

formula for the effect of hyperfine interaction, which involves Fermi and dipolar terms. This formula, however, yields positive contributions only; so it cannot provide a complete explanation of the changes in sign.

It has often been suggested that orbital and dipolar contributions, as well as the Fermi term, are important in F-F coupling.⁵

TABLE. J_{meta}^{FF} in fluorobenzenes (Hz)

Molecule	Term	Positions		
		2,4	2,6	3,5
$C_6F_5NH_2$	Fermi	-2.4	-2.6	-2.9
	Orbital	-1.0	6.3	3.6
	Dipolar	0.6	1.7	1.6
	Total	-2.8	5.4	2.3
	Expt. ¹	-8.2	6	-3
$C_6F_5NO_2$	Fermi	-3.1	-3.1	-3.8
	Orbital	9.0	-3.2	2.7
	Dipolar	2.4	0.7	3.5
	Total	8.3	-5.6	2.4
	Expt. ¹	6	-10	0
C_6F_6	Fermi	—	—	-3.5
	Orbital	—	—	2.3
	Dipolar	—	—	1.3
	Total	—	—	0.1
	Expt. ⁹	—	—	-4

The object of this communication is to report the results of some calculations on hexafluorobenzene, pentafluoroaniline, and pentafluoronitrobenzene which show that the

change in the signs of J_{24}^{FF} and J_{26}^{FF} in the last two compounds is due to the effect of the orbital term. The equations have been given by Blizzard and Santry.^{5,6}

The computations were carried out on the KDF9 computer and runs of 1–2 h were necessary to obtain convergence for the orbital and dipolar terms. The original INDO parameters⁷ were used, with bond angles of 120°, bond lengths C–C 1.40, C–F 1.33, C–N 1.40, N–O 1.24 and N–H 1.036 Å, and the corrected Hartree–Fock values⁸ $\langle r^{-3} \rangle = 7.546$ a.u., $|\psi(O)|^2 = 11.3966$ a.u.

In the three molecules, J_{ortho}^{FF} and J_{para}^{FF} were found to be almost constant, with values of -22 ± 2 Hz and 11 ± 1 Hz respectively, in good agreement with the experimental pattern. Values for J_{meta}^{FF} are shown in the Table. It can be seen that the Fermi term is always negative and the dipolar term always positive. The orbital term changes sign in the same way as the experimental values for J_{26}^{FF} and J_{24}^{FF} . Thus the effect of the substituents on the *ortho* and *para* positions shows itself through the orbital term. For J_{35}^{FF} the orbital and dipolar terms are positive and the Fermi term is negative. The small magnitude is due to the approximately equal magnitudes of the positive and negative terms. The calculations give somewhat too positive values, but the order is the same as for the experimental values.

These results for J_{24}^{FF} and J_{26}^{FF} provide the first clear-cut example of a dominant contribution from the orbital term in nuclear coupling.

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Novel Aryl-bridged Tetranuclear Copper–Lithium Cluster Compounds: Synthesis and Characterization by ¹³C and ¹H Nuclear Magnetic Resonance Spectroscopy of Bis-{2-[(dimethylamino)methyl]phenyl}copper(I) Lithium

