared well with its published[8] one.

Cyclodecanone (7).—Bromine, 162 g (*ca.* 1 mol), was added dropwise to a stirred solution of 84.1 g (0.5 mol) of **4** in 350 ml of anhydrous ether at roughly the bromine uptake rate while cooling the reaction mixture. After the addition was completed,[10] the reaction mixture was poured onto 200 g of crushed ice followed by the addition of 100 ml of water and 150 ml of benzene. The aqueous phase was separated and extracted with 100 ml of benzene. The combined organic phases were washed successively with dilute aqueous solutions of sodium sulfite and sodium hydrogen carbonate and a concentrated aqueous solution of sodium chloride, and finally dried over anhydrous sodium sulfate. The ether then was evaporated and the resulting benzene solution was added dropwise to a stirred suspension of 95 g (1.75 mol) of sodium methoxide in 300 ml of dry benzene over a period of 30 min while maintaining the reaction temperature between 20 and 25°. The mixture was stirred for an additional 5 min at room temperature followed by work-up as described for **3b**. The crude **6** was added to 350 ml of sulfuric acid (97%) followed by the addition of 350 ml of chloroform. Sodium azide, 42 g (0.65 mol) was added to the stirred reaction mixture over a period of about 20 min while maintaining the reaction temperature between 35 and 38° through cooling. Work-up as described for **4** gave on distillation 59.2 g (77% yield) of **7**: bp 94.5–95° (6 mm); mp 26° uncor, $n^{26}D$ 1.4801 (lit. bp 99–101° (8 mm),[1c] mp 25°,[8] $n^{25}D$ 1.4806).[1c] The infrared spectrum of **4** compared well with that previously published.[8]

Registry No.—**4**, 878-13-7; **7**, 1502-06-3.

Acknowledgment.—The authors are grateful for support of this work from the National Science Foundation (Grant No. G.P. 3589).

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(9) H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957).

(10) The composition of the stereoisomeric 2,11-dibromocycloundecanones obtained is about 80% *cis* and 20% *trans*.

On the Structure of the Cycloheptatriene–Tetracyanoethylene Diels–Alder Adduct

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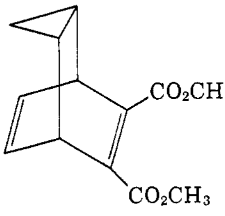
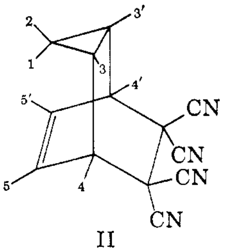
Received November 24, 1967

The reports[1] of novel reactivity of tetracyanoethylene (TCNE) with N-carbethoxyazepine prompt us to report our findings on the reactivity of the parent hydrocarbon with TCNE.

Only recently has the stereochemistry of a Diels–Alder adduct of cycloheptatriene (CHT) been rigorously established.[2] Goldstein and Gevirtz[2] combined an analysis of spectral properties and chemical correlations to demonstrate that the originally assumed[3] structure (I) of the CHT–dimethylacetylenedicarboxylate adduct was correct. These authors[2] further pointed out that the mechanism of Diels–Alder addition to cycloheptatriene was not yet firmly established. For this reason, and also because tetracyanoethylene has shown unusual reactivity,[4] we thought it important to establish conclusively the nature of the CHT–TCNE adduct.



I



II

Jordan and Elliott in the course of other work[5] reacted TCNE and CHT and obtained a product which gave the proper elemental analysis and displayed infrared absorption consistent with the presence of the nitrile group and a three-membered ring. No additional proof was offered for the proposed structure, II.

We have repeated the reaction of TCNE with CHT using benzene as solvent. The adduct II, produced in good yield, possessed physical properties which agreed with the published data.[5] The 100-MHz H^1 nmr spectrum of an acetone-d_6 solution of II containing internal TMS (see Table I), however, provides strong support for the proposed structure.