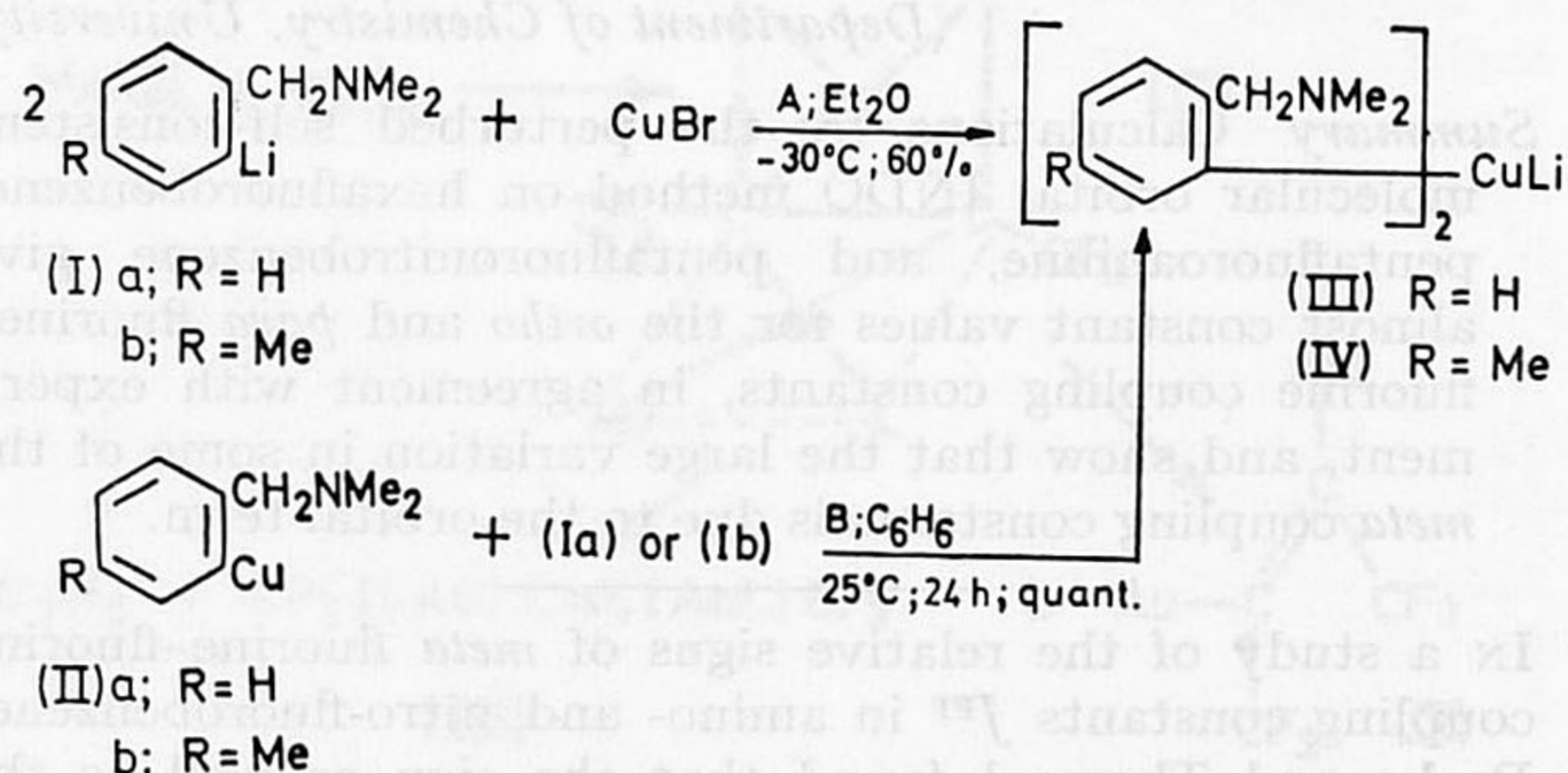
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Summary The synthesis of two dimeric bis(substituted-aryl)copper(I) lithium compounds is described; ¹H and ¹³C n.m.r. spectroscopy reveal a structure consisting of a Cu₂Li₂ cluster with aryl groups bridging a copper and a lithium atom.

LITTLE is known definitely about the structure of the organocuprates.^{1–4}

We report here the synthesis of thermostable bis(aryl)copper(I) lithium compounds and the assignment of their structure as tetranuclear mixed Cu–Li cluster compounds with bridging aryl groups.



Compounds (III) and (IV) have been prepared *via* routes A and B.† The colourless compounds‡ (III) and (IV) (decomp. 178–192 °C), which are soluble in both ether and hydrocarbon solvents, exist in benzene as discrete dimeric units $R_4Cu_2Li_2$ (by cryoscopy and by ebullioscopy).

The arrangement of the aryl groups around the Cu_2Li_2 units in (III) and (IV) follows from their 1H and natural abundance ^{13}C n.m.r. spectra. The ^{13}C resonances (relative to Me_4Si , with proton decoupling) at the lowest field [in C_6D_6 : (IIa), 157.11(s); for (III), 168.10 p.p.m. (q)]§ have been assigned to C-1, which is directly bound to the metal cluster, *i.e.* in the case of (IIa) the C-1 atom bridging two Cu atoms.¶ In the ^{13}C n.m.r. spectra of (III) and (IV) these resonances appear as quartets [for (III): J 7.1 Hz] as a result of ^{13}C - 7Li coupling of the C-1 atom with only *one* Li atom. The 1H n.m.r. spectrum of (III) displays only one quartet

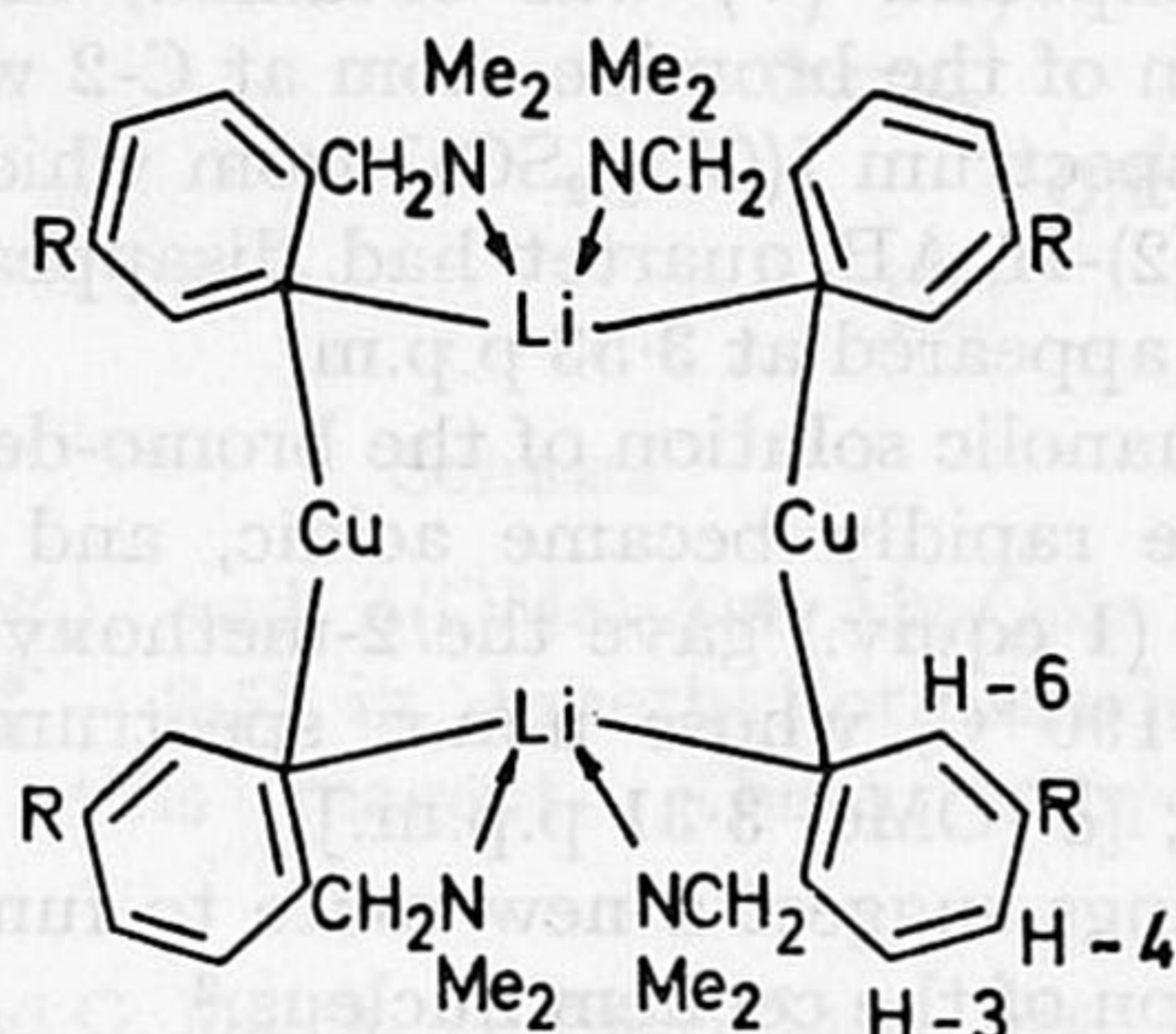


FIGURE. (III), R = H-5; (IV), R = Me

[(III) in $[^2H_8]$ toluene: 8.74 p.p.m.; $J_{5,6}$ 7; $J_{4,6}$ 1.5 Hz] for the *ortho* protons H-6 in the four aryl nuclei [(IV) displays one