TABLE I

100-MHz NMR DATA OF II

Chemical shift (τ)	Relative area	Signal appearance	Assignment
9.65	1	Doublet of triplets	H-1
		$J_{1,2} = -6.1$ Hz	
		$J_{1,3} = +3.8$ Hz	
9.25	1	Doublet of triplets	H-2
		$J_{1,2} = -6.1$	
		$J_{2,3} = +7.5$	
8.33	2	Complex	H-3, H-3′
5.77	2	Complex[a]	H-4, H-4′
3.77	2	Complex	H-5, H-5′

[a] Irradiation at 5.77 causes the 3.77 signal to collapse to a singlet and the 8.33 signal to change into a doublet of doublets ($J_{1,3} = +3.8$ Hz; $J_{2,3} = +7.5$ Hz). (All signs of coupling constants are assigned in accordance with the assumption of a positive sign for ^1J (C^{13}–H^1).)

The τ 9.65 and 9.25 signals are assigned to the *endo* (H-1) and *exo* (H-2) geminal cyclopropyl hydrogens, respectively. The higher field position of the resonance of the *endo* hydrogen is ascribable to the shielding effect of the double bond.[6]

Additional evidence for the assigned stereochemistry of II is provided by relative magnitudes of the coupling constants. The τ 9.65 signal is split by only 3.8 Hz as would be expected for *trans* vicinal coupling in a three-membered ring. The τ 9.25 signal, split by 7.5 Hz, is in accord with its assignment to the *exo* hydrogen

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(1) J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, **87**, 4819 (1965); A. S. Kende, P. T. Izzo, and J. E. Lancaster, *ibid.*, **87**, 5044 (1965).

(2) M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Lett.*, 4417 (1965).

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(5) N. W. Jordan and I. W. Elliott, *J. Org. Chem.*, **27**, 1445 (1962).

(6) We have attempted to strengthen this argument by hydrogenating the double bond. If our logic was correct we would expect to find no signal above τ 9.50 in the nmr spectrum of the dihydro derivative. However, all attempts at hydrogenation have failed! Examination of a molecular model of II indicates severe crowding above and below the double bond.

(H-2) which is *cis* oriented with respect to H-3 and H-3′.[7-9] The τ 8.33 signal reflects the deshielding effect of the proximate cyano groups on these cyclopropyl hydrogens (H-3, H-3′). Both the location and the shape of the τ 5.77 signal are consistent with the bridgehead (H-4, H-4′) assignment. The decoupling data (Table I) provide dramatically convincing evidence for the central location of the hydrogens producing this signal. Finally, the τ 3.77 signal is unexceptional and is assigned to the olefinic hydrogens (H-5, H-5′).

Registry No.—II, 16118-23-3.

[7] It is tempting to estimate the angles in the cyclopropyl ring by application of the Karplus[8] and Gutowsky, Karplus, Grant[9] correlations of *J* with vicinal dihedral and geminal angles, respectively. Since there are no polar groups directly attached to the three-membered ring, such a treatment may be reasonable. The values obtained (H_1–C–C–H_3 = 118°; H_2–C–C–H_3 = 30°; H_1–C–H_2 = 116°) agree well with predictions based on models.

[8] N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 49–50, and references cited therein.

[9] H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959); see also, R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, **7**, 335 (1966).

Synthesis of 1,4-Diketones by the Reaction of Lithium Aroyltricarbonylnickelates with Acetylenes

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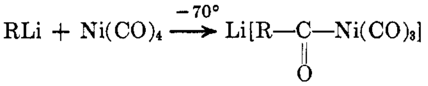
Received October 16, 1967

We have reported that aryllithiums reacted with nickel carbonyl at low temperature (−70°) in ether solution to give lithium aroyltricarbonylnickelates (I).[1]



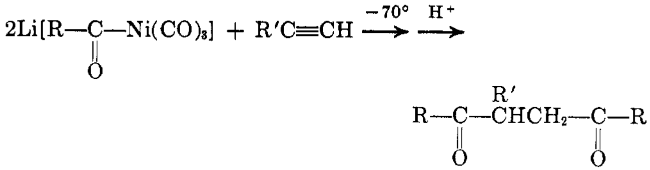
$$\mathrm{RLi} + \mathrm{Ni(CO)_4} \xrightarrow{-70^\circ} \mathrm{Li[R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Ni(CO)_3]}$$

I

Fischer and Maasböl also described the formation of lithium benzoylpentacarbonyltungstate by the reaction of phenyllithium with tungsten hexacarbonyl,[2a] and they furthermore reported the formation of several lithium acyl- or aroylcarbonylmetalates.[2b]

Although an attempt to isolate the pure complexes of these metalates was unsuccessful, their synthetic applications were investigated since lithium aroyltricarbonylnickelates showed useful reactivity. For example, these complexes were reactive toward organic halides[1b] and toward unsaturated compounds[3] such as styrene because of their carbon–nickel σ bond.

Now we have investigated the reaction of lithium aroyltricarbonylnickelates with acetylenes and found that 2 mol of these complexes added to 1 mol of acetylenes at −70° to give 1,4-diketones (II) in yields of 47–74%, and γ-lactones were produced as by-products in yields of 2–24% when the reaction was carried out at higher temperature (−30°).



$$2\mathrm{Li[R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Ni(CO)_3]} + \mathrm{R'C{\equiv}CH} \xrightarrow{-70^\circ} \xrightarrow{H^+} \mathrm{R{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}\overset{R'}{C}HCH_2{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}R}$$

II (main product)

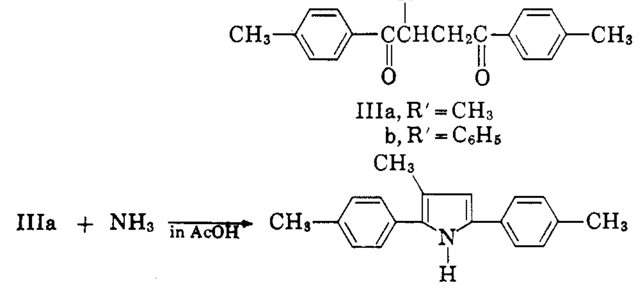
Several workers have reported that acetylenes insert between the acyl and metal carbonyl groups in acyl metal carbonyls. Heck isolated 2,3-diethyl-π-(2,4)-penteno-4-lactonylcobalt tricarbonyl in the reaction of acetylcobalt tetracarbonyl with 3-hexyne.[4] Cassar and Chiusoli reported that allylic halides react with nickel carbonyl in acetone solution containing small amounts of water in the presence of carbon monoxide and acetylene to produce γ-lactone derivatives.[5]

Thus, it was found to be probable that acetylenes insert into the bond between the acyl and metal carbonyl group to form acylvinylmetal carbonyls which may undergo CO insertion and cyclization to give unsaturated γ-lactones. However, in the reaction of lithium aroyltricarbonylnickelates with acetylenes main products are not lactones but 1,4-diketones.

In this paper, we would report the reaction of lithium aroyl- and acyltricarbonylnickelates with acetylenes which promises to be of general use for the synthesis of 1,4-diketones.

Results and Discussion

The reaction between lithium *p*-toluyltricarbonylnickelate and methylacetylene followed by hydrolysis gave 1,2-di-*p*-toluylpropane (69%), and a similar reaction with phenylacetylene gave 1,2-di-*p*-toluyl-1-phenylethane (47%). The structures of these products were confirmed by ir and nmr spectroscopy. Furthermore, the structure of 1,2-di-*p*-toluylpropane was confirmed from the formation of 2,5-di-*p*-tolyl-4-methylpyrrole by the action of ammonia in acetic acid.[6] Acetylene was treated with lithium *p*-toluyltricarbonylnickelate at −70° to give 1,2-di-*p*-toluylethane in a yield of 56%. This compound was too insoluble for nmr study, but from the chemical data and by analogy with the previous reactions this com-



IIIa, R′ = CH_3
b, R′ = C_6H_5

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[2] (a) E. O. Fischer and A. Maasböl, *Angew. Chem.*, **76**, 645 (1964); (b) E. O. Fischer and A. Maasböl, German Patent 1,214,233 (1966).

[3] M. Ryang, K.-M. Song, Y. Sawa, and S. Tsutsumi, unpublished work.

[4] R. F. Heck, *J. Amer. Chem. Soc.*, **86**, 2819 (1964).

[5] L. Cassar and G. P. Chiusoli, *Tetrahedron Lett.*, 3295 (1965).

[6] W. S. Bishop, *J. Amer. Chem. Soc.*, **67**, 2261 (1945).