doublet]. This, together with the ^{13}C n.m.r. results points out that all four 2-[(dimethylamino)methyl]phenyl groups are bound in the same manner to the metal cluster system; *i.e.* each aryl group bridges a Li and a Cu atom.** The NMe and NCH₂ proton resonance pattern [temp. dependent, for (III); NMe – 60° 1.90 (s) and 1.22 (s), collapse at 5° to a singlet, 25° 1.74 p.p.m.; NCH₂, 25° 4.12 (d) and 2.48 (d), J_{gem} 11.6 Hz, collapse at 80° to a singlet, 110° 3.36 p.p.m. (br)] indicate that: (i) the four “hard” CH₂NMe₂ ligands are co-ordinated to the same metal atom, *i.e.* to lithium in view of the HSAB principle;⁸ (ii) an exchange process $NMe_2^{coord} \rightleftharpoons NMe_2^{free}$ occurs.

The combined data are consistent with the structure presented in the Figure.

Our results indicate that organocuprates (*e.g.* R_2CuLi , R_2CuMgX ,⁴ $R_6Cu_4Mg \cdot Et_2O$ ⁹) are in fact metal-Cu cluster compounds with bridging R groups.†† The consequences of such a structure with respect to their reactivity in cross coupling and conjugate addition reactions are obvious; *e.g.* the increasing reactivity of organocopper lithium compounds when the carbon ligands are $N \equiv C^-$,¹¹ $RC \equiv C^-$,¹¹ Ar^- , and Alk^- parallels the decreasing bridging ability¹² of these groups; the metal-halogen exchange³ as a side-reaction in cross coupling reactions of aryl iodides with $(Me_2CuLi)_n$ can be explained by a nucleophilic attack of the bridged Me group on the I atom of ArI affording MeI and the more stable phenyl-bridged $CuLi$ cluster.

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† Since both the organo-lithium⁵ and copper(II)^{6,7} compounds occur as tetranuclear clusters the synthesis of (III) and (IV) *via* route B can be envisaged as an interaggregate exchange between two tetranuclear clusters.

‡ Correct Cu analysis were found; C, H, and N analyses were hampered by the extreme air sensitivity of these compounds.

§ Complete ^{13}C n.m.r. data will be published in the full paper.

¶ X-Ray diffraction analysis has established the presence of bridging aryl groups in (IIa), see ref. 7.

** In the analogous bis-{2-[(dimethylamino)methyl]phenyl}silver(I) lithium dimer the C-1 atom couples with both one Li and one Ag atom; A. J. Leusink, J. W. Marsman, G. van Koten, and J. G. Noltes, to be published.

†† Mol. wt. determinations have revealed $[2-Me_2NC_6H_4Cu]_2 \cdot CuBr^{10}$ and its $AgBr^{10}$ analogue to be hexanuclear ($R_4Cu_6Br_2$ and $R_4Cu_4Ag_2Br_2$). X-Ray diffraction analysis has established a Cu_6 cluster structure with bridging Br and R groups for the $CuBr$ complex, J. M. Guss, R. Mason, K. M. Thomas, G. van Koten, and J. G. Noltes, in preparation.

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Reactions of Cephalosporins with N-Bromosuccinimide

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Summary A 3-acetoxymethyl- Δ^2 -cephem derivative was converted into a 3-formyl- Δ^2 -cephem by oxidation with N-bromosuccinimide; a Δ^3 -deacetylcephalosporanic acid lactone formed a 2-bromo-derivative.

As part of our study of the chemistry of cephalosporins, we examined the reaction of 7-phthalimido- Δ^2 -cephalosporanic acid, methyl ester (I)† with N-bromosuccinimide (NBS). A transient brownish-red colour was observed when a degassed,

† Compound (I), m.p. 210–211 °C, was prepared (*ca.* 50%) by first heating the methyl ester of 7-aminocephalosporanic acid with phthalic anhydride and triethylamine in benzene for 2 h, followed by treatment with acetic anhydride for 18 h.